

Oxidation of 2,4,6-Trinitroresorcine Using Zero-Valent Iron

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This paper describes the character of the reduction of 2,4,6-trinitroresorcine (TNR) by zero-valent iron (ZVI) in anaerobic conditions and the oxidative reaction of amine resorcine in the system of ZVI-EDTA-O₂. The products of TNR by ZVI in anaerobic conditions were amine resorcine compounds. These compounds tend to be easier to be oxidized by the free radical OH[•] generated in the system of ZVI-EDTA-O₂. HPLC method and COD analysis have been used for monitoring efficiency of reactions. The experiments suggested that the removal of TNR from groundwater is likely implemented by two steps. The first step is reduction of TNR by ZVI to form amine resorcine. The second step is oxidation of amine resorcine in system consisting of ZVI-EDTA-O₂. From the obtained results a model for TNR contaminated groundwater treatment has been suggested.

Key Words: Oxidation, 2,4,6-Trinitroresorcine, Zero-valent iron.

INTRODUCTION

Groundwater contamination has been becoming a serious problem. The explosive chemicals such as 2,4,6-trinitrotoluene (TNT), 2,4,6-trinitroresorcine (TNR), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) disposed from munitions manufacturing plants and weapons testing areas have been a critical environmental problem. These compounds are highly stable in the environment and are somewhat soluble causing the toxicity to aquatic animals. They are also toxic to humans and can cause a host of health problems such as anemia and liver dysfunction. The EPA classifies them as a group C carcinogen; this means that they could potentially cause cancer in humans.

The TNT, TNR, RDX may be removed from groundwater by such methods as adsorption onto granular activated carbon, destruction by photo catalysis, biodegradation and incineration. Recently, zero-valent iron (ZVI) particles have been used for treatment of many recalcitrant organic compounds like nitro aromatic, chlorinated compounds¹⁻³. The chemical background of this method consists of the following reactions.

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In the absence of oxygen, we have

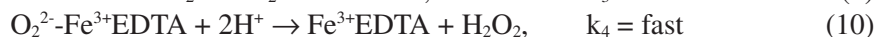


In principle, $\text{Fe}^{(0)}$, Fe^{2+} and H_2 (little) can contribute to the reduction of contaminants⁴. The predominant degradation pathway for chlorinated compounds (RX) and for nitro aromatic compounds (ArNO_2) appears to be reductive processes:



The reduced products such as RH, ArNH_2 may be easily treated by biodegradation. The reaction rates of processes^{4,5}, in practice, depend on some factors such as size, surface area of ZVI particles, pH solution, concentration of dissolved oxygen, carbonate ions, contaminant concentrations and some organic compounds, especially ethylenediaminetetraacetic acid (EDTA).

The system of Fe^{2+} - H_2O -EDTA in presence of oxygen has been demonstrated that it exhibits such a strong oxidative character that it could mineralize many refractory organic compounds. The oxidative character of this system bases on the following reactions⁵.



The Fe^{2+} EDTA complex formed in the solution plays a role of catalyst for this conversion reaction. The free radical plays the role of oxidative reagent in mineralization process.

In this paper we present the study on the mineralization of 2,4,6-trinitroresorcine (TNR) from groundwater using zero-valent iron (ZVI) in presence of EDTA and oxygen. The experimental method was carried out by two steps: (i) reduction of TNR by ZVI under anaerobic conditions to result in amine products, (ii) oxidation of amine products in a system consisting of ZVI, EDTA and oxygen. Focusing on the mineralization of TNR to be applied in environmental treatment, the efficiency of TNR mineralization has been exhibited by the variation of the COD during experiments.

EXPERIMENTAL

2,4,6-Trinitroresorcine, zero-valent iron and EDTA were obtained in high purity from Chem.-Service, R,P, China, PA. The ZVI particles have trace impurities less than 0.02 % C, 0.01 % S, 0.002 % Mn, 0.001 % P. Prior to all experiments they must be treated by a HCl diluted acid to remove the oxide layer and other contaminants.

Zero-valent iron (ZVI) pretreatment: Prior to use, the ZVI particles were hand-sieved to constrain grain size to 18-20 mesh and sonicated in HCl of 10 % (v/v) for 20 min. The clean metal was washed four times with bicarbonate buffer to avoid further surface oxidation to metal oxides. The BET surface area of the iron sample is within the range from 0.035-0.045 m²/g.

The pH solution for all experiments was controlled by an acid or basic solution, 0.1 M H₂SO₄, 0.1 M NaOH, respectively.

Reduction of TNR by ZVI particles (step 1): Batch experiments were conducted under anaerobic conditions in 500 mL round bottom flask. The flask was spiked with 0.5 mL of TNR stock solution and distilled water, to get a total volume of 250 mL with an initial concentration of 80 mg/L, pH = 5.5, the oxygen removed by N₂ gas. The TNR concentrations during the experiments, in the samples were monitored by HPLC analysis. The sample for HPLC analysis was filtered through a 0.45 μm Nalgene 4 mm nylon filter (Fisher, Pittsburgh, PA) and TNR analyzed by HPLC with diode array detector with wavelength set 270 nm. Analysis by HPLC was performed with a C-18 column (length 250 mm, ID 4.6 mm; Altech, Deerfield, IL). Two mobile phases used during different portions of experiments were a mixture of 45:55 acetonitrile/water with a flow rate of 1.0 mL/min. These experiments would allow to determine the time when almost TNR concentrations in the samples were reduced and converted into amine products.

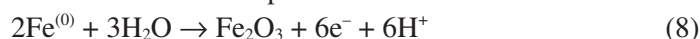
Oxidation of amine products (step 2): The amine products obtained from reduction of TNR and ZVI were filtered to remove iron particles for the further oxidation. Batch experiments were conducted under aerobic conditions in 500 mL round bottom flask. The flask contains the amine products (near 250 mL solution). In most cases, flasks received 10 g of dry, sieved iron and 84 mg EDTA. Each reactor (flask) was placed on shaker with 40 rpm at room temperature. After every 0.5 h, a sample of 10 mL was taken, filtered for measurement of chemical oxygen demand (COD). An analysis of COD was, then carried out by micrometric method. The oxidation efficiency of TNR was calculated by the expression as follows:

$$E = \frac{[\text{COD}]_0 - [\text{COD}]_t}{[\text{COD}]_0} \times 100, (\%) \quad (1)$$

Here [COD]₀, [COD]_t are the COD values corresponding to samples at the initial and t is the time of oxidation process. The influence of the EDTA amount on COD values was eliminated by a normal method.

RESULTS AND DISCUSSION

The reductive reaction of TNR by ZVI particles: In near neutral medium, in samples there is iron oxidation alone in the net production of H⁺ as shown in reaction.



When this half reaction is combined with reduction of TNR, the H⁺ are typically neutralized. The final reaction is as:



In these concrete conditions, the reductive reaction between TNR and ZVI after 1 h have been implemented nearly completely. The reaction solutions become turbid due to the appearance of Fe_2O_3 . After complete disappearance of TNR in the aqueous phase, ZVI is recovered and subjected to extraction with *n*-heptane. HPLC analysis of heptane extract indicated that there is no TNR in it. Reductive reaction of TNR carried out with dissolved ZVI does not result in TNR disappearance from the bulk solution. These finding indicate that (i) the observed TNR disappearance from bulk aqueous phase could be attributed to physical adsorption onto ZVI and (ii) the TNR reduction can be attributed to chemical reactions mediated by iron surface. After every interval of 0.5 h, the concentrations of TNR in solutions were extracted by *n*-heptane and analyzed by HPLC method. The changes of TNR concentrations in solution (soluble) *versus* the reaction time are presented in Fig. 1.

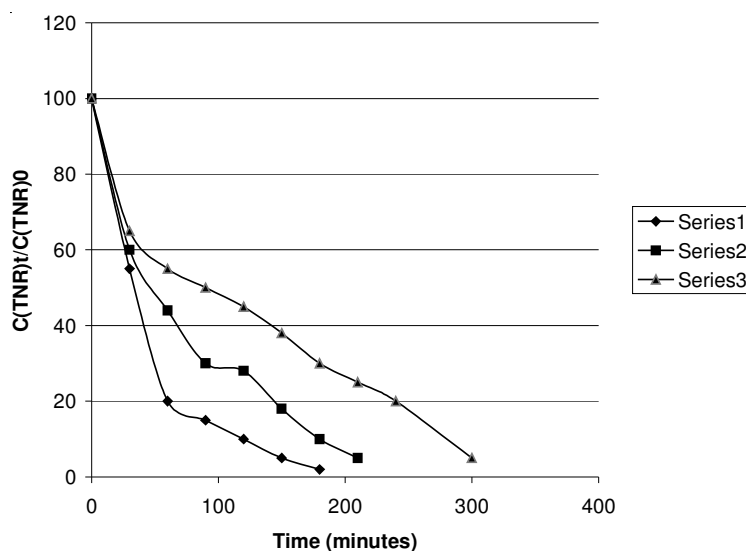


Fig. 1. Change of TNR relative concentrations $\frac{C(\text{TNR})_t}{C(\text{TNR})_0} \times 100$ by ZVI. **Series 1:** Initial TNR concentration: 80 mg/L. **Series 2:** Initial TNR concentration: 100 mg/L. **Series 3:** Initial TNR concentration: 140mg/L.

The concentrations of TNR existed in suspense and adsorbed on iron surface (not presented here) were small and neglected.

Fig. 1 indicates that with the increase of TNR concentrations (from 80-140 mg/L) the reaction rates between TNR and ZVI decrease. This was because of an influence of the initial concentrations of nitro aromatic compounds reacting with ZVI particle which has been reported by Wanaratna *et al.*³. According to these authors, the highest reaction rate (k_1) corresponds to the lowest initial TNR concentration and the lowest k_1 corresponds to the highest initial TNR concentration. These results

indicate that the reaction rate is a strong function of the number of surface active sites and therefore the ZVI:TNR molar ratio is an important reaction variable. During the reaction, the number of surface active sites decreases that causes the decrease of reaction rate. At the initial time of reaction, the number of surface active sites is high, at this moment, the reductive reaction rate of the TNR depends only on the TNR concentration. This means that the reaction kinetic order is pseudo-first order. The expression of reaction rate is as follows:

$$\frac{d[\text{TNR}]}{dt} = -k_1[\text{TNR}] \quad (2)$$

The data in Fig. 1 show that when the number of surface active sites have decreased, the reaction rates in the reactions of series 1, 2, 3 decrease significantly after 60, 45 and 40 min, respectively, when the number of surface active sites have decreased, the reaction rates decrease significantly. It means that at these times the reaction rates depend not only on the TNR concentrations but on the active surface sites of ZVI particles. The expression of these reaction rates corresponding to that times could be given as follows:

$$\frac{d[\text{TNR}]}{dt} = -k_2[\text{TNR}][\text{ZVI}] \quad (3)$$

In this case, the reduction of TNR follows a second order rate law with respect to the TNR and iron concentrations.

Comparing (2) and (3), we have

$$k_1 = k_2[\text{ZVI}] \quad (4)$$

Based on the kinetic curves of the reductive reactions between TNR and ZVI, the k_1 would be determined and then k_2 value by the expression $k_2 = \frac{k_1}{[\text{ZVI}]}$. In this case, the $k_1 = 0.015 \text{ min}^{-1}$, $k_2 = 0.022 \text{ M}^{-1}\text{L min}^{-1}$ have been determined.

Oxidative reaction of the reduced products of TNR by ZVI particles: The obtained amine products (in near 250 mL) from reductive reaction of TNR were mixed with other ZVI particles (10 g) and 84 mg of EDTA in 500 mL capacity flask, in presence of air. The efficiency of oxidative reaction of amine products by ZVI particles from present experiments was presented in Fig. 2.

The experimental data showed that the efficiency of oxidative reaction of amine products by ZVI in the studied system was much higher than the direct oxidation of TNR. After 80 min of experiments the oxidative efficiency of amine resorcinol achieved 98 %, while direct oxidation of TNR was 28 %. The oxidation of amine resorcinol or TNR compound was implemented by the free radical OH^\bullet generated in the system (see relations from 6-11). The easy oxidation of amine resorcinol than TNR may be explicated by the attack of free radical OH^\bullet on amine resorcinol is more easy than on nitro resorcinol. Some parameters such as the concentrations of TNR, ZVI, EDTA, pH solution influenced on the oxidative efficiency may become the subjects of the further studies.

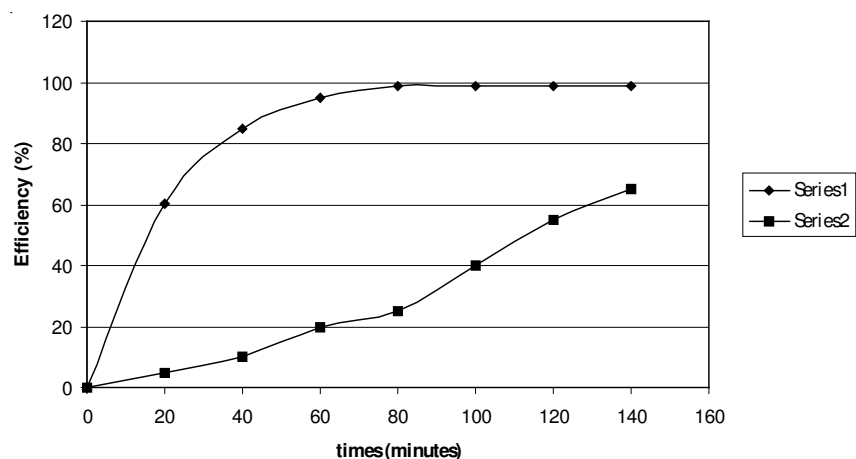


Fig. 2. Efficiency of oxidation reaction with ZVI particles in the presence of EDTA and oxygen. **Series 1.** The oxidation of amine products of the amine resorcine by ZVI. **Series 2.** The direct oxidation of TNR by ZVI

Suggested treatment model of TNR contaminated groundwater: The treatment model of TNR contaminated groundwater consists of two units given in Fig. 3.

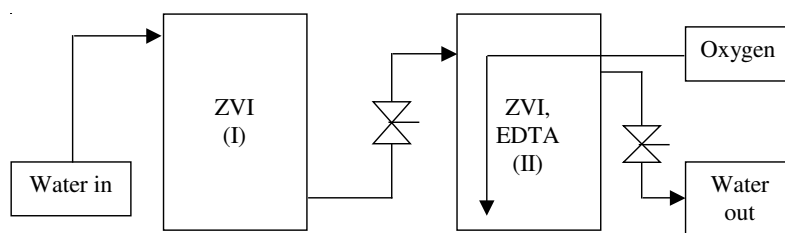


Fig. 3. Treatment model of TNR contaminated groundwater. (I) Unit containing ZVI and sand gravel. (II) Unit containing ZVI, EDTA, sand saturated by oxygen

Water from well pumped into chamber (I), where there is ZVI particles, sand and gravel. The polluted TNR compound is reduced by ZVI, form amine resorcine and Fe_2O_3 . The amine products after a certain time will flow in the second unit for the oxidation step, in presence of EDTA, sand, gravel and oxygen from air. The oxidation reaction between the amine resorcine and the free radical generated in the system will be carried out. The water come out from second unit will go to other treatment. After certain time both two units must be reactivated by a suitable diluted acid solution to remove the Fe_2O_3 layers on ZVI particles. The suggested model was applied to treat the TNR contaminated groundwater in a military plant with the capacity of $5 \text{ m}^3/\text{day}$. The TNR concentration in groundwater was decreased from 35-0.005 ppm. The system works normally, after every 2 weeks the system is reactivated by 0.02 M HCl.

Conclusion

The reduction of TNR by ZVI in anaerobic conditions and the oxidative reaction of amine resorcine in the system of ZVI-EDTA-O₂ have been important to remove TNR from groundwater. TNR compound can be reduced in the anaerobic conditions by ZVI and then its products would easily be oxidized in aerobic conditions in the system of ZVI-EDTA-O₂. HPLC method and COD analysis have been used for monitoring efficiency of reactions. From the obtained results, a model for TNR contaminated groundwater treatment has been suggested.

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REFERENCES

1. A. Agrawal and P.G. Tratnyek, *Environ. Sci. Tech.*, **30**, 1953 (1996).
2. L. McDowall, Degradation of Toxic Chemicals by Zero-Valent Metal Nanoparticles - A Literature Review, Human Protection and Performance Division, Defence Science and Technology Organisation DSTO-GD-0446, pp. 8-15 (2005).
3. P. Wanaratna, C. Christodoulatos and M. Sidhoun, *J. Hazard. Mater.*, **136**, 68 (2006).
4. M.M. Scherer, B.A. Balko and P.G. Tratnyek, *J. Am. Chem. Soc.*, **15**, 301 (1999).
5. D.F. Laine, S.D. McAllister, I.F. Cheng, *J. Electroanal. Chem.*, **608**, 111 (2007).

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