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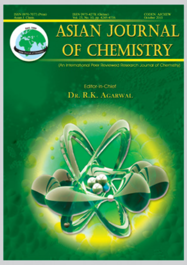

Degradation of 2,4,6-Trinitroresorcinol by Persulfate Oxidation

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2,4,6-Trinitroresorcinol 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 zero valent iron were used to oxidize organic compounds like trichloroethylene, methyl tertiary butyl ether. This work demonstrates if the zero valent iron activated persulfate oxidation of 2,4,6-trinitroresorcinol was a viable method. The experimental data have shown that the 2,4,6-trinitroresorcinol in aqueous media were oxidized by the persulfate anions activated by zero valent iron. The reaction participated in components such as 2,4,6-trinitroresorcine; its oxidized products were measured by voltammetry square wave and total organic carbon analysis. The reduced total organic carbon values in the reduced samples have demonstrated that the final oxidized products were $CO_2 + H_2O$ + other mineral compounds. The activation of the persulfate anions by zero valent iron may be implemented through the reactions between $S_2O_8^{2-}$ and zero valent iron to form sulfate free radicals ($SO_4^{-\bullet}$). The mineralization of 2,4,6-trinitroresorcinol by the persulfate anions activated by zero valent iron is favour in the pH ranged from 3 to 5.

Key Words: Persulfate anions, Zero valent iron, Persulfate oxidation, 2,4,6-Trinitroresorcine.

INTRODUCTION

Aromatic nitro compounds, such as 2,4,6-trinitroresorcinol (TNR) with m.f. $C_6H_3N_3O_8$, 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 2,4,6-trinitroresorcinol 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 physical or chemical methods. Several new activation technologies now existing to catalyze the formation of sulfate radicals have been used for the degradation of many recalcitrant organic carbons. The persulfate anion with an oxidation potential of 2.12 V is a strong oxidant, with an oxidation. However, kinetics at ordinary temperatures, the persulfate anion typically showed the 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 the 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]:

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

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:

$$S_2O_8^{2-} + 2H_2O \rightarrow H_2O_2 + 2H_sO_4^- \qquad (2)$$

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

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

Zero-valent iron 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 zero-valent iron 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+}

In presence of oxygen:

$$Fe^0 + 0.5O_2 + H_2O \rightarrow 2Fe^{2+} + 4OH^- \quad (4)$$

In absence of oxygen:

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

- Reaction to produce free sulfate radicals

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

As a result, zero-valent iron-persulfate combinations may provide a source of both oxidative and reductive destruction of nitro organic carbons including 2,4,6-trinitroresorcinol in groundwater. This work report zero-valent iron activated persulfate oxidation of 2,4,6-trinitroresorcinol.

EXPERIMENTAL

2,4,6-Trinitroresorcinol yellowish, crystalline solid (85 %), sodium persulfate ($Na_2S_2O_8$) (98 %) were purchased from a Chinese company. The zero-valent iron powder used was a carbonyl iron micro powder also supplied from China with the properties: C < 1 %; Mn= 0.3%; P= 1%; Fe = 97 %; density: 3-4 g/cm^3; particle size: 8-10 μ.

Electrochemical trace analyzer, model EG & G, USA with electrode M303 was used for the determination of 2,4,6-trinitroresorcinol concentrations in the samples. Total organic carbon determined by VE equipment, Shimadzu, Japan. An Orin model 420 A pH meter was used for pH measurement.

Preparation of experimental solutions: 2,4,6-Trinitroresorcinol stock solutions with the concentration of 160 mg/L were prepared with distilled water in 250 mL brown glass bottles. Persulfate stock solutions with concentration of 200 mg /L were also prepared in 250 mL brown glass bottles. Stock solutions of 2,4,6-trinitroresorcinol and persulfate were pre mixed to meet the various required molar ratios for experiments.

Zero-valent iron 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 2,4,6-trinitroresorcinol solution, persulfate solution and zero-valent iron powder to make up the desired molar of the sample. The pH of the experimental solution was then adjusted using 0.1 M sulfuric acid or sodium hydroxide to a pH 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 placed on an orbit shaker at 100 rpm and allowed to react for the certain times. After 1 h time period, the 50 mL of sample was taken out and was filtrated in blue paper to separate zero-valent iron and its products. The filtrated solutions were used for analysis of total organic carbon and 2,4,6-trinitroresorcinol.

Determination of the total organic carbon (TOC): The determination of total organic carbon was based on the studies[9].

Determination of 2,4,6-trinitroresorcinol: Determination of 2,4,6-trinitroresorcinol concentrations by square wave voltammetry method with the following parameters: 5 mL sample taken plus 5 mL NH_4Cl 0.1 M were added in a polarographic vessel to determine 2,4,6-trinitroresorcinol 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 min. The concentrations of 2,4,6-trinitroresorcinol were determined by the addition method. The evaluation of 2,4,6-trinitroresorcinol concentrations was determined by the polarogram peak at - 0.56V.

RESULTS AND DISCUSSION

Preliminary experiments: The preliminary experiments of this research were to establish the zero-valent iron activated persulfate oxidation of 2,4,6-trinitroresorcinol. The experiments were conducted as follows:

The experiment N_1 with 2,4,6-trinitroresorcinol (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 $Na_2S_2O_8$/L. The experimental data were presented in the Fig. 1(a), (b), (c). The peaks appeared corresponding to 2,4,6-trinitroresorcinol (-0.460 V) and to Fe^{2+} (-1.34V). pH of all samples was adjusted at 4.5.

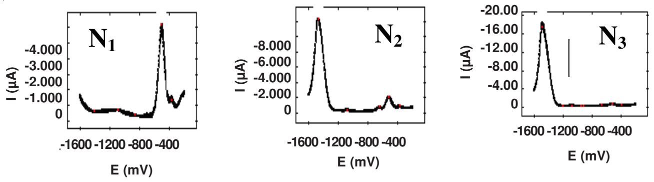

Fig. 1. Voltammetry curve profile of samples; a: N_1 corresponding to the 2,4,6-trinitroresorcinol initial concentration (80 mg/L); b: N_2 corresponding to the Fe^{2+} and 2,4,6-trinitroresorcinol concentrations for 2 h; N_3 corresponding to the sample for 2 h

The obtained experimental data have shown that the role of persulfate anions with zero-valent iron is to increase the degradation rate of 2,4,6-trinitroresorcinol in the sample (N_3). The decrease in amount of 2,4,6-trinitroresorcinol in the samples N_2, N_3 may be due to the degradation converting 2,4,6-trinitroresorcinol 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 2,4,6-trinitroresorcinol in the samples N_2 and N_3. This problem must be studied in detail with determination of total organic carbon of the samples.

Analysis of 2,4,6-trinitroresorcinol and total organic carbon: The samples were carried out in the different time intervals of 0.5 h from 0 to 3 h. The analysis of 2,4,6-trinitroresorcinol and total organic carbon for the different time intervals was presented in Fig. 2. The experimental data have shown that the decrease rate (%) of 2,4,6-trinitroresorcinol and total organic carbon is different. In the sample N_2 (Fig. 2a), the decrease rate of 2,4,6-trinitroresorcinol is significant compared to total organic carbon rate. The significant reduction of 2,4,6-trinitroresorcinol (N_2) is due to converting 2,4,6-

trinitroresorcinol onto amine inactive voltammetry products[10]. In the sample N_3 (Fig. 2b), there are both the high decrease of 2,4,6-trinitroresorcinol and total organic carbon but having a difference.

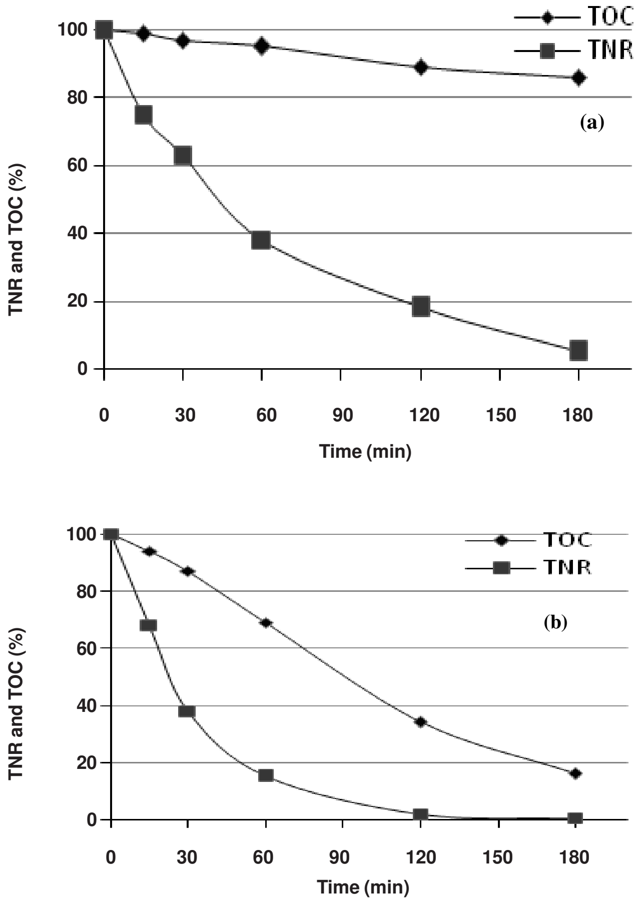

Fig. 2. The decrease of 2,4,6-trinitroresorcinol and total organic carbon for the times; (a) The decrease of 2,4,6-trinitroresorcinol and total organic carbon in the sample N_3; (b) The decrease of 2,4,6-trinitroresorcinol and total organic carbon in the sample N_2

In the sample N_3 (Fig. 2b) at initial time, the decrease (%) of 2,4,6-trinitroresorcinol is much more than for the 1 h, while the decrease (%) of total organic carbon is slower at the initial time. The decrease of total organic carbon in the sample N_3 is a proof for the mineralization of 2,4,6-trinitroresorcinol or its intermediate products to form CO_2 and H_2O. This phenomenon may be illustrated by the activation of persulfate anions by zero-valent iron to generate free sulfate radical[5]. The overall reactions to form free sulfate radical is following:

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

$$Fe^{2+} + S_2O_8^{2-} \rightarrow SO_4^{-\bullet} + SO_4^{2-\bullet} + Fe^{3+} \quad (8)$$

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

Here TNR: 2,4,6 -trinitroresorcine.

By this way with the presence of persulfate, Fe^0 might be a good Fe^{2+} source 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 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 zero-valent iron can be chosen[11]. For this study the molar ratio approximates to10/1/1. The following research may focus on the influence of pH on the oxidative efficiency of the persulfate oxidation by zero-valent iron.

Influence of pH experiments: The experimental data have shown that pH plays a prominent role in catalyzed and iron mediated reactions for mineralization of 2,4,6-trinitroresorcinol in the samples (Fig. 3).

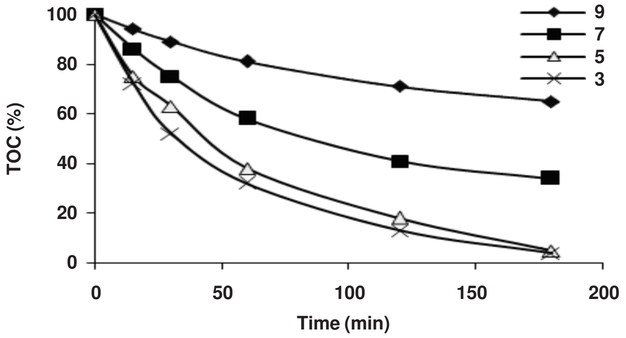

Fig. 3. The influence of pH on the total organic carbon for the time, the molar ratio of sulfate anions/2,4,6-trinitroresorcinol/zero-valent iron is 10/1/1, pH from 3 to 9

The experimental data in this study showed that for the time more 2 h, greater than 80 % of total organic carbon was reduced at pH range from 3 to 5. This means that pH plays a prominent role in the oxidation of 2,4,6-trinitroresorcinol, but by what way. We know that zero-valent iron has reductive properties and therefore by the time, in the sample it would most likely be able first to reduce the 2,4,6-trinitroresorcinol by zero-valent iron to form amine products then these products would be oxidized. In practice, the oxidation of 2,4,6-trinitroresorcinol 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 as follows:

$$mFe^0 + \text{2,4,6-trinitroresorcinol} + nH^+ \rightarrow m\ Fe^{2+} + \text{Amine Products} \quad (10)$$

$$\text{Amine products} + 2SO_4^- \rightarrow CO_2 + NO_2^-/NO_3^- + H_2O + SO_4^{2-} \quad (11)$$

$$TNR + SO_4^- \rightarrow CO_2 + NO_2^-/NO_3^- + H_2O + SO_4^2 \quad (12)$$

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.

Suggestion of the oxidation path way of 2,4,6-trinitroresorcinol: From the reactions (10- 2) they have shown that the 2,4,6-trinitroresorcinol (TNR) mineralization process may depend on three steps: (i) the reduction of 2,4,6-trinitroresorcinol to form amine products, (ii) the oxidation of the amine products and (iii) the direct oxidation of 2,4,6-trinitroresorcinol. The schema of the mineralization may be presented as follows:

$$TNR \rightarrow \text{P (Amine products)} \rightarrow \text{(F) } CO_2 + H_2O + \text{others} \quad (13)$$

Conclusion

By the experimental data it is shown that the 2,4,6-trinitroresorcinol in aqueous media was oxidized by the persulfate anions activated by zero-valent iron. The reaction components such as 2,4,6-trinitroresorcinol, oxidized products of 2,4,6-trinitroresorcinol were measured by voltammetry square wave and total organic carbon analysis. The total organic carbon 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 zero-valent iron may be implemented through the reactions between $S_2O_8^{2-}$ and zero-valent iron. The mineralization of 2,4,6-trinitroresorcinol by the persulfate anions activated by zero-valent iron is favour in the pH range from 3 to 5.

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