International Journal of Environmental Engineering and Management.
ISSN 2231-1319, Volume 4, Number 3 (2013), pp. 177-184

http://www.ripublication.com/ ijeem.htm

Treatment of Endosulfan by High Carbon Iron Filings (HCIF)

Yangdup Lama[a], Alok Sinha[b*] and Gurdeep Singh[c]

[a]*Research Scholar, Department of Environmental Science And Engineering, ISM, Dhanbad.*
[b]*Assistant Professor, Department of Environmental Science And Engineering, ISM, Dhanbad.*
[c]*Professor, Department of Environmental Science And Engineering, ISM, Dhanbad.*

Abstract

Use of organochlorine pesticides has significantly increased due to exceptional intensification and modernization of agricultural activities. These pesticides are persistent in environment and may pose serious threat to human health even at very low concentrations in drinking water. Continued use has allowed these priority pollutants to leach into the groundwater and decontamination of such aquifers is quite expensive. Building Zero Valent Iron (ZVI) Permeable Reactive Barriers (PRBs), across the contaminated aquifers, may be a feasible solution for in-situ remediation of contaminated subsurface. In this study the High Carbon Iron Filings (HCIF) were contacted with aqueous solution of endosulfan in batch reactors. The study revealed that the aqueous concentration of endosulfan declined due to reductive dehalogenation as well as adsorption. The reaction of endosulfan with HCIF could be described as pseudo-first order reaction with an observed rate constant (k_{obs}) of 0.053 hr^{-1}. The decline in total concentration (C_T) of endosulfan can be expressed as a function of aqueous concentration (C_a) and can be described by equation $\frac{dC_T}{dt} = -k_1 M C_a^n$ where M is the mass concentration of HCIF. The values of n and k_1 were determined to be 0.597 and 4.207 x 10^{-4} h^{-1} g^{-1} HCIF L. The equilibrium partitioning of endosulfan to HCIF can be described by Freundlich isotherm, $C_s = K [C_a]^m$, such that K = 1.842 x 10^{-3} g^{-1}L and m= 0.888.

Keywords: High Carbon Iron Filings (HCIF), Endosulfan, in-situ, Groundwater.

1. Introduction

Many halogenated organic compounds, i.e., chlorinated solvents, organo-chlorine pesticides and herbicides, etc. are toxic to humans and other flora and fauna. However, such compounds are widely used in industrial applications and as pesticides and herbicides in household and agricultural applications. Uncontrolled release of such compounds to the environment causes widespread air, water, and soil pollution, and ingestion by human being and other flora and fauna. Of special concern is the pollution of groundwater resources by chlorinated organic compounds. Chlorinated solvents are sufficiently toxic at low concentrations to render water unsuitable for drinking, and most have been found to have long half-lives in natural environments (Vogel *et al.*, 1987; Jeffers *et al.*, 1989). Among volatile compounds, inhalation of Vinyl Chloride (VC) has been shown to cause liver, brain and lung cancer in humans (Joyce McCann *et al.*, 1975). The U.S. EPA classifies VC as a known human carcinogen. Inhalation of perchloroethylence (PCE) has been shown to result in an increased occurrence of liver tumors in mice and kidney tumors and leukemias in rats (Lazarew, 1929; Kylin *et al.*, 1962). 1,2-Dibromoethane is a potential carcinogen and can cause liver and kidney damage (Rajagopal *et al.*, 1999). Polychlorinated biphenyls, a very toxic group of compounds, are very persistent and hence resistant to natural degradation. About 400 million Kg of PCBs are dispersed into geo-, aqua-, atmo-, and biosphere, with majority being concentrated into geo-sphere because of their low volatility, low solubility in water, and high affinity for particulates (Panel on haz. Trace subs., 1972). Chlorinated phenols, benzenes, and napthalenes are toxic to aquatic animals (Verschueren K., 2nd Ed). Systemic effects of acute toxic doses of monochlorobenzene included damage to the liver and kidney, and effects on bile and pancreatic flow (Verschueren K., 2nd Ed). Among pesticides and herbicides, alachlor is listed as a probable human carcinogen and metolachlor is listed as a possible carcinogen (Eykholt & Davenport, 1998). Chlorinated pesticides like Aldrin, Chlordane were reported as toxic to aquatic life and ingestion by rats can cause liver damage (Martin H., 1968; Khan *et al.*, 1979). Dieldrin has been reported as carcinogenic (Joyce McCann *et al.*, 1975).

Traditional remediation method for groundwater contaminated with halogenated organic compounds involves pumping the contaminated groundwater to the surface and passing it through a treatment process train. During such treatment, the contaminant is either degraded, as in the case of advanced oxidation systems (Pignetallo & Baher, 1994), or transferred to another medium, as in case of air stripping and granular activated carbon adsorption. The decontaminated water is then returned to the subsurface through surface recharge (Mackay & Cherry, 1989). Of late, issues of long term effectiveness and economic feasibility have gradually shifted remediation trends away from such ‘pump and treat’ systems and towards *in situ* methods. The main advantage of *in situ* treatment is that it allows ground water to be treated without being brought to the surface, resulting in significant cost savings (Gillham & O'Hannesin, 1994).

This paper deals with the remediation of halogenated pesticide, Endosulfan, by using High Carbon Iron Filings (HCIF). The HCIF surface not only reductively dehalogenate the halogenated organic compounds but also adsorbs the compounds (Sinha and Bose, 2006; 2007; 2009a; 2009b; 2011). In this study the kinetic rate constant for reduction and adsorption of endosulfan by HCIF surface have been determined.

2. Materials and Methods

Commercially available high carbon iron was chipped on a lathe machine and then ground into iron filings in a ball mill. The fraction of filings passing through 425 μm (40 mesh) sieve and retained on 212 μm (80 mesh) sieve was used as High Carbon Iron Filings (HCIF). For a typical experiment, approximately 5 g of HCIF was added to a 20 mL vial, with the exact weight of HCIF added being determined gravimetrically. Vials were fully filled with de-oxygenated aqueous solution of 1 mg/L Endosulfan prepared in deionized Milli-Q water and screwed tight such that no headspace existed. Stock solutions of Endosulfan was prepared in methanol. Aqueous volumes in the vials were determined gravimetrically. Approximate mass of a compound added to a vial was 20 μg. Control vials, containing 20 μg of Endosulfan, but no HCIF were also prepared. All vials were placed on a roller drum and rotated at 50 rpm such that the vial axis remained horizontal at all times. Ambient temperature was approximately 30 ± 1^0C during mixing. Vials were removed at specified times, for sampling and analysis. Vials were removed at 1,2,5,12,24, 48 and 60 hrs and analyzed for aqueous and solid phase concentration.

500 μL aliquots of aqueous phase from various control vials were sampled using a micro syringe pierced through the septa, while adding deoxygenated deionized Milli-Q water into the vial using another syringe pierced through the septa to maintain headspace free conditions during sampling. The aqueous sample was added to a GC auto-sampler vial containing 750 μL n-hexane as solvent and sealed. The GC vial contents were then mixed on a vortex mixer, followed by analysis of the solvent phase by gas chromatograph equipped with an electron capture detector (GC-ECD). Extraction efficiency for endosulfan was 95%. For determining sorbed mass of endosulfan on HCIF the aqueous content of the 20 mL vial was transferred to another vial containing by air displacement using a cannula. 10 mL of n-hexane was added to the HCIF remaining in the vials and vortex mixed for 10 minutes. This sample was analyzed on GC to give the sorbed mass of endosulfan.

3. Results and Discussion

Endosulfan dehalogenation experiments were carried out in batch reactors over a 60 hour period. The pH measured during the entire experimental duration increased to 9.

Redox potential measured at various times during the experimental duration varied between -300mV to -400mV. At any time during endosulfan interaction with HCIF in batch systems,

$$C_T\,(\mu\text{moles L}^{-1}) = \left[C_s\,(\mu\text{moles g}^{-1}\text{ iron}).M(\text{g iron L}^{-1})\right] + C_a\,(\mu\text{moles L}^{-1}) \qquad (1)$$

where C_a, C_s and C_T are the aqueous, sorbed and total endosulfan concentrations and M is the concentration of HCIF. The total pesticide concentration, C_T, decreased with time due to dehalogenation through interaction with the metallic iron surface. Therefore, rate of change of total endosulfan concentration,

$$\frac{dC_T}{dt} = -k_1.M.(C_a)^n \qquad (2)$$

Where, k_1 and n are reaction rate constant and order respectively of the dehalogenation reaction. Experimental data on the decline in total aqueous concentration with time is presented in Figure 1. The decline aqueous concentration can be expressed as pseudo first order reaction as reported earlier by many researchers (Gillham and O'Hannesin, 1994; Matheson and Tratnyek, 1994). The aqueous concentration at any instant of time (C_t) may be expressed as:

$$C_t = C_0 \exp^{-kt} \qquad (3)$$

Where C_0 is the initial aqueous concentration and k is the observed rate constant. Equation 3 can be linearized as:

$$\text{Ln } C_t / C_0 = -kt \qquad (4)$$

The linearized plot between Ln C_t/ C_0 and time is shown in Figure 2. Observed rate constant (k) as calculated from linearized plot is 0.053 hr^{-1}. Equation 2 was linearized for the determination of k_1 and n,

$$\text{Ln}\left[-\frac{dC_T}{dt}\right] = \text{Ln}[M.k_1] + n.\text{Ln}[C_a] \qquad (5)$$

A plot of $\text{Ln}\left[-\frac{dC_T}{dt}\right]$ versus $\text{Ln}[C_a]$ is presented in Figure 3. $\frac{dC_T}{dt}$ was calculated from experimental data using numerical differentiation techniques. The values of k_1 and n obtained from Figure 3 were 4.207 x 10^{-4} hr^{-1} g^{-1} iron L and 0.597 respectively.

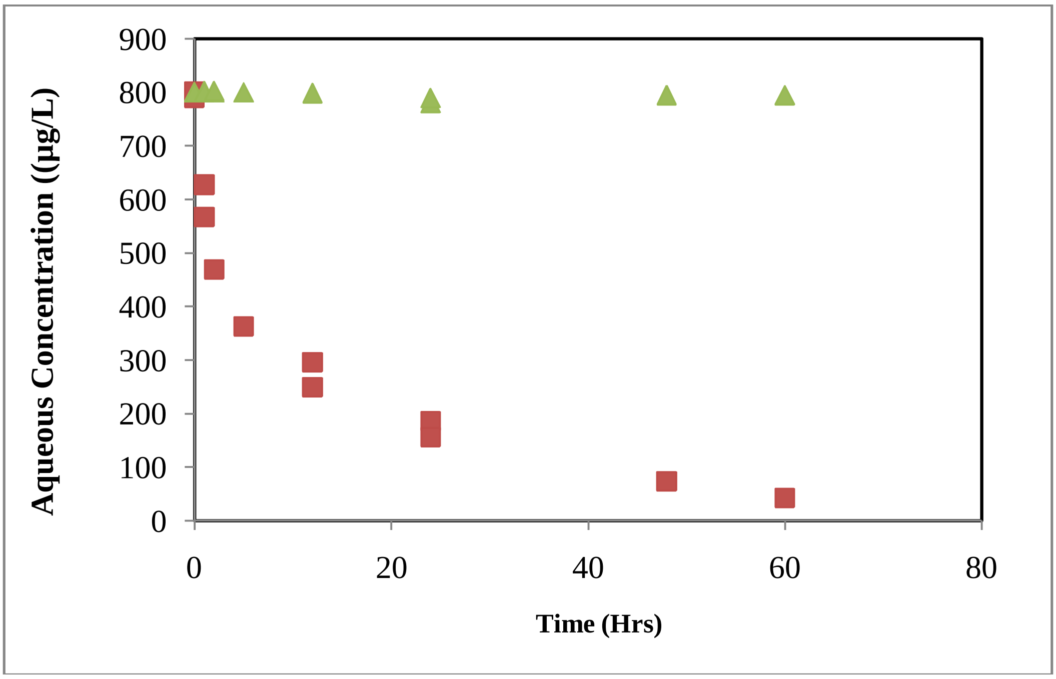

Figure 1: Decline in aqueous concentratiuon of Endosulfan with time in batch reactors.

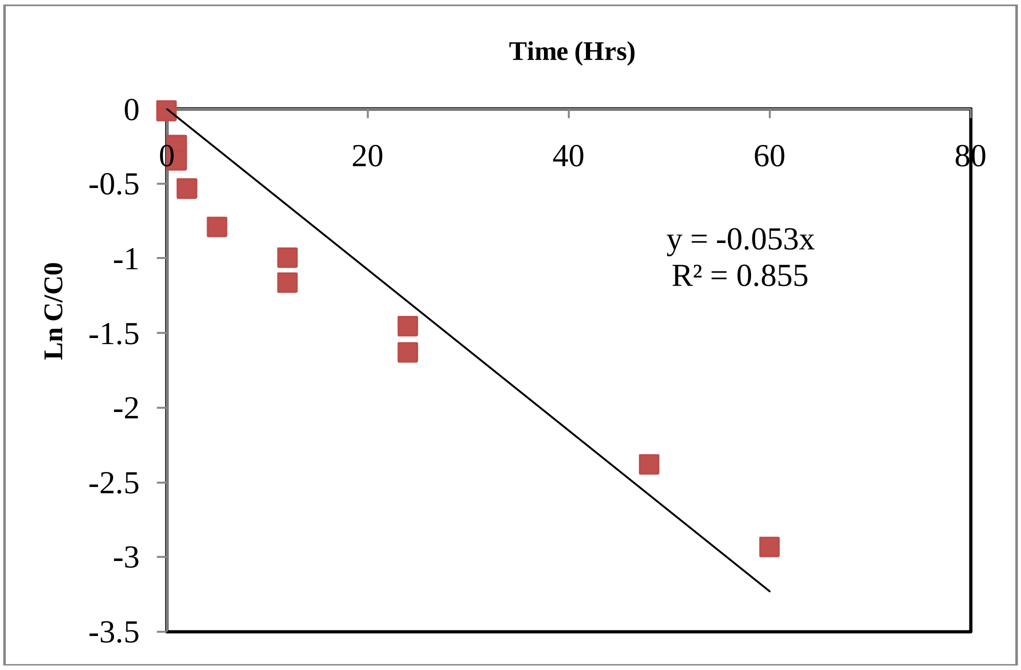

Figure 2: Plot of Ln C_t/ C_0 vs time.

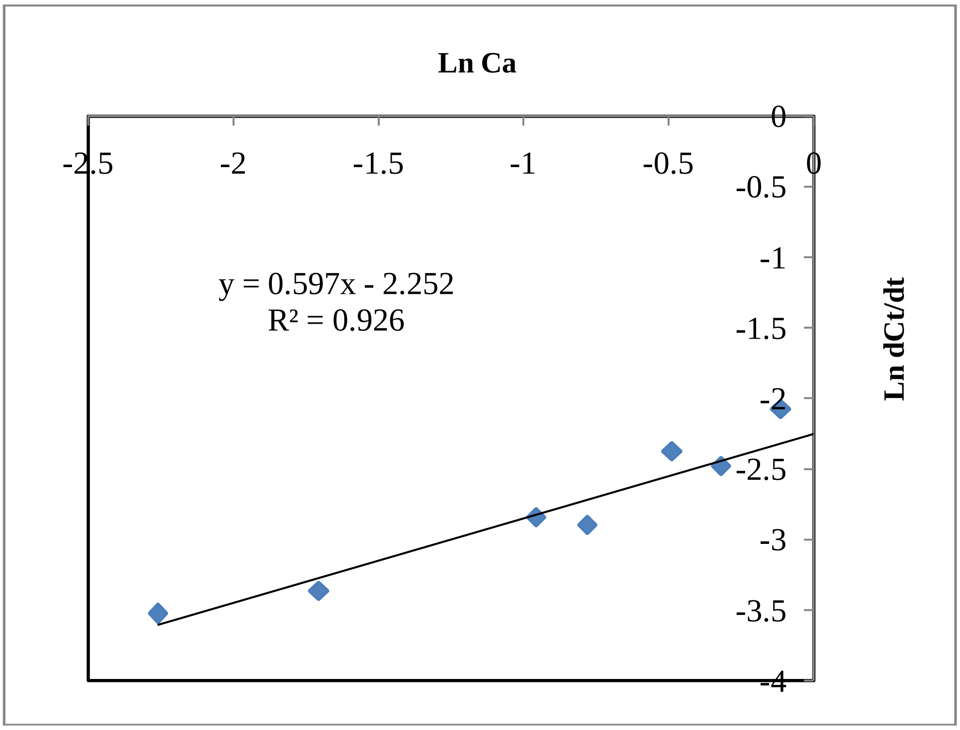

Figure 3: Linearized Plot of Rate of Endosulfan Degradation Versus Aqueous Phase Endosulfan Concentration.

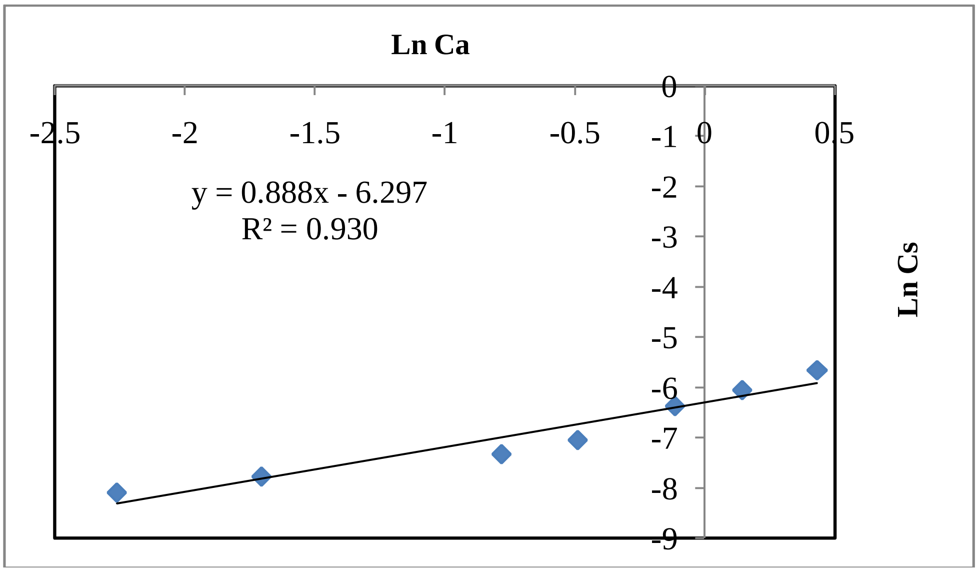

Figure 4: Freundlich Isotherm Describing Equilibrium Partitioning of Endosulfan between Solid and Aqueous Phases During Interaction with HCIF.

Endosulfan partitions to graphite inclusions present in HCIF (Sinha and Bose, 2006; 2007; 2009a; 2009b; 2011). It is assumed that such partitioning is non-specific in nature, i.e., the number of adsorption sites on the graphite surface is constrained only by the number of Endosulfan molecules that can be fitted on the graphite surface. Under such conditions, partitioning of Endosulfan between solid and aqueous phases can be represented by a Freundlich isotherm,

$$C_s = K.[C_a]^m \tag{6}$$

A linearized plot of Ln C_a versus the corresponding Ln C_s for Endosulfan, presented in Figure 4, show that the data could be adequately represented by the Freundlich isotherm with $K = 1.842 \times 10^{-3}$ $g^{-1}L$ and m= 0.888.

4. Conclusion

Batch experiments demonstrated that the Organo Chlorine Pesticide, Endosulfan, can be successfully dehalogenated by using cast iron particles. Endosulfan reduced to 94.6% of its original concentration within 60 hrs of contact time. The study revealed that the adsorption of endosulfan plays an important role in reducing the aqueous concentration of endosulfan in batch reactors in initial stage. The adsorption phenonmenon of endosulfan to graphite nodules present on HCIF surface can be described by Freundlich isotherm. Later, sorption-desorption and simultaneous reduction plays an important role in the decline of total concentration of endosulfan. Hence, HCIF can be used as a reactive material for *in-situ* remediation of groundwater contaminated with organochlorine pesticide, endosulfan. Further studies involving reduction of endosulfan, in flow through system, simulating groundwater conditions, are required to be carried out and pathways of reduction of endosulfan are also a matter of concern.

5. Acknowledgements

The author heartily acknowledge ISM Dhanbad for providing all necessary assistance, under the research project FRS (1)/2009-2010/1/ESE, for completion of this research work.

References

[1] Eykholt, G.R. & Davenport, D.T. (1998) "Dechlorination of the Chloroacetanilide Herbicides Alachlor and Metolachlor by Iron Metal". *Environ. Sci. Technol.,* 32, 1482-1487

[2] Gillham, R.W. & O'Hannesin, S.F. (1994) "Enhanced Degradation of Halogenated Aliphatics by Zero-Valent Iron". *Ground Water,* 32, 958-967.

[3] Jeffers, P.M., Ward, L.M., Woytowitch, L.M. and Wolfe, N.L. (1989) Homogeneous hydrolysis rate constants for selected chlorinated methanes, ethanes, ethenes, and propanes. *Environ. Sci. and Technol.,* 23, 965-969.

[4] Joyce McCann et al. (1975) "Detection of carcinogens as mutagens in the salmonella/microsome test: Assay of 300 chemicals". *Proc. Nat. Acad. Sci. USA,* 72(12), 5135-5139.

[5] Keum, Y-S and Li, Q.X. (2004) "Reduction of nitroaromatic pesticides with zero-valent iron"Chemosphere, 54, 225-263.

[6] Khan, M.A.Q., Feroz, M. & Sudershan, P. (1979) "Metabolism of Cyclodiene insecticides by fish". *Pesticide and Xenobiotic Metabolism in Aquatic Organisms,* American Chemical Society, Symposium Series 99.

[7] Lazarew, N.W., *Arch. Exp. Path. Pharmakol.,* 1929, 141, 19.

[8] Mackay, D.M. & Cherry, J.A. (1989) "Groundwater Contamination: Pump-and-Treat Remediation". *Environ. Sci. Technol.,* 23, 630-636.

[9] Martin, H. (1968) *"Pesticide Manual"* British Corp Protection Council, Clacks Farm, Boreley, Ombersley, Doritwich, Worcester, U.K.

[10] Panel on Hazardous Trace Substances. *Environ. Res.,* 1972, 5, 249-362.

[11] Rajagopal, V.K. and Burris, D.R. (1999) Reduction of 1,2-dibromoethane in the presence of zero-valent iron. *Environ. Toxicol. Chem.,* 18, 1779-1782.

[12] Sinha, A. and Bose, P. (2006) "Dehalogenation of 2-chloronapthalene by cast iron". *Water Air and Soil Pollution,* 172 (1-4), pp. 375-390.

[13] Sinha, A. and Bose, P. (2007) "Interaction Of 2-Chloronaphthalene with High Carbon Iron Filings (HCIF): Adsorption, Dehalogenation And Mass Transfer Limitations". *Journal of Colloid and Interface Science,* 314 (2), pp. 552-561.

[14] Sinha, A. and Bose, P. (2009) "Interaction Of Chloroethanes And Chloroethenes With Un-Rusted And Rusted High Carbon Iron Filings". *Journal of Environmental Engineering Science,* 26(1), pp. 61-70.

[15] Sinha, A. and Bose, P. (2009) "Interaction of 2,4,6-Trichlorophenol with High Carbon Iron Filings: Reaction and Sorption Mechanisms". *Journal of Hazardous Materials,* 164(1), pp. 301-309.

[16] Sinha, A. and Bose, P. (2011) "2-Chloronaphthalene Dehalogenation by High Carbon Iron Filings (HCIF): Impact of Formation of Corrosion Products on HCIF Surface" *Journal of Environmental Engineering Science,* 28(10): 701-710.

[17] Verschueren, K. (1983) "Handbook of Environmental Data on Organic Chemicals" 2nd Ed., Van Nostrand Reinhold Company Inc., New York.

[18] Vogel, T.M., Criddle, C.S. and McCarty, P.L. (1987) Transformations of halogenated aliphatic compounds. *Environ. Sci. and Technol.,* 8, 722-736.