

Detoxification of Chlorinated Chemicals by the Reductive Dehalogenation Process

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1. INTRODUCTION

Halogenated aliphatic compounds(HACs) are used in a broad range of industrial, agriculture, and domestic applications. They are found in groundwaters, as a result of past practices in landfilling and in toxic chemical disposal. They are also major compounds of landfill leachates and hazardous wastes. The production and use of HACs and their potential hazard to human health have prompted investigations concerning their fate in the aquatic environments, and in the treatments facilities. Air-stripping and sorption onto activated carbon have been used for above groundwater treatment of contaminated water. These methods merely transfer the contaminants from one environmental compartment to another, without destroying them. More recently biological oxidation is being used to destroy HACs both above ground and in situ. Bioremediation is limited to low concentrations of the HACs and is only effective for dissolved HACs(Alvarez et al., 1989). Studies of carbon tetrachloride reduction by iron sulfides and hydroquinones suggest possible reaction pathways for the reduction of halogenated aliphatic compounds(HACs). It has been hypothesized that iron sulfide and hydroquinones are electron transfer mediators which form highly reactive and reduced intermediates, being able to reduce the oxidized contaminant(1,2) Once the electron transfer mediator is oxidized by the contaminant, it can be assumed to be reduced back to the initial state by a "bulk" electron donor, which may be present in excess of the mediator. If the concentration of reduced mediator is large with respect to the concentration of the oxidized substrate, the extent of cycling of the mediator may be small. Some hydroquinones have been found to be efficient

electron transfer mediators with either Fe^{2+} or HS^- as the bulk electron donor(3). NOM(Natural Organic Matter) has recently been shown to increase the rate of reduction of HACs in the presence of HS^- , and it was proposed that the hydroquinone/quinone type couple was the electron transfer mediator(4). This is consistent with the known properties of model hydroquinones and the redox properties of NOM. This hydroquinone/quinone-type couple is believed to dominate the redox properties of humic acid(5). It has been suggested that HS^- also reduces quinone groups to the corresponding hydroquinone group in humic acid(6,7).

In this work, it was hypothesized that both simple hydroquinones and hydroquinone groups in NOM can mediate the reduction of CCl_4 . More specifically, the objectives are to test the hypothesis that CCl_4 could be reduced by a simple hydroquinone and to determine the reduction of CCl_4 with HS^- as the bulk electron donor if iron sulfide can mediate. The objective is also given to estimate rates of the reduction of CCl_4 in the different experimental systems.

2. METHODOLOGY

Experimental Approach. The rate of reduction of CCl_4 by hydroquinone was investigated, and results were compared with experiments conducted with iron sulfide. The effect of its addition of HS^- to the NOM(Natural Organic Matter) was also investigated. Experiments were also conducted in solutions containing carbon tetrachloride and HS^- . The initial concentrations of carbon tetrachloride was $10.0 \mu\text{M}$ in all cases, and the initial molar ratio of electron donor to acceptor was 100 or greater. The influence of adding humic acid to the iron sulfide and HS^- solution was also tested.

Equipment The atmosphere in the glove box was 90% N_2 /10% H_2 . The gas chromatograph used was a Younglin, Model M600D, equipped with FDD detector. The column was type DB-1, 50m \times 0.2mm with a 0.11 μm film thickness from Hewlett Packard. The column, injector, and detector temperatures were 42 $^\circ\text{C}$, 225 $^\circ\text{C}$ and 250 $^\circ\text{C}$, respectively. The make-up gas was 95%Ar/5% CH_4 and a pressure of approximately 2.5kg/cm². The flow rate of the carrier gas, He, was 8ml/min.

3. RESULTS AND DISCUSSION

Reduction by Hydroquinone. Figure 1 illustrates the transformation of CCl_4 to CHCl_3 in the presence of $250 \mu\text{M}$ hydroquinone at pH 7.2 and 50°C . The observed disappearance of CCl_4 fit the first-order model ($r^2=0.90$), and the formation of the CHCl_3 appears to be quantitative. This is evident by comparing the CHCl_3 data with the CHCl_3 concentrations calculated by assuming quantitative conversion of CCl_4 to CHCl_3 .

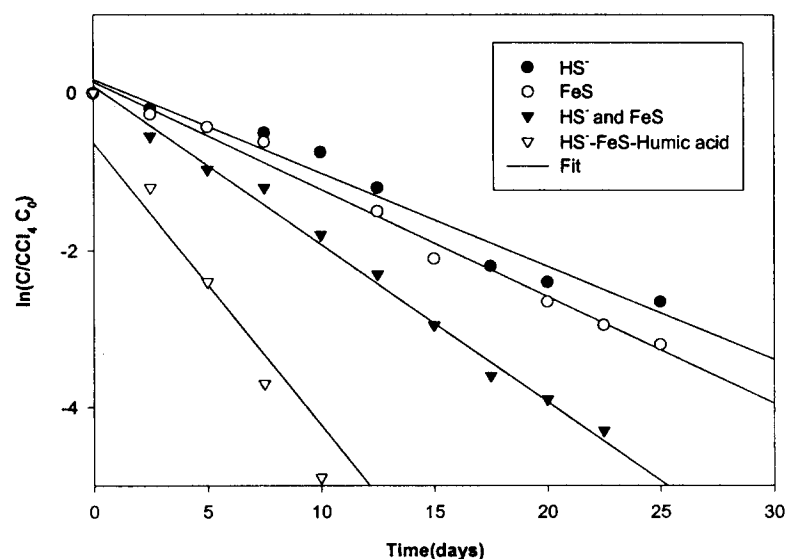


Figure1. First-order plots of CCl_4 transformation at 36.7°C in the presence of iron sulfide ($\text{SC}=75\text{m}^2/\text{L}$) without and with 1mM HS^- . Lines indicate fit of first-order model to the data

Effect of Iron sulfide and Humic acid on CCl_4 Transformation. Figure 2 shows the effect of iron sulfide ($\text{SC}=75\text{m}^2/\text{L}$) and humic acid on the transformation rate of $10 \mu\text{M CCl}_4$ in the presence of 1mM HS^- at pH 8.6, 50°C . The result shows that the disappearance of CCl_4 is first order ($\alpha=1$), the minerals increase the transformation rate of CCl_4 over the rate that occurs in homogeneous solution, and humic acid accelerates the transformation rate of CCl_4 reacted with iron sulfide and HS^- solution.

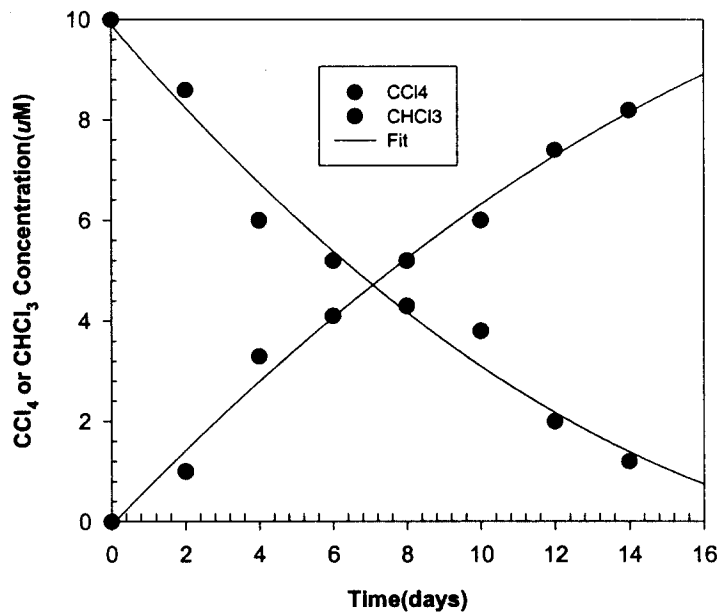


Figure 2. Disappearance of 10µM CCl₄ and appearance of CHCl₃ in the presence of 250µM hydroquinone at 50°C and pH7.6

4. CONCLUSIONS

This work demonstrates that iron sulfide and hydroquinone can effectively reduce CCl₄ in aqueous solutions at 50°C and pH 7.2. NOM sample, humic acid, transformed CCl₄ more rapidly upon the addition of a bulk electron donor. The transformation of CCl₄ in NOM solutions with iron sulfide or HS⁻ as the bulk electron donors is consistent with NOM acting as electron transfer mediator and hydroquinone groups being the reactive sites. Therefore, detailed studies are needed to confidently characterize NOM as an electron transfer mediator.

5. REFERENCES

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