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The interactive biotic and abiotic processes of DDT transformation under dissimilatory iron-reducing conditions

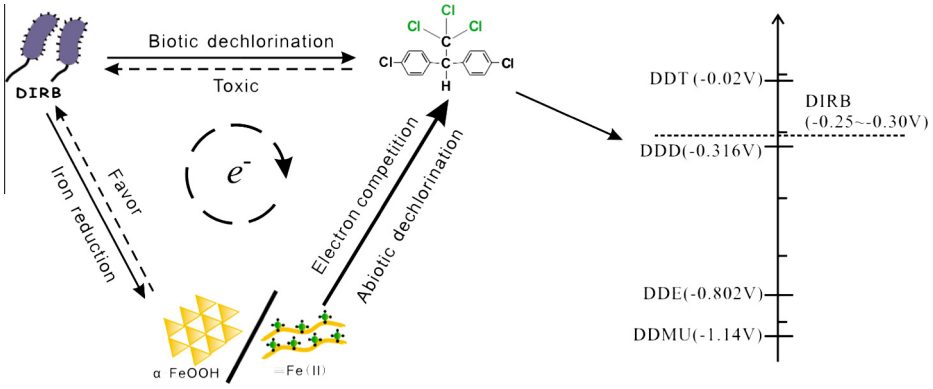
Xin Jin [a], Fang Wang [a], Chenggang Gu [a], Xinglun Yang [a], Fredrick O. Kengara [b], Yongrong Bian [a], Yang Song [a], Xin Jiang [a,*]

[a] State Key Laboratory of Soil and Sustainable Agriculture, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, China
[b] Department of Chemistry, Maseno University, Maseno 40105, Kenya

HIGHLIGHTS

- DDT dechlorination is well described by a modified first-order kinetics model.
- α-FeOOH enhances reductive dechlorination, while increases electron competition.
- The reduced Fe^{II} mainly exists as a weakly adsorbed complex in natural pH.
- DDD which is the main metabolite, and DDE, DDMU are too recalcitrant to be degraded.
- The dechlorination stability of organochlorine may be predicted from the E_1 value.

GRAPHICAL ABSTRACT



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ABSTRACT

The objective of the study was to elucidate the biotic and abiotic processes under dissimilatory iron reducing conditions involved in reductive dechlorination and iron reduction. DDT transformation was investigated in cultures of *Shewanella putrefaciens* 200 with/without α-FeOOH. A modified first-order kinetics model was developed and described DDT transformation well. Both the α-FeOOH reduction rate and the dechlorination rate of DDT were positively correlated to the biomass. Addition of α-FeOOH enhanced reductive dechlorination of DDT by favoring the cell survival and generating Fe^{II} which was absorbed on the surface of bacteria and iron oxide. 92% of the absorbed Fe^{II} was Na-acetate (1 M) extractable. However, α-FeOOH also played a negative role of competing for electrons as reflected by the dechlorination rate of DDT was inhibited when increasing the α-FeOOH from 1 g L^{-1} to 5 g L^{-1}. DDT was measured to be toxic to *S. putrefaciens* 200. The metabolites DDD, DDE and DDMU were recalcitrant to *S. putrefaciens* 200. The results suggested that iron oxide was not the key factor to promote the dissipation of DDX (DDT and the metabolites), whereas the one-electron reduction potential (E_1) of certain organochlorines is the main factor and that the E_1 higher than the threshold of the reductive driving forces of DIRB probably ensures the occur of reductive dechlorination.

1. Introduction

2,2-bis(4-Chlorophenyl)-1,1,1-trichloroethane (DDT) was widely used in the 1940s and 1950s for controlling agricultural

* Corresponding author at: 71 East Beijing Road, Nanjing 21008, China.
E-mail address: jiangxin@issas.ac.cn (X. Jiang).

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pests and malaria vectors. It has been banned for decades in some developed countries because of its high environmental persistence and potential carcinogenicity. In 2007, DDT was re-introduced by the World Health Organization to control malaria because it is inexpensive yet highly effective (WHO, 2011). In South Africa, the special application as an indoor residual spray applied 2 g m^{-2} DDT on indoor wall (Humphries, 2013). The residual concentrations of DDT and its metabolites in some natural soils, sediments, and contaminated sites are still high (Liu et al., 2008). And there is evidence of new point sources: For instance, dicofol and antifouling paint, continues to contribute to DDT concentrations in various environmental compartments (Guo et al., 2009; Jia et al., 2011). Therefore, DDT is still a compound of environmental concern.

Dissimilatory iron-reducing bacteria (DIRB) are prevalent microorganisms in subsurface environments (Lovley et al., 2004). They are distinguished by their strategy of oxidizing readily degradable organic carbon or H_2, and transferring the generated electrons to extracellular electron acceptors like ferric iron oxide. Organic and inorganic pollutants such as nitroaromatic compounds, polyhalogenated alkanes, chromium (VI), and uranium (VI) can also act as alternative terminal electron acceptors (Lovley et al., 2004; Luan et al., 2009; Picardal et al., 1993; Guha et al., 2001). Therefore, there is increasing interest in DIRB for the potential application in in-situ remediation of contaminated sites and natural attenuation of industrial wastes (Hofstetter et al., 1999; Wei and Finneran, 2011). Ferrous iron, when bound to mineral surfaces, was found to have a high reductive activity on pollutants of nitro- and halo-compounds (Amonette et al., 2000; Charlet et al., 1998). Under conditions where DIRB and iron oxide were combined, the transformation rate of certain target compound was enhanced due to beneficial interaction of DIRB and iron oxide (Kim and Picardal, 1999). Previous studies have shown that DIRB can transform DDT to DDD (2,2-bis(4-Chlorophenyl)-1,1-dichloroethane) (Li et al., 2010). However the detailed biotic and abiotic processes, and their relative contributions, in reductive dechlorination and iron reduction, are still not clear. Once in the environment, DDT is usually known to be broken down into metabolites, DDE and DDD, which are highly recalcitrant, it is necessary to further investigate and evaluate the degradation potential of DIRB for not only DDT but its metabolites as well.

This study attempts to (i) study the fate of DDT degrading by the DIRB *Shewanella putrefaciens* 200 associated with and without iron oxide, and thus to elucidate the interactive biotic and abiotic processes involved in reductive dechlorination and iron reduction; (ii) evaluate the reductive dechlorination potential of DIRB to DDX (DDT and the metabolites).

2. Materials and methods

2.1. Basic medium

A modified Westlake medium (Obuekwe and Westlake, 1982) was used for DDT degradation. It contained 0.5 g L^{-1} K_2HPO_4, 1.0 g L^{-1} NH_4Cl, 0.15 g L^{-1} $CaCl_2$, 0.1 g L^{-1} $MgSO_4{\cdot}7H_2O$, 30 mM Na-lactate, 30 mM PIPES (1,4-Piperazinediethanesulfonic acid, Sigma–Aldrich, Co., China) and 1 g L^{-1} or 5 g L^{-1} α-FeOOH when was necessary. Lactate was added not only as the carbon source but also as the electron donor to provide electrons for the reductive dechlorination of DDT and the reduction of α-FeOOH. The final pH of the medium was adjusted to 7.0. The ionic strength was 0.06 M. 100 mL of the medium was prepared in a 120 mL glass bottle (SCHOTT DURAN, Germany) and screwed using a PBT screw cap with a PTFE-coated silicon seal. After sterilization (121 °C, 30 min), the bottles were stored in an anoxic chamber (CIMO YQX-II, Shanghai) filled with N_2/H_2 (97:3; Pd catalyst; 30 °C; BOC Industrial Gases, Shanghai) for at least 3 d to remove the dissolved oxygen.

2.2. DDT transformation by S. putrefaciens 200 associated with/without α-FeOOH

The DIRB *S. putrefaciens* 200 (Obuekwe and Westlake, 1982) was used as the model DIRB. DDT transformation was studied in iron-free culture (containing *S. putrefaciens* 200 without α-FeOOH) and ferric iron culture (containing *S. putrefaciens* 200 with 1 g L^{-1} α-FeOOH or with 5 g L^{-1} α-FeOOH). α-FeOOH was synthesized from $Fe(NO_3)_3$ and KOH (Schwertmann and Cornell, 2000) following electrodialysis to remove excessive NO^{3-} and K^+. *S. putrefaciens* 200 were first cultivated in Tryptic Soy Broth (Qingdao Hope Bio-tech. Co., China) medium overnight under aerobic conditions and harvested by centrifugation (5000 rpm, 20 min). The pellet was washed three times with phosphate buffer saline (pH 7.0). Then about 2 mL of the concentrated cells were re-suspended into the modified Westlake medium to get an initial cell density of $\sim 2 \times 10^8$ cells mL^{-1}. The culture with sterilized *S. putrefaciens* 200 (121 °C, 30 min) served as the control. The liquid cultures were equilibrated for 4 h in an anoxic chamber to consume any traces of oxygen. Next, acetone-based *p,p′*-DDT (Dr. Ehrenstorfer, Germany) was spiked to give the concentration of 15.7 ± 0.1 μM. The cultures were incubated in a water bath shaker in the dark (150 rpm, 30 °C). Each experiment was performed in triplicate.

In order to evaluate how the initial DDT concentration impacts on its dechlorination behavior, batch experiments at different initial *p,p′*-DDT concentrations (from 1 to 40 μM) were conducted in the iron-free culture and ferric iron culture (with 1 g L^{-1} and 5 g L^{-1} α-FeOOH).

To maintain anoxic conditions, all reaction bottles were tightly screwed and sealed with paraffin wax after each sampling. Sampling, over time, was performed in an anaerobic chamber. Sample aliquots were withdrawn for analysis of the concentrations of *p,p′*-DDT, the metabolites, Fe^{II}, and the biomass of *S. putrefaciens* 200. *p,p′*-DDT and its metabolites were extracted using a hexane-dichloromethane (1/1, v/v) mixture and analyzed by GC-ECD (Agilent 6890, USA). Details of analytical procedures are provided in SI, Section S1 and S2.

2.3. α-FeOOH reduction

The Fe^{II} in ferric iron cultures (1 g L^{-1} and 5 g L^{-1} α-FeOOH, 15.4 μM DDT) was monitored throughout the whole incubation period. The dissolved Fe^{II} was determined by filtration of the culture medium through a 0.22 μm polyethersulfone membrane. The Fe^{II} was also extracted individually by 1 M Na-acetate, 0.5 M HCl and 3 M HCl for 24 h each. The 1.0 M Na-acetate extracts the chelated and weakly adsorbed Fe^{II} complex, as well as the dissolved Fe^{II}. The 3 M HCl further extracts the fixed Fe^{II} which should be strongly adsorbed or bonded onto the mineral and cell surface. The Adsorbed Fe^{II} was calculated by subtracting the dissolved Fe^{II} from the 0.5 M HCl extractable Fe^{II}. Fe^{II} was analyzed by the ferrozine method (Viollier et al., 2000), and provided in SI, Section S3 in detail.

2.4. Degradation of DDT metabolites by S. putrefaciens 200

In order to evaluate the potential of bacteria *S. putrefaciens* 200 on degrading DDT metabolites, *p,p′*-DDD, *p,p′*-DDE, and *p,p′*-DDMU were individually introduced into the cultures of *S. putrefaciens* 200