Application of Nanoscale Zero-Valent Iron in the Remediation of DDT from Contaminated Water

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Abstract: Nanoscale zero-valent iron (NZVI) was synthesized and tested to remediate DDT (Dichlorodiphenyltrichloroethane) from the contaminated water. The influence of experimental variables such as reaction time, NZVI particle dosage and pH were studied. Mixing an aqueous solution of 3 mg L^{-1} DDT with 30 mg L^{-1} Fe^0 resulted in 99.2% loss of DDT within 4 h. Solvent extraction of the Fe^0 revealed that DDT removal was not through adsorption and as Fe^0 treatment of DDT lead to new chromatographic peaks (degradation products) in GC analysis and chloride release, removal occurred through dechlorination. GC/MS analysis confirmed the formation of completely dechlorinated hydrocarbon skeleton of DDT namely, diphenylethane (DPE), as the end product in this treatment; thereby implying the removal of all five chlorine atoms (three alkyl and two aryl) of DDT.

Keywords: Nano zero-valent iron, DDT, Remediation, Water

Introduction

Most POPs (persistent organic pollutants) are organochlorine pesticides, namely, aldrin, endrin, clordane, DDT, heptachlor, mirex, toxaphene and hexachlorobenzene. They have been banned for agricultural or domestic uses in Europe, North America and many countries of South America in accordance with the Stockholm Convention (ratified in 2004). However, some organochlorine pesticides are still used - *e.g*. DDT [(1,1-bis(4-chloro-phenyl)-2,2,2-trichloroethane)] (Figure 1) which is used to control malaria in some developing countries[1-4]. WHO classified the DDT among the twelve persistent organic pollutants to eliminate urgently because it is characterized by a strong solubility in greases, which involves an accumulation in fat tissues of the living organisms. Its molecular structure contains chlorinated aliphatic and aromatic structures that impart great chemical stability. The toxicity of DDT is mainly due to its chlorine atoms and dechlorination may reduce its environmental risk and biotoxicity.
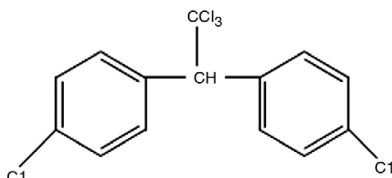
Figure 1. Chemical structure of DDT (Dichlorodiphenyltrichloroethane)

The chemicals used by farmers for pest removal are drawn off by precipitation and thus the infested water flows into the streams and rivers. Among the most serious diseases caused by pesticide poisoning, the following distinguish: neurological disorders, internal organs disorders, skin disorders and cancer[5-7]. The infiltration of halogenated compounds to ground water has generated considerable interest in engineering a reducing environment in aquifers for remediation purposes. Some of these chemicals are biodegradable and decompose quickly in harmless or less harmful substances, but the non-degradable are the most common ones that persist for a long period of time. Under reducing conditions, many of these contaminants can be detoxified through reductive dehalogenation reactions. Copious evidence indicates that reducing or removing electron-withdrawing moieties from parent structures generally results in more biodegradable products[8,9]. Based on this premise, one technology gaining widespread acceptance is the use of zero-valent metals for remediating ground water contaminated with halogenated compounds.

Nowadays, the versatility of nanometer-scale zero-valent iron (NZVI) material has been demonstrated for potential use in environmental engineering[10]. NZVI is an effective reductant for a wide variety of reducible contaminants including chlorinated organic compounds, heavy metal ions and oxo-anions which is non-toxic and relatively inexpensive[11-13]. The practical applicability of these NZVI particles lies in the fact to get oxidized into +2 and +3 oxidation states thereby reducing other organic as well as inorganic impurities (Figure 2). Metallic iron (Fe^0) serves effectively as an electron donor:

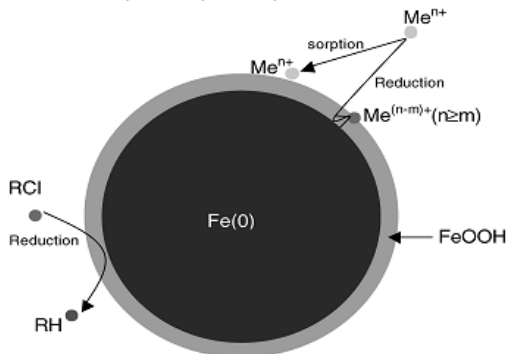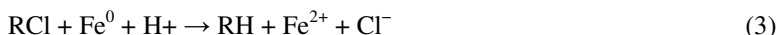$$Fe^0 \rightarrow Fe^{2+} + 2e^- \tag{1}$$

Figure 2. Core shell model of nano zero-valent iron showing various chemical mechanisms

Chlorinated hydrocarbons on the other hand accept the electrons and undergo reductive dechlorination:

$$RCl + H^+ + 2e^- \rightarrow RH + Cl^- \tag{2}$$

From a thermodynamic perspective, the coupling of the reactions [1] and [2] is often energetically highly favorable:

$$RCl + Fe^0 + H+ \rightarrow RH + Fe^{2+} + Cl^- \tag{3}$$

Due to the extremely small particle size, large surface area and high *in-situ* reactivity, these materials have great potential in a wide array of environmental applications such as soil, sediment and groundwater remediation[14-15]. The goal of this study is to investigate the application of laboratory-synthesized NZVI for the remediation of DDT from contaminated water.
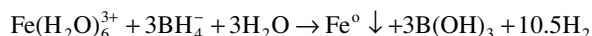
Experimental

DDT (98%) and 2,2',3,4',5,5',6-heptachlorobenzene (internal standard) were purchased from Supelco. Analytical grade acetone, hexane, dichloromethane (DCM) and acetonitrile (ACN) supplied by Aldrich Chemical Co. The chemical reagents used in the study ($FeCl_3.6H_2O$, H_2SO_4, NaOH and $NaBH_4$) were reagent grade obtained from Aldrich Chemical Co.

Apparatus

Morphology of the particles was observed with a Phillips EM 400ST transmission electron microscope (TEM) to characterize the particle and distribution of the iron particles. Powder x-ray diffraction (XRD) patterns of the solid products were obtained in the 2θ range of 5°-80° using a PW-1840 diffractometer from Philips Co. with Cu-$K\alpha$ radiation (λ=1.54178 A^o). Ion chromatography (IC) determinations were carried out in a S 1122 Sykam ion chromatograph to measure the chloride. pH measurements were performed with a Metrohm 691 pH meter. An Agilent 7890 GC equipped with a DB-XLB capillary column (30 m × 0.250 mm×0.25 μm) and electrolytic conductivity detector (ELCD), model 5320A. GC– MS analyses were performed using Varian model CP3800 gas chromatography instrument interfaced with electron ionization ion source and equipped with a quadrupole mass spectrometer model 1200 as detector. A factor- four, VF-5 ms capillary column (30 m × 0.250 mm × 0.25 μm) was used with helium as the carrier gas.

NZVI synthesis

The NZVI material was synthesized by drop wise addition of 1.6 M $NaBH_4$ aqueous solution to a Ne gas-purged 1 M $FeCl_3.6H_2O$ aqueous solution at room temperature with magnetic stirring as described by Wang and Zhang[10]. Ferric iron (Fe^{3+}) was reduced and precipitate according to the reaction:

$$Fe(H_2O)_6^{3+} + 3BH_4^- + 3H_2O \rightarrow Fe^o \downarrow + 3B(OH)_3 + 10.5H_2$$

The solution was stirred for 20 min and centrifuged at 6000 g for 2 min and the supernatant solution was replaced by acetone. Acetone-washing prevented the immediate rusting of NZVI during purification leading to a fine black powder product after freeze-drying. All Fe materials were stored in a N_2-purged desiccator.

Batch experiment

The batch experiments were carried out in a 250 mL flask under N_2 at room temperature which kept in the dark by covering the reactor with aluminum foil. Desired concentration (3 mgL^{-1}) of DDT was added into the reactor and reaction was initiated by the addition of NZVI (3-30 mgL^{-1}). Just after that, the electrode of the pH-meter was immersed in the solution and the pH was adjust at 2.0 (±0.1) by addition of some drops of 3 M H_2SO_4 solution. The closed reactors were mixed by a rotary shaker at 130 rpm. 30 mL of the suspensions samples were taken at 0, 1, 2, 3, 4 and 5 h with a pipette and then separated by centrifugation at 4500 rpm for 30 min to get the supernatant for analysis. It was introduced into a 50 mL separating funnel containing 3 mL of sodium hydroxide solution (2.5 N). This

later was used to stop the dechloration reaction. The analysis method derives from method 8081B - determination of organochlorine pesticides by gas chromatography. According to this method, extraction was carried out by twice 5 mL of dichloromethane, with agitation during 5 min each time. The organic phases were recovered and then concentrated at a volume of 0.5 mL under a weak flow of nitrogen. During concentration the solvent is changed with hexane. The concentrated extracts were analyzed by GC/ELCD to measure the residual concentration of DDT. The identity of dechlorinated end products was determined by GC–MS analyses.

Reactions proceeded for 10 h. After 10 h, the DDT-treated NZVI was separated and gently washed with water and then was agitated for 18 h with 20 mL DCM. Aliquots of supernatant solution were filtered (0.45 µm) and analyzed for adsorbed DDT by GC/ELCD. Besides GC analysis, 0.50 mL of the solution at aforementioned times was removed for chloride analysis by ion chromatography

Analysis of samples

For drawing the calibration curve, stock solution (30 mgL^{-1}) of the DDT was prepared in hexane and diluted to lower working concentrations to prepare standard solutions with the concentrations. All samples were spiked with 2,2',3,4',5,5',6-heptachlorobenzene as an internal standard. The response factor (RF) of the DDT standards relative to the internal standard, was carried out by injecting the standard together with the internal standard. 2,2',3,4',5,5',6-heptachlorobenzene was chosen since it is not likely to be found in real environmental samples. Also 2,2',3,4',5,5',6-heptachlorobenzene is detectable by ELCD with its peak well separated from DDT.

The sample was analyzed in the Agilent GC/ElCD instrument in the following conditions: temperature of the reactor = 1100 °C; electrolyte (*n*-propanol) flow = 40 µL/min; hydrogen flow =35 mL/min; helium flow in the column = 1.5 mL/min and 20 mL/min in the detector. The column temperature was programmed to ramp from 150 °C (5 min hold) to 280 °C (10 min hold) at a rate of 10 °C/min. The splitless injector was maintained at 250 °C to prevent the DDT breakdown at the injector port.

GC–MS analyses were performed in the following conditions: the column temperature was ramped from 150 to 280 °C at 10 °C/min. Electron impact (70 eV) mass spectra were used to identification of the intermediates and end products with reasonable certainty.

Results and Discussion

Characterization of NZVI: Structure and particle size determination by TEM and XRD

Figure 3 shows the images of NZVI nanoparticles observed by transmission electron microscopy. It indicates that iron particles have a nearly spherical shape with a grain size range about 20- 50 nm.

Figure 4 shows the XRD spectrum of NZVI nanoparticles. The main reflection at 44.7° corresponding to Fe°. The weakly diffract peak of Fe° indicates that nano-scale ZVI synthesized by NaBH$_4$ in the aqueous solution is poorly crystalline. XRD presents the three major peaks of Fe^0 at 45, 65 and 85 (2-theta degree), consistent with nano zero-valent iron particles (14, 22). The peaks were found to have low intensity because of the presence of an amorphous iron phase (14).
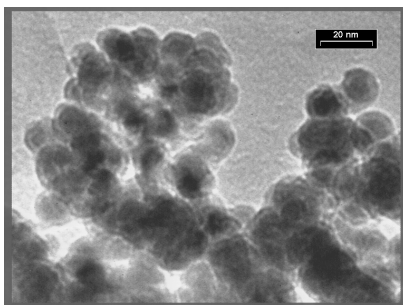
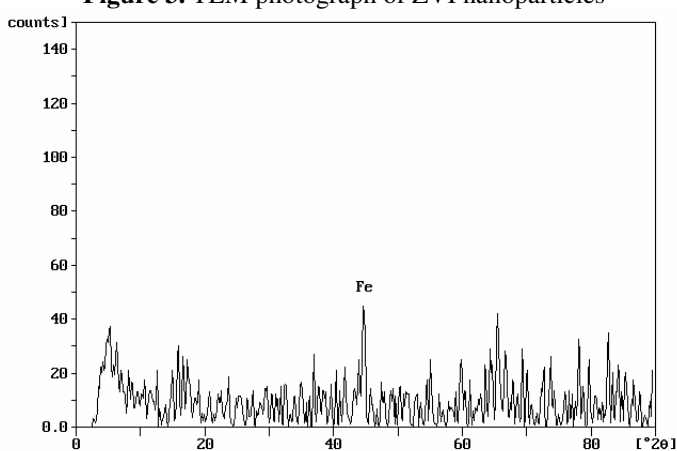**Figure 3.** TEM photograph of ZVI nanoparticles

Figure 4. XRD spectrum of ZVI nanoparticles

Effect of NZVI dosage

The maximum acceptable concentration (MAC) of DDT and its metabolites in drinking water is 0.03 mg/L. Experiments of DDT removal with Fe^0 were performed at an initial concentration of 3 mg L^{-1}, which is 100 times more than it's considered MAC in drinking water.

In Figure 5, results of DDT removal using different Fe^0 concentrations in the range of 3-30 mg L^{-1} are shown. There was an exponential decrease in the concentrations of DDT in contact with Fe^0 with increasing time. The results revealed that increasing the Fe^0 concentration increased the amount of removed DDT. Maximum DDT loss (99.2% within 240 min) occurred in the presence of 30 mgL^{-1} Fe^0, while only 14.7% DDT loss occurred during the first 4 h when 3 mg L^{-1} Fe^0 was used. This is because the more NZVI particles are able to provide more iron surface-active sites for collision with DDT molecules to accelerate the DDT removal efficiencies. Thus, the DDT removal efficiencies were gradually swelling from 14.7, 26.5, 52.3, 86.5, to 99.2% by raising NZVI dosage from 3, 6, 12, 24 to 30 g L^{-1} as shown in Figure 5. Results show that 30 mgL^{-1} is an optimal amount of NZVI, beyond which no improvement of removal was obtained.

Effect of pH

The pH was also one of the important factors in the DDT removal by zerovalent iron. When the ferrous ions dissolved from the iron surface, collided with hydroxyl ions in alkaline solution and precipitation of produced ferrous hydroxide on the iron surface occupy the reactive sites

to hinder the reaction. Also, lower pH gives rise to a greater extent of acid washing of ion oxides on metallic iron surfaces and reduces passivation of metal by enhancing solubility of metal hydroxide. So, the chemical reduction of DDT by NZVI is favorable in acid conditions.
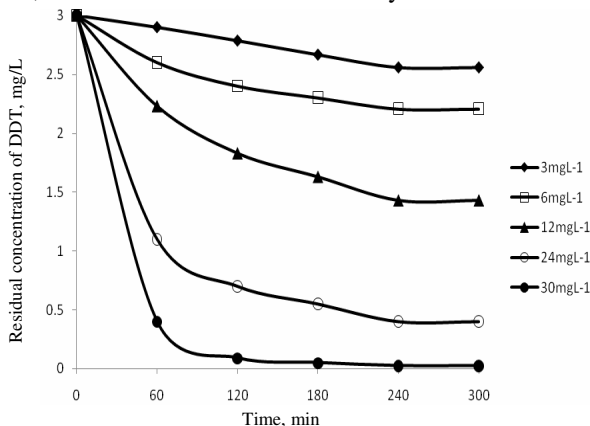

Figure 5. DDT residual concentration versus time; initial DDT concentration: 3 mg L^{-1} with various NZVI dosages

The pH effect on DDT removal is illustrated in Figure 6 (NZVI dosage: 30 mgL^{-1} and DDT concentration: 3 mg L^{-1}). Comparing the removal efficiencies of DDT by NZVI, for pH 9 and pH 2, were showed 99.2% removal of DDT after a treatment time of 240 min for the later, while the former had 26% removal efficiency. Therefore the result of the DDT degradation with different pH shows the importance of working in acid medium.
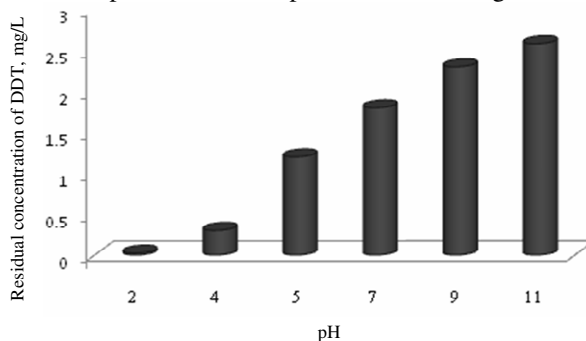

Figure 6. Effect of pH on DDT removal by NZVI

Ion chromatographic results

One mole of DDT ($C_{14}H_9Cl_5$) fully degraded will release 5 mol of chloride ions into solution. Therefore it is possible to understand the extent of DDT degradation by measuring the incremental chloride concentration. This chloride will fully account for the degradation product and any volatile loss of DDT to air will not be included.

Figure 7 shows the effect of Fe^0 degradation of 3 mg/L of DDT. This concentration is reduced to 0.09 mg/L after 120 min and to less than 0.030 mg/L after 240 min accounting for more than 90% removal. The chloride concentration increased correspondingly with remediation time. Therefore change in chloride under Fe^0 application is a sufficient indication of the progress of DDT destruction.
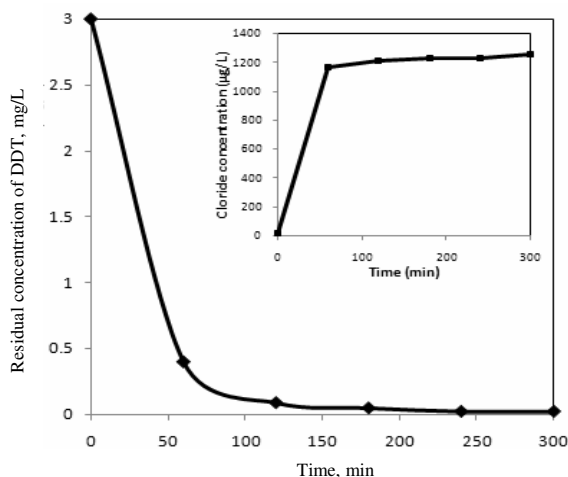
Figure 7. Plot of DDT and chloride concentration during the treatment by Fe^0; initial concentration of DDT: 3 mg/L and zero percent dosage: 30 mgL^{-1}

Adsorption or dechlorination

As new chromatographic peaks (degradation products) were observed during GC analysis and chloride release was detected during Fe^0 treatment, dechlorination of DDT by the iron surface is occured. In addition, the analysis of the extract of DDT-treated NZVI by GC/ELCD revealed no DDT traces which proves that DDT removal was not through adsorption.

Identification of intermediate products

A DDT solution (3 ppm) was treated by the Fe^0 (30 mgL^{-1}) within 1 and 4 h under acidic conditions (Figure 8). As can be seen dechlorination is complete and no DDT peak is observed at the end of 4 h but some intermediates are detected after 1 h by GC-ELCD.
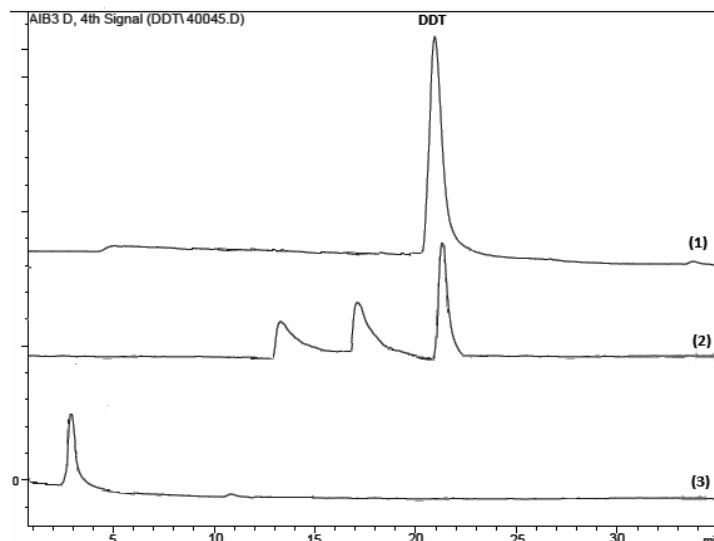

Figure 8. Comparison of GC-ELCD profiles of (1): untreated (control) and (2) & (3):Fe^0

The identity of intermediates and end products formed following dechlorination reaction of DDT with NZVI for 1 h and 4 h were determined through GC/MS. Figure 9 presented the results of TIC (total ion current) chromatograms of these samples.
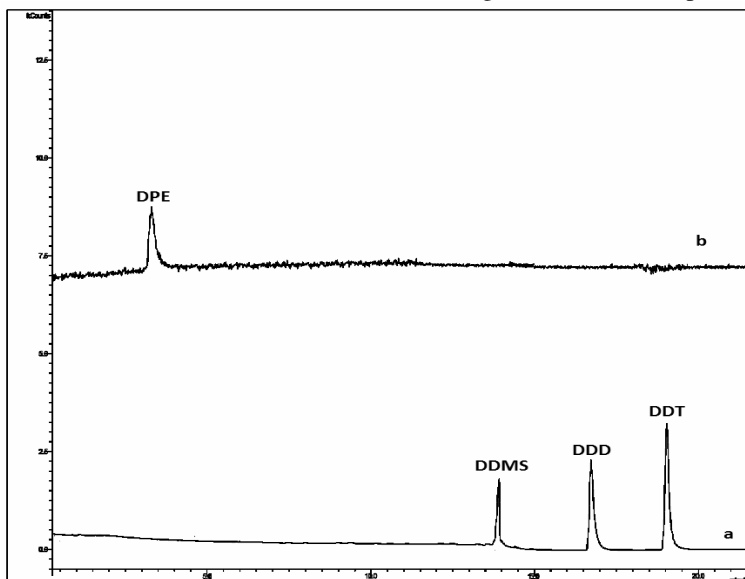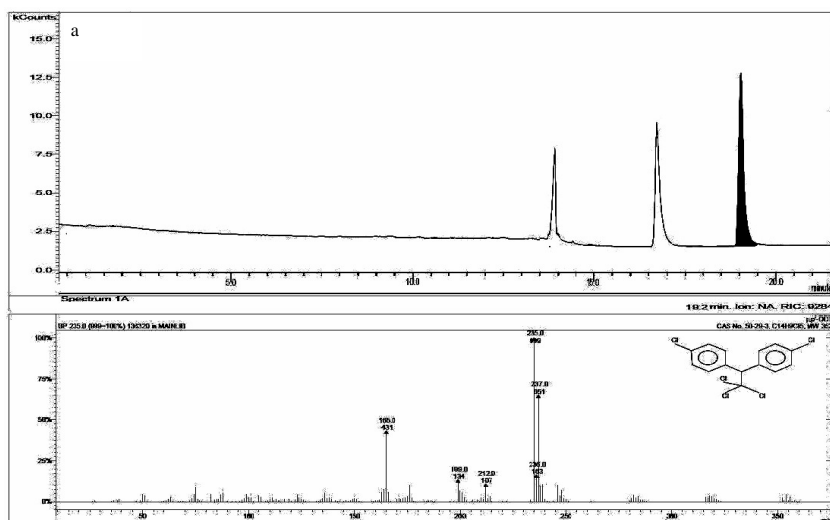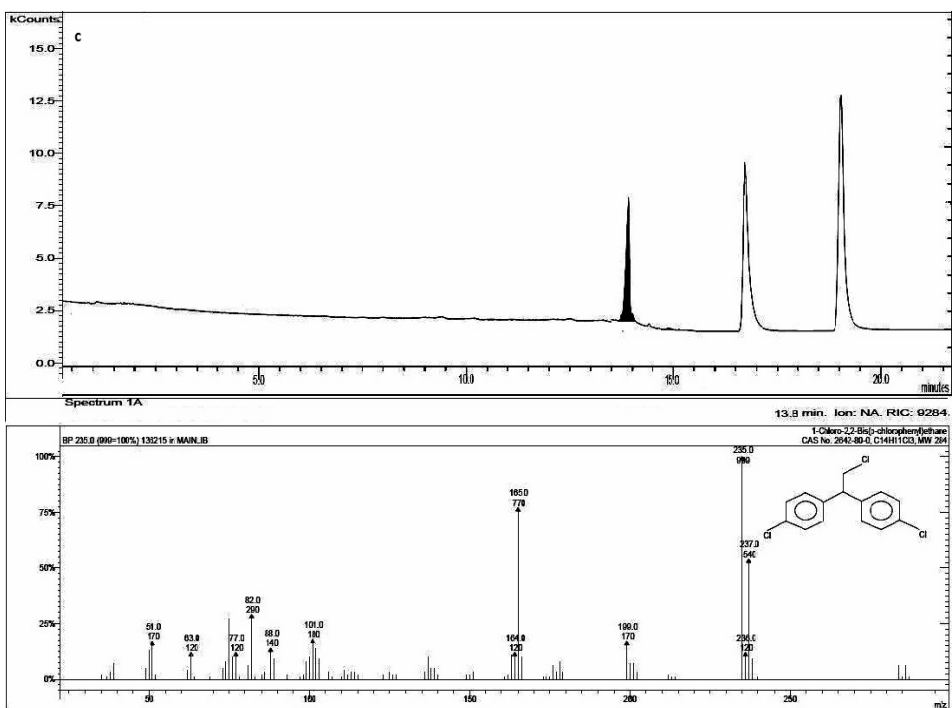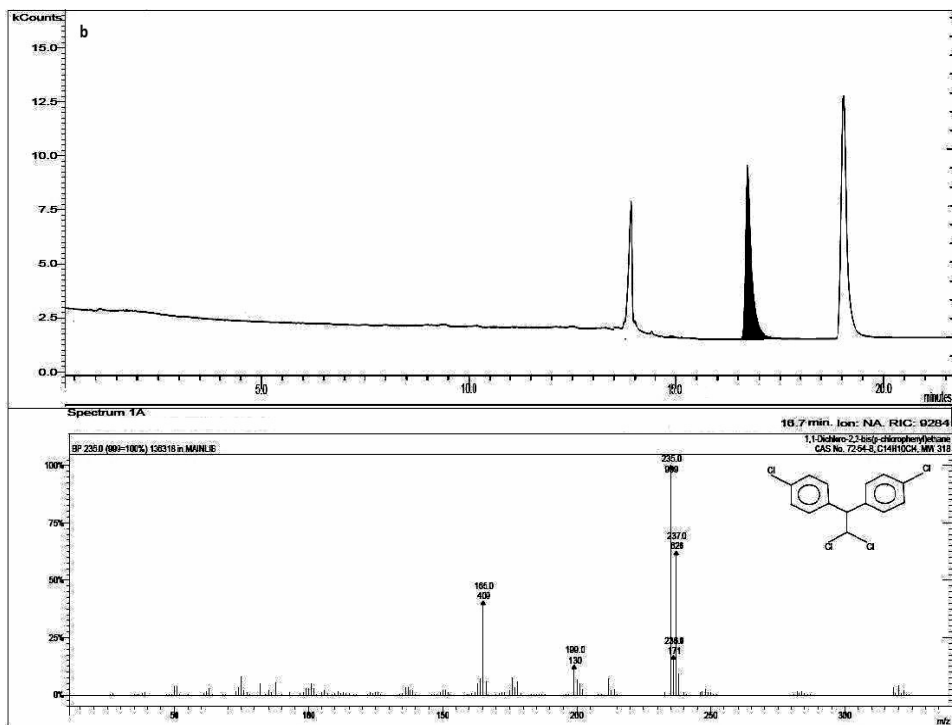

Figure 9. GC/MS elution profiles of product formed following 1(a) and 4(b) h reaction of 3 mg L^{-1} DDT with 30 mgL^{-1}NZVI

In the GC–MS pattern following 1 h of the reaction of DDT with Fe^0 two intermediates appeared and the presence of DDT at the retention times of 23 min was confirmed (Figure 10a). Based on the molecular ion peaks and the unique fragmentation peaks, the compounds appeared at the retention times of 21.5 and 19.5 min in GC chromatogram were identified to be (1,1-dichloro-2,2-bis(4-chlorophenyl)ethane)DDD (Figure 10b) and 1-chloro-2,2-bis (*p*-chlorophenyl)-ethane (DDMS) (Figure 10c), respectively.
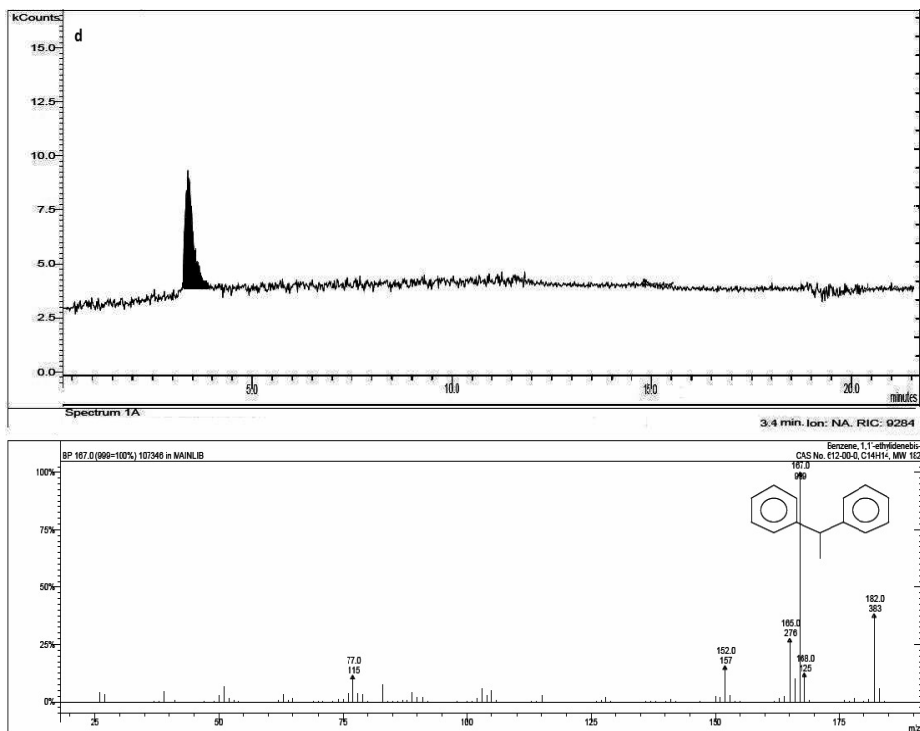
Figure 10. GC/MS fragmentation pattern for the compounds eluting at (a) 19.2 min; (b) 16.7 min; (c) 13.8 min and (d) 3.4 min

The GC–MS pattern following 4 h of the reaction of DDT with Fe^0 revealed the presence of only one peak at 5.0 min. Based on the molecular ion fragmentation pattern of this peak, the end product of DDT dechlorination was identified as DPE (diphenyl ethane), characterized by *m/z* of 182 (Figure 10d). Formation of DPE as the end product suggests removal of three alkyl and two aryl chlorine atoms. Based on detected intermediates and the final products, the proposed pathway of DDT degradation with NZVI can be summarized as below (Figure 11).
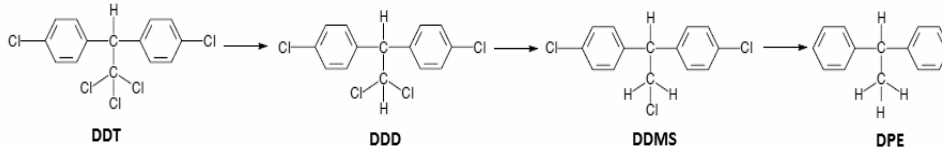

Figure 11. Observed pathway of DDT dechlornation in this study

Conclusion

Nanoscale Fe^0 was synthesized through a reductive method in this paper. The capability of powdered nanoscale zero-valent iron to dechlorinate DDT and related compounds at room temperature was studied. Batch experiments were performed to investigate the reduction of DDT by Nanoscale Fe^0. The pH (in acid conditions) was also important factor in the DDT removal. The identify of intermediates and end products formed following dechlorination

reaction of DDT with NZVI were determined by GC/MS. The obtained results show DDT, DDD, DDMS and DPE transformation by powdered Nanoscale Fe^0. The Nanoscale Fe^0 was successful at dechlorinatind DDT, DDD and DDMS.

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