

Single-step treatment of 2,4-dinitrotoluene via zero-valent metal reduction and chemical oxidation

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Abstract

Many nitroaromatic compounds (NACs) are considered toxic and potential carcinogens. The purpose of this study was to develop an integrated reductive/oxidative process for treating NACs contaminated waters. The process consists of the combination of zero-valent iron and an ozonation based treatment technique. Corrosion promoters are added to the contaminated water to minimize passivation of the metallic species. Water contaminated with 2,4-dinitrotoluene (DNT) was treated with the integrated process using a recirculated batch reactor. It was demonstrated that addition of corrosion promoters to the contaminated water enhances the reduction of 2,4-DNT with zero-valent iron. The addition of corrosion promoters resulted in 62% decrease in 2,4-DNT concentration to 2,4-diaminotoluene. The data shows that iron reduced the 2,4-DNT and ozone oxidized these products resulting in a 73% removal of TOC and a 96% decrease in 2,4-DNT concentration.

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1. Introduction

Past environmental practices included the disposal of presently classified hazardous organics compounds in unlined lagoons causing soil and groundwater contamination. For example, the groundwater surrounding many Army Ammunition Plants (AAPs) has shown contamination with nitroaromatic compounds (NACs) [1]. These NACs include 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), 2,6-dinitrotoluene, and nitrobenzene. These compounds have shown to be cancerous in lab animals as well as toxic at relatively low concentrations [2]. Current concerns over the depletion of groundwater supplies make it important that the contaminated groundwater surrounding the AAPs be treated so it may be used safely for irrigation and human consumption.

Current NAC treatment techniques include granular activated carbon (GAC) and advanced oxidation processes (AOPs).

Activated carbon is a non-destructive technology that transfers contaminants from the liquid phase onto the solid phase of the carbon surface. Studies have shown that activated carbon can be effective in removing NAC from contaminated water at concentrations up to 100 mg L^{-1} [3]. However, regeneration of activated carbon typically involves exposing the activated carbon to high temperatures, which could create unsafe operating conditions when dealing with spent carbon with adsorbed explosive compounds. Consequently, the spent carbon is disposed of in a hazardous waste landfill. This practice may result in future liability and increase the operating cost of GAC system for treating NACs contaminated waters.

Because nitro groups are electrophilic (electron withdrawing groups), the reaction of NACs with ozone (another electron withdrawing species) is relatively slow and generate difficult to oxidize and potentially toxic by-products [4]. For methylated NACs, oxidation attacks the methyl group initially [5]. In the case of 2,4-DNT, oxidation produces 1,3-dinitrobenzene, a hazardous organic and carcinogenic compound [4].

Over the past decade, zero-valent metals (ZVMs) have been used to treat a number of hazardous organic compounds [6–11]. In particular, ZVMs (electron donating species) have shown to be effective in the reduction of NACs to produce aromatic amines

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[7]. The aromatic amines produced still pose a threat to the environment and must be treated further. An effective method of mineralizing aromatic amines is the application of oxidation technologies [12].

Oh et al. [13] researched a two-step system in which TNT and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) were first treated with zero-valent iron (ZVI) and then treated with Fenton's Reagent. The Fenton's reaction generates hydroxyl radicals by the reaction of ferrous ions and hydrogen peroxide. The hydroxyl radical is a relatively strong chemical oxidizer. This study showed that mineralization of NACs was achievable utilizing a two-step system of reduction and oxidation. Hernandez [14] evaluated ZVM reduction followed by peroxone (combination of ozone and hydrogen peroxide) for remediating TNT contaminated waters. The results showed that some mineralization was achieved; however, the reduction products adsorbed very strongly to the surface of the ZVM making mineralization of the reduction products difficult. Bell et al. [15] investigated a sequential treatment of nitrobenzene using ZVM and biodegradation. The results showed that this technique was effective in the treatment of nitrobenzene.

Another issue with ZVMs as a water treatment technique is deactivation of the metal. As the ZVM donates electrons to the NACs the surface forms an oxide layer that can hinder the transfer of electrons [16]. One method of removing this oxide layer is to introduce chloride into the system. The chloride dissolves the oxide layer as well as forms pits and cracks in the surface of the metal that enhance electron transfer [17,18]. Once it starts, pitting corrosion is an autocatalytic process, the rate of pitting formation and pit dissolution accelerates with time. However, depending on chloride concentration and the presence of passivating agents, such as carbonates, the pitting formation rate caused by chloride-based corrosion promoters diminishes over time [19].

This study explores the effectiveness of an integrated reduction/oxidation of 2,4-DNT using zero-valent iron (ZVI) and ozonation. The hypothesis is that the metal will reduce (donate electrons) 2,4-DNT at the nitro group and the ozone will oxidize the methyl group. This double site attack in an integrated system will result in faster degradation and mineralization of 2,4-DNT. Chloride was used to accelerate the reduction reaction and minimize passivation of the ZVI. Experiments were conducted to evaluate separately the performance of the reductive and oxidative systems, and the integrated system for treating 2,4-DNT contaminated water.

Fig. 1 depicts the hypothesized mechanism of the double site attack. The nitro groups adsorb onto the surface of the ZVI and are reduced by electrons donated from the ZVI. The reduction of these nitro groups allows them to be more easily oxidized since amino groups are electron donors. At the same time the methyl group on the 2,4-DNT molecule is attacked by the ozone molecule. This double site attack leads to ring breakage and ultimately the mineralization of the molecule.

2. Experimental methods

2.1. 2,4-DNT reduction

All experiments were conducted in a recirculated batch system (see Fig. 2) under ambient temperature and atmospheric pressure. A similar recirculating batch system was proposed by Devlin et al. [9]. The reactor system consisted of a 500 mL European style flask (Ace Glass Inc.), a variable speed pump (Cole Palmer Inc., Model 7553-20), and a 30 cm × 1 cm glass column (Ace Glass Inc.). The operation of the reactor system consisted of test solution being pumped out of the reactor vessel, through the glass column containing the ZVI, and back into

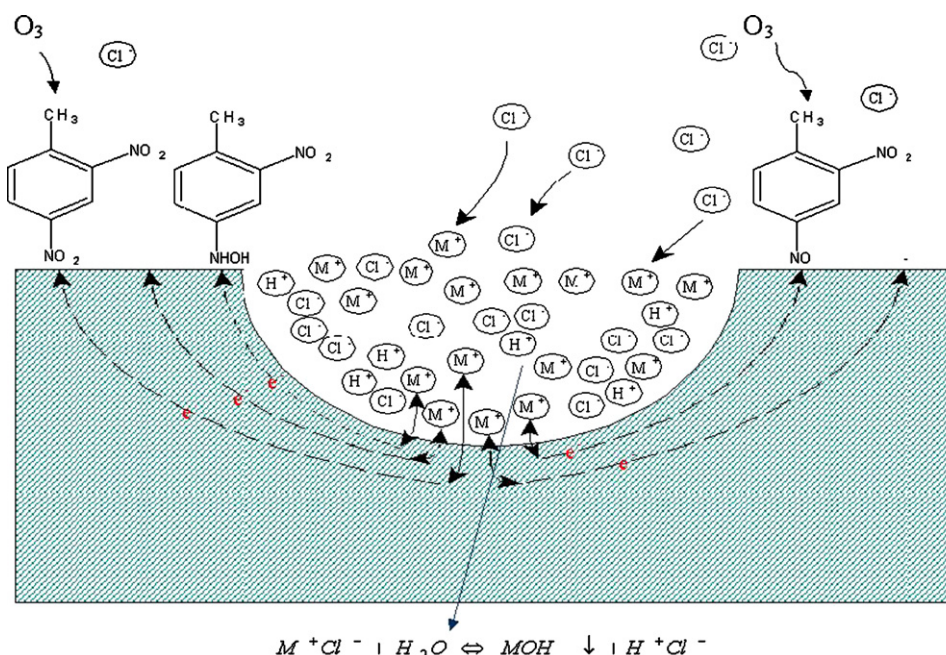


Fig. 1. Diagram of hypothesized reaction mechanism.

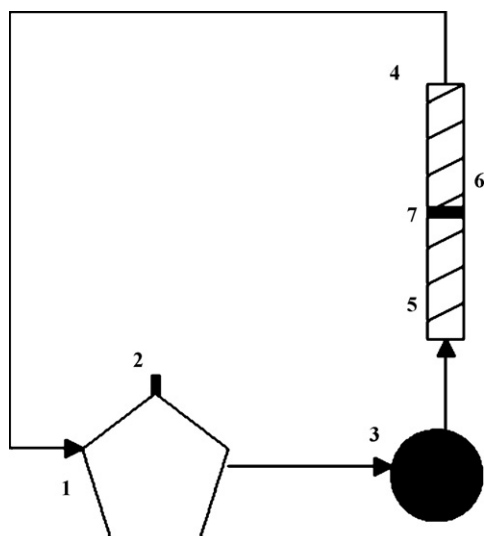


Fig. 2. Diagram of the recirculating batch system. 1, Reactor; 2, sample port; 3, pump; 4, glass column; 5, glass beads; 6, crushed glass; 7, metal sample.

the reactor vessel. The column contained 2 g of ZVI granules with 1–2 mm diameter and 99.98% pure. The ZVI was used without any surface pre-treatment to remove the oxide layer. The iron packed zone was approximately 0.5 cm. All reactions were continuously stirred with a magnetic stir bar and a stir plate. All experiments were stirred at the same setting. The reactor was charged with 500 mL of 20 mg L⁻¹ 2,4-DNT solution. The 2,4-DNT solution was made by dissolving solid 2,4-DNT (97%, Avocado Research Chemical Ltd.) in DI water. A stream of oxygen was then bubbled through the reactor for 30 min at 2.5 ft³ (STP) h⁻¹ prior to running the experiment to achieve a dissolved oxygen concentration of approximately 45 mg L⁻¹. Oxygen concentration was assessed using a DO probe (Orion). The test solution was oxygenated to emulate the conditions of an integrated system using ozonation. An ozonated stream contained approximately 95% oxygen by weight. After aerobic conditions were reached in the reactor, 10 μM to 3 mM of either FeCl₃ (97%, Sigma–Aldrich) or NaCl (99%, Fisher Scientific) was added to the reactor and the pump turned on at a speed of 12 mL s⁻¹. The concentration range of corrosion promoter was based on the USEPA regulation for chloride concentration in drinking water and previous studies conducted with ZVI and corrosion promoters [14]. The reaction was conducted for 180 min with periodic sampling. Samples were collected using a glass syringe and placed in 2 mL amber HPLC vials. The effect of chloride on 2,4-DNT reduction was measured via comparison with experiments conducted without chloride additions.

The glass column in the reactor system was packed with 4–6 mm diameter glass beads (Fisher Scientific) and crushed glass to secure the ZVI samples. The ZVI species used for this study was Fe (99.98%, Alfa Aesar). The ZVI concentration was 4 g of metal per liter of 2,4-DNT solution. All experiments were conducted in duplicate. The data points in each of the figures represent an average value.

2.2. Single-step reduction and oxidation of 2,4-DNT

Experiments were conducted in the same reactor system as described in Section 2.1. A 2% by weight O₃ stream was added to the reactor to oxidize the reduction products. The O₃ was produced by an oxygen fed ozone generator (Ozonology, Model LC-1234). It was continuously sparged through the system over the course of the reaction at 2.5 ft³ (STP) h⁻¹. The reactor was operated and the column was packed in the same manner as previously described in Section 2.1.

Experiments were conducted in which the 2,4-DNT solution was ozonated without the addition of ZVI or FeCl₃. Experiments were also conducted in which ozonation of the 2,4-DNT solution occurred separately from the reduction step. After the reduction step was completed, the ZVI was removed from the system and ozone was sparged into the system for an additional hour.

2.3. Analytical methods

Concentration of 2,4-DNT was determined by using a high performance liquid chromatograph (HPLC) (Agilent, Model 1100) and USEPA Analytical Method 8330. The HPLC was equipped with a diode array detector and a Hypersil BDS-C18 column (Agilent, 100 mm × 4 mm, particle size 3 μm). The injection volume, mobile phase flow rate, and wavelength were 0.100 mL, 0.500 mL min⁻¹, and 280 nm (with reference at 360 nm), respectively. The mobile phase consisted of 60% DI water and 40% methanol (Fisher Scientific, HPLC grade). The instrument was calibrated using serial dilutions of 2,4-DNT and 2,4-diaminotoluene (DAT) standards (Supelco Inc.).

For the single-step reduction and oxidation experiments, total organic carbon (TOC) was analyzed using an UV/persulfate TOC analyzer (Tekmar-Dohrman, Phoenix 8000 Model). The TOC analyzer utilizes a 10% sodium persulfate/5% phosphoric acid reagent to break down organic carbon to CO₂ that is then detected using a non-dispersive infrared detector. TOC calibrations were conducted with serial dilutions of TOC stock solution.

Also, for the single-step reduction and oxidation experiments, nitrate concentration was analyzed using a DX-Ion Chromatography System (Dionex Corp.). The system used an Ion Pac[®] AS11-HC analytical separation column (Dionex Corp., 4 mm × 250 mm) and an ED40 Electronic Detector (Dionex Corp.). The injection volume and mobile phase flow rate were 0.025 mL and 1.0 mL min⁻¹, respectively. The mobile phase consisted of DI water. Calibrations were conducted using serial dilutions of nitrate in DI water and mid-range calibrations were analyzed every 10 samples to ensure quality control.

3. Results and discussion

3.1. Aerobic 2,4-DNT reduction results

Fig. 3 illustrates the concentration of 2,4-DNT over time when reacted with ZVI and 10 μM–3 mM concentrations of FeCl₃. The results are normalized based on the initial concentration of 2,4-DNT. The objective of chloride addition is to create

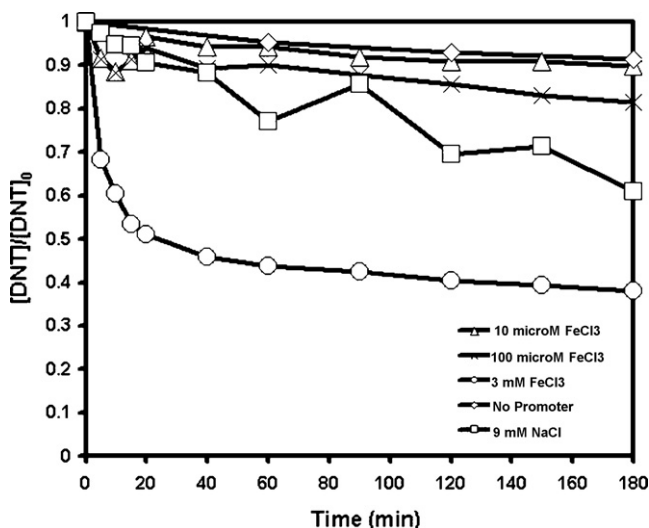


Fig. 3. Time course reduction of 2,4-DNT with ZVI and 0–3 mM FeCl₃ under aerobic conditions.

pits in the metal, provide a continuous flow of electron to the metal surface, and consequently, accelerate conversion of 2,4-DNT into 2,4-DAT. The flow of electrons to the metal surface by the introduction of chloride was investigated by Scherer et al. and Hernandez et al. [17,18]. Higher conversion of 2,4-DNT into DAT will improve the efficiency of the integrated reductive/oxidative process. The highest degradation of 2,4-DNT (62%) was obtained using 3 mM FeCl₃. The other concentrations evaluated (10 μM FeCl₃ and 100 mM FeCl₃) did not increase the 2,4-DNT degradation significantly over the no promoter reaction. The results indicate that a specific concentration of chloride is necessary before the oxide layer on the surface of the metal is pitted causing the acceleration of 2,4-DNT degradation. Fig. 3 also indicates that FeCl₃ results in greater 2,4-DNT removal than NaCl. The corrosion literature indicates that FeCl₃ is a better corrosion promoter compared to NaCl [20]. It can be observed that a 9 mM NaCl (equivalent to a chloride concentration of 3 mM FeCl₃) removed 39% of the 2,4-DNT compared to 62% using 3 mM FeCl₃ (results not shown). This higher degradation could be caused by the combination of two mechanisms:

- (1) Fe³⁺ can accept an electron from the ZVI surface and transfer this electron to the 2,4-DNT in the bulk solution. Therefore the 2,4-DNT would transform to DAT by homogeneous and heterogeneous reactions.
- (2) Several investigators have determined that Fe²⁺ adsorbed on an oxide layer with a ZVI core has a catalytic effect on reduction reactions [21,22]. The Fe³⁺ added to the system could be reduced on the ZVI oxide surface becoming Fe²⁺. This species may be adsorbing to the oxide layer and catalyzing 2,4-DNT degradation.

3.2. Ozonation of 2,4-DNT

Fig. 4 illustrates the effect of ozonation on TOC and 2,4-DNT concentration. It was assumed that the loss of NACs due to ozone stripping was negligible. The results show that less

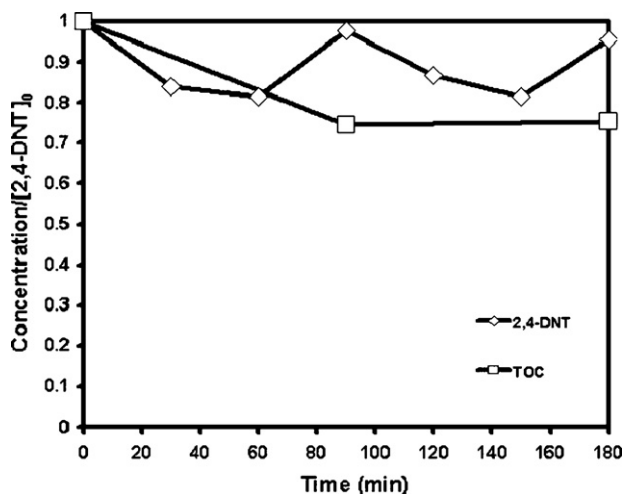


Fig. 4. Time course oxidation of 2,4-DNT via ozonation.

than 5% of the 2,4-DNT was removed by ozonation in 3 h. As mentioned above, mineralization of NACs is a relatively slow reaction. Ozone is an electrophilic molecule and will attack 2,4-DNT at the methyl group generating 2,4-dinitrobenzene (2,4-DNB), which is more difficult to oxidize than 2,4-DNT.

3.3. Two-step reduction and oxidation results

Aromatic amines such as 2,4-DAT, the terminal reduction product of 2,4-DNT, are organic compounds of environmental concern [23]. Remediation technologies are necessary to transform parent compounds into non-hazardous species. Oxidation has been shown effective to mineralize aromatic amines [12]. Fig. 5 shows the concentration of 2,4-DNT, TOC, and nitrate over time for a two-step reduction and oxidation reaction with ZVI, 3 mM FeCl₃, and O₃. The figure illustrates that the reduction step removes approximately 30% of the initial 2,4-DNT and 20% of the initial TOC. It is speculated that the TOC disappearance during the reduction step is caused by the adsorption

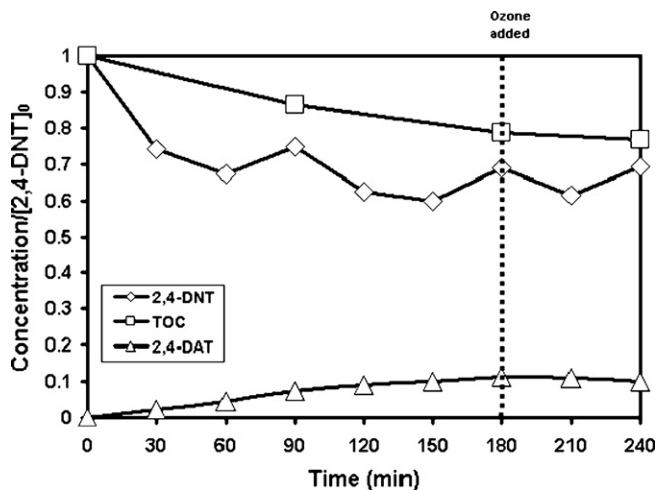


Fig. 5. Time course two-step degradation of TOC from 2,4-DNT using ZVI (4 mg L⁻¹) in the presence of FeCl₃ (3 mM) and ozonation (2% O₃ and 2.5 SCFH).

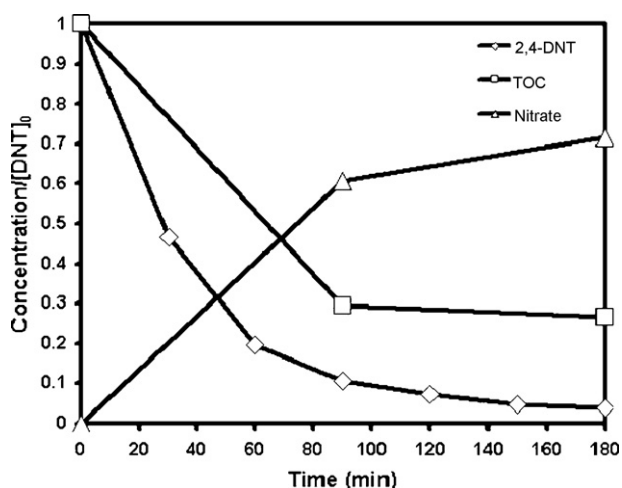


Fig. 6. Time course single-step reduction and oxidation of 2,4-DNT with ZVI, 3 mM FeCl₃, and O₃.

of reduction by-products onto the ZVI surface. A mass balance accounting for all reaction by-products was not completed because several unknown peaks were detected by the HPLC. It was assumed that these species are reaction intermediates between the 2,4-DNT and 2,4-DAT. Time-course of 2,4-DAT formation (see Fig. 5) indicates that approximately 10% of the original 2,4-DNT was detected in solution as 2,4-DAT. It is speculated that most of the 2,4-DAT generated is strongly adsorbed to the ZVI surface. Hofstetter et al. [22] determined that reduction products of NACs adsorbed strongly on the iron oxide surface.

The ZVI was filtered from solution and the reactor was connected to the ozone generator after completion of the reduction step. Fig. 5 shows 2,4-DNT and TOC did not degrade during the oxidation step.

Fig. 6 illustrates the single-step reaction of 2,4-DNT with ZVI and O₃. The results show a 73% decrease in TOC concentration and a 96% removal of 2,4-DNT from the system. These results indicate that oxidation of the organic species is taking place. The decrease in TOC concentration supports the hypothesis that mineralization of the reduction by-products is occurring. The results show that oxidation of the reaction by-products leads to greater removal of 2,4-DNT from the system. Mineralization results in the availability of more reactive sites on the metal surface for reduction and oxidation reactions. The results support the hypothesis that the double site attack of the molecule achieve mineralization of 2,4-DNT and result in higher overall degradation of 2,4-DNT.

Previous experiments indicated that reduction of nitroaromatic compounds occurs at the nitro groups [7]. Zappi [5] concluded that the methyl groups of nitroaromatic compounds are attacked by hydroxyl radicals (strong oxidizing agent). This double site attack breaks open the ring structure and ultimately leads to the mineralized products water, carbon dioxide, and nitrates. The experimental results (Fig. 6) indicate a decrease in TOC concentration, suggesting that the organic carbon is being converted to carbon dioxide. The experimental results also show an increase in nitrate concentration, indicating that the nitrogen is being removed from the organic molecule.

Fig. 1 offers one possible mechanism for the single-step reduction and oxidation of 2,4-DNT. In this mechanism, the 2,4-DNT adsorbs to the iron oxide surface and the nitro groups are reduced. While the 2,4-DNT is adsorbed, the ozone molecules attack the methyl group on the 2,4-DNT molecule. This double site attack leads to ring breakage and ultimately the mineralization of the 2,4-DNT molecule and a reduction in TOC concentration. However, this is not the only possible mechanism for the removal of TOC from the solution. Another possible mechanism is the reaction of ozone with the 2,4-DNT molecule that results in a new organic species that adsorbs strongly to the iron oxide surface. It is also possible that increased iron oxide surface area can lead to greater adsorption of organic molecules to the surface that will result in lower TOC concentration. One possible method for determining if the loss of TOC concentration is due to mineralization is to utilize radio labeled carbon to follow the carbon through the system. Future work will need to be done to isolate the reaction mechanisms that are occurring and the fate of the TOC concentration.

4. Conclusions

This work has shown that a single-step reduction and oxidation of 2,4-DNT is possible, and that it is likely that mineralization of 2,4-DNT is occurring. The results support the hypothesis that the ZVI reduces the nitro groups on the 2,4-DNT to form a molecule that is more easily oxidized. This molecule is then attacked at the methyl group by ozone. This double attack leads to ring breakage and ultimately mineralization. The results also show that the single-step reduction and oxidation of 2,4-DNT enhances the overall removal of 2,4-DNT from the system. Future work will need to be done to address the potential ZVI deactivation, oxides formation caused by ozonation, as well as the fate of the organic molecules to confirm mineralization.

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