ANALELE UNIVERSITATII BUCURESTI
Department of Physical Chemistry
4-12 Regina Elisabeta Blvd, District 3, Bucharest
phone: +40-21-3143508; fax: +40-21-3159249
*p*ISSN: 1220-871X *e*ISSN: 1844-0401

ARS DOCENDI PUBLISHING HOUSE
Sos. Panduri 90, District 5 Bucharest
phone/fax: +40-21-4102575
e-mail: arsdocendi@yahoo.com

DEGRADATION OF 2,4,6-TRINITRORESORCINE (TNR) BYPERSULFATE OXIDATION ACTIVATED WITH ZERO-VALENT IRON (ZVI)

T.V. Chung *, D.S. Quang *, D.V. Bay ** and T.D. Luong **

abstract: 2,4,6-Trinitroresorcine (TNR) with molecular formula $C_6H_3N_3O_8$ is one of the aromatic nitro compounds ranging slight to strong oxidizing agents causing environmental contamination. The persulfate anions activated by ZVI were used to oxidize organic compounds like trichloroethylene (TCE), methyl tertiary butyl ether (MTBE). The content of this paper was to demonstrate if the ZVI activated persulfate oxidation of TNR was a viable method. The experimental data have shown that the TNR compounds in aqueous media were oxidized by the persulfate anions activated by ZVI. The reaction participated in components such as TNR; its oxidized products were measured by Voltammetry square wave and TOC analysis. The TOC values in the samples reduced have demonstrated that the final oxidized products were CO_2 + H_2O + other mineral compounds. The activation of the persulfate anions by ZVI may be implemented through the reactions between $S_2O_8^{2-}$ and ZVI to form sulfate free radicals ($SO_4^{-\bullet}$). The mineralization of TNR by the persulfate anions activated by ZVI is favor in the pH range from 3 to 5.

key words: Persulfate anions with ZVI; Persulfate oxidation of TNR; Mineralization of TNR; 2,4,6-Trinitroresorcine.

received: February 23, 2011 *accepted*: May 01, 2011

1. Introduction

Aromatic nitro compounds, such as 2,4,6-Trinitroresorcine (TNR) with molecular formula $C_6H_3N_3O_8$, also called styphnic acid range from slight to strong oxidizing agents. If mixed with reducing agents, including hydrides, sulfides and nitrides, they may begin a vigorous reaction that culminates in a detonation. The presence of TNR in ground water or wastewater may produce irritating, corrosive and toxic for environment and body health. The aromatic nitro contaminated water may be treated by many methods [1] such as physical, chemical. Several new activation technologies now existting to catalyze the formation of sulfate radicals have been used for degradation of many recalcitrant organic

---

* Institute of Chemistry and materials, Hanoi, Vietnam.
corresponding author e-mail: tranchunghhvl@gmail.com
** Hanoi National University of Education, daobaydhsph@yahoo.com

Analele Universităţii din Bucureşti – Chimie (serie nouă), vol 20 no. 1, pag. 41 – 47

compounds. The persulfate anion is a strong oxidant, with an oxidation potential of 2.12 V. However, kinetics at ordinary temperatures, the persulfate anion typically has slow oxidative, for most contaminant species it must to be activated. As a result, persulfate is typically activated for use to oxidize most organic contaminants. In the presence of certain activators such as H_2O_2, Fe^{2+}, OH^-, persulfate anion can be converted to the free sulfate radical, an even stronger oxidant [1-3]:

$$S_2O_8^{2-} + \text{Activator} \rightarrow 2\ SO_4^{-\bullet} \text{or } SO_4^{-\bullet} + SO_4^{2-} \qquad (1)$$

The free sulfate radical is one of the strongest aqueous oxidizing species with a redox

potential estimated to be 2.6 V, similar to that of the hydroxyl radical, 2.8 V. This potential is higher than the redox potential for the redox potentials of $S_2O_8^{2-}$ (2.1 V), MnO_4^- (1.7V). In addition to its oxidizing strength, sulfate radical oxidation has several advantages over other oxidant systems such as kinetically fast rate, the sulfate radical more stable than the hydroxyl radical, able to transport greater distances in the solutions.

Under acidic conditions, persulfate anion can hydrolyze to form hydrogen peroxide:

$$S_2O_8^{2-} + 2\ H_2O \dashrightarrow H_2O_2 + 2\ HSO_4^- \qquad (2)$$

Hydrogen peroxide itself has an oxidation potential of 1.77 V, and in the presence of various activators like Fe^{2+}, can form the Fenton reagents. Under stronger acidic conditions, persulfate can form peroxymonopersulfate anions, with an oxidation potential of 1.44V:

$$S_2O_8^{2-} + H_2O \dashrightarrow HSO_5^- + HSO_4^- \qquad (3)$$

ZVI is a reductive technology that has been used to treat chlorinated solvent contaminated sites[4]. Recently, it has been found that persulfate can be activated by zero valent iron well recognized reducing agent for chlorinated compounds [4-8]. It has been suggested that the mechanism of persulfate activation is by a two steps, whereas the ZVI is the source of divalent iron, which can be used to generate sulfate radicals from persulfate.The reactions may be as follows:

– Reaction to produce Fe^{2+}

When in presence of oxygen:

$$Fe^{(0)} + \tfrac{1}{2}\ O_2 + H_2O \dashrightarrow Fe^{2+} + 2\ OH^- \qquad (4)$$

When absence of oxygen:

$$Fe^{(0)} + 2H_2O \dashrightarrow Fe^{2+} + 2OH^- + H_2 \qquad (5)$$

– Reaction to produce free sulfate radicals

$$S_2O_8^{2-} + Fe^{2+} \dashrightarrow Fe^{3+} + SO_4^{-\bullet} + SO_4^{2-} \qquad (6)$$

As a result, ZVI – persulfate combinations may provide a source of both oxidative and reductive destruction of nitro organic compounds including TNR in groundwater.The object of this paper is to determine if the ZVI activated persulfate oxidation of TNR is possible method .

2. Experimental part

2.1. Materials

TNR yellowish, crystalline solid (85%), sodium persulfate ($Na_2S_2O_8$) (98%) were purchased from a Chinese Company.

The ZVI powder used was a carbonyl iron micro powder also supplied from China with the properties: C ≤ 1 %; Mn ≤ 1 ; P ≤ 1 Fe = 97 %; density: 3-4 g/cm^3; particle size: 8-10 microns.

2.2. Equipments

– Electrochemical Trace Analyzer, model EG&G, USA with electrode M303 was used for the determination of TNR concentrations in the samples.

– TOC -V_E equipment, Shimadzu, Japan.

An Orin model 420 A *p*H meter was used for *p*H measurement.

2.3. Experimental methods

2.3.1. Preparation of experimental solutions

– TNR stock solutions with the concentration of 160mg/L were prepared with distillated water in 250ml brown glass bottles.

– Persulfate stock solutions with concentration of 200 mg /L were also prepared in 250mL brown glass bottles

– Stock solutions of TNR and persulfate were pre mixed to meet the various required molar ratios for experiments.

2.3.2. ZVI activated persulfate oxidation

– The reaction vessels used in the experiments were 100 mL-glass bottles. Each 100 mL bottle was filled up with the amount of TNR solution, persulfate solution and ZVI powder to make up the desired molar of the sample. The *p*H of the experimental solution was then adjusted using 0.1M sulfuric acid or sodium hydroxide to a *p*H of 3, 5, 7 and 9. The bottles were capped with Teflon lined screw caps to minimize the loss due to volatilization. The bottles then were paced on an orbit shaker at 100 rpm and allowed to react for the certain times. After the one hour time period, the 50 mL of sample was taken out and was filtrated in Blue Paper to separate ZVI and its products. The filtrated solutions were use for analysis of TOC and TNR.

– Determination of the total organic compound (TOC). The determination of TOC was based on the stud [9].

– Determination of TNR concentrations by Square Wave Voltammetry method with the following parameters:

5 mL sample taken plus 5mL acetate buffer 0.1M were added in a polarographic vessel to determine TNR with the following parameters:

Dropping mercury electrode: S size.

The initial potential: –1.6 V.

The final potential: –0.2 V.

The scan increment: 2mV.

The frequency: 100 Hz,

The Pulse height: 20 mV

The oxygen in the samples was eliminated by nitrogen current for 10 minutes.

The concentrations of TNR were determined by the addition method.

The evaluation of TNR concentrations was determined by the polarogram peak at – 0.56V.

3. Results and discussion

3.1. Preliminary experiments

The preliminary experiments of this research were to establish the ZVI activated persulfate oxidation of TNR. The experiments were conducted as follows:

The experiment N_1 with TNR (80 mg/L) in NH_4Cl 0.1M;

The experiment N_2 consisting of N_1+20 mg $Fe^{(0)}$/L and the experiment N_3 consisting of N_2+ 800 mg $Na_2S_4O_8$/L. The experimental data were presented in Fig. 1 (a),(b),(c). The peaks appeared corresponding to TNR (–0.460 V) and to Fe^{2+}(–0.34V). The *p*H of all samples was adjusted at 4.5.

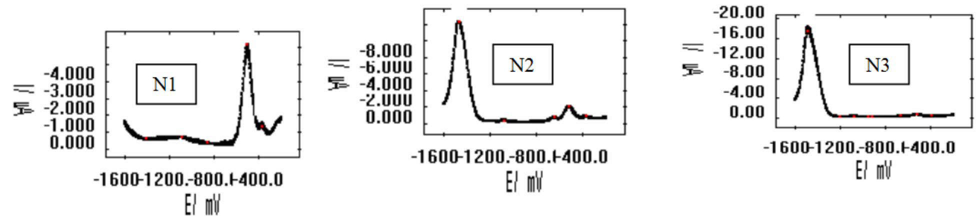
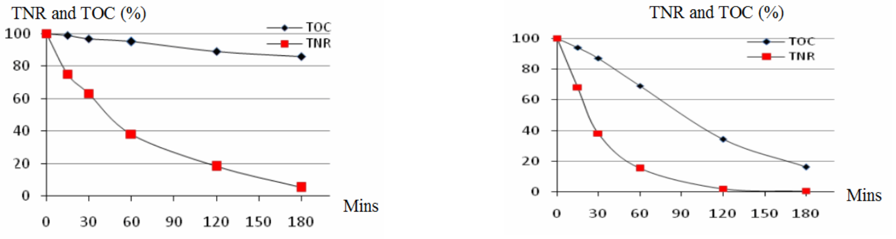


Fig. 1 *Voltammetry curve profile of samples*
N_1 corresponding to the TNR initial concentration (80mg/l); N_2 corresponding to the Fe^{2+} and TNR concentrations for 120 mins; N_3 corresponding to the sample for 120mins.

The obtained experimental data have shown that the role of persulfate anions with ZVI is to increase the degradation rate of TNR in the sample (N_3). The decrease in amount of TNR in the samples N_2, N_3 may be due to the degradation converting TNR onto amine products (inactive Voltammetry) and other mineral products such as CO_2, H_2O. It means that there are both two processes such as reduction and oxidation for TNR in the samples N_2 and N_3. This problem must be studied in detail with determination of TOC of the samples.

3.2. Analysis of TNR and TOC

The samples were carried out in the different time intervals of 30 mins from 0 to 180 mins. The analysis of TNR and TOC for the different time intervals was presented in Fig. 2. The experimental data have shown that the decrease rate (%) of TNR and TOC is different. In the sample N_2 (Fig. 2a), the decrease rate of TNR is significant compared to TOC rate. The significant reduction of TNR (N_2) is due to converting TNR onto amine inactive Voltammetry products [10]. In the sample N_3 (Fig. 2b), there are both the high decrease of TNR and TOC but having a difference.



a *b*

Fig. 2 *The decrease of TNR and TOC for the times*

a: The decrease of TNR and TOC in the sample N_3; b: The decrease of TNR and TOC in the sample N_2.

In the sample N_3 (Fig.2b) at initial time, the decrease (%) of TNR is much more than for the 60 mins, while the decrease (%) of TOC is slower at the initial time. The decrease of TOC in the sample N_3 is a proof for the mineralization of TNR or its intermediate products to form CO_2 and H_2O. This phenomenon may be illustrated by the activation of persulfate anions by ZVI to generate free sulfate radical[5]. The overall reactions to form free sulfate radical is following:

$$Fe^{(0)} + S_2O_8^{2-} \rightarrow 2\ SO_4^{2-} + Fe^{2+} \tag{7}$$

$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{-\bullet} + SO_4^{2-} + Fe^{3+} \tag{8}$$

$$\text{TNR (or Products)} + 2\ SO_4^{-\bullet} \rightarrow CO_2 + NO_2^{-}/NO_3^{-} + H_2O + SO_4^{2-} \tag{9}$$

By this way with the presence of persulfate, Fe(0) might be a good Fe^{2+} provider for the activation of persulfate to sulfate radicals. It is evident that the free sulfate radical may react with other components presented in the sample such as $Fe^{(0)}$, Fe^{2+} therefore it may reduce the effectiveness of the free sulfate radical oxidation. To increase the oxidative effectiveness, a suitable molar ratio of persulfate anion, target contaminant and ZVI can be chosen [11]. For this study the molar ratio approximates to 10/1/1. The following research may focus on the influence of *p*H on the oxidative efficiency of the persulfate oxidation by ZVI.

3.3. The influence of *p*H experiments

The experimental data have shown that *p*H plays a prominent role in catalyzed and iron mediated reactions for mineralization of TNR in the samples (see Fig. 3).

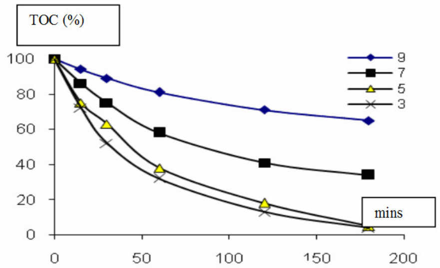


Fig. 3 *The influence of pH on the TOC for the time, the molar ratio of sulfate anions/TNR/ZVI is 10/1/1, pH from 3 to 9.*

The experimental data in this study showed that for the time more 120 mins, greater than 80 percent of TOC was reduced at pH range from 3 to 5. This means that *p*H plays a prominent role in the oxidation of TNR, but by what way. We know that ZVI has reductive properties and therefore by the time, in the sample it would most likely be able first to reduce the TNR by ZVI to form amine products then these products would be oxidized. In practice, the oxidation of TNR by the free sulfate radical is more difficult than the oxidation of its reduced products (amine products). The chemical process in the sample would be suggested as follows:

$$\text{mFe}^{(0)} + \text{TNR} + \text{n H}^{+} \rightarrow \text{m Fe}^{2+} + \text{Amine Products} \qquad (10)$$

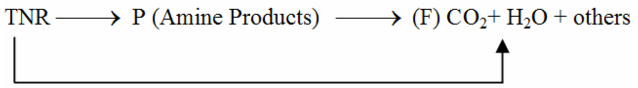
$$\text{Amine Products} + 2\,\text{SO}_4^{-\bullet} \rightarrow \text{CO}_2 + \text{NO}_2^{-}/\text{NO}_3^{-} + \text{H}_2\text{O} + \text{SO}_4^{2-} \qquad (11)$$

$$\text{TNR} + \text{SO}_4^{-\bullet} \rightarrow \text{CO}_2 + \text{NO}_2^{-}/\text{NO}_3^{-} + \text{H}_2\text{O} + \text{SO}_4^{2} \qquad (12)$$

On the other hand, in acidic media the ferrous ions are enough stable to activate the persulfate anions in the sample to form free sulfate radicals so that increase the oxidative process.

3.4. The suggestion of the oxidation path way of TNR

From the reactions (10- 12) they have shown that the TNR mineralization process may depend on three steps: (i) the reduction of TNR to form amine products, (ii) the oxidation of the amine products, and (iii) the direct oxidation of TNR, The schema of the mineralization may be presented as follows:



(13)

4. Conclusions

By the experimental data it has shown that the TNR in aqueous media was oxidized by the persulfate anions activated by ZVI. The reaction components such as TNR, oxidized products of TNR were measured by Voltammetry square wave and TOC analysis. The TOC values in the samples reduced have demonstrated that the final oxidized products were CO_2+H_2O + other mineral compounds. The activation of the persulfate anions by ZVI may be implemented through the reactions between $S_2O_8^{2-}$ and ZVI. The mineralization of TNR by the persulfate anions activated by ZVI is favor in the pH range from 3 to 5.

Acknowledgments: The authors are grateful to The National Foundation for Science & Technology Development (NAFOSTED) for the financial support to do this work.

REFERENCES

1. Peroxygen Talk. “Choosing the Right Activator”, Jan 2006. (www.klozur.com)
2. Block, P.A., R.A. Brown and D. Robinson. “Novel Activation Technologies for Sodium Persulfate In Situ Chemical Oxidiation”, 4th International Conference on the Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, 2004.
3. Klozur Technical Bulletin #1 – Activator Selection Guide (see Klozur Resource Center, www.klozur.com).
4. Brown, R.A., D. Robinson and P.A. Block. “Simultaneous Reduction and Oxidation: Combining Sodium Persulfate and Zero Valent Iron”. 3rd Oxidative – Reductive Technology (ORT) Conference, 2004.
5. Padmanabhan, A.R. “Novel Simulataneous Reduction / Oxidation Process for Destroying Organic Solvents”. Master’s Thesis: Worcester Polytechnic Institute, 2008.
6. Liang, C. and M.C. Lai. “Trichloroethylene Degradation by Zero Valent Iron Activated Persulfate Oxidation”, Env. Eng. Sci. 25, p 1071 – 1077, 2008.
7. Oh, S.Y., H.W. Kim, J.M. Park, H.S. Park and C. Yoon. “oxidation of polyvinyl alcohol by persulfate activated with heat, Fe (II) and zero valent iron”. J. Haz Mat 168, p 346 – 351, 2009.
8. Oh, S.Y., S.G. Kang and P.C. Chiu. “Degradation of 2,4-dinitrololuene by persulfate activated with zero valent iron”. Science of the Total Environment 408, p 3464 – 3468, 2010.
9. Total Organic Carbon (TOC) Analysis: Chapter 11: GEOCHEMICAL METHODS AND EXPLORATION, Daniel M. Jarvie, *AAPG Special Volumes* Volume TR: Source and Migration Processes and Evaluation Techniques, Pages 113 - 118 (1991).
10. L.Q.Trung, N.V.Chat, N.D. Hung, T.V.Chung and I.F.Cheng, Two steps oxidation of 2,4,6-Trinitroresorcine TNR) and its application in removal of TNR from groundwater. ANALELE Universitatii BUCURESTI, 2009, Vol 18, No.2,pag.77-83.
11. Sharma Sachin Slurry Test Evaluation for In-Situ Remedation of TCE Contamination Aquifer. Worcester Polytechnic Institute. Master of Science Thesis.