# **USING LOW-COST IRON BYPRODUCTS FROM AUTOMOTIVE MANUFACTURING TO REMEDIATE DDT**

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**Abstract.** Water, soil and sediment contaminated with DDT poses a threat to the environment and human health. Previous studies have shown that zerovalent iron (ZVI) can effectively remediate water contaminated with pesticides like DDT, metolachlor, alachlor. Because the type of iron can significantly influence the efficiency and expense of ZVI technology, finding a cheaper and easily available iron source is one way of making this technology more affordable for field application. This study determined the effects of iron source, solution pH, and presence of Fe or Al salts on the destruction of DDT. Batch experiments demonstrated successful removal of DDT  $(>95\%$  in 30 d) in aqueous solutions by three different iron sources with the following order of removal rates: untreated iron byproduct  $(1.524 d^{-1})$  > commercial ZVI  $(0.277 d^{-1})$  > surface-cleaned iron byproduct  $(0.157 d^{-1})$ . DDT removal rate was greatest with the untreated iron byproduct because of its high carbon content resulted in high DDT adsorption. DDT destruction rate by surface-cleaned iron byproduct increased as the pH decreased from 9 to 3. Lowering solution pH removes Fe (III) passivating layers from the ZVI and makes it free for reductive transformations. By treating DDT aqueous solutions with surfacecleaned iron byproduct, the destruction kinetics of DDT were enhanced when Fe(II), Fe(III) or Al(III) salts were added, with the following order of destruction kinetics: Al(III) sulfate  $>$  Fe(III) sulfate  $>$ Fe(II) sulfate. Cost analysis showed that the cost for one kg of surface-cleaned iron byproduct was \$12.33, which is less expensive than the commercial ZVI. Therefore, using surface-cleaned iron byproduct may be a viable alternative for remediating DDT-contaminated environments.

**Keywords:** zerovalent iron, remediation, organochlorine pesticides, DDT, sulfate salts

### **1. Introduction**

DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane] is a pesticide once widely used to control insects in agriculture and health proposes. Due to its persistence and lipophilic nature, DDT tends to bioaccumulate in flora and fauna, and was therefore banned in many countries in the early 1970s (USEPA, 1980; Bolt and Degen, 2002). Although banned in Thailand in 1994, DDT has been detected in surface and ground water in central and northeastern Thailand (Sakulthiengtrong *et al*., 2002). In 2005, the pesticide research division (department of agriculture, Thailand) reported that many rivers in Thailand were contaminated with persistent

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organic pollutant (POP) pesticides. More than a half of water and sediment samples collected from the major rivers around the agricultural areas were contaminated with DDT, endosulfan, dieldrin, aldrin, heptachlor, dicofol, hexachlorocyclohexane (BHC), endrin, and chlordane. Residue concentrations of DDT and other POPs in water and sediments ranged from  $0.01-1.20 \mu g L^{-1}$ , and  $0.01-7.43 \text{ mg kg}^{-1}$ , respectively (Hungtrakul *et al*., 2005).

Many pesticides normally considered persistent in aerobic environments are not as persistent under anaerobic conditions (Comfort *et al*., 2001). Thus, generating a reduced (electron-rich) environment in soils, sediments, and aquifers has recently become a popular remediation approach. One example of this type of technology uses zerovalent iron (ZVI) as a chemical reductant. Under aerobic conditions, oxygen is the usual electron acceptor, while in anoxic environments, electron release from the reaction of ZVI with water can be coupled to the reaction of chlorinated and nitroaromatic compound (Gillham and O'Hannesin, 1994). Treatment with ZVI can promote rapid abiotic degradation via reductive dechlorination. When halogonated organic pollutant is treated with ZVI, oxidation of ZVI and Fe(II) provides electrons for dechlorination:

$$
\text{Fe}^{0} + \text{R-C1} + \text{H}^{+} \rightarrow \text{Fe}^{2+} + \text{R-H} + \text{Cl}^{-} \tag{1}
$$

$$
\text{Fe}^{2+} + \text{R-C1} + \text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + \text{R-H} + \text{OH}^- + \text{Cl}^- \tag{2}
$$

ZVI has been successfully used to transform several halogenated organic compounds (Gillham and O'Hannesin, 1994; Eykholt and Davenport, 1998; Satapanajaru *et al*., 2003a), such as atrazine (Singh *et al*., 1998), nitroaromatics (Agrawal and Tratnyek, 1996; Park *et al*., 2004), nitrates (Till *et al*., 1998; Huang *et al*., 2003), and metals (Blowes *et al*., 1997; Fiedot *et al*., 1998). Sayles *et al*. (1997) found that zerovalent iron successfully dechlorinated DDT and its derivatives, DDD [1,1,1-dichloro-2,2-bis(4-chlorophenyl) ethane] and DDE [2,2-bis (4 chlorophenyl) ethane].

Manipulating the  $Fe<sup>0</sup>$ -soil-water system by adding various electrolytes and optimizing pH has also been shown to increase ZVI's effectiveness (Satapanajaru *et al*., 2003a). The type or source of iron can significantly influence the efficiency and cost of the ZVI technology. Thus, finding a cheaper and easily available iron source is one way of making ZVI technology more affordable for field applications. Because ZVI can be obtained in bulk as an industrial byproduct, this technology has the potential to be cost-effective, efficient and environmentally safe method for remediating DDT contaminated water, soil and sediment.

One difficulty in treating DDT is its extremely low water solubility. DDT, DDD and DDE have low water solubility of  $3 \mu g L^{-1}$ ,  $160 \mu g L^{-1}$ , and  $40 \mu g L^{-1}$  respectively (Sayles *et al*., 1997), so DDT and its derivatives are retained to a greater degree by soil and sediment (WHO, 1989). Increasing the concentration of contaminant in solution is usually desirable for efficient remediation. Previous studies have shown that surfactants increase the aqueous solution concentration of hydrophobic

organic compounds by partitioning the solute into the hydrophobic interior of micelles when surfactant concentrations are above the critical micelle concentration (Kile and Chiou, 1989; Park *et al*., 2005). You *et al.* (1996) indicated that Triton X-114, an alkylphenol ethoxylate, increases the apparent solubility of DDT and consequently, enhances its anaerobic degradation.

Our objective was to quantify the effectiveness of different ZVI sources to degrade high concentrations of DDT in aqueous solutions in the presence of surfactant Triton X-100. We also determined the effects of iron and aluminum salts on DDT degradation kinetics by surface-cleaned iron byproduct of automotive industry. We used a pH-stat to determine the optimum pH for DDT degradation.

# **2. Materials and Methods**

# 2.1. MATERIALS

DDT [1,1,1-trichloro-2,2-bis(4-chlorophenyl) ethane] was obtained from Chem Service (West Chester, PA). Ferrous sulfate  $[FeSO<sub>4</sub>·7H<sub>2</sub>O]$ , ferric sulfate  $[Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>·2H<sub>2</sub>O]$ , aluminum sulfate  $[Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>]$ , and TritonX-100 were purchased from Aldrich Chemical Co. (Milwaukee, WI). We used two sources of  $Fe<sup>0</sup>$  in our experiments: commercial zerovalent iron (ZVI) and iron by product from automotive spare parts industry. Commercial ZVI was obtained from Safe and Science Company (Bangkok, Thailand). The second source of iron was the byproduct of the machining processes (milling and drilling processes) of steel used to make spare parts of automobiles and motorcycles.

## 2.2. MORPHOLOGY OF IRON BYPRODUCT

Iron byproduct was screened through a sieve (dia.  $\lt 1$  mm) prior to use. The iron surface was cleaned by washing in analytical grade hexane and heating at  $500\degree$ C in a furnance (Thermolyne 48000 series) for 2 h. The surface morphology of the iron sources was compared by mounting with carbon tabs, sputtercoating with gold-palladium, and observing with a Jeol JSM-5600LV scanning electron microscope (SEM) operated at 15 KV connected with electron dispersive X-ray (EDX). EDX was used to quantify  $%$  Fe and  $%$  C in the iron sources. A quantitative analysis was conducted by standardless analysis. A standardless analysis quantifies Fe and C by calculating the area under the peak of each identified element and after taking account for the accelerating voltage of the beam to produce the spectrum, performs calculations to create sensitivity factors that converts the area under the peak into atomic percent. The surface area of iron sources was determined by BET surface area analyzer, (Micromeritics, FlowSorb II 2300, Norgross, GA).

### 2.3. BATCH EXPERIMENTS

An aqueous phase experiment was conducted to compare the efficacy of various ZVI sources to degrade DDT. The iron sources were: commercial ZVI, iron byproducts from automotive spare parts industry, and surface-cleaned iron from automotive spare parts industry. The initial DDT concentration was  $5 \text{ mg } L^{-1}$ . This DDT concentration was representative of the concentration released with surfactant from the DDT-contaminated sediment. Preliminary experiment was conducted to find the optimal amount of surfactant Triton X-100 required to dissolve 5 mg  $L^{-1}$ . Five mg of DDT was dissolved in one liter of deionized water with 1, 2, 3, 4 and 5% (w/v) of Triton X-100. The results indicated that DDT (5 mgL<sup>-1</sup>) was completely dissolved by 3, 4 and 5% Triton X-100 in aqueous solution.

Aqueous solution of 5 mg L<sup>-1</sup> DDT was prepared in deionized water with 3% (v/v) of Triton X-100. Batch procedures included treating 150 mL of aqueous DDT with 5% (w/v) of three different iron sources in 250 mL Erlenmeyer flasks. Flasks were covered with Parafilm M (American National Can, Chicago, IL) and agitated on an orbital shaker at 150 rpm in ambient temperature. The experiments were performed in triplicate. DDT concentration was measured in samples at preselected times. Eh/pH was also monitored in each treatment. A combination redox probe was used to monitor temporal changes in Eh, while pH was measure by pH meter (Fisher Scientific Model AR-15). Redox measurements were converted to a standard hydrogen electrode (SHE) reference by adding 200 mV to observed values (Light, 1972). After one month of shaking experimental units, iron was removed from flasks into 50 mL Teflon tubes. Fifty mL of hexane was then added to the tubes with no headspace. DDT adsorbed on iron particles was extracted by hexane with the aid of a sonic disruptor. The sonic disruptor bombarded iron with sonic waves, facilitating the transfer of DDT into hexane. After 12 h, the aliquots were removed and transferred to 1.5 mL GC bottles for GC analysis.

#### 2.4. EFFECTS OF PH AND SALTS

An experiment was conducted to optimize pH desired for ZVI treatment of DDTcontaminated water. We used a pH-stat apparatus (Metrohm Titrino 718S; Brinkman Instruments, Westbury, NY) to control the pH in the ZVI-DDT matrix. A single treatment consisting of 5% (w/v) ZVI (surface-cleaned iron byproduct) was used. The ZVI-DDT solutions were maintained at pH 3, 7 and 9. Acidic pH was adjusted by 0.1 *N* HNO3 while basic pH was adjusted by 0.2 *N* NaOH. Temporal changes in DDT concentration were measured in samples at preselected times for 1 month.

An experiment was conducted to determine the capacity of ZVI to degrade DDT in the presence of iron and aluminum salts. Aqueous DDT (5 mg L<sup>−</sup>1) was treated with 5% (w/v) ZVI (surface-cleaned iron byproduct) and equal concentrations of FeSO<sub>4</sub>, Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, or Al<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> [0.5% (w/v)]. All treatments were conduced in triplicate. Changes in DDT concentration were measured for 1 month. Eh and pH was monitored in each treatment. On 30th day of experiment, Fe(II) concentration was measured by the Ferrozine method (Stookey, 1970). One hundred  $\mu$ L of sample was added to 50 mL DI water in 125 mL flask. One mL of Ferrozine solution [5.14 g ferrozine, 100 g of hydroxylamine hydrochloride in 500 mL HCl and diluted to 1 L] was added. Sample was heated and held at boiling point for 10 min. After cooling, 49 mL of sample was transferred to 50 mL volumetric flask and 1 mL of buffer solution [400 g ammonium acetate in 350 mL of ammoniumhydroxide, and dilute to 1 L with DI water] was added. After 10 min, sample was measured by UV spectrophotometer at 562 nm.

# 2.5. SAMPLE PREPARATION AND ANALYSIS OF DDT

At preselected times, multiple 1.2 mL aliquots were removed and transferred to 1.5 mL polypropylene microcentrifuge tubes, centrifuged at  $13000 \times g$  for 10 min, and then the aliquots were transferred to 5 mL glass vials. Two mL GC grade hexane was added to glass vials to extract DDT from water. The solutions were then leached through anhydrous sodium sulfate  $[Na_2(SO_4)]$  column. The samples were analyzed by gas chromatograph (GC) (Hewlett Packard, Model HP6890 series) equipped with electron capture detector (ECD), and 30-m fused silica capillary column. Nitrogen was the carrier gas with a flow rate of 1 mL min<sup>−</sup>1. Injection was set at splitless mode. Injection port and detector temperature were 240 and 300 ◦C, respectively. The DDT determination method was adapted from US EPA Method 8080A (US EPA, 1994).

# **3. Results and Discussion**

# 3.1. EFFECTS OF IRON SOURCES

We determined the feasibility of using iron byproduct to remediate DDT in aqueous solutions. The specific surface area,  $\%$  Fe and  $\%$  C of different Fe<sup>0</sup> sources are shown in Table I. The results showed that specific surface area and % Fe were lower in low cost iron waste as compared to commercial ZVI. Percent C determined by EDX analysis was about 10 times higher in iron byproduct than the commercial ZVI. Higher C content mainly came from the oil and grease associated with the milling equipment. This higher % C on the surface of iron waste may result in DDT adsorption. Thus, the surface of low cost iron byproduct was cleaned by washing with hexane and heating at 500 °C. Cleaning the surface of iron waste resulted in removal of 96% of C and thus could help in decreasing DDT adsorption on surface of iron byproduct. SEM photos in Figure 1 revealed a sharp contrast between rough surface of untreated iron byproduct and smooth surface of surface-cleaned iron byproduct. The smooth surface of surface-cleaned iron byproduct probably resulted from the high temperature treatment. Gaber *et al*. (2002) indicated that

### TABLE I

% Fe, % C, and specific surface area of different sources of zerovalent iron



 $\mathbf B$ 

A



*Figure 1*. Scanning electron microscope photos of iron byproduct of automotive industry (A)  $\times$  35 & (B)  $\times$  450, and surface-cleaned iron byproduct (C)  $\times$  35 & (D)  $\times$  450.

annealed iron (heated the iron under a hydrogen and nitrogen atmosphere) with smooth surface can be more resistant to corrosion in aqueous solution. This unique quality protects the surface of ZVI from being coated with iron oxides.

Treating aqueous solutions of DDT with 5% (w/v) zerovalent iron revealed that DDT removal rates were significantly different ( $\alpha = 0.5$ ) among iron sources

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TABLE II

Types of ZVI	DDT Conc. $(mgL^{-1})$
Commercial ZVI	0.53
Iron byproduct of automotive industry	2.95
Surface-cleaned iron byproduct of automotive industry	0.85
9	
8	
5% commercial ZVI 7 5% Iron by product С	
필 5% Surface cleaned iron byproduct Control ▽	
6	
5	
4	
600	
400	
200	
$\mathbf{0}$	
Eh (mV vs. SHE)	
$-200$	
$-400$	
5 15 20 10 25 30 $\mathbf{0}$	5 15 10

*Figure 2*. Degradation of DDT, formation of DDD by 5% (w/v) commercial ZVI, iron byproduct and surface-cleaned iron waste byproduct and pH/Eh of each treatment.

(Figure 2). Although nearly 100% removal of DDT occurred from solution with the various zerovalent iron treatments, mass balance studies showed a 60% recovery of DDD as dechlorination product from the commercial zerovalent iron but only 20% recovery of DDD from the untreated iron byproduct. Sixty percent recovery of dechlorinated product (DDD) was observed after treating DDT with surfacecleaned iron byproduct. There likely was some adsorption of DDT on the iron surface that resulted in lower recovery of dechlorinated products. After 30 days of treatment, the samples were extracted with hexane to remove any adsorbed DDT (Table II). About 60% DDT was recoverd in the treatment of DDT with untreated iron byproduct whereas only 11% and 17% was recovered in commercial ZVI and surface-cleaned iron byproduct treatments, respectively (Table II). It shows that higher % C in untreated iron byproduct resulted in higher adsorption of DDT on the surface of untreated iron byproduct as compared to commercial ZVI and surface-cleaned iron byproduct.

As adsorption phenomenon in the untreated iron byproduct treatment affected the degradation kinetic rate, we reported the rates of decreasing DDT concentration as DDT removal rate. DDT removal rate for the untreated iron byproduct was 1.524 d<sup>−</sup>1. For commercial ZVI and surface-cleaned iron treatments, first order DDT degradation kinetic rates  $(k_{obs})$  were observed as:

$$
-\frac{d[DDT]}{dt} = k_{\text{obs}}[DDT]
$$

The degradation kinetic rates ( $k_{obs}$ ) were 0.277 d<sup>-1</sup> for commercial ZVI, and 0.157  $d^{-1}$  for the surface-cleaned iron byproduct. For comparison, degradation kinetic rates can be normalized by the specific surface area of iron. The specific surface area for 50 g L<sup>-1</sup> iron (5% w/v) of this commercial ZVI and surface-cleaned iron byproduct were 22.5 and 17.5 m<sup>2</sup> L<sup>-1</sup>, respectively. ( $k_{obs}$ ) = ( $k_{SA}$ ) $\rho_a$ , where  $k_{SA}$  is the specific reaction rate constant (L m<sup>-2</sup>h<sup>-1</sup>), and  $\rho_a$  is the surface area concentration of ZVI (m2 L<sup>−</sup>1) (Johnson *et al*., 1996). Specific first-order rates were 0.00051 and 0.00037 L m<sup>-2</sup> h<sup>-1</sup> for commercial ZVI and surface-cleaned iron, respectively. Sayles *et al*. (1997) reported that specific first-order rate of DDT dechlorination by Fe<sup>0</sup> with Triton X-114 surfactants was  $0.029 \pm 0.008$  L m<sup>-2</sup>h<sup>-1</sup>. Comparing  $k_{SA}$  from our experiment with rates from Sayles *et al.* (1997) revealed large difference among iron sources. These differences may be attributed to the high purity of iron used by Sayles *et al*. (1997) (99.9% purity) and the lower purity of iron byproduct (69.2% purity) used in our experiment.

DDT degradation products were analysed at the preselected times. DDD[1,1,1-dichloro-2,2-bis(p-chloro-phenyl) ethane] was the major degradation product. We also found small amount of DDE [2,2'-bis(p-chloro-phenyl)-(1,1'dichloroethylene)], DDMS [2,2-bis (p-chlorophenyl) 1 chloroethane] and DDMU [1-chloro-2,2 bis (p-chlorophenyl)-ethylene]. From the metabolic pathway of DDT proposed by Quensen *et al*. (2001), DDD is the main product from the reductive dechlorination of DDT, especially, under anaerobic conditions. The redox potentials in our treatments were between  $-78$  and  $-350$  mV (SHE) (Figure 2), which were low enough to make treatment system highly anaerobic. In addition, losses of DDD were found in the system after 5 days because DDD can be potentially degraded to DDMS by ZVI under the similar conditions. Sayles *et al*. (1997) assumed that DDD was transformed to DDMS or other products, but not DDMU. This assumption was proved by Eggen and Majchercyzk (2006). They found that the increase in DDMU was related to the decrease in DDE. Small amounts of DDE and DDMU were also found in our treatment. DDE was actually an impurity in DDT formulation, which could be transformed to DDMU by ZVI.

The untreated iron byproduct removed most of DDT by adsorption but washing the iron byproduct with hexane effectively degraded DDT to DDD and other degradation products. Although commercial ZVI degraded DDT more quickly, surface-cleaned iron waste was also successful in degrading >95% DDT within 30 days.

## 3.2. EFFECTS OF PH

An additional experiment was conducted using surface-cleaned iron byproduct to study the effect of pH on DDT degradation. Using a pH-stat, we controlled the pH of the surface-cleaned iron waste treatment. DDT destruction rate constant  $(k_{obs})$ increased as the pH decreased from 9 to 3 (Figure 3). Destruction kinetic rates were 0.704 d<sup>-1</sup> for pH 3, 0.107 d<sup>-1</sup> for pH 7 and 0.034 d<sup>-1</sup> for pH 9. Slower destruction kinetics with increasing pH has previously been observed while treating metolachlor (Satapanajaru *et al*., 2003a), nitrite (Alowitz and Scherer, 2002) or nitrate (Huang *et al*., 2003) with ZVI. Several factors may explain this trend. One is the formation of secondary reductants (Fe(II) or Fe(II)-containing oxides and hydroxides) on



*Figure 3.* Degradation of DDT and formation of DDD with 5% (w/v) surface-cleaned iron byproduct under constant pH.

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the surface of ZVI (Alowitz and Scherer, 2002). Various iron (hydr)oxides such as goethite formed at high pH passivate the iron surface (Satapanajaru, *et al*., 2003a,b). This hinders the access of contaminant molecules to the ZVI surface (Dombek *et al*., 2001). Low pH would remove these passivating layers from ZVI core and render it free for reaction with the halogenated molecules (Satapanajaru*, et al*., 2003a; Dombek *et al*., 2001).

### 3.3. EFFECTS OF FE AND AL SULFATE SALTS

DDT degradation rate constants  $(k_{obs})$  were enhanced when Fe(II), Fe(III) or Al(III) salts were added, with the following order of destruction kinetics: Al(III) sulfate > Fe(III) sulfate > Fe(II) sulfate (Table III, Figure 4). Past research has shown that high concentration of salts can slow passivation by moving the reaction products away from ZVI surface (Farrell *et al*., 2000). This same trend was observed by Satapanajaru *et al*. (2003a) while treating metolachlor with ZVI and various catalytic salts. Moreover, availability of Al(III), Fe(II) and Fe(III) during ZVI oxidation facilitates incorporation into the oxidized Fe structure (Huang *et al*., 2003; Schwertman and Cornell, 1991) and results in release of Fe(II) into bulk solution. At 30 days, we determined the Fe(II) concentration in each treatment. High concentration of Fe(II) was found in the treatments where sulfate salts were added. The Fe(II) concentration was  $1023 \text{ mgL}^{-1}$  in ferrous sulfate treatment, 1290 mgL<sup>−</sup><sup>1</sup> in ferric sulfate treatment and 1810 mgL<sup>−</sup><sup>1</sup> in aluminum sulfate treatment. By comparison, Fe(II) concentrations were between 98 and 202 mgL<sup> $-1$ </sup> in the treatment with no salts. This supports that availability of Al(III), Fe(II) and Fe(III) during ZVI oxidation results in increasing Fe(II) in the DDT treatment system thus favoring the DDT degradation kinetics. The role of Fe(II) on the mineral surfaces has environmental significance because surface-

TABLE III	

Comparison on the degradation rate constant of DDT Degradation by surface-cleaned iron byproduct augmented with iron or aluminum salts





*Figure 4*. Degradation of DDT, formation of DDD by 5% (w/v) surface-cleaned iron byproduct and Fe and Al salts and Eh/pH of each treatment.

bound Fe(II) has been shown to be an important reductant in the transformation of chlorinated and nitrogenated contaminants (Klausen *et al*., 1995; Amonette *et al*., 2000, Gregory *et al*., 2004). Moreover, it is likely that salts can lower the pH (Figure 4) in the ZVI-DDT-aqueous system. Lowering solution pH might cause faster disappearance of ZVI and hence decrease the ZVI surface concentration and increased Fe(II) in the remediation system.

# 3.4. COST ANALYSIS

Our results have proved that surface-cleaned iron byproduct was successful for DDT removal in aqueous phase in the presence of surfactant. However, another important factor in evaluating ZVI remediation technology is cost. Although factoring in labor, capital outlays and equipment depreciation is complicated, listing chemical expenditures per mass of pollutant treated is relatively straightforward (Comfort *et al.,* 2001). Given that the equal mass of DDT was treated with the same amount of different iron sources, with no treatment time required, the only factor affecting the treatment cost is the price of iron. We calculated the cost of pretreated iron (surfacecleaned iron) as: iron byproduct (\$0.5/kg), hexane AR grade from JT Baker (\$11.56 per L) and energy cost (\$0.0747 per Killowat (KW)-hour (Metropolitan Electricity Authority, Bangkok, Thailand). In our treatment, iron byproduct was heated by a

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Furnance Thermolyne 48000 series/1650 Watt for 2 h. The total cost for 1 kg of pretreated iron byproduct was \$12.33 [\$0.5 + \$11.56 + \$0.2651 (\$0.0747 / KWh.  $\times$  1.65 KW  $\times$  2 h)]. The commercial ZVI, purchased from Safe and Science company, Thailand, costed \$100 per kg. Moreover, it costs \$158 per kg for granular iron if ordered from Aldrich, USA. The electronically produced ZVI (Sayles *et al*. (1997) used for DDT degradation) from Fisher Scientific Company, USA is \$252 per kg. We acknowledge that bulk pricing could be far less expensive. Nonetheless, purchasing the byproduct iron from the automotive industry is clearly a cheaper alternative.

# **4. Conclusions**

Our results indicate that low-cost surface-cleaned iron byproduct can be successfully used to remediate water contaminated with organochlorine pesticides like DDT. Surface-cleaned iron byproduct was successful in removing  $>95\%$  DDT within 30 days. Lowering the pH from 9 to 3 increased the destruction kinetic rates of DDT by surface-cleaned iron byproduct. Moreover, sulfate salts of Fe(II), Fe(III) and Al(III) can successfully increase destruction of DDT, DDD and DDE by lowcost surface-cleaned iron that is a byproduct of automotive industry. In addition, cost of surface-cleaned iron byproduct is much less than that of other commercial ZVI and it is easily available. Contrasting results in destruction rates due to iron sources, pH, and the effects of surrounding electrolytes indicated that the mineralogy on the iron surface must be considered to accurately predict reaction rates. Results from this study can be applied to remediate DDT-contaminated sediments in the field. Using industrial wastes byproducts as iron sources may offer a more cost-effective, efficient and environmentally safe means of remediating contaminated sites with organochlorine pesticides like DDT and other organic pollutants.

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#### **References**

Agrawal, A., & Tratnyek, P.G. (1996). Reduction of nitro aromatic compounds by zerovalent iron metal. *Environmental Science and Technology*, *30*, 153–160.

- Alowitz, M.J., & Scherer, M.M. (2002). Kinetics of nitrate, nitrite and Cr(VI) reduction by iron metal. *Environmental Science and Technology*, *36*, 299–306.
- Amonette, J.E., Workman, D.J., & Kennedy, D.W. (2000). Dechlorination of carbon tetrachloride by Fe(II) associated with goethite. *Environmental Science and Technology*, *34*, 4606–4613.
- Blowes, D.W., Ptacek, C.J., & Jabor, J.L. (1997). In situ remediation of Cr(VI)-contaminated groundwater using permeale reactive walls: Laboratory studies. *Environmental Science and Technology*, *31*, 3348–3357.
- Bolt, H.M., & Degen, G.H. (2002). Comparative assessment of endocrine modulators with oestrogenic activity. II Persistent organochlorine pollutants. *Archives of Toxicology*, *76*, 187–193.
- Comfort, S.D., Shea, P.J., Machacek, T.A., Gaber, H., & Oh B.-T. (2001). Field scale remediation of a metolachlor-contaminated spill site using zerovalent iron. *Journal of Environmental Quality*, *30*, 1636–1643.
- Dombek, T., Dolan, F., Schultz, J., & Klarup, D. (2001). Rapid reductive dechlorination of atrazine by zero-valent iron under acidic conditions. *Environmental Pollution*, *111*, 21–27.
- Eggen, T., & Majcherczyk, A. (2006). Effects of zero-valent iron  $(Fe<sup>0</sup>)$  and temperature on the transformation of DDT and its metabolites in lake sediment. *Chemosphere*, *62*, 1116–1125.
- Eykholt, G.R., & Davenport, D.T. (1998). Dechlorination of the chloroacetanilide herbicide alachlor and metolachlor by iron metal. *Environmental Science and Technology*, *32*, 1481–1487.
- Farrell, J., Kason, M., Melitas, N., & Li, T. (2002). Investigation of the long-term performance of zero-valent iron for reductive dechlorination of trichloroethylene. *Environmental Science and Technology*, *34*, 514–521.
- Fiedor, J.N., Bostick, W.D., Jarabek, R.J., & Farrel, J. (1998). Understanding the mechanism of uranium removal from groundwater by zero-valent iron using X-ray photoelectron spectroscopy. *Environmental Science and Technology*, *32*, 1466–1473.
- Gaber, H.M., Comfort, S.D., Shea, P.J., & Machacek, T.A. (2002). Metolachlor dechlorination by zerovalent iron during unsaturated transport. *Journal of Environmental Quality*, *31*, 62–969.
- Gillham, R.W., & O'Hannesin, S.F. (1994). Enhanced degradation of halogenated aliphatics by zerovalent iron. *Groundwater*, *32*, 958–967.
- Gregory, K.B., Larese-Casanova, P., Parkin, G.F., & Scherer, M.M. (2004). Abiotic transformation of hexahydro-1,3, 5-trinitro-1,3,5-triazine by FeII bound to magnetite. *Environmental Science and Technology*, *38*, 1408–1414.
- Hongtrakul, T., Chulintorn, P., Thangnipon W., & Sakulthiengtrong, S. (2005). POPs pesticides in Thailand' abstract, UNU International Symposium on Ecosystem Impacts of POPs, Bangkok, Thailand April 26–27, 2005.
- Huang, Y.H., Zhang, T.C., Shea, P.J., & Comfort, S.D. (2003). Effects of oxide coating and selected cations on nitrate reduction by iron metal. *Journal of Environmental Quality*, *32*, 1306– 1315.
- Johnson, T.L., Scherer, M.M., & Trantnyek P.G. (1996). Kinetics of halogenated organic compound degradation by iron metal. *Environmental Science and Technology*, *30*, 2634–2640.
- Kile, D. E., & Chiou, C. T. (1989). Water solubility enhancements of DDT and TCB by some surfactants below and above the critical micelle concentration. *Environmental Science and Technology*, *23*, 832–838.
- Klausen, J., Trober, S.P., Haderlein, S.B., & Schwarzenbach, R.P. (1995). Reduction of substituted nitrobenzenes by Fe(II) in aqueous mineral suspensions. *Environmental Science and Technology*, *29*, 2396–2404.
- Light, T.S. (1972). Standard solution for redox potential measurement. *Analytical Chemistry*, *44*, 1038–1039.
- Park, J., Comfort, S.D., Shea, P.J., & Machacek, T.A. (2004). Remediaitng munitions-contaminated soil with zerovalent iron and cationic surfactants. *Journal of Environmental Quality*, *33*, 1305– 1313.

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- Park, J., Comfort, S.D., Shea, P.J., & Kim, J.S. (2005). Increasing Fe<sup>0</sup>-mediated HMX destruction in highly contaminated soil with didecyldimethylammoniumbromide surfactant. *Environmental Science and Technology*, *39*, 9683–9688.
- Quensen III, J.F., Tiedje, J.M., Jain, M.K., & Mueller, S.A. (2001). Factors controlling the rate of DDE to DDMU in Palos Verdes Margin under anaerobic condition. *Environmental Science and Technology*, *35*, 286–291.
- Sakulthiengtrong, S., Wesyanon, M., Baiadul, P., & Hruth-aithanasun, P. (2002). Contamination of hazardous materials in groundwater. Proceedings of 4th department of hazardous material conferences, Karbi, Thailand pp. 64–73.
- Satapanajaru, T., Comfort, S.D., & Shea, P.S. (2003a). Enhancing metolachlor destruction rates with aluminum and iron salts during zerovalent iron treatment. *Journal of Environmental Quality*, *32*, 1726–1734.
- Satapanajaru, T., Shea, P.J., Comfort, S.D., & Roh, Y. (2003b). Green rust and iron oxide formation influences metolachlor dechlorination during zerovalent iron treatment. *Environmental Science and Technology*, *37*, 5219–5227.
- Sayles, D.G., You, G., Wang, M., & Kupferle, M.J. (1997). DDT, DDD, and DDE dechlorination by zerovalent iron. *Environmental Science and Technology*, *31*, 3448–3454.
- Schwertmann, U., & Cornell, R.M. (1991).*Iron oxides in the laboratory*. New York: VCH Publication.
- Singh, J., Shea, P.J., Hundal, L.S., Comfort, S.D., Zhang, T.C., & Hage, D.S. (1998). Iron-enhanced remediation of water and soil containing atrazine. *Weed Science*, *46*, 381–388.
- Stookey, L.L. (1970). Ferrozine- a new spectrophotometric reagent for iron. *Analytical Chemistry*, *42*, 779–781.
- Till, B.A., Weathers, L.J., & Alvarez, P.J.J. (1998). Fe(0)-supported autotrophic denitrification. *Environmental Science and Technology*, *32*, 634–639.
- USEPA (United State Environmental Protection Agency). (1994). *Method 8080A: organochlorine pesticides and polychlorinated biphenyls by gas chromatography*. Washington, DC. USA: U.S. Environmental Protection Agency.
- USEPA (United State Environmental Protection Agency) (1980). *Ambient water quality criteria for DDT' EPA 440/5-80-038*. Washington, DC. USA: U.S. Environmental Protection Agency.
- WHO (World Health Organisation) (1989). *DDT and its derivatives: Environmental aspects*. Geneva, Switzerland: Environmental Health Criteria 83. WHO, pp. 6–11.
- You, G.R., Sayles, G.D., Kupferle, M.J., Kim, I.S., & Bisphop, P.L. (1996). Anaerobic DDT biotransformation:enhancement by application of surfactants and low oxidation reduction potential. *Chemosphere*, *32*, 226–2284.