



## Degradation of Nitrobenzene by Persulfate Activated with Zero-valent Iron

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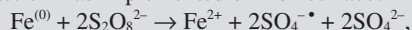
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The properties of zero-valent iron is useful in remediation of aromatic nitro compounds by reducing them to convert onto the amino products which may also lead to oxidize or mineralize them with the presence of persulfate anion ( $S_2O_8^{2-}$ ). In practice, with the zero-valent iron, persulfate anion ( $E^0 = 2.01$  V) may be activated to produce free sulfate radical ( $SO_4^{\cdot-}$ ) with the higher standard reduction potential ( $E^0 = 2.60$  V). It is an active reagent for the mineralization of nitrobenzene in the studied samples. The activation process of persulfate in solution with zero-valent iron to produce  $SO_4^{\cdot-}$ , may be implemented by the following pathways:

In the heterogeneous system the activation reaction was implemented on iron surface:



In homogeneous case, the activation process was implemented in solution:



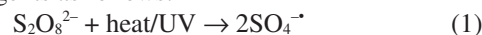
In the studied system zero-valent iron is a source producing  $Fe^{2+}$  to keep the activation of persulfate anion. The free sulfate radical formed *in situ* oxidizes nitrobenzene causing the decrease of the total organic carbon in the samples. The experimental data have shown that the nitrobenzene concentration of 80 mg/L in the system consisting of 500 mg/L of  $Na_2S_2O_8$  and 1 g/L of zero-valent iron, pH = 5, the efficiency of nitrobenzene mineralization may reach for 98 % for 40 min. The nitrobenzene was first reduced with zero-valent iron then transported for the further oxidation with free sulfate radical, the mineralization nitrobenzene may reach for 95 % for 0.5 h. This means that amine products are easily oxidized than its nitro compounds. The obtained experimental data have suggested that the reduction of nitrobenzene by zero-valent iron may be combined with the oxidation process with persulfate activated with zero-valent iron to enhance the nitrobenzene degradation efficiency and the efficiency of zero-valent iron used. The factors such as ratios of persulfate/zero-valent iron/ nitrobenzene, pH, the addition of  $Fe^{2+}$  influencing on the efficiency of nitrobenzene mineralization have been investigated.

**Key Words:** Activation of persulfate, Persulfate oxidation, Persulfate activated with zero-valent iron.

### INTRODUCTION

The chemical oxidation has been used in environmental technology to degrade many organic contaminants<sup>1</sup>. The oxidant agents such as  $H_2O_2$ ,  $O_3$ ,  $KMnO_4$  and their combination with UV have been investigated in laboratory and field for organic compound remediation. Although these chemicals have high standard reductive potential, but their application for the environmental treatment has been limited due to the low effectiveness, short life spans and selective reactivity toward unsaturated organic compounds<sup>2</sup>. In recent years, the oxidation persulfate anion activated with chemical agents including zero-valent iron which received a great attention in the mineralization of the recalcitrant organic compounds<sup>3</sup>. In practice persulfate anion ( $S_2O_8^{2-}$ ) with a high standard reductive potential ( $E^0 = 2.01$  V), but when it is activated produces free sulfate radical

with the higher reductive potential ( $E^0 = 2.60$  V)<sup>4</sup>. The activation of persulfate anion would be implemented with many physical and chemical agents as follows:



here,  $Me^{n+}$  denoted metal ions like  $Mn^{2+}$ ,  $Ag^+$  or  $Fe^{2+}$ .

The activation of persulfate by some of these agents has been applied for removal of toxic organic compounds such as methyl-*tert*-butyl ether, benzene, toluene, xylene, chlorinated solvents<sup>5</sup>. The zero-valent iron in an aqueous media oxidized to produce ion  $Fe^{2+}$  used for activation of persulfate anion has received a growing attention<sup>6</sup>. This is a new application of the activated persulfate anion producing the high oxidation effectiveness in treating recalcitrant organic compounds. The remediation of aromatic nitro compounds is of interest because they are common environmental contaminants with a large amount

produced from industry of munitions, insecticides, herbicides and pharmaceuticals<sup>7</sup>. In practice aromatic nitro compounds may easily react with zero-valent iron under reducing conditions to be transformed into amine compounds. However in presence of zero-valent iron and persulfate anion, the aromatic nitro compounds may take part in two main processes such as reduction and oxidation. In this paper, we have focused on the degradation of aromatic nitro compounds with persulfate activated by zero-valent iron, in which nitrobenzene has been selected as a represented model system. In the system consisting of zero-valent iron, persulfate anion and nitrobenzene there is a zero-valent iron dissolution to produce  $\text{Fe}^{2+}$ , reduction of nitrobenzene, activation of persulfate and others. The role of zero-valent iron in the degradation process of nitrobenzene with persulfate anion (consisting of reduction of nitrobenzene with zero-valent iron and then its oxidation by free sulfate radical) would be illustrated by experimental data. The experimental data were analyzed by voltammetry and measuring total organic carbon (TOC). So that the all problems relating with the degradation of nitrobenzene by zero-valent iron and the activated persulfate would be resolved in this paper.

## EXPERIMENTAL

The chemicals used for the experiments were purchased from a Chinese company with following parameters: Zero-valent iron powder with surface area of  $1.20 \text{ m}^2/\text{g}$  corresponding to the mean diameter of  $10 \mu\text{m}$  and the chemical components of zero-valent iron are  $\text{C} \leq 1\%$ ;  $\text{Mn} \leq 1$ ;  $\text{P} \leq 1$ ;  $\text{Fe} = 97\%$ ; density:  $3\text{--}4 \text{ g}/\text{cm}^3$ ; sodium persulfate ( $\text{Na}_2\text{S}_2\text{O}_8$ ) with 99 % purity; nitrobenzene with 98 % purity with stock solution  $80 \text{ mg}/\text{L}$ .  $\text{CH}_3\text{COONa}\text{--}\text{CH}_3\text{COOH}$  (0.1 M) as buffer solution was used as an electrolyte for voltammetry analysis. All the solutions were prepared in deionized water.

### Bath experiments

**Bath reduction experiments:** A series of 100 mL of nitrobenzene solution ( $80 \text{ mg}/\text{L}$ ) and 0.1 g of zero-valent iron were added to 250 mL Erlenmeyer flasks, which was shaken at 150 rpm in an electric shaker at the room temperature. The sample was then filtrated to remove the solid part and the obtained solution was used for the further bath oxidation experiments.

**Bath oxidation experiments:** Every 100 mL of above filtrated reduced nitrobenzene solution with 0.1 g zero-valent iron and 50 mg of  $\text{Na}_2\text{S}_2\text{O}_8$  were added to a 250 mL of Erlenmeyer flask, which was shaken at 150 rpm at the room temperature. After a different time interval, samples were taken for analyzing nitrobenzene concentrations and total organic carbon.

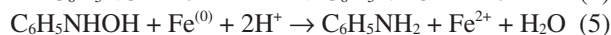
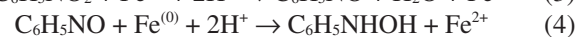
**Determination of nitrobenzene concentration and total organic carbon:** Determination of the total organic carbon (TOC) was based on the study<sup>8</sup>. The concentration changes of nitrobenzene in the samples were determined with square wave voltammetry by electrochemical trace analyzer (Princeton applied research- M394). The measurements were set up with the following parameters: initial potential of  $-0.2 \text{ V}$ , the final potential of  $-1.6 \text{ V}$ , dropping mercury electrode with S size, the scan increment of  $2 \text{ mV}$ , the frequency of  $100 \text{ Hz}$ , the pulse height of  $20 \text{ mV}$ . A  $5 \text{ mL}$  sample taken plus  $5 \text{ mL}$  acetate buffer  $0.1 \text{ M}$  was added to a polarographic vessel to determine nitrobenzene. The oxygen in the samples was eliminated by

purging nitrogen current for 10 min. The concentrations of nitrobenzene were determined by the addition method. The evaluation of nitrobenzene concentrations was determined by the peak height at  $-0.47 \text{ V}$ . The experiments were implemented by the following steps: (i) Reduction of nitrobenzene with alone zero-valent iron, calculation of nitrobenzene-reduction efficiency and the efficiency of zero-valent iron used for the reduction. (ii) Oxidation of the reduced nitrobenzene by persulfate activated with zero-valent iron, calculation of nitrobenzene-reduction efficiency and the efficiency of zero-valent iron used for the reduction. (iii) Direct oxidation of nitrobenzene by persulfate activated with zero-valent iron.

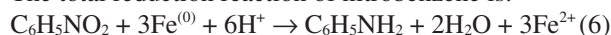
## RESULTS AND DISCUSSION

### Reduction of nitrobenzene by zero-valent iron powder

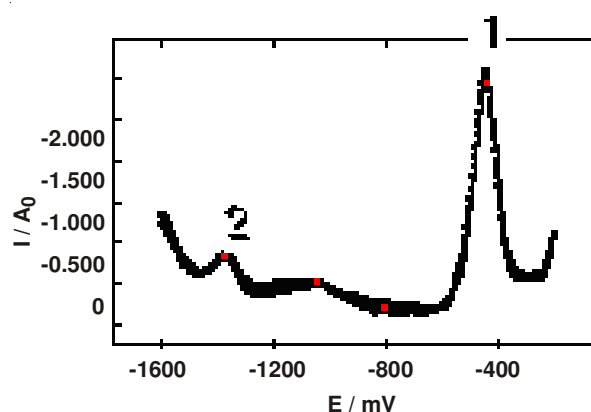
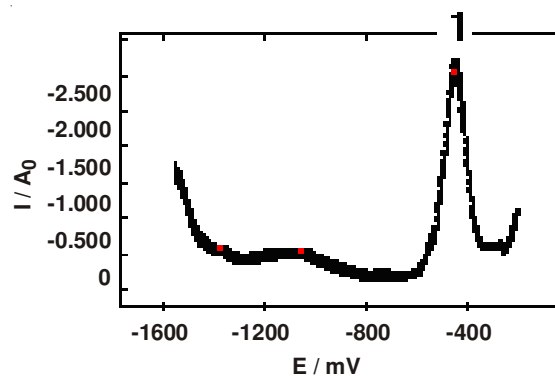
**Efficiency of nitrobenzene reduction:** The reduction of nitrobenzene by zero-valent iron was studied by bath experiment. The reaction pathway of  $\text{Fe}^{(0)}$  and nitrobenzene was implemented in the bath as follows:



The total reduction reaction of nitrobenzene is:



In this experiment, the nitrobenzene concentration may be determined by square wave voltammetry corresponding to the reduction of nitrobenzene to aniline. The peak appeared at the potential of  $-0.47 \text{ V}$  in  $0.1 \text{ M}$  - acetate buffer corresponding to the reduction of nitrobenzene to aniline was used to determine its concentration in the sample [Fig. 1(a-c)].



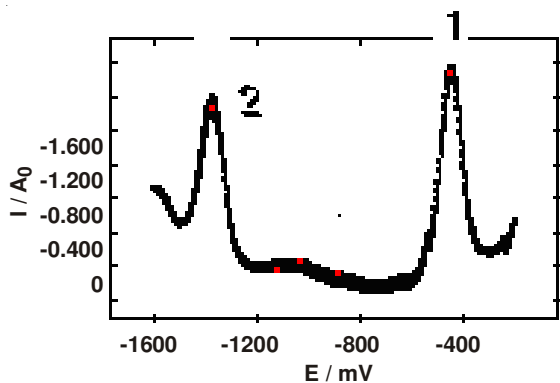


Fig. 1. Voltammetry square wave of nitrobenzene and  $\text{Fe}^{2+}$  in the sample containing electrolyte sodium acetate buffer 0.1 M: a) nitrobenzene 0.64 mM; b) nitrobenzene: 0.64 mM +0.1 g  $\text{Fe}^{(0)}$  for the reaction time of 5 min, c) nitrobenzene 0.64 mM +0.1 g  $\text{Fe}^{(0)}$  for the reaction time of 10 min, (1):nitrobenzene peak -0.47 V; (2): $\text{Fe}^{2+}$  peak-1.32 V

In present experiment, due to the higher concentration of zero-valent iron than nitrobenzene concentration, the conversion of nitrobenzene ( $E_{\text{ff}}$ ) onto aniline (eqn. 6) would be established by the expression as follows:

$$E_{\text{ff}} (\%) = \left(1 - \frac{h_{\text{peak}}^t}{h_{\text{peak}}^0}\right) 100 \quad (7)$$

here  $h_{\text{peak}}^0$ ,  $h_{\text{peak}}^t$ , denote the peak height of nitrobenzene at the initial time and after  $t$ -time, respectively. The conversion of nitrobenzene depends on the zero-valent iron mass (g/100 mL) and the initial concentration of nitrobenzene. The obtained experimental data of  $E_{\text{ff}}$  (%) are presented in the Figs. 2 and 3.

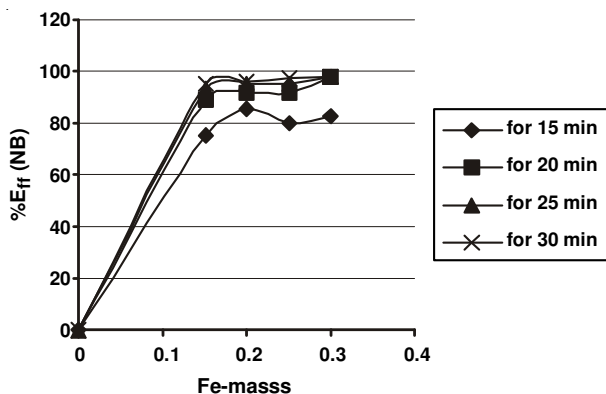


Fig. 2. Influence of  $\text{Fe}^-$  mass on  $E_{\text{ff}}$ ; nitrobenzene conc. = 80 mg/L, pH = 5

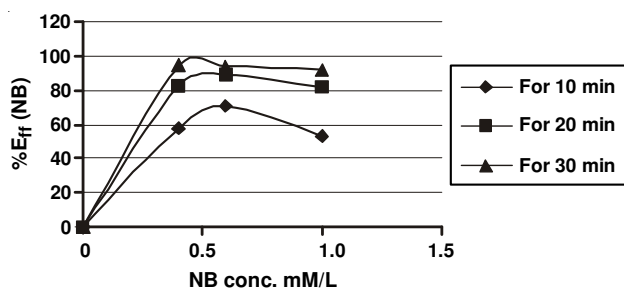


Fig. 3. Influence of nitrobenzene conc. on  $E_{\text{ff}}$ ;  $\text{Fe}^-$  mass = 0.1 g/100 mL, pH = 5

The experimental data from Figs. 2 and 3, let us select the nitrobenzene concentration of 80 mg/L and 0.1g/100mL of zero-valent iron for the reduction bath experiments to have high efficiency (> 95 %). The final main product of the conversion of nitrobenzene with zero-valent iron is aniline. It is consistent with the work of Barry *et al.*<sup>9</sup>. The obtained reduced nitrobenzene products are transported to the further oxidation with persulfate activated by zero-valent iron.

**Efficiency of zero-valent iron:** By square wave voltammetry, the concentration of  $\text{Fe}^{2+}$  in the samples may be determined by the peak height ( $h_{\text{peakFe}}^t$ ) at the potential of -1.32 V. The efficiency of zero-valent iron used ( $\text{Fe} (\%)$ ) for the reduction of nitrobenzene to produce aniline may be calculated based on the expression<sup>9</sup>, as follows:

$$\text{Fe} (\%) = \frac{1}{3h_{\text{peakFe}}^t} \left(1 - \frac{h_{\text{peak}}^t}{h_{\text{peak}}^0}\right) 100$$

The obtained  $\text{Fe} (\%)$  data in the experimental samples are presented in Fig. 4.

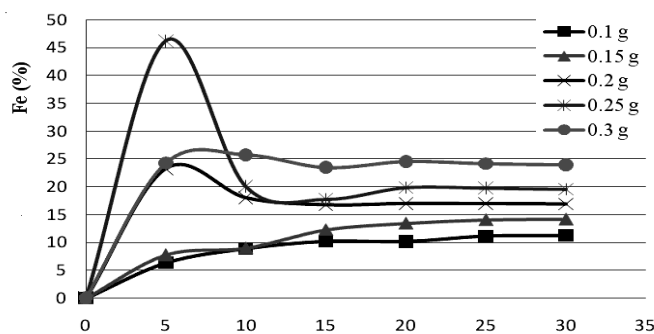
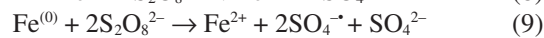
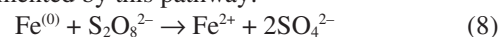


Fig. 4. Efficiency of zero-valent iron used

The data from Fig. 4, show that the efficiency of Fe used ranged from 10 to 25 %. The low efficiency of Fe used can be attributed to the oxidation of Fe by oxygen and  $\text{H}_2\text{O}$  in the samples to produce a certain amount of  $\text{Fe}^{2+}$ . This result is consistent with the work of Bary *et al.*<sup>9</sup>. The enhancement of the efficiency of Fe used for reaction with nitrobenzene can be done by reducing oxygen in the sample or addition of persulfate salt ( $\text{Na}_2\text{S}_2\text{O}_8$ ). The addition of  $\text{S}_2\text{O}_8^{2-}$  to the samples exhibits excellent advantages due to available  $\text{Fe}^{2+}$  and  $\text{Fe}^{(0)}$  in the sample for the activation to produce  $\text{SO}_4^{\cdot-}$ . The obtained sulfate free radical can oxidize nitrobenzene and its intermediate products, convert them to  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other minerals. Hence after the reduction, the samples were transported into the oxidation with  $\text{S}_2\text{O}_8^{2-}$  that is an optimal selection.

**Oxidation of reduced nitrobenzene products with persulfate activated zero-valent iron:** In the experimental system consists of  $\text{S}_2\text{O}_8^{2-}$ ,  $\text{Fe}^{(0)}$ ,  $\text{Fe}^{2+}$ , pH = 5 the activation of  $\text{S}_2\text{O}_8^{2-}$  can be done<sup>10</sup> to produce  $\text{SO}_4^{\cdot-}$ . The formation of  $\text{SO}_4^{\cdot-}$  may be implemented by this pathway:



The formed  $\text{SO}_4^{\cdot-}$  reacts with the reduced nitrobenzene products from reduction bath to produce  $\text{CO}_2$ ,  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ , etc. Besides, free sulfate radical can reacts with  $\text{Fe}^{(0)}$  and  $\text{Fe}^{2+}$ . The experiment has indicated that the efficiency of this oxidation

depends on the factors such as (i) the molar ratio of reduced nitrobenzene products (aniline) with  $\text{Fe}^{(0)}$  and persulfate, (ii) pH of samples, (iii) rate of revolution. From the previous studies<sup>6,10</sup> the factors influenced on the oxidation of nitrobenzene have been chosen for these experiments. Under these conditions, the oxidation of persulfate anion activated with zero-valent iron is presented by the decrease in  $\text{TOC}/\text{TOC}^0$  in the studied samples. The decrease of  $\text{TOC}/\text{TOC}^0$  was presented in Fig. 4.

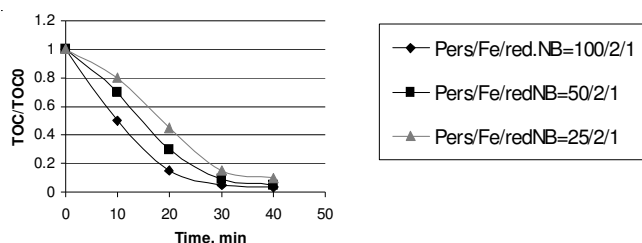


Fig. 4. Dependence of  $\text{TOC}/\text{TOC}^0$  on persulfate anion, pH = 5.0

The experimental data have indicated that for a constant amount of zero-valent iron and nitrobenzene the TOC decrease in samples depends on the amount  $\text{S}_2\text{O}_8^{2-}$ . The oxidation of nitrobenzene in the sample may reach *ca.* 95 % for 0.5 h when the ratio of persulfate/Fe/nitrobenzene is 25/2/1. With an addition of  $\text{S}_2\text{O}_8^{2-}$  the efficiency of zero-valent iron used in this case, Fig. 5, may reach to 70 %. This may be explained by the activation of  $\text{S}_2\text{O}_8^{2-}$  to produce  $\text{SO}_4^{\bullet-}$  that oxidizes nitrobenzene and its intermediate substrate.

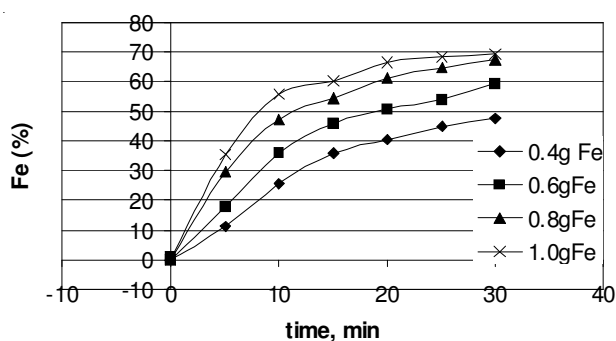


Fig. 5. Efficiency of zero-valent iron used for the oxidation of the reduced nitrobenzene, 80 mg/L

**Direct oxidation of nitrobenzene with persulfate activated zero-valent iron powder:** For the direct oxidation of nitrobenzene, the experiments were repeated with 100 mL of nitrobenzene taken instead of the reduced nitrobenzene. The oxidation results are presented in Fig. 6.

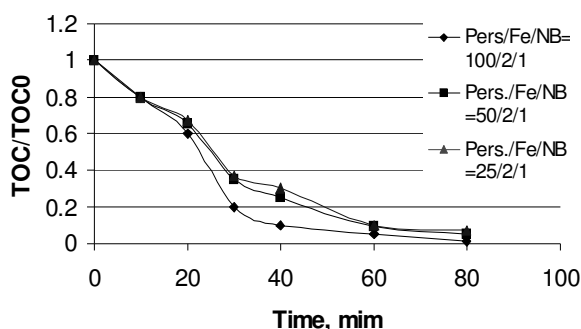


Fig. 6. Direct oxidation of nitrobenzene with  $\text{S}_2\text{O}_8^{2-}$  activated by zero-valent iron

The obtained plots show that for the initial 20 min, the ratio of  $\text{TOC}/\text{TOC}^0$  decreases slowly and then more quickly for the time from 20 to 40 min. This phenomenon may be explained by the following pathway.

At the initial time the process of nitrobenzene reduction to produce amine products is predominated (eqns. from 3 to 5). After 20 min when there are enough  $\text{Fe}^{2+}$  ions in the sample to activate  $\text{S}_2\text{O}_8^{2-}$  anion producing  $\text{SO}_4^{\bullet-}$ , the oxidation process would be implemented causing the quick decrease of  $\text{TOC}/\text{TOC}^0$ . The decrease of  $\text{TOC}/\text{TOC}^0$  in the samples is a proof for the mineralization of organic components to produce  $\text{CO}_2$ ,  $\text{H}_2\text{O}$  and other mineral components. Fig. 4 shows the removal efficiency of nitrobenzene may reach to 98 % for 40 min. The efficiency of zero-valent iron used for this process (Fig. 5) is about more than 55 %.

## Conclusion

The degradation of the aromatic nitro compounds by persulfate activated with zero-valent iron is a field that has received a growing attention. In this paper the degradation of nitrobenzene by  $\text{S}_4\text{O}_8^{2-}$  activated with zero-valent iron has been studied. The obtained experimental data have shown that the reduction of nitrobenzene by zero-valent iron may be combined with the oxidation process with persulfate activated with zero-valent iron to enhance the nitrobenzene degradation efficiency and the efficiency of zero-valent iron used. The simultaneous reduction/oxidation process for destroying nitrobenzene with persulfate activated with zero-valent iron has been briefly studied.

## ACKNOWLEDGEMENTS

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