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# Chemical Degradation of Chlorinated Organic Pollutants for *In Situ* Remediation and Evaluation of Natural Attenuation

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## 1. Introduction

Chlorinated organic compounds, prevalent contaminants found in the geo-environment, pose an ecological risk even at trace concentrations. More volatile chlorinated compounds such as VOCs (volatile organic compounds) have been detected in urban areas and industrial zones because of the use of these compounds as components of industrial solvents and both raw and intermediate synthetic products. Chlorinated organic compounds quickly evaporate from surface water but remain in groundwater and soil for a long time. Recently, several remediation techniques have been developed that can entirely remediate chlorinated organic compounds to non-toxic materials. However, high molecular weight chlorinated organic compounds (e.g., polychlorinated biphenyls (PCBs) and dichloro-diphenyl-trichloroethane (DDT)) are highly toxic chemicals that persist for long periods of time in the environment and bioaccumulate. They are categorized as persistent organic pollutants (POPs). Although the amount and date of use vary by country, POPs were widely used for pesticides and disease control in crop production and industrial processes during the period of industrial production after World War II around the globe. DDT, PCBs and dioxins are the best known POPs. DDT is used to control mosquitoes, which carry malaria, and PCBs were useful in electrical transformers and large capacitors. Among these POPs, PCBs, hexachlorobenzene (HCB), chlordanes, dichloro-diphenyl-dichloroethane (DDE) and dieldrin show significant ecological accumulation, such as in human milk, human blood and other biological media.

The Stockholm Convention is intended to protect human health and the environment, starting with the reduction or elimination of the production, use, and/or release of 12 species of POPs (PCBs, HCB, aldrin, dieldrin, endrin, DDT, chlordane, heptachlor, toxaphene, mirex, polychlorinated dibenzo-*p*-dioxins (dioxins), and polychlorinated dibenzofurans (furans). The 9 additional chemicals adopted in amendments to the Stockholm convention as new POPs are  $\alpha$ -hexachlorocyclohexane,  $\beta$ -hexachlorocyclohexane, chlordecone, hexabromobiphenyl, hexabromobiphenyl ether and heptabromobiphenyl ether, Lindane, pentachlorobenzene, perfluorooctane sulfonic acid and its salts and perfluorooctasulfonyl fluoride, tetrabromobiphenyl ether and pentabromobiphenyl ether in 2009. The Stockholm Convention has led to a general global

decline in the concentration of these chemicals in the environment. However, some individual POPs still persist and accumulate in fatty tissue and are present in higher concentrations at higher levels in the food chain, with long-range mobility through natural processes, because complete removal of POPs from the environment is difficult.

Experimental degradation methods for POPs at room temperature have been reported, using chemical catalysis, bacteria, UV, photocatalysis, Fenton reagent and other methods. Among these techniques, reductive dechlorination processes encounter difficulty in achieving complete dechlorination and degradation of the chemical structure. Powerful oxidative processes are assumed to show some possibility for complete degradation of POPs. Reports of complete degradation of POPs are few, even when oxidative processes are applied for on-site remediation over a very extensive polluted area.

This chapter reviews remediation methodology for chlorinated organic pollutants and chemical remediation methods using ferric sulphide compared with reaction with zero-valent iron, which widely used as a practical in-situ remediation method for soil and groundwater pollution by VOCs. Ferric sulphides also have outstanding ability to degrade chlorinated organic pollutants, but the dechlorination processes differs from that of zero-valent iron. The natural remediation capability, reaction products, and reaction mechanisms using ferric sulphide for trichloroethylene, dieldrin and chlorinated benzenes are reported in this chapter.

## 2. Reported remediation methods for chlorinated organic pollutants

Several remediation methodologies for chlorinated organic pollutants such as bioremediation, bioaugmentation, and chemical or physical remediation have been reported by many researchers. In these remediation methodologies, chlorinated organic contaminants can be transformed chemically, photochemically, or biochemically by oxidation or reduction in the soil and the groundwater environments.

Bioremediation technology has developed rapidly in the last 15 years, and the application of this technology has been extended to several species of contaminants, including volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs). Reductive dechlorination by microorganisms under anaerobic conditions is an advantageous process because reductive dechlorination allows the reoxidation of metabolic intermediates. For VOCs, PCE (tetrachloroethylene) or TCE (trichloroethylene), which is most widely reported chemicals, are capable of reductive dechlorination by dehalococcoides, dehalobacter and desulfuromonas (Hollinger *et al.*, 1993; Gerritse *et al.*, 1996, 1999; Löffler *et al.*, 1999; Krumholz *et al.*, 1996; Maymo-Gatell, 1997). These microorganisms dechlorinated the PCE/TCE to cis-dichloroethylene (cis-DCE) or vinyl chloride (VC). Dehalococcoides especially (including the culture) is reported to have achieved complete dechlorination of PCE/TCE to ethylene. In aerobic or oxidizing environments, chlorinated ethylenes are oxidized to CO<sub>2</sub> and the chlorinated ethylenes are co-metabolized to CO<sub>2</sub> via trichloroacetate, trichloroethanol, trichloroethylene epoxide, dichloroacetate, glyoxylate, formate, oxalate, etc. The reaction pathway and the number of intermediates differ according to the species of bacteria in the local environment (Newman and Wackett, 1991, 1995, 1997; Weightman *et al.*, 1985, 1993; Li and Wackett, 1992; Kim *et al.*, 2009; Rosenzweig *et al.*, 1993; Oldenhuis *et al.*, 1989; Motosugi *et al.*, 1982). Oxygen served as the electron acceptor in the aerobic oxidation, and non-specific microbial oxygenase enzymes produced by aerobic microorganisms participated in co-metabolism reactions.

Anaerobic microbial communities in sediments also dechlorinate PCBs. The ease of dechlorination of positions on aromatic rings is usually meta > para > ortho, and on biphenyl rings, mono-ortho- and ortho-chlorobiphenyls were not degraded after one year of reaction (Teidje *et al.*, 1993). PCE was also oxidatively degraded by *Pseudomonas* strain sp. P2. In this reaction, PCE is metabolized to chlorobenzoic acids with one to three chlorine atoms. At the actual reaction site, reductive and oxidative biological reaction is estimated to occur because of conditions at the site. Each reaction is therefore assumed to proceed partly under anaerobic conditions and partly under aerobic conditions at one polluted site, and this collaboration of reactions under different sets of conditions leads to complete remediation at the natural site.

Many chemical remediation methods have been investigated for rapid in-situ or off-site remediation of soil and groundwater. Among the chemical and photochemical dechlorination methods, zero-valent iron (ZVI) has frequently been reported as the remediation technique for reductive dechlorination of chlorinated ethenes and ethanes. Among actual chemical remediation techniques, the ZVI methodology is widely used for in situ remediation for soil (e.g., injection by direct drilling) and groundwater (application in a reactive permeable barrier). The chlorinated organic materials degrade under anaerobic (reducing) conditions using ZVI. This reductive dechlorination is generally divided into hydrogenolysis and reductive elimination. Both reaction mechanisms are accompanied by a net transfer of two electrons. Although reductive dechlorination is occasionally referred to as hydrolytic reduction, this term is misleading because hydrolysis is incidental to the actual reduction. Some other zero-valent metals such as zinc and platinum are also reported as reductive remediation catalysts instead of ZVI. The reaction pathway for TCE using ZVI and other metals is the same as the reductive dechlorination process using bioremediation.

Although the application of ZVI for remediation of high molecular weight persistent organic compounds is difficult, zero-valent metals such as Pd, Pt, Ni and Cu are also used as catalysts in the ZVI methodology for dechlorination of PCBs. Metal catalysis enhances the reductive dechlorination capability of ZVI. In the case of persistent organic compounds, electrochemical methods using metal electrodes are used for reductive dechlorination.

Fenton reaction and photochemical reaction are the predominant oxidative dechlorination processes and can remediate contaminants rapidly. The Fenton reaction is the oxidation of organic substrates by iron(II) and hydrogen peroxides. The Fenton reagent is effective in treating various industrial wastewaters polluted by chlorinated organic compounds, aromatic amines, pesticides, and surfactants. This oxidation system is based on the formation of reactive oxidizing species able to degrade the contaminants effectively in wastewater. In the Fenton chemistry, a two-reaction pathway is advanced as the first step. Production of hydroxyl radicals and a non-radical pathway using ferric ion production have been reported (Barbusinski, 2009). The nature of the oxidizing species is still controversial. Some researchers showed that the hydroxyl radical is the major species in the Fenton mechanism, and other groups showed that this reaction includes the formation of reactive oxidizing species such as ferric ion. Considering that the Fenton reaction occurs chemically and biologically as well as in the natural environment, there is a possibility that both mechanisms coexist in the Fenton reaction. Several hazardous pollutants can be oxidized by the Fenton reaction; for example, chlorophenol is degraded to hydroxyacetic intermediates (Barbeni *et al.*, 1987a) and perchloroethylene is transformed to dichloroacetic acid, formic acid and CO<sub>2</sub> (Leung *et al.*, 1992). More detailed information about Fenton reaction is discussed in the chapter "Fenton's Process for the Treatment of Mixed Waste Chemicals".

In natural waters exposed to solar radiation, the Fenton reaction is often perceived as a possible source of hydroxyl radical in sunlit waters. The photolysis of nitrates, metal-to-ligand charge transfer reactions, and photoFenton reactions are included as other possibilities for the Fenton reaction, and  $\text{H}_2\text{O}_2$  and Fe(II) are photochemically produced in these sunlit waters. Photochemical dechlorination is reported for persistent high molecular weight organic compounds such as DDT and PCBs (Mochizuki 1977; Van Beek *et al.*, 1982; Shimakoshi *et al.*, 2004). Photochemical PCBs dechlorination in alkaline isopropyl alcohol effectively degrades PCBs to biphenyl, chloride ions, acetone and water (Mochizuki, 1977). Dechlorination of DDT was catalyzed by hydrophobic vitamin B12 (heptamethyl cobyrinate perchlorate) with irradiation by visible light (Shimakoshi *et al.*, 2004). The Co(I) species of cobalamin and the related cobalt complex are supernucleophiles and react with an alkyl halide to form alkylated complexes with dehalogenation (Shimakoshi H. *et al.*, 2004). In this reaction, DDT is mono-dechlorinated to DDD. Photocatalytic treatment assisted by  $\text{TiO}_2$  is also widely reported for TCE, DDT, chlorinated phenol, chloroform, etc. (Ahmed and Ollis, 1984; Barbeni *et al.*, 1986, 1987b; Dible and Raupp, 1990, 1992; D'Oliveria *et al.*, 1990; Kondo and Jardim, 1991; Borello *et al.*, 1989) These oxidative degradations proceed by radicals arising from the photoreaction of other compounds present in the system.

In a similar reaction, UV/ $\text{H}_2\text{O}_2$  and UV/Fenton are used for the remediation of chlorinated ethylenes and ethanes, chlorobenzenes, benzenes, and chlorinated phenols (Frolich, 1992; Moza *et al.*, 1988; Sundstrom *et al.*, 1986, 1989; Weie *et al.*, 1987). UV/ $\text{H}_2\text{O}_2$  oxidation involves the dissociation of  $\text{H}_2\text{O}_2$  to form the hydroxyl radical. The hydroxyl radical oxidizes toxic organic materials by abstraction of protons to produce organic radicals. Some toxic materials degrade to lower molecular weight acids and finally transform to  $\text{CO}_2$ . However, many reports only estimate degradation ability and reaction kinetics and do not mention reaction products, especially when high molecular weight persistent organic compounds are involved.

These strong chemical oxidation technologies such as Fenton reagent, UV radiation, catalysis and photochemical treatment have the prospect of degradation of persistent organic pollutants to non-toxic compounds.

### 3. Remediation ability of ferric sulphides

The metal sulphides show a great diversity in electrical and magnetic properties. The sulphides of the transition metals can be considered as intermediate between the transition metal oxides. The small particles of metal sulphide are often superior in electrical and chemical properties, as well as in catalysis.

Pyrite is the most abundant metal sulphide mineral and is treated as industrial waste at many mining sites. An outcrop including pyrite leads to oxidation in aerobic weathering processes and causes acidification of environmental water. Pyrite is also distributed in acidic coastal sulphate soils, which are naturally formed under waterlogged anaerobic conditions. These acidic sulphide soils are located in tropical coastal areas in West Africa, South and Southeast Asia, and northeast South America. These acidic conditions are mainly developed in recent or semi-recent sediments close to the sea. In these environments, the sulphur in pyrite is derived from the sulphate in seawater, which is biologically reduced to sulphide in the anaerobic mud. The organic matter which serves as the energy source for the sulphate-reductive bacteria is usually abundant in plants in the coastal area. Ferrous iron is also derived from reduction of insoluble ferric compounds resulting from the weathering of clay.

The reactivity of pyrite when the surface is exposed to H<sub>2</sub>O, O<sub>2</sub>, and a mixture of H<sub>2</sub>O and O<sub>2</sub>, has been studied experimentally by Guevremont *et al.* (1997, 1998a, b, c, d). The pyrite surface exposed to H<sub>2</sub>O vapour up to 1 bar was oxidized, although the reaction site is limited to the defect site on pyrite surface. The surface reaction with O<sub>2</sub> vapour showed no oxidation. Substantial surface reaction is observed in the reaction with the H<sub>2</sub>O/O<sub>2</sub> mixture. The intermediate oxidation products, sulphur oxoanion and zero-valent sulphur, are also identified and removed by use of either the O<sub>2</sub> or H<sub>2</sub>O (Kendelewicz *et al.*, 2004). The oxidation mechanism of pyrite with the H<sub>2</sub>O/O<sub>2</sub> mixture involves competitive adsorption of O<sub>2</sub> and H<sub>2</sub>O at the surface Fe site, oxidation of surface Fe sites by O<sub>2</sub>, dissociation of co-adsorbed H<sub>2</sub>O at Fe sites, and charge redistribution in surface S atoms (Rosso *et al.*, 1999). This pathway allows for the production of hydroxyl radicals from dissociated water and subsequent nucleophilic attack of these hydroxyl radicals at surface S sites. The oxygen in the final product sulphate arises from water molecules (Taylor *et al.*, 1984; Usher *et al.*, 2004, 2005). The hydroxyl radical from the pyrite oxidation process causes the degradation of chlorinated organic compounds.

### 3.1 Degradation ability for major volatile organic compounds

Chlorinated ethylenes are widespread groundwater and soil contaminants. Due to the prevalent pollution and the efforts to treat these compounds, substantial research has been conducted to identify the mechanism of reaction under various environmental conditions. As mentioned above, the chemical dechlorination method using ZVI is in wide use as a practical in situ remediation technique for soil and groundwater pollution with TCE. This reductive dechlorination reaction process includes hydrogenolysis,  $\beta$ -elimination and a hydrogen addition reaction, and degrades chlorinated ethylenes and ethanes to ethylene and ethane. The dechlorination of TCE by pyrite (ferric sulphide) under anaerobic conditions is also reported to be reductive dechlorination like ZVI (Weerasooriya R., 2001; Lee and Batchelor, 2002, 2003). Other chlorinated ethylenes and ethanes are also reductively dechlorinated under anaerobic conditions (Kriegman-King and Reinhard, 1994; Lee and Batchelor, 2003). The reductive dechlorination of chlorinated compounds occurs by the transfer of electrons from the mineral surface.

Fig. 1 shows the dechlorination of TCE by metallic sulphides and zero-valent iron. In this reaction, 100 ppm of TCE is dechlorinated with powdered pyrite and Milli-Q-grade-ultrapure water under closed aerobic conditions. TCE is detected by a headspace method using gas chromatography (GC) (GC17A, Shimadzu Co. Ltd.). Pyrite and chalcopyrite showed an outstanding dechlorination rate, and complete dechlorination was confirmed by the mass balance of chloride ion. According to the recent pyrite oxidation work, the most reactive surface component is S<sup>2-</sup>, and the second most reactive surface component is the surface atom of the first disulphide layer (S<sub>2</sub><sup>2-</sup>) with sulphur atoms of the disulphide groups beneath the surface layer being least reactive. Oxidized iron (Fe<sup>3+</sup>) states are proposed to arise after fracturing of S-S bonds by electron transfer from Fe<sup>2+</sup> to this S<sup>-</sup> state, which then reacts rapidly to sulphate (Nesbitt *et al.*, 1998; Schaufuss *et al.*, 1998). If this oxidation reaction is similar with metallic sulphide, the S-S bonds in metallic sulphide oxidize chlorinated contaminants, as assumed from this oxidation model. Disulphide metallic minerals involving S-S bonds are therefore assumed to have greater degradation ability than the mono-sulphide metals. In our experimental estimation in Figure 1, the disulphide metallic minerals are only pyrite and chalcopyrite, which have superior degradation ability relative to the other mono-sulphide metals and ZVI.

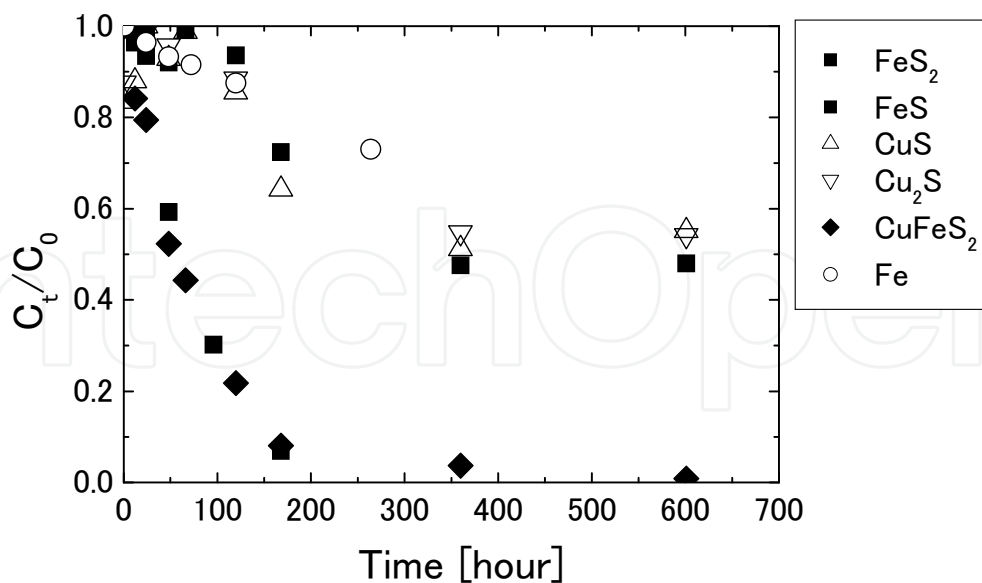
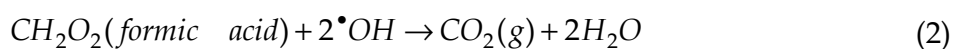
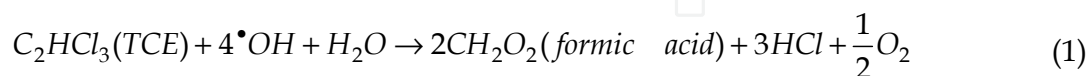


Fig. 1. Dechlorination of trichloroethylene (TCE) by metallic sulphide and zero-valent iron under aerobic conditions.  $C_0$  is the initial concentration of TCE (100 mg/L),  $C_t$  is the concentration of TCE at time  $t$ . The reaction was represented as the evaluation of the normalized remaining percentage of TCE with time.

TCE is also degraded by pyrite under aerobic conditions (Hoa *et al.*, 2008). TCE dechlorination in anaerobic and aerobic pyrite suspensions is observed with time, but there is no outstanding degradation under anaerobic conditions and the dechlorination rate of TCE is proportional to the increase in oxygen. Fig. 2 shows the disappearance of TCE, the reaction intermediates and the final product in the reaction of TCE with a pyrite suspension under aerobic conditions. Under aerobic conditions, 98 % of TCE was degraded after about 2 weeks. The TCE degrades to dichloroacetic acid, glyoxylic acid, formic acid, oxalic acid and  $\text{CO}_2$  by oxidative processes (Hoa *et al.*, 2009). This degradation process is similar to the oxidative metabolic pathway of TCE (Kim *et al.*, 2009; Li *et al.*, 1992). Figure 3 shows the expected dechlorination pathway of TCE by pyrite under aerobic conditions. The dechlorination pathway of TCE is divided into three pathways. All pathways show direct dechlorination of three chlorine atoms in TCE. The main pathway is degradation of TCE to formic acid (Eq. (1)).



Formic acid has toxicological properties toward aquatic organisms, but the degradation rate of formic acid by pyrite suspensions is also high, similar to the dechlorination of TCE to formic acid, and formic acid continuously transforms to  $\text{CO}_2(\text{g})$  without accumulation (Eq. (2)).

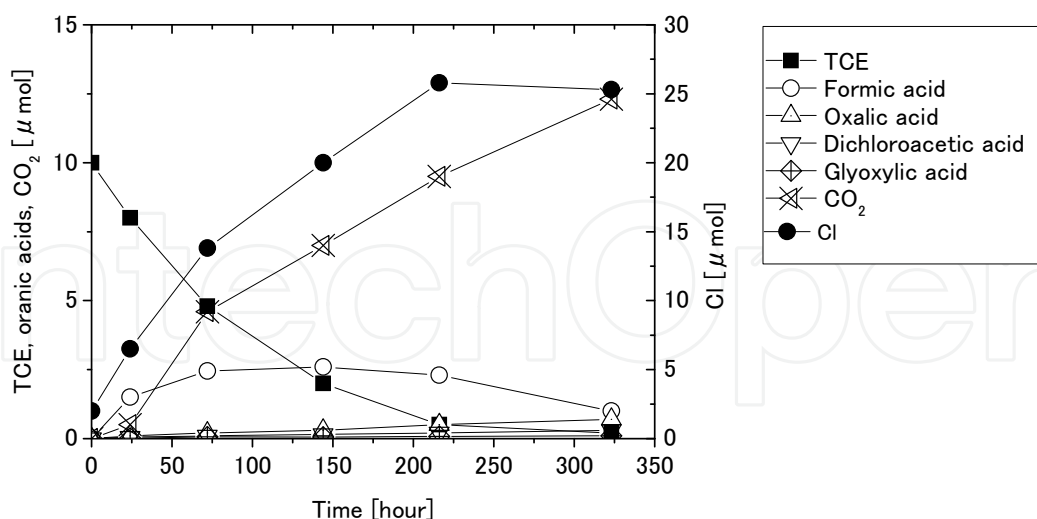


Fig. 2. Transformation of trichloroethylene (TCE) and detected reaction products in pyrite suspension (Edited from Hoa *et al.* (2008)). The initial TCE concentration is 10  $\mu\text{mol}$ , the oxygen volume is 0.268 mmol/L, and pyrite is 10  $\text{m}^2/\text{L}$ . The left side of the Y-axis shows the molecular weight of TCE,  $\text{CO}_2$  and organic acids (formic acid, oxalic acid, dichloroacetic acid, glyoxylic acid). The right side of the Y-axis shows the chloride molecular weight as degraded from TCE.

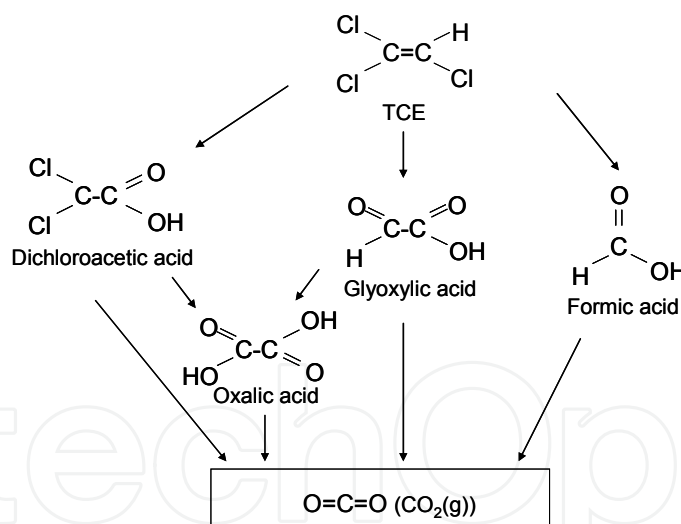


Fig. 3. Degradation pathway of trichloroethylene (TCE) using a pyrite suspension under aerobic conditions (Edited from Hoa *et al.* (2009)).

### 3.2 Degradation capability for dieldrin

Dieldrin is a cyclodiene pesticide which has persisted in the soil over decades in some agricultural fields. Some agricultural crops and animals accumulate dieldrin through the food chain. From the previous report of TCE dechlorination by pyrite, we see that TCE is able to be reductively degraded under anaerobic conditions and oxidatively degraded under aerobic conditions. The reductive dechlorination under anaerobic conditions is not observed using pyrite suspensions. Dieldrin has a higher persistence than TCE and is less amenable to



reductive dechlorination under anaerobic conditions. Remediation techniques for dieldrin (UV/Fenton reagent, UV/chemical reaction, Pd/C catalyst, solar photocatalysis, and bioremediation) have been reported (Books, 1980; Maule *et al.*, 1987; Bandala *et al.*, 2002; Kusvuran and Erbatur, 2004; Chiu *et al.*, 2005; Zinovyev *et al.*, 2005; Dureja *et al.*, 1987; Baczynski *et al.*, 2004), but dieldrin transforms to mono- or di- dechlorinated intermediates still having a bicyclic ring structure. A study of the use of Fenton reagent for aldrin reports the transformation from aldrin to oxalic acid, acetic acid, chlorohexanone, cyclohexanol, cis-2-hydroxy-cyclohexanone, cis-2-methyl-cyclohexanol, 4-hydroxycyclohexanone, cis-4-methylcyclohexanol, 1-cyclopropyl-1-hydroxyethylene, and trans-dihydroxycyclohexane (Kusvuran and Erbatur, 2004).

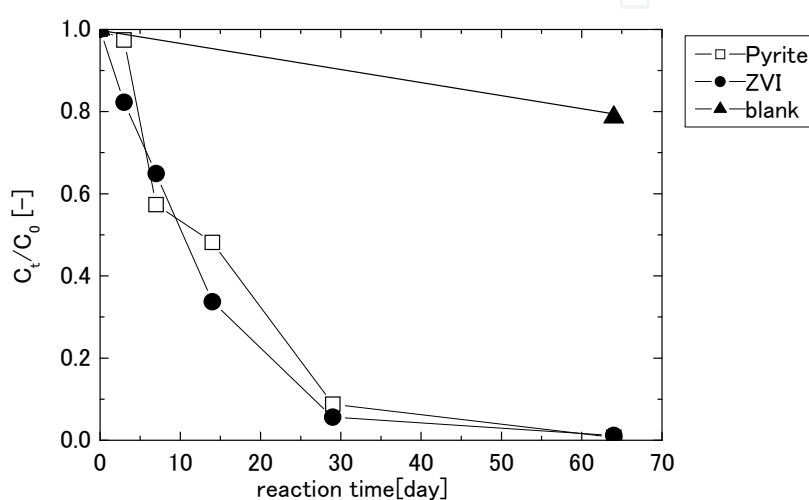


Fig. 4. Degradation profile of dieldrin using pyrite and zero-valent iron under aerobic conditions. The blank denotes the non-metallic catalysis condition.  $C_0$  is the initial concentration of dieldrin ( $0.131 \mu\text{mol}$ ),  $C_t$  is the concentration of dieldrin at time  $t$ . (Edited from Hara *et al.*, (2009)

The degradation of dieldrin using ZVI and pyrite under anaerobic conditions is shown in Fig. 4. ZVI and pyrite have similar dechlorination capabilities for dieldrin, but the reaction process differs completely for the two reagents (Hara *et al.*, 2009). In the case of ZVI, dieldrin partially transforms to nono-dechlorinated products ( $\text{C}_{12}\text{H}_9\text{Cl}_5$ ,  $\text{C}_{12}\text{H}_9\text{Cl}_5\text{O}$ ) and aldrin ( $\text{C}_{12}\text{H}_8\text{Cl}_5$ ). This reaction is a reductive dechlorination proceeded by the generation of  $\text{H}^+$  and an electron arising from oxidation of ZVI. This reaction is stopped only this pathway. In contrast, the mono-dichlorinated reaction intermediates and aldrin are not detected in the reaction using pyrite. Dieldrin is oxidatively degraded to water-soluble reaction intermediates by pyrite.

Fig. 5 shows the dechlorination rate of dieldrin using pyrite under anaerobic to aerobic conditions, changing with oxygen concentration ( $\text{O}_2 = 0 \sim 833 \mu\text{mol}$ ). Dieldrin was gradually degraded under every condition of oxygen concentration, except for the  $\text{O}_2 = 0 \mu\text{mol}$  condition. In Fig. 5, 5 ppm ( $0.131 \mu\text{mol}$ ) of dieldrin is used with a powdered pyrite suspension under each oxygen condition. Dieldrin is detected by GC/MS (Shimadzu Co. Ltd.) after solvent/solvent extraction using acetone and hexane. The water-soluble reaction intermediates are detected by IC-TOF/MS (ICS-3000 (Dionex) and JMS-T 100LP (JEOL)). A little oxygen ( $\text{O}_2 = 10 \mu\text{mol}$ ) accelerates the dechlorination of dieldrin in

comparison to the anaerobic conditions. Approximately 99 % of the dieldrin was degraded after about one month under the most enhanced reaction conditions ( $O_2 = 10 \mu\text{mol}$ ), and approximately 43 % of dieldrin remained under  $O_2 = 300 \mu\text{mol}$  in the same reaction time, which is the slowest dechlorination condition. In these reactions, chloride ion resulting from the dechlorination was detected in the aqueous phase. The mass balance of dechlorinated chloride and degraded dieldrin is 90 % in the most degraded condition ( $O_2 = 10 \mu\text{mol}$ ). This discrepancy in mass balance is obvious in the anaerobic conditions, but the mass balance agrees well under aerobic conditions ( $O_2 = 300$  and  $833 \mu\text{mol}$ ).

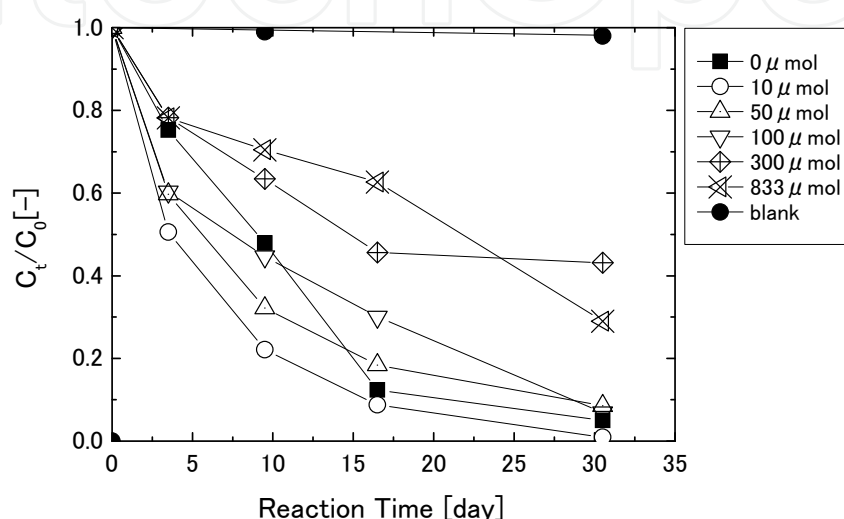


Fig. 5. Oxygen dependence on degradation of dieldrin in pyrite suspension (Hara, 2011).  $C_0$  is the initial concentration of dieldrin ( $0.131 \mu\text{mol}$ ),  $C_t$  is the concentration of dieldrin at time  $t$ .  $O_2 = 833 \mu\text{mol}$  denotes the air volume conditions in this experiment. The blank is without pyrite.

As reaction products, formic acid, oxalic acid, malonic acid, succinic acid, acetoxyacetyl, lactic acid, and pyruvic acid are detected as the main reaction products in the case of aerobic conditions ( $O_2 = 833 \mu\text{mol}$ ). Acetic acid, glycolic acid, hydroxybutyric acid, glyoxylic acid, propionic acid, glutaric acid, levulinic acid and sulphur-containing organic acids such as methanesulphonic acid, sulphopropionic acid, etc. are also detected as minor reaction products. Formic acid is predominantly generated, as shown in (Eq. (3)).



Formic acid is also detected in TCE dechlorination by a pyrite suspension under aerobic conditions, and the formic acid continuously degrades to  $CO_2$  (Eq. (2)). Dieldrin is therefore assumed to finally transform to  $CO_2$  as a main reaction pathway.

In the case of a low  $O_2$  volume or anaerobic conditions, these low molecular weight organic acids generated under oxygen-rich conditions are much lower in abundance and some organic acids are not detected. Instead of the generation of organic acids, 3-chloro-4-methyl-2-pentanol ( $C_6H_{13}ClO$ ) and dibutyl phthalate ( $C_{16}H_{22}O_4$ ) are generated. One part of these intermediates is continuously degraded to a low molecular weight organic acid, but the residual volume is also higher than the volume observed under aerobic conditions.

The reaction pathway of dieldrin proceeds mostly by oxidative degradation under anaerobic and aerobic conditions. Although the oxidative ability is obviously different from the content of oxygen, the active oxidant to degrade the dieldrin is promoted from both the pyrite/H<sub>2</sub>O and pyrite/O<sub>2</sub> interface reaction, due to oxidants produced under either aerobic or anaerobic condition. The difference of degradation ability in oxygen volume is assumed to depend on the difference of radical species arising from pyrite/H<sub>2</sub>O and pyrite/O<sub>2</sub> interface.

Considering the reaction products, the degradation pathway of dieldrin results mainly in the direct production of organic acids, which are easy to produce under oxygen-rich conditions. Under anaerobic or micro-aerobic conditions, the pathway of ring opening and the addition reaction of low molecular weight organic acids arising from C<sub>16</sub>H<sub>22</sub>O<sub>4</sub> and the pathway of generation of chlorinated hydrocarbons arising from C<sub>6</sub>H<sub>13</sub>ClO (which continuously transforms to formic acid and malonic acid) become predominant.

### 3.3 Degradation ability for chlorinated benzenes

Dieldrin having a bicyclic ring could be decomposed by pyrite. This section discusses the ability to dechlorinate chlorobenzenes whose main structure is the benzene ring.

Chlorobenzenes are divided into 12 species based on the number and configuration of chlorine in the molecule: monochlorobenzene (mono-CB), 3 types of dichlorobenzene (1,2-, 1,3-, 1,4- di-CB), 3 types of trichlorobenzene (1,2,3-, 1,2,4-, 1,3,5- tri-CB), 3 types of tetrachlorobenzene (1,2,3,4-, 1,2,3,5-, 1,2,4,5- tetraCB), pentachlorobenzene (penta-CB), and hexachlorobenzene (hexa-CB). The chlorobenzenes are used in pesticides, deodorants, or as intermediates in a chemical synthesis process. Some tri- or tetra-chlorinated benzenes are extensively used as insulating materials. The risk associated with chlorinated benzenes increases relative to the increase in the chlorine number, because of their increasing lack of volatility with increasing chlorine number, the highest level of risk is associated with the misuse or accidental release of the mono- to trichlorinated benzenes. These compounds spread into the atmosphere are reported to be photolyzed or chemically reacted, and that in groundwater and soils these compounds are mainly remediated by microbial degradation. However, the residence time is increased because of the organic constituents present in the soil and groundwater, which results in adsorption and accumulation in the soil ecosystems. The major remediation method for more the accumulation of chlorobenzenes with a higher chlorination level in soils is incineration at high temperatures for digging out of soils.

In the previous reports of electrochemical dehalogenation of chlorinated benzenes (Miyoshi *et al.*, 2004; Mohammad and Dennis, 1997; Farwell *et al.*, 1975; Kargina *et al.*, 1997; Guena *et al.*, 2000), the chlorine is eliminated step by step from the highly chlorinated benzenes to yield less-chlorinated benzenes and finally transform to benzene. Farwell *et al.* (1975) reported on chlorobenzenes and the main cathodic reaction pathway for hexachlorobenzenes as follows: hexachlorobenzene → pentachlorobenzene → 1,2,3,5-tetrachlorobenzene → 1,2,4-trichlorobenzene → 1,4-dichlorobenzene → monochlorobenzene → benzene. This dechlorination pathway is promoted by the electrochemical reductive dechlorination. Benzene is detected as the final reaction product.

Oxidative dechlorination of chlorobenzenes has been reported using bacteria, Fenton reagent, UV/H<sub>2</sub>O<sub>2</sub>, and TiO<sub>2</sub>-assisted photocatalysis. In the microbial metabolism reported by Reineke and Knackmuss (1984), chlorobenzene was gradually degraded to 3-chloro-cis-1,2-dihydroxycyclohexa-3,5-diene, 3-chlorocatechol, 2-chloro-cis,cis-muconate, trans-4-carboxymethylenebuten-4-olide, maleylacetate, and 3-oxoadipate. Fenton reagent effectively

degrades chlorobenzene to chlorohydroxycyclohexadienyl radical in the first step, and the radical dimerizes to produce dichlorobiphenyls, with bimolecular disproportionation to produce chlorophenol and chlorobenzene under non-oxygen conditions or in the absence of other strong oxidants (Reineke W. and Knackmuss H-J, 1984). In the presence of oxygen or other strong oxidants, reactions of the oxidant ( $O_2$ ) with chlorohydroxycyclohexadienyl radical is predominant and results in lower concentrations of dichlorobiphenyl, which decreases remarkably, and chlorobenzoquinone is formed. Chlorophenol isomers were further oxidized by hydroxyl radical and formed chlorinated and non-chlorinated diols. Chlorobenzenes were also dechlorinated by the UV/ $H_2O_2$  treatment method (Sundstrom *et al.*, 1989), and chlorobenzene was degraded to phenol, biphenyl, chlorobiphenyl isomers, and benzaldehyde with only UV, and chlorobenzenes also transform to chlorophenol and various isomers of chlorobiphenyl and dichlorobiphenyl in the UV/ $H_2O_2$  system.

Degradation of chlorobenzenes in pyrite suspensions is shown in Fig. 6 and in Table 1, with four volatile species: mono-chlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene. The concentrations of these compounds were determined by headspace methods. The experiments were conducted at 25 °C at 200 rpm in the pyrite suspension under anaerobic conditions. The initial concentrations of chlorobenzenes were set to 10 mg/L using the each pure chlorobenzenes dissolved in hexane water. The initial rate of degradation is 1,2,4-trichlorobenzene > 1,2-dichlorobenzene > monochlorobenzene > 1,3-dichlorobenzene, and more than 90 % of these chlorobenzenes were dechlorinated after merely 10 days. The degraded amount of chlorobenzenes is not sensitive to differences in the distribution of their isomers. However, the amount of chloride ion arising from dechlorination of chlorobenzenes is less than the entire chlorine content from each of the chlorobenzenes. This disagreement in mass balance also shows less than one chloride ion degraded from each chlorobenzene. The order of total dechlorination ability is 1,2-dichlorobenzene > monochlorobenzene > 1,2,4-trichlorobenzene > 1,3-dichlorobenzene. Among the 4 species of chlorobenzenes estimated here, 1,3-dichlorobenzene is the hardest to degrade because it has a meta-site chloride configuration. The meta-site dechlorination is not easier than 1,2-(ortho) and 1,4-(para-) dichlorobenzenes.

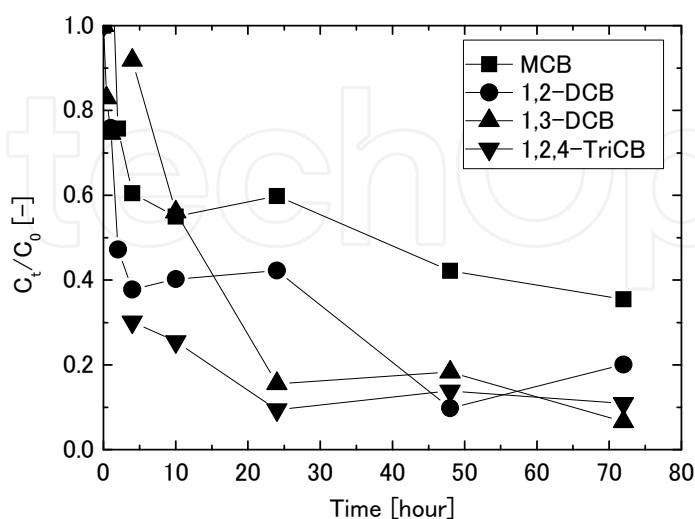


Fig. 6. Degradation of monochlorobenzene, 1,2- and 1,3-dichlorobenzene, and 1,2,4-trichlorobenzene in pyrite suspension under aerobic conditions.  $C_0$  is the initial concentration of chlorobenzenes (10 mg/L),  $C_t$  is the concentration of chlorobenzenes at time  $t$ .

species	$-\Delta C_{\text{CBs}}^t / C_{\text{CBs}}^0$ [mol%]	$+\Delta C_{\text{Cl}}^t / C_{\text{CBs}}^0$ [mol%]
MonoCB	88.1	76.5
1,2-DiCB	96.4	88.4
1,3-DiCB	89.1	56.6
1,2,4-TriCB	95.6	68.7

Table 1. The fraction of degraded chlorinated benzenes and chloride ion arising from chlorinated benzenes after 10 days.

Fig. 7 shows the ratio of the residual chlorinated chlorobenzenes relative to the degradation of all species of chlorinated benzenes by pyrite suspension. Table 2 is the fraction of dechlorinated chloride ion from each chlorobenzene and the initial chloride content of the chlorobenzenes. The volatile chlorinated benzenes, mono-, 1,2-di-, 1,3-di- and 1,2,4-trichlorobenzenes were analyzed by the headspace method in addition to solvent extraction analysis to determine their concentrations. The non-degraded volatile chlorobenzenes adsorbed on the pyrite surface are correctly estimated here. The reaction products were also analyzed by GC/MS after eluting in the organic solutions along with the other chlorinated benzenes.

The ratio of complete dechlorination is higher for low molecular weight chlorobenzenes, and 1,2-dichlorobenzene is easier to degrade than 1,3-dichlorobenzene. The greater electron deviation due to chlorine configuration allows the degradation of chlorobenzenes. More than 80 to 90 % of mono-, di-, tri-chlorobenzenes, and 1,2,3,4- and 1,2,3,5-tetrachlorobenzene are degraded from the original concentrations. These compounds are easy to degrade, but there is a small variation depending on chlorine configuration. The residual ratio is 1,2- < 1,3- < 1,4- among the dichlorobenzenes, and 1,2,3- < 1,2,4- < 1,3,5- among the trichlorobenzenes. There is a significant difference in dechlorination ability for the tetrachlorobenzene isomers. The symmetrical chlorine configuration, 1,2,4,5-, on the benzene ring is stable and hard to degrade, so 1,2,4,5-tetrachlorobenzene, tetra- and hexachlorobenzenes with the 1,2,4,5-chlorine configuration are extremely difficult to degrade. Considering the mass balance of persistent chlorobenzenes and chloride ions, di-, tri-, and tetra- (limited to 1,2,3,4- and 1,2,3,5-) chlorobenzenes are transformed into chlorinated intermediates because the detected concentration of chloride ion is only one mole of chloride ion per one mole of chlorobenzene and that corresponds to a decline of the initial concentration of each of the chlorobenzenes.

The GC/ MS analysis of the solvent-extracted samples after 10 days indicates the presence of one or more dechlorinated chlorobenzenes from the initial materials for each chlorobenzene, except for hexachlorobenzene. In the experimental dechlorination of hexachlorobenzene, pentachlorobenzene is detected after 10 days. Hexachlorobenzene is assumed to have a slow dechlorination rate so that a little of the compound could be detected. As an example of reaction products, Fig. 8 shows the analytical result of GC/MS and NMR analysis for the solvent extracted from the reaction system of monochlorobenzenes.  $C_9H_{14}(OH)Cl$ ,  $C_{13}H_{17}(OH)_3$ ,  $C_{16}H_{23}SO_2$  are detected by MS together with cyclic sulphur molecules such as  $S_6$ ,  $S_7$ ,  $S_8$ . The other saturated or unsaturated straight-chain hydrocarbons, such as 3-decyne ( $C_{10}H_{18}$ ), 8,10-dodecadienal ( $C_{12}H_{20}O$ ) and 2,2,6-trimethyl-1,4-cyclohexanedione ( $C_9H_{14}O_2$ ) are detected as one of the reaction

products of tri- to hexachlorobenzenes. The NMR spectrum also shows the alcohol, ether, and aromatic methyl peaks ( $-\text{CH}_2\text{OH}$ ,  $-\text{O}-$ ,  $-\text{COH}$ ,  $\text{C}_6\text{H}_6\text{-CH}_3$ ) with the benzene and chlorobenzene peaks. One part of the benzene ring structure is assumed to be opening in this reaction process.

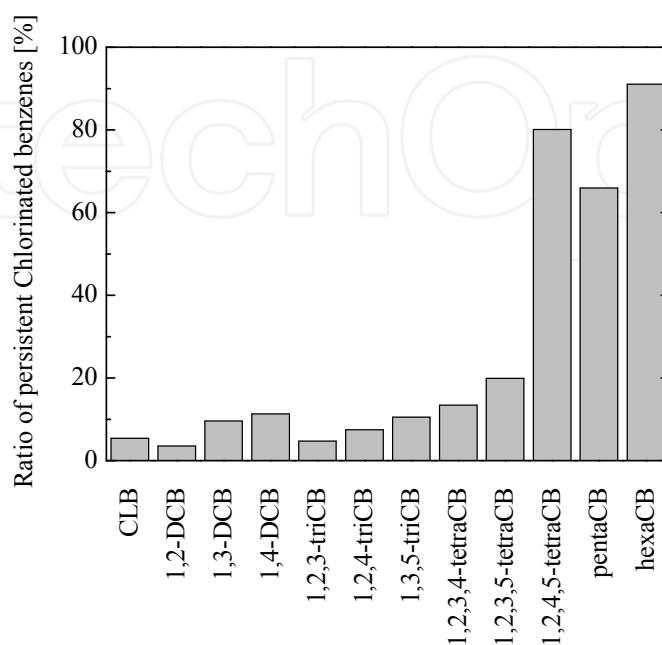


Fig. 7. Residual ratio of 12 species of chlorinated benzenes estimated under aerobic conditions in pyrite suspension after 10 days (Hara *et al.* (2006)).

species	$+\Delta\text{C}_{\text{Cl}}^t / \text{C}_{\text{Cl}}^0$ [mol%]
monochlorobenzene	89
1,2-dichlorobenzene	47
1,3-dichlorobenzene	45
1,4-dichlorobenzene	45
1,2,3-trichlorobenzene	30
1,2,4-trichlorobenzene	29
1,3,5-trichlorobenzene	30
1,2,3,4-tetrachlorobenzene	20
1,2,3,5-tetrachlorobenzene	18
1,2,4,5-tetrachlorobenzene	11
pentachlorobenzene	7.5
hexachlorobenzene	5.5

Table 2. The fraction of dechlorinated chloride ion from each chlorobenzene and initial chloride content of chlorobenzenes.

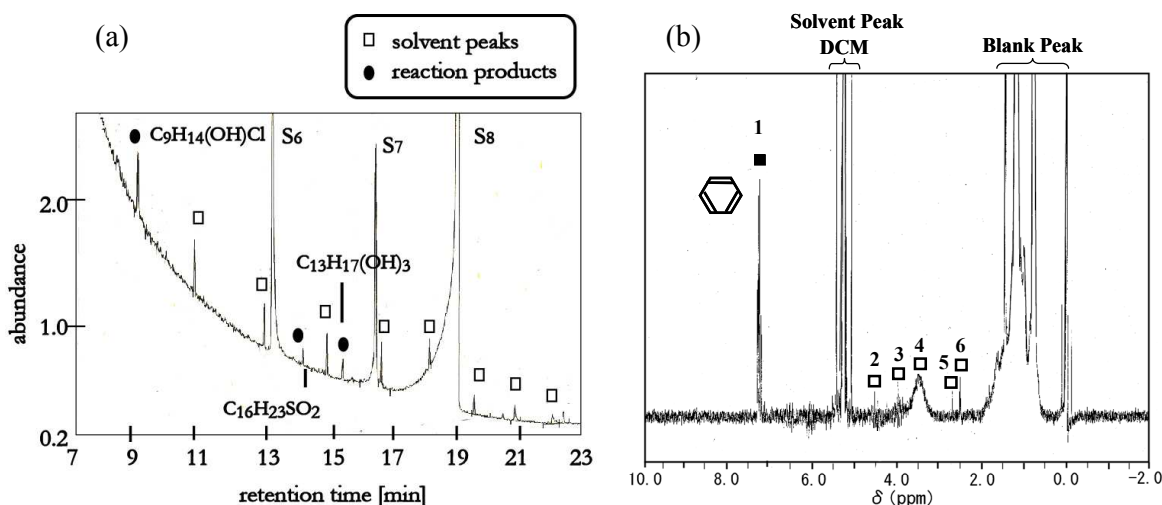


Fig. 8. The spectrum of reaction intermediates arising from transformation of monochlorobenzene in pyrite suspension. (a) MS spectrum. (b) MNR spectrum. In the NMR spectrum, 1. aromatic peak (benzene and monochlorobenzene), 2-4. alcohol and ether peak (-CH<sub>2</sub>OH, -O-, -COH), 5. aromatic methyl (methylbenzene).

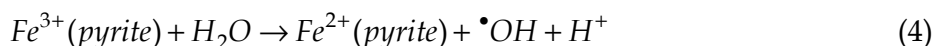
From the analytical results, the benzene ring could have been opened by the dechlorination process. One part of the benzene ring opened to straight chain unsaturated hydrocarbons and these hydrocarbons polymerized with other straight chain unsaturated hydrocarbons. Some polymerized straight chain hydrocarbons remain, and some hydrocarbons are combined with unsaturated ring structures. A ring-opening reaction of benzene is assumed to be a common reaction for every chlorobenzene under our experimental conditions, not only turning into cyclohexanes. These reactions are initiated when one chlorine site is dechlorinated by pyrite. Therefore, at least one mole of chlorine ions was dissolved in solution for every mole of chlorinated benzene molecules that reacted with pyrite. Furthermore, non-detected chlorine ions may still bind the carbon atoms that are produced by this reaction.

The reactions are proceeded by the oxidant arising on the pyrite interface. The polymerization and ring-opening reactions are similar to the dechlorination of Dieldrin under anaerobic conditions.

#### 4. Discussion

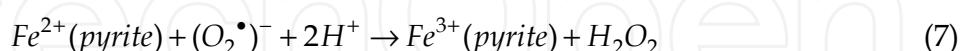
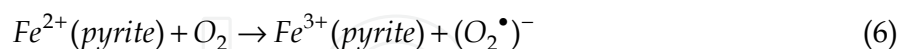
Pyrite suspension shows degradation ability predominantly for TCE, Dieldrin and chlorobenzenes as shown in Section 3. These degradations of chlorinated organic compounds are initiated by the oxidant arising from the pyrite interface reaction.

The surface reaction of pyrite/H<sub>2</sub>O and pyrite/O<sub>2</sub> produces the radical as follows (Cohn *et al.*, 2006). In the pyrite/H<sub>2</sub>O interface under non-oxygen conditions, H<sub>2</sub>O is hydrolysed to •OH and H<sup>+</sup> (Eq. (4) and Eq. (5))

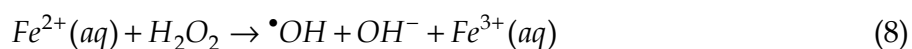


Commonly, the radical is apt to arise under aerobic conditions, but the hydroxyl radical can be generated under anaerobic conditions and it acts as an oxidant.

In the presence of oxygen (aerobic conditions), superoxide ( $O_2\bullet^-$ ) was detected as an intermediate from  $H_2O_2$  formation. The superoxide ( $O_2\bullet^-$ ) is generated by the oxidation of iron on the pyrite surface as follows:



The reactions of the pyrite/ $O_2$  interface generate hydroxyl radicals from hydrogen peroxide by the oxidation of surface iron (Eq. (6) and Eq. (7)), and hydrogen peroxide is also used for the reduction of ferric to ferrous ion in the reaction shown in Eq. (8). However, the hydroxyl radicals are not noticeably produced under aerobic condition.



Under aerobic conditions, superoxide and hydrogen peroxide are dominant oxidants used for degradation of chlorinated organic compounds.

Although there is a difference in oxidative ability among oxidants, oxidants arise from the pyrite interface under both aerobic and anaerobic conditions. The hydroxyl radical has an oxidant ability superior to superoxide and hydrogen peroxide, but the total amount of ferrous ion on the pyrite surface is limited under anaerobic conditions; therefore, the total volume of the hydroxyl radical is also limited under anaerobic conditions as opposed to aerobic conditions. The difference between reaction products under aerobic and anaerobic conditions is caused by thus radical character of the pyrite interface.

The oxidation and polymerization of chlorinated organic compounds are caused by several radicals arising from the pyrite/ $H_2O$ , pyrite/ $O_2$  interface reaction.

## 5. Conclusion

This chapter reviews several remediation methods for chlorinated organic pollutants, and emphasizes the degradation ability of natural ferric sulphide (pyrite) for TCE, Dieldrin and chlorobenzenes. The transformation of TCE and Dieldrin under aerobic conditions becomes clear and the main reaction product is formic acid, which continuously degrades to  $CO_2$ . Although the 1,2,4,5-chloride configuration in the chlorobenzene and benzene ring structure is hard to degrade, one part of the benzene ring is transformed into several hydrocarbons.

The oxidative reaction of the pyrite suspension has great degradative ability not only for low molecular weight organic pollutants such as VOCs but also for high molecular weight persistent organic compounds with a stable benzene ring and bicyclic rings. Natural ferric sulphide has a remediation ability predominantly for chlorinated organic pollutants.

Iron and ferric sulphides (e.g., pyrite) are widely distributed in the subsurface layer in the global environment. The reductive degradation ability of iron and the oxidative degradation ability of ferric sulphides assist the innovative remediation techniques that are conducted at in situ normal temperature and pressure. The ferric ion and ferric sulphide latent in natural systems have a potential for natural attenuation of contamination.



Pyrite is also widely distributed at mining sites and soils in coastal regions of the Asian and the Pacific areas located in tropical, subtropical and temperate climate areas. For instance, the Mekong Delta in Vietnam is a vast acidic sulphate soil region that includes metallic sulphide. Garvalho *et al.* (2008) reported the agrochemical and polychlorobiphenyl residues in the Mekong River Delta. Several chlorinated compounds, such as DDT, HCH (hexachlorocyclohexane), PCBs and endosulfan were detected in sediment and biota. However, the concentrations of PCBs and pesticide residues in the aquatic environment in the Mekong River Delta are lower than the values reported in other regions of Vietnam and Asia. The aquatic environment of the Mekong Delta is endowed with natural ferric sulphide and water, and consequently the natural environment in this region is assumed to enhance PCB degradation. The acidic sulphate soils distributed in coastal area assumes to actually attenuate the contamination of chlorinated organic compound and prevent the expansion of pollution.

## 6. Acknowledgments

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## **Organic Pollutants Ten Years After the Stockholm Convention - Environmental and Analytical Update**

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Ten years after coming into force of the Stockholm Convention on Persistent Organic Pollutants (POPs), a wide range of organic chemicals (industrial formulations, plant protection products, pharmaceuticals and personal care products, etc.) still poses the highest priority environmental hazard. The broadening of knowledge of organic pollutants (OPs) environmental fate and effects, as well as the decontamination techniques, is accompanied by an increase in significance of certain pollution sources (e.g. sewage sludge and dredged sediments application, textile industry), associated with a potential generation of new dangers for humans and natural ecosystems. The present book addresses these aspects, especially in the light of Organic Pollutants risk assessment as well as the practical application of novel analytical methods and techniques for removing OPs from the environment. Providing analytical and environmental update, this contribution can be particularly valuable for engineers and environmental scientists.

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