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DEGRADATION OF DICHLORODIPHENYLTRICHLORO-ETHANE (DDT) USING ZERO-VALENT IRON

¹Josephine Q. Borja, ¹Lorraine M. Cangco, ¹Belinda Monica C. Chan, ¹Keith Timothy A. Chua, ¹Joseph Auresenia
¹Chemical Engineering Department, De La Salle University

Abstract. This study investigated the degradation of DDT in water matrix using micro-scale zero-valent iron (ZVI) in both non-emulsified and emulsified forms. A second metal, cobalt was added to ZVI. The initial concentration of DDT was varied at 10, 15, and 20 ppm. The effect of initial DDT concentration and ZVI loading on the extent of DDT degradation was determined using a full factorial design of experiment. All experimental runs were carried out at room temperature in batch mode, each batch lasting for 4 h. The initial pH of the test solutions was set at 2.0. The concentration of DDT was determined using GC-ECD. Results show that the non-emulsified metals performed better than their emulsified counterparts but was totally corroded compared to the emulsified variant which was partially corroded after 4 h of reaction. The highest amount of DDT degraded at 246.5 mg DDT per g metal per liter solution was achieved when the initial DDT concentration was 20 ppm using pure non-emulsified ZVI. Among the emulsified variants, the extent of DDT degradation was highest at 155.02 mg DDT per g metal per liter solution. This occurred when the initial DDT concentration was 15 ppm using pure ZVI. At this the extent of DDT degradation was almost the same for the non-emulsified and emulsified metals, in both cases, pure ZVI was used. Results also show that the addition of cobalt had minimal effect on the extent of DDT degradation. It was the initial concentration of DDT that exhibited significant effect. The kinetic study conducted showed that the non-emulsified variant of pure ZVI exhibited first order kinetics with a specific rate constant of 0.0192/min. All the other conditions resulted in second order kinetics.

Key words: zero valent iron; emulsified zero valent iron; DDT; bimetal ZVI

1. INTRODUCTION

Dichlorodiphenyltrichloroethane (DDT) is a stable organic compound that was introduced and manufactured on a large scale in 1942 as an agent to control the spread of Malaria during the World War II (Beard, 2006). Because of its remarkable insecticidal properties its use was extended to agriculture to combat a wide variety of insects. It became the most widely used pesticide for many years because of its stability and persistence of insecticidal action. However, these desirable characteristics of DDT have become the very reason for its negative impacts to the environment, animals and humans. It does not degrade under natural conditions and since it is lipophilic, it tends to bioaccumulate in fatty tissues and is biomagnified



up the food chain. It was found that bone density was reduced among men and women exposed and a higher risk of developing pancreatic cancer was observed among those involved with agriculture and forestry. Exposure to DDT was also correlated with lung cancer and neurological disorders among animals exposed to DDT. Because of this, DDT was listed as one of the “Dirty Dozen” under the Stockholm Convention on Persistent Organic Compounds.

The degradation of DDT has been the subject of various researches using different methods. A promising method is the use of zero-valent iron (ZVI). ZVI has become a popular choice for treatment of toxic wastes and for the remediation of pesticide-contaminated sites (Li et al., 2006). However, there are concerns as to whether ZVI can retain its reactivity for a long time. The decrease in the reactivity of ZVI may be due to surface passivation layer formation or maybe due to the precipitation of metal hydroxides like $\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$ and metal carbonates [$\text{Fe}(\text{CO}_3)$] on the surface of iron (Zhang, 1998). The mobility of ZVI is another concern. Studies have shown that these problems could be overcome by using a second metal which could retard the corrosion of metal. As to mobility, an emerging technology is encapsulating ZVI in a hydrophobic membrane producing an emulsified ZVI (Cook, 2009). This does not only promote better mobility but also protects the ZVI from reacting with other inorganic constituents that might compete with DDT. In addition, encapsulating ZVI also slows down its corrosion.

This study compared the performance of encapsulated and non-encapsulated ZVI combined with cobalt in terms of the extent of DDT degradation.

2. METHODOLOGY

Emulsification of ZVI, Co and ZVI-Co

Micro-scale zero valent iron and cobalt were emulsified using a mixture of water, corn oil and the surfactants Brij-35 and Tween 80. Brij 35 aids in the mobilization of the metal (Rios, 2010), while Tween 80 served as emulsifying agent. Emulsification was done following Echols (2009). To 0.8 g metal (total weight), 2 ml of corn oil was added, then 2 ml of water- Brij 35 surfactant mixture (10:1) added slowly with continuous manual mixing. The process was completed with the addition of 2 drops Tween 80.

Preparation of DDT Stock Solution

The simulated DDT stock solution (1000 ppm) was prepared by dissolving DDT (Sigma Aldrich) in acetone (Gautam et al., 2006). Lower concentrations were made by diluting a sample of the stock solution with deoxygenated water or acetone solution with the addition of surfactant to final water-acetone ratio of 9:1. Desired initial pH was also adjusted in this solution by dilute H_2SO_4 solution.

Degradation of DDT

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The degradation of DDT was carried out using both non-emulsified and emulsified ZVI, Co, and ZVI-Co. The effect of initial DDT concentration and ZVI loading (%) on the extent of DDT degradation was determined. Initial DDT concentration was varied at 10, 15, and 20 ppm, while ZVI loading was varied at zero, 50, and 100%. Experiments were implemented following a full factorial design of experiment.

Aqueous solutions of DDT of varying concentrations (6 ml) were placed in 15-ml vials with Teflon-lined screw caps. To each of the DDT solution, 0.08g of metal was added. For the emulsified variant, since it already contains 4 ml of water and oil, the amount of DDT solution was adjusted accordingly to maintain the desired initial DDT concentration in the solution. The pH of the solution was adjusted to 2.0 with 1-2 drops hydrochloric acid. Regardless of the nature of metal used the solutions were subjected to continuous shaking using a rocking shaker (Thermo Scientific, bi-directional rotation, 30rpm, 20° angle of rotation shaker). In each experimental run, five vials were used, each vial served as a sample. Sampling was done at 48, 96, 144, 192 and 240 minutes. Each experimental run lasted for 4 hours and were done in duplicate.

Analytical Technique

The sample was extracted with hexane following a modified procedure of Bedard et al. (1987). The content of the vial was first centrifuged for 5 minutes, the liquid portion was transferred to another vial and 4 ml of hexane and 0.1 g sodium sulphate were added. Sodium sulfate prevented emulsification of the sample. The mixture was vortexed for 2 minutes, sonicated for 30 minutes at 30°C, and then centrifuged for 15 minutes. The solvent phase was transferred to 1.5 ml amber vials and crimp-sealed. The extract was analyzed with GC-ECD with ELITE-5 column to determine the DDT concentration.

Treatment of Data

The extent of DDT degradation was calculated for each experimental run and was expressed as mg DDT removed per g-metal per li solution. These data were analysed using Minitab. Analysis of variance was performed to determine whether the factors were significant, which was also confirmed through the main effects plot.

The kinetics of DDT degradation was determined by considering an n^{th} order of reaction shown in Equation 1. Evaluating Equation 1 gives Equation 2. The experimental data obtained were fitted to Equation 2 to determine the order of reaction and the rate constant.

$$-\frac{dC_{DDT}}{dt} = kC_{DDT}^n \quad (\text{Eq. 1})$$

where C_{DDT} = concentration of DDT at time t
 k = apparent rate constant

$$\frac{1}{C_{DDT}^{n-1}} = \frac{1}{C_{(DDT)_0}^{n-1}} + (n-1)kt \quad (\text{Eq. 2})$$

3. RESULTS AND DISCUSSION

Degradation of DDT

During experimentation there were observed varying changes in color of the DDT solution the %ZVI loading. It was observed that the corrosion of cobalt resulted in light pink or cloudy pink solution while the iron exhibited light yellow to dark orange solution. The darker the color the more corroded the metals were. It was also observed that the centrifuged samples revealed that the iron fillings that settled at the bottom of the vial were orange while the cobalt particles were dark maroon. This was difficult to observe during the experiment.

The extent of DDT degradation after 4 hours for each of the experimental runs is shown in Table 1.

Table 1. Extent of DDT degradation

Run	Percent ZVI loading	Initial DDT concentration	mg DDT degraded per g-metal per li of solution	
			Non-emulsified	Emulsified
1	0	10	115.98	60.53
2	50	10	115.58	77.28
3	100	10	122.83	82.57
4	0	15	165.14	142.31
5	50	15	187.50	116.46
6	100	15	157.29	155.02
7	0	20	209.05	79.01
8	50	20	205.74	120.03
9	100	20	246.51	150.84

It can be observed that the performance of non-emulsified metals was better than that of the emulsified variant for all ZVI loading and initial DDT concentrations tested. The highest amount of DDT degraded was obtained when the initial DDT concentration was 20 ppm. On the other hand, for the emulsified variant, highest DDT removal was obtained when the initial DDT concentration was 15 ppm. In both cases, pure ZVI was used. Considering that the reaction time was fixed at 4 hours, the inferior performance of the emulsified metals could be due to the delayed contact time between the DDT molecule and the metal that may have been limited by the diffusion of the DDT molecule across the boundary layer between the bulk solution and emulsion. This is not the case for the non-emulsified variant as there was immediate contact

between the DDT molecule and the metal. Though the non-emulsified variant gave higher amount of DDT removed, corrosion rate was faster. After 4 hours, the non-emulsified variant was completely corroded, whereas only partial corrosion was observed in the emulsified variant. The emulsion served as a protective layer against corrosion which could be caused by inorganic impurities and other oxidizing agents (Cook, 2009). This suggests that if the reaction time were extended beyond 4 hours, higher DDT removal could be attained. It is also possible that for the same reaction time, less ZVI could be used. Whether the metal is emulsified or not, corrosion was most noticeable in pure ZVI, followed by the ZVI+Co, and pure Co being the least corroded.

In the emulsified metals, for the same amount of ZVI, ZVI+Co and Co and volume of the solution, it was at 15 ppm initial DDT concentration where the highest DDT removal was obtained. This could be explained by the number of electrons that the metal could release (Quinn, 2002), which is responsible for the dechlorination of DDT. The number of electrons released could be correlated to the corrosion behaviour of the metal. For the same amount of the ZVI, ZVI+Co, and Co, ZVI can release the most number of electrons. As such, it was the eZVI that gave higher DDT removal for all DDT concentrations tested. In the e(ZVI+Co), initially, ZVI releases electrons attracting DDT into the emulsion. As reaction progresses ZVI starts to corrode and to aid the reaction Co releases electrons resulting in more electrons available to attract and degrade DDT molecules into the emulsion. When this happens, the Co starts to corrode until its rate of corrosion surpasses that of ZVI. When the initial DDT concentration was 10 ppm the amount of DDT removed was higher than in the 20ppm solution, there may not have been enough electrons to attract DDT.

In comparing the non-emulsified and emulsified variants, the amount of DDT removed increased when the initial DDT concentration was increased from 10 to 15 ppm. When the initial concentration was raised to 20 ppm, the non-emulsified variant exhibited further increase in DDT removal, but it was the reverse for the emulsified variant. The trend that was observed in the emulsified variant could be explained by mass transfer limitation. The DDT molecules may have competed in diffusing into the eZVI droplet causing less DDT to react with ZVI.

To determine which factor was more significant, analysis of variance was done at 5% significance level. Results showed that initial DDT concentration was more significant than ZVI loading. Also, in the non-emulsified variant the two factors do not interact; in the emulsified variant, the two factors interact but only at 15 and 20 ppm DDT concentration.

Kinetics of DDT Degradation

The experimental data were plotted according to Equation 2 to determine the order of reaction and rate constant. The average values of the rate constants obtained are shown in Table 2. Based on the units, it can be observed that only the non-emulsified pure ZVI exhibited first order kinetics, the rest are all second order kinetics.

Table 2. Average values of rate constants of all metal variants

average k values	non-emulsified			emulsified		
	ZVI min ⁻¹	Co L-mg ⁻¹ min ⁻¹	ZVI + Co L- mg ⁻¹ min ⁻¹	eZVI L- mg ⁻¹ min ⁻¹	eCo L- mg ⁻¹ min ⁻¹	e(ZVI+ Co) L- mg ⁻¹ min ⁻¹
	0.0156	0.0029	0.0032	0.0009	0.0004	0.0004

4. CONCLUSIONS

This study dealt with the degradation of DDT in water matrix using zero valent iron and cobalt and combination of the two in non-emulsified and emulsified forms. The effect of initial DDT concentration and ZVI loading on DDT removal was determined. The performance of non-emulsified and emulsified metals was compared. The non-emulsified metal performed better in terms of DDT removal, however, corrosion was faster compared to the emulsified variant. The Highest DDT removal was obtained in the non-emulsified pure ZVI at DDT initial concentration of 20 ppm. As to the effect of initial DDT concentration, DDT removal increased with increase in initial DDT concentration. On the other hand, in the emulsified variant, DDT removal increased when the initial concentration was increased from 10 to 15 ppm, but beyond this concentration, there was an observed decrease in DDT removal. The ZVI loading did not have significant effect on DDT removal.

For the kinetics of DDT degradation a first order kinetics was obtained for the non-emulsified pure ZVI, and second order for all the other variants.

5. ACKNOWLEDGEMENT

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