

Catalytic degradation of nitroaromatic explosives with Fenton's reagent

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Abstract

Oxidation of the nitroaromatic explosives namely, 2,4,6-trinitrophenol (PA), ammonium picrate (AP), 2,4-dinitrotoluene (DNT) and 2,4,6-trinitrotoluene (TNT) by Fenton's reagent has been investigated in this study. The initial concentrations of nitroaromatics were in the range of 1.0×10^{-5} to 3.0×10^{-4} M. For the Fenton oxidation of the four nitroaromatics, the structural characteristic is the major factor affecting the decomposition rate rather than the interference effect coming from the oxidation intermediates. Oxidation rate of the explosives in the Fenton process were in the following sequence: DNT > PA > AP > TNT. The results were in good agreement with kinetic model, assuming the pseudo-steady-state hypothesis of hydroxyl radical formed by the Fenton reaction. Thus, a half-life prediction model was proposed and compared with the half-lives calculated from pseudo-first-order equation to prove the interference effect resulted from the oxidation intermediates.

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1. Introduction

Military sites and battle fields represent a seriously and potentially hazardous contamination problem of growing environmental concern. Especially at former ammunition production plants and battle zones, improper treatment of explosives during manufacture, transportation, maneuver and disposal has caused very serious pollution in groundwater and soil. Nitroaromatic explosives were usually used during the two World Wars, since they are the main component of bombs and propellants. These include 2,4,6-trinitrophenol (PA), ammonium picrate (AP), 2,4-dinitrotoluene (DNT), and 2,4,6-trinitrotoluene (TNT). Most nitroaromatic explosives are toxic to humans, and the azoxy- and azo-compounds deriving from their environmental transformation products and condensed products are equal to or more toxic than the parent nitroaromatics [1].

Dave et al. [2] showed the toxicity of PA, which the EC₅₀ values for *Daphnia magna* are 200 and 86 mg/l after 24 and 48 h, respectively. Since the sensitivity of AP is lower than that of PA, it is usually packed in armor-piercing shells [3]. Additionally, their high solubility in water will contaminate the groundwater

easily. TNT represents an environmental hazard because of its toxicity to human, fish, algae, and microorganisms. It is mutagenic to *Salmonella typhimurium* and can cause cancer [4]. DNT is a precursor of TNT, which exhibits 14-day LC₅₀ values of 12.5 mg/l and also causes liver cancer in rats [5]. In the United States, the Department of Defense has identified more than 1000 explosive-contaminated sites, which are polluted over 95% by TNT [6]. The treatment of nitroaromatics contaminated water and soil becomes a more urgent issue. Therefore, Rodgers and Bunce [7] reviewed technologies that were available or under investigation to remediate areas contaminated with these compounds.

The Fenton process is one of the most powerful advanced oxidation processes (AOPs), and can be used to destroy a variety of explosive ammunition residues in the environment [8]. In the Fenton process, ferrous ion reacts with hydrogen peroxide to produce hydroxyl radical (a strong oxidant; $E^0 = -2.8$ V), which then reacts with ferrous ion to form ferric ion or reacts with explosives. Since the hydroxyl radical is the major oxidant in the Fenton process, the removal behavior of explosives is highly related with the hydroxyl radical formation. Li et al. [9] showed that the Fenton reaction could be used successfully to achieve the remediation goal of 17.2 mg TNT/kg established for the Nebraska Ordnance Plant (NOP). The NOP site had successfully remedied 10,000 tonnes of soil polluted by hexahydro-1,3,5-

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trinitro-1,3,5-triazine (RDX) to a concentration of 5.8 mg/kg through the Fenton process in 1998 to meet the US EPA regulations [8]. In addition, Zoh and Stenstrom [10] showed that the high explosives RDX and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) could be effectively mineralized with Fenton reagents. Moreover, Oh et al. [11] observed that the waste water of TNT and RDX could be degraded more completely by enhancing the Fenton oxidation through pretreatment with zero-valent iron.

Lu et al. [12] set up a kinetic model to predict the half-lives in photocatalytic oxidation of various dichlorvos concentrations using TiO₂. Results showed that the difference between estimated values and observed values increased with increasing initial concentration. Kawaguchi and Inagaki [13] also set up a kinetic model estimating the half-lives of 2-chlorophenol to assess the effect of ferric ion on the performance of photocatalytic reaction. Fenton oxidation of nitroaromatics has been widely investigated. It could be an effective process for the degradation of nitroaromatics. However, there was no report comparing the oxidation kinetics of various initial concentrations under the same experimental conditions. Therefore, decomposition kinetics for the selected explosives, namely PA, AP, DNT and TNT were compared to evaluate the effect of substituents of the phenyl ring on the Fenton decomposition reaction rate. The molecular structures, chemical formula and physical characteristics of these investigated explosives are listed in Table 1 [14]. In addition, in order to estimate half-lives of explosive decomposition at various initial concentrations, a kinetic model was proposed to predict the decomposition half-lives. The interference effect of intermediates was also quantified through the kinetic model.

2. Experimental

2.1. Chemicals

Technical grade 2,4,6-trinitrophenol (PA), ammonium picronitrate (AP), and 2,4,6-trinitrotoluene (TNT) were obtained from the Army Chemical Laboratory, R.O.C. Reagent grade 2,4-dinitrotoluene (DNT, 95%) was obtained from Lancaster Synthesis (Morecambe, England). Ferrous sulfate and sodium phosphate were purchased from the Baker Company. Hydrogen peroxide (purity, 30%) was provided by the Ferak Company, and the rest of the reagents were of reagent grade. Aqueous solutions used for oxidation reaction were prepared with Millipore Milli-Q water.

2.2. Process operation and water analyses

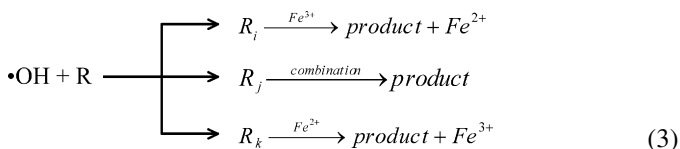
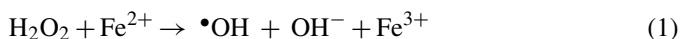
All reaction solutions were adjusted to pH 3.0 with 0.5N nitric acid. Fenton reactions were initiated by adding 1.5 ml of 30% hydrogen peroxide and 0.5 ml of ferrous ions into a 250 ml-flask containing 48 ml of explosive chemical solution, yielding an initial concentration of 0.29 M hydrogen peroxide and 0.72 mM of ferrous ions. The flask was placed on a shaker at room temperature (25 ± 2 °C) at 130 circular rpm. In this experiment, 5, 10, 30, 50, 70, 90 and 120 min

were used as the time points for water sampling and analysis. As previously reported [15], the Fenton reaction was quenched instantly by adding 0.5 ml of 0.01 M sodium dibasic phosphate solutions into 2.0 ml of withdrawn samples before analysis. The changes in the explosive concentrations with reaction time were determined by high performance liquid chromatography (HPLC, Perkin-Elmer). A Supelco LC-18-DB column (25 cm × 4.6 mm × 5 μm) was used with an isocratic mixture of CH₃OH–H₂O (60:40, v/v) at the flow rate is 1.0 ml/min. Nitroaromatics were detected spectrophotometrically at 254 nm and quantified by comparison with high purity standard.

3. Results and discussion

3.1. Effect of initial concentration

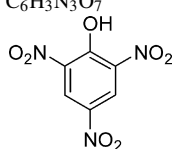
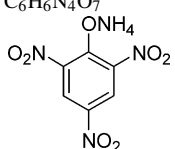
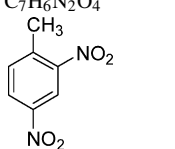
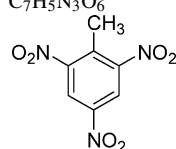
The Fenton process is one of the advanced oxidation processes commonly used in the treatment of wastewater contaminated with organic compounds. In the Fenton process, ferrous ions react with hydrogen peroxide to produce hydroxyl radicals which then oxidize organic compounds [11]. The reaction may occur according to the following three steps:



It may be speculated from Eq. (3) that the intermediates would react with hydroxyl radical, resulting in the competition of hydroxyl radical with nitroaromatics. In this study, various initial nitroaromatics concentrations were used in the Fenton reaction to clarify the effect of the initial concentration on the decomposition kinetics of nitroaromatics.

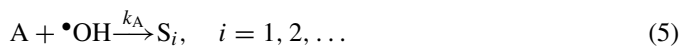
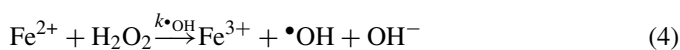
The dependence of the decomposition reaction of PA, AP, DNT and TNT on initial concentrations is shown in Fig. 1(A–D). In the decomposition of PA (Fig. 1(A)), the decomposition percentage was over 80% after 50 min when the initial concentration was higher than 2×10^{-4} M, and was over 93% when the initial concentration of PA was below 1.5×10^{-4} M. Similar trends can be observed for AP, DNT and TNT in Fig. 1(B–D). The decomposition percentages of AP were 78.3% and 90.4% as initial concentrations are 3×10^{-4} and 2×10^{-4} M, respectively. Over 90% were oxidized when AP concentration was lower than 1.5×10^{-4} M. It is notable that the DNT possessed the highest decomposition rate, and the decomposition percentages were 67.3, 86.5, 93.8, 99.2 and 100% at 20 min when the initial concentrations of DNT were 3.5×10^{-4} , 2×10^{-4} , 1×10^{-4} , 5×10^{-5} and 3×10^{-5} M, respectively. On the other hand, TNT possessed the lowest decomposition rate with decomposition ratio less than 61%. All four plots in Fig. 1 show that the decomposition rates were dependent on

Table 1
Physical and chemical properties of investigated explosives

Property	PA	AP	2,4-DNT	2,4,6-TNT
Formula	$C_6H_3N_3O_7$	$C_6H_6N_4O_7$	$C_7H_6N_2O_4$	$C_7H_5N_3O_6$
Molecular structure				
M.P. (°C)	122	265–271	69	80.1
B.P. (°C)	>300	423	300	240
Appearance	Colorless or yellow needles	Yellow or red bitter crystals	Light yellow powder	Yellow powder
Solubility in water 20–25 °C (mg/l)	14,000 (soluble)	10,000 (slight soluble)	270 (insoluble)	100 (insoluble)
Explosive	Explosive	Flammable	No	Flammable
Sensitivity	Medium	Very low	Very low	Very low

the initial concentration, and decreased with increasing initial concentration.

The dependence of the reaction rate on the initial concentration can be illustrated by means of construction of a kinetic model using a mechanism involving by-product intermediates interference. The reaction mechanism can be expressed as



where $k_{\bullet OH}$ is the rate constant for $\bullet OH$ formation reaction, k_A the rate constant for nitroaromatic explosive decomposition reaction, k_i represent the rate constants for decomposition reaction of by-products S_i , A is target compound, namely the nitroaromatic explosive, and B is the final product, which does not further react with $\bullet OH$. The decomposition rate of nitroaro-

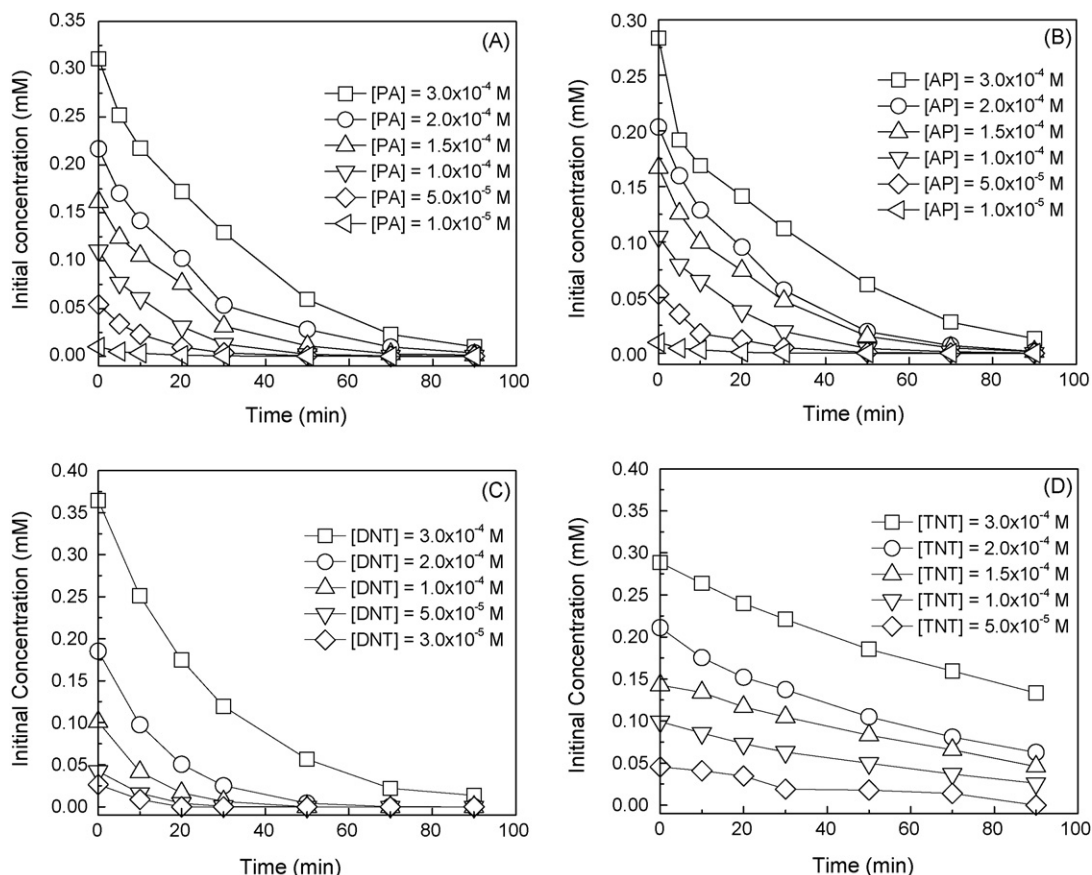


Fig. 1. Dependence of Fenton oxidation reaction on the initial concentration for PA (A), AP (B), DNT (C) and TNT (D). Experimental conditions: 0.72 mM Fe^{2+} , 0.29 M H_2O_2 at pH 3.0 and 25 °C.

Table 2
Rate constants (k) and half-lives ($t_{1/2}$) for the Fenton oxidation of nitroaromatics various initial concentrations

Initial concentration ($\times 10^4$ M)	PA		AP		DNT		TNT	
	k ($\times 10^2$ min $^{-1}$)	$t_{1/2}$ (min)	k ($\times 10^2$ min $^{-1}$)	$t_{1/2}$ (min)	k ($\times 10^2$ min $^{-1}$)	$t_{1/2}$ (min)	k ($\times 10^2$ min $^{-1}$)	$t_{1/2}$ (min)
3.0	3.775	18.4	3.24	21.4	3.781	18.3	0.85	81.6
2.0	4.49	15.4	4.08	17.0	6.67	10.4	0.96	72.4
1.5	5.54	12.5	4.68	14.8	–	–	1.11	62.4
1.0	6.95	10.0	6.32	11.0	9.26	7.5	1.40	49.6
0.5	8.85	7.8	7.55	9.2	11.7	5.9	2.12	32.7

matic explosive according to Eq. (5) can be expressed as

$$r = k_A[A][\bullet\text{OH}] \quad (8)$$

By applying mass balance for $\bullet\text{OH}$,

$$r_{\bullet\text{OH}} = k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2] - k_A[A][\bullet\text{OH}] - k_1[\text{S}_1][\bullet\text{OH}] - k_2[\text{S}_2][\bullet\text{OH}] \cdots - k_n[\text{S}_n][\bullet\text{OH}]$$

In the experiment, since excess amounts of H_2O_2 were provided from Fenton reagent ($[\text{Fe}(\text{II})] = 0.72$ mM, $[\text{H}_2\text{O}_2] = 0.29$ M) at pH 3.0, $[\bullet\text{OH}]$ should be constant during the reaction. Therefore, pseudo-steady-state-hypothesis (PSSH) can be applied when $r_{\bullet\text{OH}}$ is zero, and $[\bullet\text{OH}]$ can be expressed as $[\bullet\text{OH}]_{\text{SS}}$ at steady state.

$$\begin{aligned} k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2] &= k_A[A][\bullet\text{OH}] + k_1[\text{S}_1][\bullet\text{OH}] \\ &\quad + k_2[\text{S}_2][\bullet\text{OH}] + \cdots + k_n[\text{S}_n][\bullet\text{OH}] \\ &= k_A[A][\bullet\text{OH}] + \sum k_i[\text{S}_i][\bullet\text{OH}] \end{aligned}$$

$$[\bullet\text{OH}]_{\text{SS}} = \frac{k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k_A[A] + \sum k_i[\text{S}_i]} \quad (9)$$

By substitution of Eq. (9) into Eq. (8), the following reaction rate can be obtained:

$$r = -\frac{d[A]}{dt} = k_A[A] \frac{k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k_A[A] + \sum k_i[\text{S}_i]} \quad (10)$$

In this study, since the reaction was taken as pseudo-first-order, the last term in Eq. (10) is incorporated into rate constant k_A as

$$r = k[A], \quad \text{where } k = \frac{k_{\bullet\text{OH}}k_A[\text{Fe}^{2+}][\text{H}_2\text{O}_2]}{k_A[A] + \sum k_i[\text{S}_i]}$$

Therefore, when $[A]$ is high, the numerator value is high, giving a lower k value; when $[A]$ is low, the numerator value is low, giving a higher k value.

All of the values for the pseudo-first-order reaction rate constant, k , were calculated from the linear regression of the $\ln[A]$ and time with regression coefficients higher than 0.95. The reaction rate constants and half-lives times are summarized in Table 2. As illustrated in Table 2, the decomposition rate constants increased with decreasing initial concentrations, and the half-lives decreased with decreasing initial concentrations, indicating a faster reaction rate at lower initial concentration.

According to the structural characteristics, the resonance natures of the phenyl ring in nitroaromatics make the electrophilic aromatic substitution feasible. In addition, different substituents bearing on the phenyl ring would act as activating groups or deactivating groups due to different electronegativity. Therefore, DNT is the most easily degraded compound of four explosives, as shown in Table 2. Li et al. [16] has also reported that the Fenton oxidation rate of nitroaromatic explosives was consistent with electrophilic attack by the hydroxyl radical: 2-nitrotoluene > 4-nitrotoluene > 2,4-DNT > 2,6-DNT > TNT. In the Fenton oxidation of nitroaromatic explosives, the reaction rate depends on the number of the nitro groups on the aromatic ring. The tendency of degradation rate is related to the molecular structures of explosives. Nitro group, the common substituent of the four nitroaromatic explosives studied, acted as a strong deactivating group due to its electron-withdrawing nature. Therefore, the reactivity of compounds would be reduced when nitro groups were attached to the phenyl ring. In addition, $-\text{OH}$, $-\text{ONH}_4$, and $-\text{CH}_3$ groups have electron-releasing abilities, leading to increase in the reactivity of nitroaromatics. Such functional groups can enhance the resonance effect of aromatic ring and become a good leaving group. In this case, DNT bearing only two nitro groups on the phenyl ring has the highest decomposition rate. Therefore, the oxidation rate of the explosives followed the sequence: DNT > PA > AP > TNT. This result obtained in this study completely fits the theoretical prediction as shown in Table 2.

3.2. Interference effect of intermediates and prediction of half-lives

The interference effect of the intermediate by-products in the Fenton oxidation of nitroaromatic explosives has been illustrated by means of kinetic deduction through Eq. (4) to Eq. (10). Zepp et al. [17] announced that the rate of $\bullet\text{OH}$ formation is equal to the rate of $\bullet\text{OH}$ combination with intermediates in a photo Fenton system. Therefore, a pseudo-steady-state hypothesis of $\bullet\text{OH}$ concentration in the Fenton reaction is reasonable. Hence, the decomposition rate of nitroaromatic explosives can be expressed as Eq. (10).

When neglect of interference from intermediates was assumed, $k_A[A] \gg \sum k_i[\text{S}_i]$, Eq. (10) can be reduced to a second-order reaction.

$$-\frac{d[A]}{dt} = k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2] \quad (11)$$

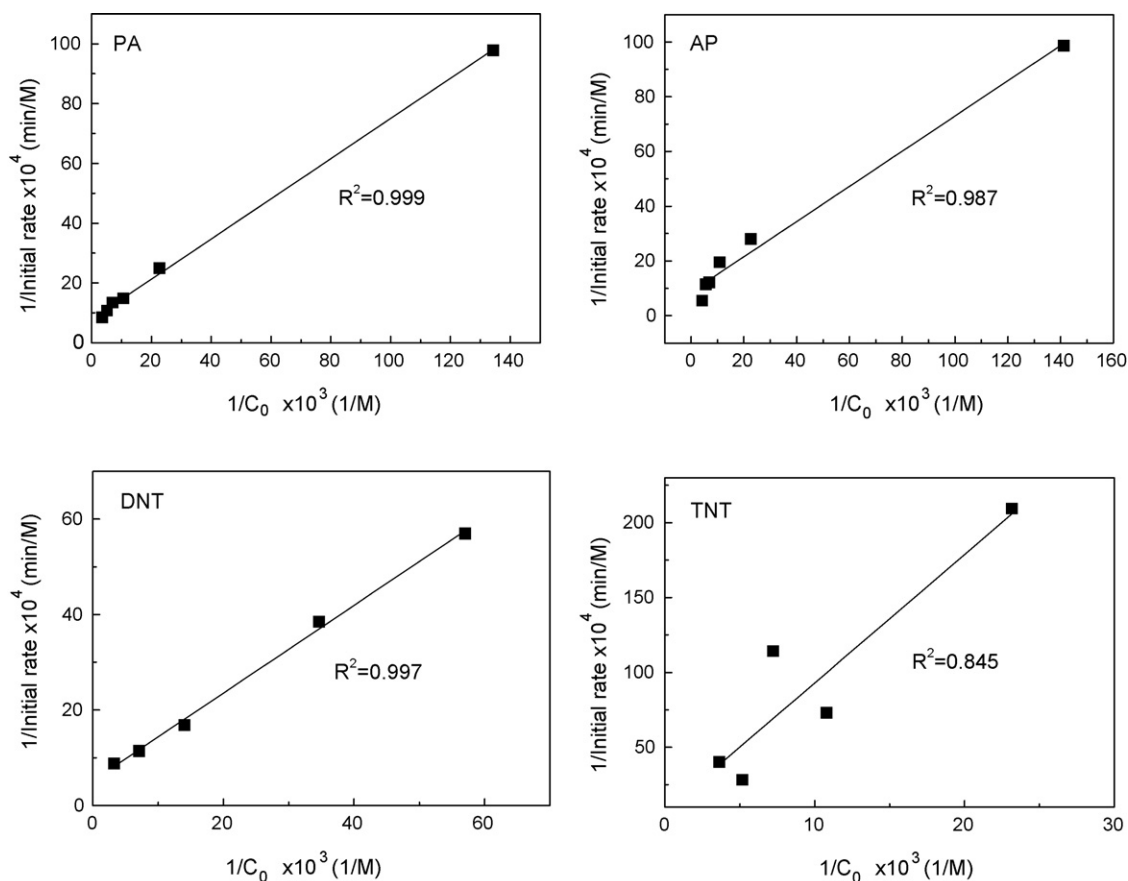


Fig. 2. The reciprocal kinetic plots for Fenton oxidation of nitroaromatic explosive obtained from regression using initial rate at various initial concentration.

The reciprocal form of Eq. (10) gives a linear relationship between $1/r$ and $1/[A]$, as shown below,

$$\frac{1}{r} = \frac{1}{k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]} + \frac{\sum k_i[S_i]}{k_A k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]} \frac{1}{[A]} \quad (12)$$

Integration of Eq. (10) gives

$$t = \frac{\sum k_i[S_i]}{k_A k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]} \ln \frac{[A]_0}{[A]} + \frac{1}{k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]} \times ([A]_0 - [A]) \quad (13)$$

Therefore, the half-life is

$$t_{1/2} = \frac{\sum k_i[S_i]}{k_A k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]} \ln 2 + \frac{[A]_0}{2k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2]} \quad (14)$$

As indicated in Fig. 2, the plot of the reciprocal initial rate r^{-1} as a function of the reciprocal initial concentration C_0^{-1} yields a straight line with slope and intercept being $\sum k_i[S_i]/(k_A k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2])$ and $1/(k_{\bullet\text{OH}}[\text{Fe}^{2+}][\text{H}_2\text{O}_2])$, respectively. By substituting the slope and the intercept into Eq. (14), the estimated half-lives for PA, AP, DNT and TNT are obtained. Since the initial rate and initial concentration were used in the equation, the interference from the intermediates was negligible. On the other hand, a half-lives expression has been proposed previously based upon the assumption of pseudo-first-

order reaction, in which the interference effect was incorporated into the rate constant k . Comparison of the two models is presented for PA, AP, DNT and TNT in Fig. 3. It is obvious that the values are almost identical at low initial concentrations for all four nitroaromatic explosives.

However, the difference between the two models increased with increasing initial concentrations. This suggests that the decomposition by-products may inhibit the oxidation of the nitroaromatic explosives to lengthen the half-lives of the reactions. Li et al. [18] and Tanaka et al. [19] reported that these end byproducts contained NO_3 groups, oxalic acid and organic acids in the Fenton oxidation of TNT. In addition, in our previous investigations about the degradable mechanism of nitroaromatic, these medium byproducts were unidentified as 1,3,5-trinitrobenzene, 1-methyl-2,4-dinitrobenzene, 2,5-dinitrobenzoic acid and 1,3-dinitrobenzene by using GC/MS [20]. By the formation of these byproducts, the mechanisms of the methyl group oxidation, decarboxylation, aromatic ring breakage, and hydrolysis could be recognized and demonstrated in the Fenton oxidation of nitroaromatics [20,21]. Therefore, higher initial concentrations produce more byproducts and hence the difference increases due to the byproducts competing hydroxyl radicals with the parent compound.

In this study, $k_{\bullet\text{OH}}$ was obtained from the intercept in Eq. (12) and k_A was calculated from the pseudo-first-order reaction rate equation using the reciprocals of the initial reaction rate ($1/r$)

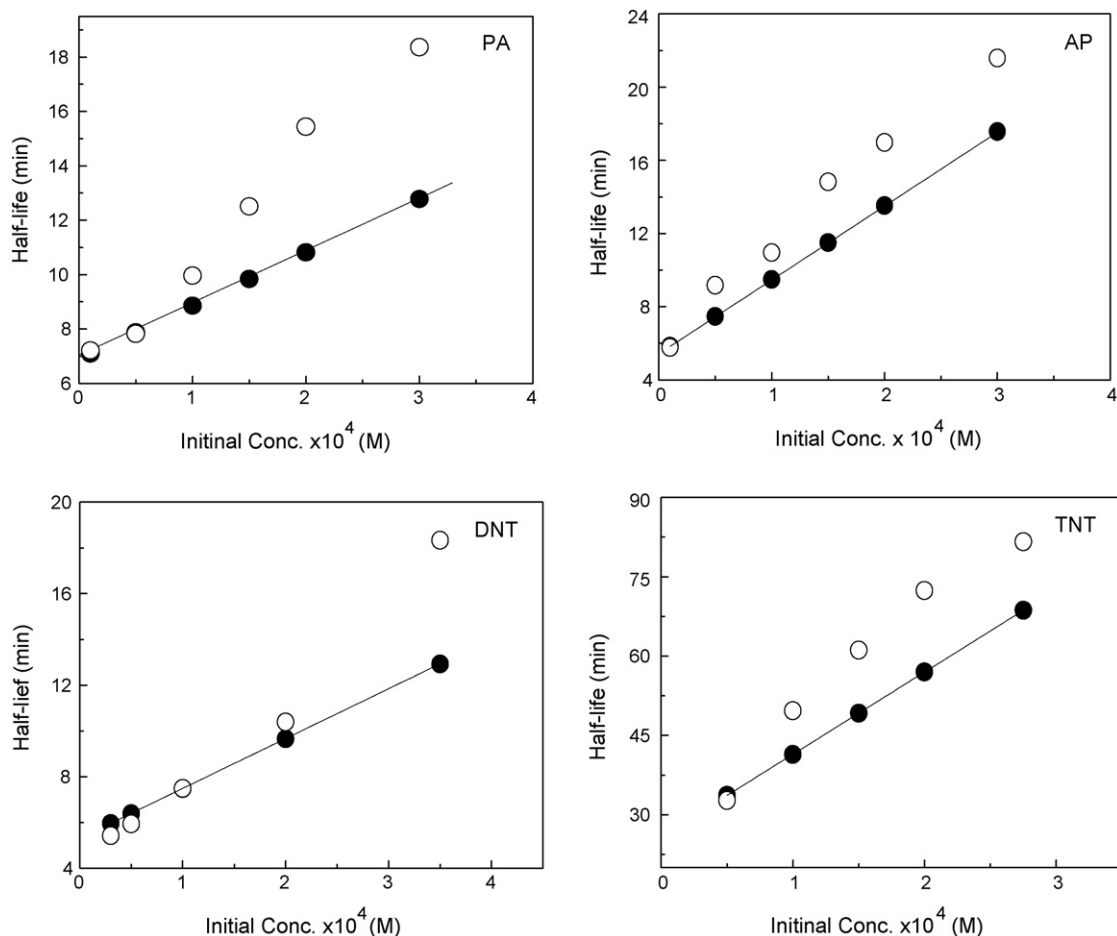


Fig. 3. Comparison of the half-life obtained from pseudo-first-order hypothesis (○) with proposed model calculated using initial conditions (●).

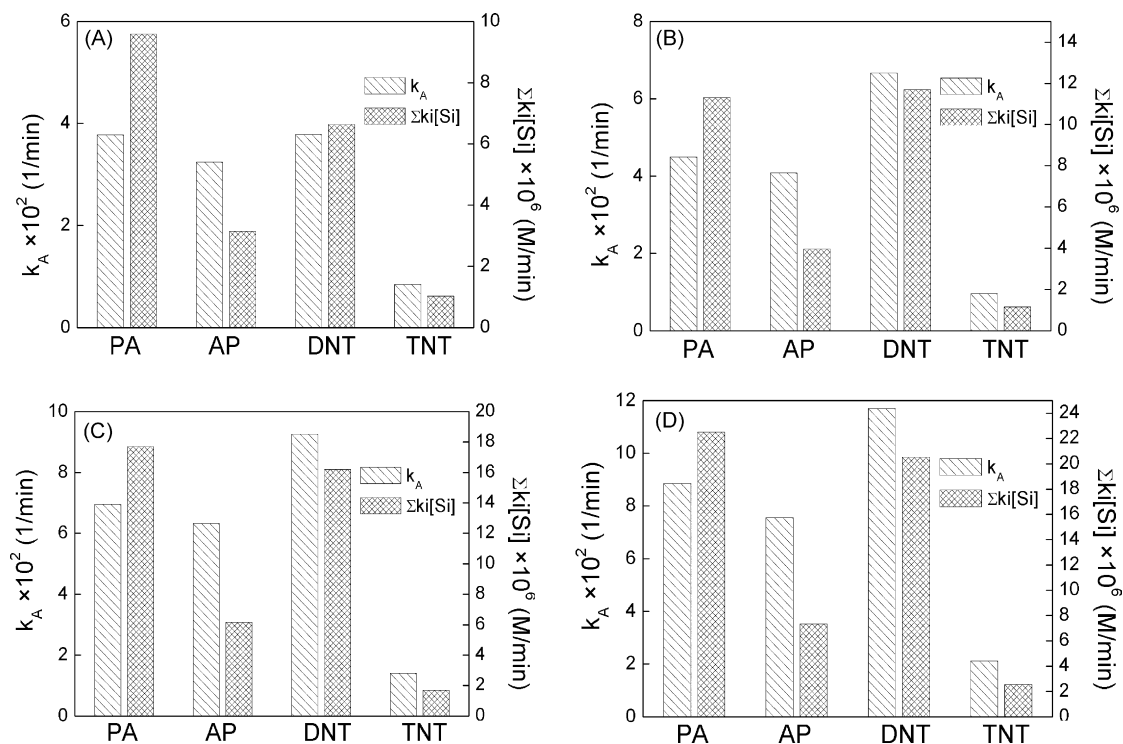


Fig. 4. Comparison of kinetic parameters for degradation of nitroaromatic explosives and their by-products for initial concentration = 3.0×10^{-4} M (A); 2.0×10^{-4} M (B); 1.0×10^{-4} M (C); 5.0×10^{-5} M (D). (The k_A values were shown on y-axis left side, and the $\sum k_i[S_i]$ values were shown simultaneously on y-axis right side.)

Table 3
Kinetic parameter for degradation of nitroaromatics by-products at various initial concentrations

Nitroaromatics	$\sum k_i[S_i]$ ($\times 10^6$ M/min) (initial concentration)			
	3.0×10^{-4} M	2.0×10^{-4} M	1.0×10^{-4} M	5.0×10^{-5} M
PA	9.59	11.3	17.7	22.5
AP	3.15	3.97	6.15	7.34
DNT	6.63	11.7	16.2	20.5
TNT	1.02	1.15	1.68	2.54

and initial concentration ($1/C$). By substituting the $k_{\bullet\text{OH}}$ and k_A into the slope in Eq. (12), $\sum k_i S_i$ can be obtained and are listed in Table 3. Kinetic parameters $\sum k_i[S_i]$ and k_A for nitroaromatic oxidation at various concentrations are presented in Fig. 4.

When the four nitroaromatics for $\sum k_i[S_i]$ were compared, which represent the influences from intermediates, the interference effect decreased in the order of PA > DNT > AP > TNT. According to the sequence of the interference effect, the decomposition reaction rates were supposed to be in the order of TNT > AP > DNT > PA. However, the actual reaction rates were in the order of DNT > PA > AP > TNT. The sequence is consistent with the decomposition tendency derived from their structural characteristics. Consequently, for the Fenton oxidation of the four nitroaromatics, the structural characteristic is the major factor affecting the decomposition rate rather than the interference effect coming from the oxidation intermediates.

In order to take the intermediate interference effect into consideration, the slope and the intercept were recalculated by linear regression of the reciprocal reaction rate $1/r$ and the reciprocal concentration $1/C$ obtained during the Fenton oxidation for each explosive at various time intervals. A typical linearized reciprocal kinetic plot is shown in Fig. 5. Hence, the intermediates are carefully considered as a hydroxyl radical competitor according to the kinetic model. The estimated half-lives and R^2 for linear regression of $1/r$ vs. $1/C$ during the Fenton oxidation of nitroaromatic explosives are listed in Table 4. Slopes and intercepts were also obtained from the plots according to Eq. (12). Substitutions of the slopes and the intercepts into Eq. (14) give new sets of half-lives, which take into account the interference effect from the decomposition byproducts. The half-lives were further compared with the experimental data shown in Fig. 1, and are demonstrated in Fig. 6. As observed in the plots, the estimated values agree with the experimental values very well

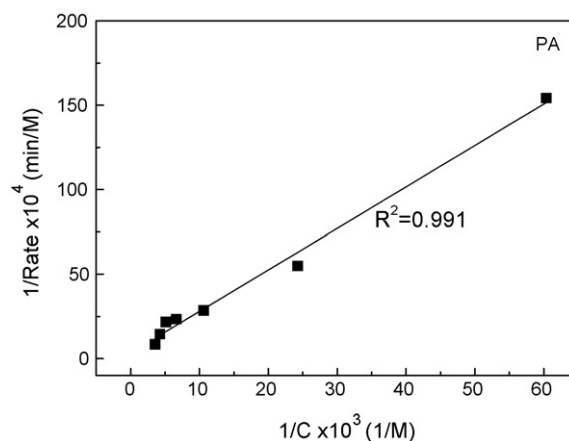


Fig. 5. Typical linear relationship of $1/r$ with $1/C$ during Fenton oxidation of nitroaromatic explosives. Experimental conditions: $[PA] = 3.0 \times 10^{-4}$ M, $[H_2O_2] = 0.29$ M, $[Fe(II)] = 7.2 \times 10^{-4}$ M.

for all nitroaromatic explosives. The agreements of the estimated values with the observed values manifests the kinetic model described above, and also implies the applicability of the pseudo-steady-state hypothesis of hydroxyl radical in the Fenton reaction.

It is also obvious that the dependence of half-lives on initial concentration shows good linearity for all nitroaromatics except TNT as shown in Fig. 6. This is not unusual since the linear relationship has been described in Eq. (14), where the slope is $1/(2k_{\bullet\text{OH}}[Fe^{2+}][H_2O_2])$ and the intercept is $((\sum k_i[S_i])/(k_A k_{\bullet\text{OH}}[Fe^{2+}][H_2O_2])) \ln 2$. However, the poor linearity in TNT may be due to the recalcitrant nature of TNT.

From Eq. (14) the $k_{\bullet\text{OH}}$ values can be obtained using the slopes of $t_{1/2}-[A]_0$ plots in Fig. 6. Based on the assumption that $[Fe^{2+}]$ and $[H_2O_2]$ are constants through the reaction, $k_{\bullet\text{OH}}$ can be calculated by $1/(\text{slope} \times [Fe^{2+}][H_2O_2])$. The $k_{\bullet\text{OH}}$ values in the oxidation reactions of PA, AP, DNT and TNT are thus 1.43, 2.04, 2.69 and 0.58, respectively. Except for TNT, the $k_{\bullet\text{OH}}$ values are all close to each other. This is doubtless since $k_{\bullet\text{OH}}$ is independent of the initial concentration and reactants, but a function of temperature. On the other hand, by comparing the intercepts of $t_{1/2}-[A]_0$ plots in Fig. 6, it is surprising to find that all plots have similar intercept values except for TNT. From Eq. (14), the intercept is $((\sum k_i[S_i])/k_A)(\ln 2/(k_{\bullet\text{OH}}[Fe^{2+}][H_2O_2]))$, assuming that $\ln 2/(k_{\bullet\text{OH}}[Fe^{2+}][H_2O_2])$ is a constant, the intercept can be regarded as reaction rate ratio of byproducts to nitroaromatics, $\sum k_i[S_i]/k_A$, and the degree of competition effect from the

Table 4
Half-lives ($t_{1/2}$) and R^2 for linear regression of $1/r$ vs. $1/C$ during Fenton oxidation of nitroaromatic explosives

Initial concentration ($\times 10^4$ M)	PA		AP		DNT		TNT	
	$t_{1/2}$ (min)	R^2	$t_{1/2}$ (min)	R^2	$t_{1/2}$ (min)	R^2	$t_{1/2}$ (min)	R^2
3.0	22.5	0.991	29.5	0.962	21.4	0.987	84.4	0.955
2.0	19.4	0.991	16.9	0.993	11.7	0.999	51.9	0.911
1.5	18.2	0.984	17.5	0.999	–	–	58.4	0.933
1.0	11.1	0.992	14.2	0.991	8.52	0.999	49.3	0.854
0.5	8.9	0.995	12.09	0.999	8.9	0.998	–	–

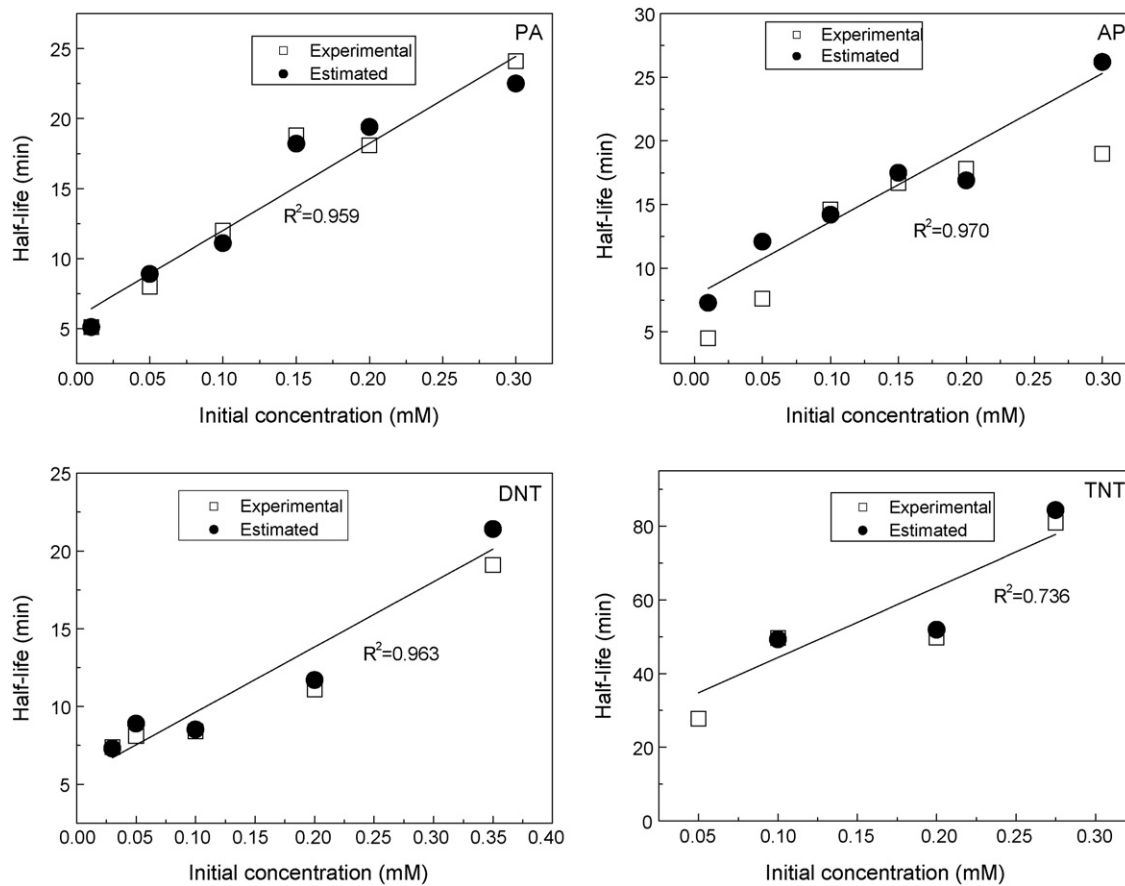


Fig. 6. Comparison of the estimated half-lives (●) with the experimental values (□). The straight line is the linear regression of the estimated values.

intermediates. Similar intercept values suggested that all the intermediates have a similar effect on the oxidation reaction. In this study, the four nitroaromatic explosives have a similar structure of nitro groups attached on the phenyl ring and therefore would result in a similar oxidation mechanism.

4. Conclusions

The removal rate of nitroaromatic is highly dependent on the $\bullet\text{OH}$ formation rate over the entire oxidation process. Four nitroaromatic explosives were selected and compared for their reaction rate constants and half-lives at various initial concentrations. By comparing the four nitroaromatics at the same initial concentration, the decomposition reactions are found to be dependent on the characteristics and numbers of substituents on the phenyl rings. Furthermore, a kinetic model for the nitroaromatic explosives decomposition has been proposed which describes the effect of decomposition byproducts on the oxidation reaction. The structural characteristic is proved to be the major factor in the Fenton oxidation by comparing the interference effect and the decomposition rate. The proposed model has been also proved to successfully coincide with the experimental results, and can be applied to estimate the half-lives of the decomposition reaction. Moreover, it also demonstrates the competition of hydroxyl radical between nitroaromatic explosive and oxidation byproducts.

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