TWO STEP OXIDATION OF 2,4,6-TRINITRORESORCINE (TNR) USING ZERO-VALENT IRON (ZVI) AND ITS APPLICATION IN REMOVAL OF TNR FROM GROUNDWATER

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abstract: This paper describes the character of the reduction of TNR by ZVI in anaerobic conditions and the oxidative reaction of amine resorcine in the system of ZVI-EDTA-O_2. The products of TNR by ZVI in anaerobic conditions were amine resorcine compounds. These compounds tend to be easier to oxidize by the generated in the system of ZVI-EDTA-O_2. HPLC and Chemical Oxygen Demand analysis (COD) were used to monitor the efficiency of reactions. The experiments have suggested that the removal of TNR from groundwater should be implemented by a two step process. The first step is reduction of TNR by ZVI to form amine resorcine. The second step is oxidation of amine resorcine in a system consisting of ZVI-EDTA-O_2. From the obtained results, a model for TNR contaminated groundwater treatment has been suggested and tested.

key words: TNR compounds; Reduction of TNR; Oxidation of TNR; Treatment of TNR.

1. Introduction

Groundwater contamination has become a serious problem. 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 monitions 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.

The TNT, TNR, and RDX may be removed from groundwater by such methods as adsorption onto granular activated carbon, destruction by photo catalysis, biodegradation and incineration. Recently ZVI particles have been used for treatment of many recalcitrant

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organic compounds like nitro aromatic, chlorinated compounds [1-3,5-8]. The chemical background of this method consists of the following reactions:
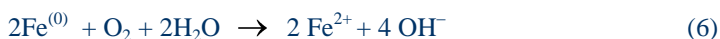
In the absence of oxygen, we have:

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

$$Fe^{2+}_{(sur)} \rightarrow Fe^{3+}_{(sur)} + 1e^- \tag{2}$$

$$2H_2O + 2e^- \rightarrow H_2(g) + 2OH^- \tag{3}$$

In principle, $Fe^{(0)}$, Fe^{2+}, and H_2 can contribute to the reduction of contaminants [4]. The predominant degradation pathway for chlorinated compounds (RX) and for nitro aromatic compounds ($ArNO_2$) appears to be reductive processes:

$$RX + H^+ + 2 e^- \rightarrow RH + X^- \tag{4}$$

$$ArNO_2 + 6 e^- + 6 H^+ \rightarrow ArNH_2 + 2 H_2O \tag{5}$$
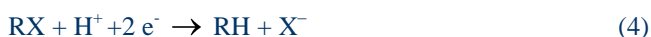
The reduced products such as RH, $ArNH_2$ may be easily treated by biodegradation. The rates of Reactions 4 and 5, depend on the factors such as size, surface area of ZVI particles, pH of solution, concentration of dissolved oxygen, carbonate ions, contaminant concentrations, and some organic compounds, especially ethylendiamineteraacetic acid (EDTA).

The system of Fe^{2+}- H_2O - EDTA in the presence of oxygen has demonstrated such a strong oxidative character that it mineralizes many refractory organic compounds. The oxidative character of this system is based on the following reactions [5,9-12]:

$$2Fe^{(0)} + O_2 + 2H_2O \rightarrow 2 Fe^{2+} + 4 OH^- \tag{6}$$

$$Fe^{(II)}EDTA + O_2 \rightarrow O_2 Fe^{(II)}EDTA, \qquad k_1 = 10^3 \ M^{-1}s^{-1} \tag{7}$$

$$O_2 Fe^{(II)}EDTA \rightarrow Fe^{(III)}EDTA + O_2^- \qquad k_2 = 10^2 M^{-1}s^{-1} \tag{8}$$

$$Fe^{(II)}EDTA + O_2^- \rightarrow O_2^{2-} - Fe^{(III)}EDTA , \qquad k_3 = 10^6 \ M^{-1}s^{-1} \tag{9}$$

$$O_2^{2-} - Fe^{(III)}EDTA + 2H^+ \rightarrow Fe^{(III)}EDTA + H_2O_2, \quad k_4 = fast \tag{10}$$

$$Fe^{(II)}EDTA + H_2O_2 \rightarrow Fe^{(III)}EDTA + OH^- + OH^{\bullet}, \quad k_5 = 10^3 \ M^{-1}s^{-1} \tag{11}$$

The $Fe^{(II)}$EDTA complex formed in the solution plays in role of catalyst for this conversion reaction. The free radical $OH^{\bullet}$ plays the role of oxidative reagent in mineralization process.

In this paper we present the study on the mineralization of 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 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.

2 Experimental

2.1 Chemicals: 2,4,6-trinitroresorcine, zero-valent iron and ethylendiamineteraacetic acid (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.

ZVI pretreatment: Prior to use, the ZVI particles were hand-sieved to constrain grain size to 18-20 mesh and sonicated in 10% (v/v) HCl for 20min. to remove the oxide layer and other contaminants. 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 was between 3.5 to 4.5 m^2/g.

The *p*H solution for all experiments was controlled by an acid or basic solution, H_2SO_4 0.1M, NaOH 0.1M respectively

2.2 Reduction of TNR by ZVI particles (step 1)

Batch experiments were conducted under anaerobic conditions in 500 ml round flask. The flask was spiked with 0.5 ml TNR stock solution and distilled water, to get a total volume of 250 ml with an initial concentration of 80mg/L, pH = 5.5, with the oxygen removed by N_2 purge. The TNR concentrations during the experiments 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 340nm. Analysis by HPLC was performed with a C- 18 column (length 250mm. ID 4.6 mm; Altech, Deerfield,IL). The mobile phase used was a mixture of 45:55 accetonitrile/water with a flow rate of 1.0 ml/min. These experiments allowed us to determine the time when the most TNR in the samples was converted into amine products.

2.3 Oxidation of amine products (step 2)

The amine products obtained from reduction of TNR by ZVI were filtered to removal iron particles before oxidation. Batch experiments were conducted under aerobic conditions in 500- ml open round flask. The flask contains the amine products (near 250ml solution). The flasks received 10g of dry, sieved iron and 84mg EDTA. Each reactor (flask) was placed on shaker with 40 rpm at room temperature every 30 minutes, a sample of 10ml was taken, filtered for measurement of COD. An analysis of COD was then carried out by titrimetric method.Analysis offerrous was conducted by using the modified 1,10-phenatroline colorimetric method at 510 nm. The oxidation efficiency of TNR was calculated by the expression as follows:

$$E = \frac{[COD]_0 - [COD]_t}{[COD]_0} 100 \, , \, (\%) \tag{12}$$

Here $[COD]_0$, $[COD]_t$ are the COD values corresponding to samples at the initial and t- time of oxidation process. The influence of the EDTA amount on COD values was eliminated by the blank in the same conditions, but withou TNR.

3 Results and discussion

3.1 The reductive reaction of TNR by ZVI particles

In near neutral medium, there is spontaneous iron oxidation with the production of hydrogen ions as shown in reaction 13.

$$2\ Fe^{(0)} + 3\ H_2O\ \rightarrow\ Fe_2O_3 + 6e^- + 6H^+ \qquad (13)$$

When this half reaction is combined with reduction of TNR, the hydrogen ions are typically neutralized. The final reaction is given:

$$C_6H_3(OH)_2(NO_2)_3 + 3\ H_2O + 6\ Fe\ \rightarrow\ C_6H_3(OH)_2(NH_2)_3 + 3\ Fe_2O_3 \qquad (14)$$

In these conditions, the reduction of TNR by ZVI after 60 minutes was 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 the direct interaction between $Fe^{(0)}$ and TNR, (ii) the TNR reduction can be attributed to chemical reactions mediated by iron surface. After every interval of 30 minutes, the concentrations of TNR in solutions were extracted by n-heptan and analyzed by HPLC method. The changes of TNR concentrations in solution (soluble) versus the reaction time are presented in Fig. 1.
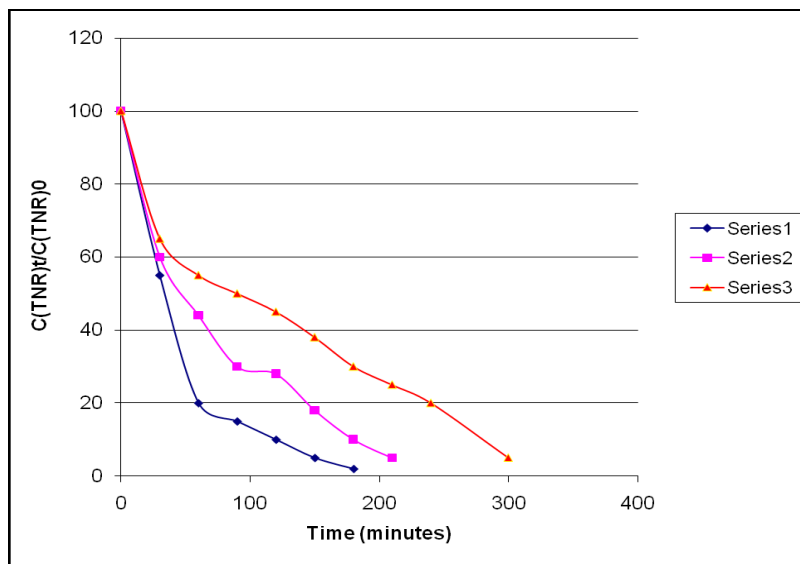

Fig. 1 *The change of TNR relative concentrations* $\frac{C(TNR)_t}{C(TNR)_0} 100$ *by ZVI*

Series 1: The initial TNR concentration: 80mg/L.
Series 2: The initial TNR concentration: 100mg/L.
Series 3: The 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 80mg/L to 140mg/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 [2,3, 4]. 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 which causes the decrease of reaction rate. At the initial time, the number of surface active sites is high, and the reduction reaction rate of the TNR depends only on the TNR concentration. This means that the reaction kinetic order is pseudo-first one. The expression of reaction rate is as follows:

$$\frac{d[TNR]}{dt} = -k_1[TNR] \qquad (15)$$

The data in Fig. 1 show that after 60, 45 and 40 minutes, when the number of surface active sites have decreased, the reaction rates in the reactions of series 1, 2 and 3 respectively 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 those times could be given as follows:

$$\frac{d[TNR]}{dt} = -k_2[TNR][ZVI] \qquad (16)$$

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 $\qquad k_1 = k_2[ZVI] \qquad (17)$

Based on the kinetic curves of the reductive reactions between TNR and ZVI, k_1 was determined and then k_2 was determined from k_1, by the expression $k_2 = \dfrac{k_1}{[ZVI]}$. In this case, the $k_1 = 0.015$ mn^{-1}, $k_2 = 0.022$ M^{-1}L.mm^{-1} have been determined.

3.2 Oxidative reaction of the reduced products of TNR by ZVI particles

The obtained amine products (approx. 250 ml) from reductive reaction of TNR were mixed with fresh ZVI particles (10g) and 84mg of EDTA in a 500 ml flask, in presence of oxygen from air. The efficiency of the oxidative reaction of amine products by ZVI particles from our experiments was presented in Fig. 2.
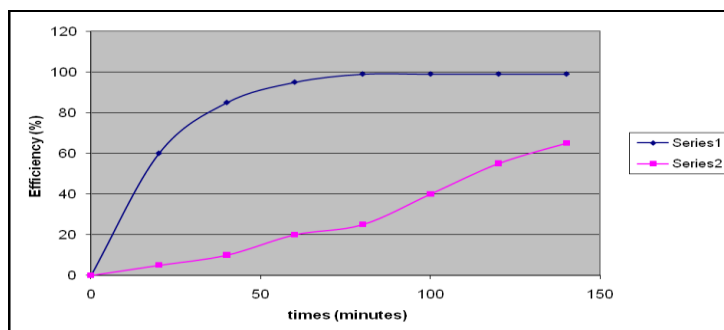
Fig. 2 *The efficiency of oxidation reaction with ZVI particles in the presence of EDTA and oxygen*
Series 1. The oxidation of amine products of the amine resorcine by ZVI.
Series 2. The direct oxidation of TNR by ZVI.

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 minutes the oxidative efficiency of amine resorcine achieved 98%, while the direct oxidation of TNR was 28%. The oxidation of amine resorcine or TNR compound was implemented by the free radical $OH^\bullet$ generated in the system (see relations from 6 to 11). The ease of amine resorcine oxidation compared to TNR may be because $OH^\bullet$ reacts faster with amine resorcine than on nitro resorcine. 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.

3.3 The suggested treatment model of TNR contaminated groundwater

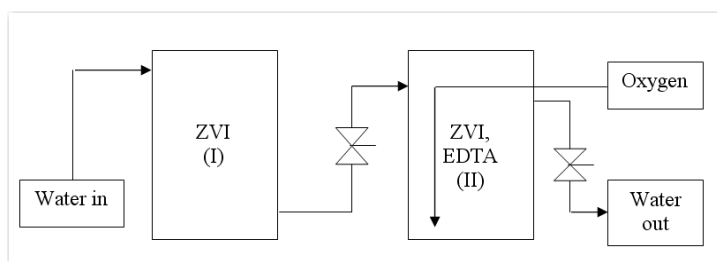The treatment model of TNR contaminated groundwater consists of two units given in Fig. 3.

Fig. 3 *The treatment model of TNR contaminated groundwater*
(I) Unit containing ZVI and sand gravel
(II) Unit containing ZVI, EDTA, sand, and saturated with air.

Water from a well is pumped into compartment (I), where the polluted TNR compound is reduced by ZVI to form amine resorcine and Fe_2O_3. The amine products after reacting will flow into the second compartment for the oxidation step, where there is EDTA, sand, gravel and oxygen from air. The oxidation reaction between the amine resorcine and the free radical $OH^\bullet$ generated in the system will be carried out. The water from the second unit will then go on to other treatments. Periodically both two units must be reactivated by flushing with diluted acid to remove the Fe_2O_3 layers on ZVI particles. The suggested model was

applied to treat TNR contaminated groundwater in a military plant with the capacity of $5m^3$/day. The TNR concentration in the groundwater was decreased from 35ppm to 0.005ppm. Every two weeks the system was reactivated with 0.02 M HCl.

Conclusion

The reduction of TNR by ZVI in anaerobic conditions and the oxidation reaction of amine resorcine in the system of ZVI-EDTA-O_2 has been very important for studying to removal of TNR from groundwater. TNR can be reduced in the anaerobic conditions by ZVI and then its products can easily be oxidized in aerobic conditions in the system of ZVI-EDTA-O_2. HPLC method and analysis by COD was used to monitor the efficiency of reactions. From the obtained results, a model for TNR contaminated groundwater treatment has been suggested and successfully demonstrated

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