Catalytic degradation of explosives with goethite and hydrogen peroxide

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Abstract

Goethite (α-FeOOH), one of soil contents, can be dissolved in acidic water to produce ferrous ions initiating Fenton reaction with hydrogen peroxide to degrade explosive. In this study, a series of catalytic degradation of nitro aromatic explosives, namely picric acid (PA) and ammonium picrate (AP) have been investigated using the FeOOH/H_2O_2 process. The controlling factors, such as adsorption of goethite dosage, hydrogen peroxide concentration and UV-light exposure on the oxidation of nitro aromatic explosives were investigated. The results showed that target compounds were adsorbed on the surface of goethite while the oxidation was proceeding. Furthermore, inhibition effect of nitro aromatic intermediates on the reaction was also discussed. A half-life kinetic model has been proposed to predict the half-lives of explosive oxidation in the goethite/H_2O_2 system.
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1. Introduction

Nitroaromatic compounds, i.e. 2,4,6-trinitrophenol (PA) and ammonium picrate (AP), are the main component of bombs and propellants and have been widely used as solid fuel oxidants for thruster and ammunitions. These explosives are known to be toxic to aquatic and terrestrial organism, causing very serious pollution in groundwater and soil, especially in former ammunition production plants and battle zones [1,2]. Dave et al. [3] had set up EC_{50} values of pitric acid for *D. magna* of $200\,\mathrm{mg\,L^{-1}}$ after 24 h and $86\,\mathrm{mg\,L^{-1}}$ after 48 h. Similar values were also reported by Kuhn et al. [4,5]. Lower toxic concentrations have been reported for algae system [6] and American oysters system [7].

Advanced oxidation processes are commonly used for the treatment of wastewater containing recalcitrant organic pollutants [8–10] and can be used to destroy a variety of explosive ammunition residues in the environment [11]. These methods are so attractive because of the possibility of the mineralization of the target compounds. Of these chemical processes, Fenton-type systems, employing iron salts and hydrogen peroxide in acidified soil suspensions (pH 2–3) to produce hydroxyl radical (a strong oxidant; $E^\circ = -2.8\,\mathrm{V}$), have been studied as a potential technology for soil remediation [12]. Li et al. [13,14] have shown that Fenton reaction could be used successfully to achieve the remediation goal for TNT and RDX for Nebraska Ordnance Plant (NOP). Similar researches about Fenton-type systems have been carried out [15,16]. Hundal et al. [17] also reported the mineralization conversion of RDX with Fe^0 alone, Fe^0 followed by H_2O_2 or Fe^0 in combination with biotic treatment. Moreover, Ravikumar and Gurol [18] found that iron oxide/H_2O_2 system is excellent in the decomposition of chlorophenols, such as PCP and TCP, on the surface of contaminated soil.

The required agents for the Fenton process are hydrogen peroxide (H_2O_2) and iron oxide, where H_2O_2 is a safe and economic oxidant. However, hydrogen peroxide is not an excellent oxidant for most organic substance of interest. In general, hydrogen peroxide is combined with UV-light, iron salts or ozone to produce a high concentration of hydroxyl radicals. Recently, the use of goethite (α-FeOOH) with hydrogen peroxide was found to effec-

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tively oxidize organic compounds due to the catalysis on goethite surface and ferrous ion generation [19,20]. Khan and Watts [21] reported that adding appropriate amount of H_2O_2 into the contaminated soils in the presence of goethite produced the reactive OH radicals, degrading most organic pollutants. Lu [19] also indicated that 2-chlorophenol can be decomposed with H_2O_2 catalyzed by goethite. Moreover, the capability of degradation can be greatly improved by the combination of goethite and UV/H_2O_2 [21]. This advantage is mainly due to the generation of more hydroxyl radicals from H_2O_2 when exposed to UV-light [22].

In the goethite/H_2O_2 process, ferrous ions are generated by the reductive dissolution of goethite shown as below [23]:

$$\alpha\text{-FeOOH} + \tfrac{1}{2}H_2O_2 + 2H^+ \rightarrow Fe^{2+} + \tfrac{1}{2}O_2 + 2H_2O \qquad (1)$$
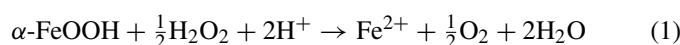
Ferrous ions are dissolved into the solution and then mixed with hydrogen peroxide to produce hydroxyl radicals (OH•), commonly described as Fenton reaction [24]:

$$H_2O_2 + Fe^{2+} \rightarrow OH^{\bullet} + OH^- + Fe^{3+}$$

$$OH^{\bullet} + Fe^{2+} \rightarrow OH^- + Fe^{3+}$$
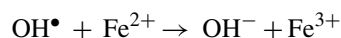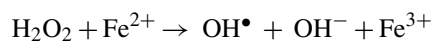
The Fenton reaction is recognized as one of the most powerful oxidizing reactions that can be used to decompose wide a range of refractory synthetics or natural organic compounds, including nitroaromatic explosives, such as PA and AP [25].

This research describes the heterogeneous catalytic reactions of H_2O_2 with granular size goethite (α-FeOOH) particles in aqueous solution under various experimental conditions. PA and AP solutions at various initial concentrations were prepared under acidic condition (pH 2.8) to perform Fenton-like oxidation reaction. The objective of this study was to investigate the oxidation of explosives, namely AP and PA, by goethite/H_2O_2 process. A kinetic model was proposed to successfully predict nitroaromatic decomposition half-lives. In addition, the inhibition and adsorption effect of intermediates on the parent compound oxidation can be quantified through this kinetic model.

2. Material and methods

2.1. Chemicals

Goethite with particle size between 30 and 50 mesh was purchased from the Aldrich Chemical Company. The explosive chemicals, PA (2,4,6-trinitrophenol) and AP (ammonium picronitrate), were obtained from the Army Chemistry Laboratory of the ROC. Hydrogen peroxide, with a purity of 30%, was provided by the Ferak Company. All other reagents were reagent grade. Aqueous solutions used for oxidation reaction were prepared with Millipore Milli-Q water.

2.2. Procedure and analysis

Aqueous solutions containing explosives were prepared by stirring an excess amount of explosives in pure water overnight.

All reaction solutions were adjusted to pH 2.8 with 0.5N nitric acid. Tests for blank absorption effect were first performed with 0.1, 0.2 and 0.4 g of goethite in 50 mL of total PA solution. The flasks were placed on a shaker at room temperature ($25 \pm 2\,^\circ$C) and 130 rpm. After 50 and 120 min, the remaining concentration of PA was detected. In the next section, 48.5 mL of 2.0×10^{-4} M PA and AP were mixed with goethite and hydrogen peroxide. UV-light was also applied to increase the oxidation rate. For data quality, replicated experiments were carried out in this study.

The residual amounts of explosive concentration were determined by a high performance liquid chromatography (HPLC) equipped with a multiple UV wavelength detector set at 254 nm. The samples (2 mL) taken from the solution at certain time intervals were mixed with 0.5 mL of 10^{-2} M sodium perphosphate to quench the Fenton reaction. A Supelco LC-18-DB column (25 cm × 4.6 mm × 5 μm) with an isocratic mixture of CH_3OH–H_2O (60:40, v/v) was used at the flow rate of 1.0 mL/min. Nitro aromatics were detected spectrophotometrically at 254 nm and quantified by comparison with high purity standard.

3. Results and discussion

3.1. Factors affecting the oxidation reaction

3.1.1. Effect of catalyst adsorption

Higher catalyst loading leads to higher degradation efficiency. Adding excess goethite could provide more surface areas for reaction interface. Thus, more explosives adhered on the surface of goethite. This is what we called "the adsorption effect". When excess goethite was added, the adsorption effect of PA on goethite was significant and it sometimes restrains the overall degradation efficiency. It is because the dense covering of explosives on goethite reduces the area available for the dissolution of ferrous ions into the solution and blocks the active sites that can participate in the catalysis of the Fenton-like reaction. Similar phenomena were also reported that very low iron ion was generated when $0.8\,g\,L^{-1}$ of goethite was used [19].

Since the adsorption occurs on the interface of heterogeneous reaction, this phenomenon must be taken into consideration and be calculated from the control experiment. In this paper, we use Langmuir–Hinshelwood kinetic equation [15] to describe this phenomenon on the heterogeneous catalysis. The blank adsorption tests were carried out at the following conditions: 0.1, 0.2 and 0.4 g 2,4,6-trinitrophenol (PA) mixed with 50 mL of goethite. As can be seen in Fig. 1, the remaining PA (0.1 g per 50 mL of goethite) was 0.89 g after 50 min. The residual ratio was further decreased to 82% after 120 min.

3.1.2. Effect of H_2O_2 concentration

The kinetic decomposition of H_2O_2 over goethite was also studied with ranging pH, H_2O_2 concentration and goethite concentration. Valentine and Wang [26] had established a linear relationship between the observed first-order decomposition coefficient (k_{obs}) of H_2O_2 to the mass of oxide present, allowing a mass normalized catalytic activity, k_{mass}, to be defined and a
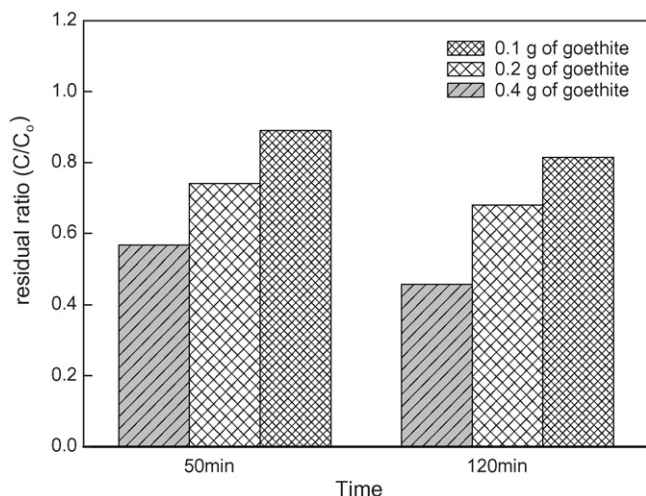
Fig. 1. Comparisons of residual ratios (C/C_o) for the degradation of PA without H_2O_2 at the concentrations of 0.1, 0.2, and 0.4 g of goethite per 50 mL of solution. Residual ratios (C/C_o) are normalized with the initial concentration (C_o: 2.0×10^{-4} M).

second-order rate expression to be derived,

$$\frac{d[H_2O_2]}{dt} = k_{obs}[H_2O_2] = k_{mass}[H_2O_2][oxide] \tag{2}$$

where $k_{mass} = k_{obs}[oxide]^{-1}$ and [oxide] is the concentration of oxide. k_{obs} is the rate of the reaction. k_{mass} is a constant at the same condition related to the temperature (T) and activated energy (E_a). Lin and Gurol [27] had also demonstrated that H_2O_2 at low concentration does not affect the dissolution kinetics of iron oxide and the surface reactivity. However, the dissolution kinetics and degradation are interacted as the ratio of [H_2O_2]/[explosive] is increased over 1000. In order to understand whether the iron ion leached out from goethite would contribute significantly to the decomposition of H_2O_2, a control experiment of goethite dissolution using 1.5 mL of 30% H_2O_2 in 48.5 mL goethite solution was conducted. Results showed that 2.46×10^{-6} M of the total dissolved Fe ions was detected in the solution after 50 min.

In our previous study [28], 2-chlorophenol (CP) was selected as the model compound to explore the oxidation with H_2O_2 in the presence of goethite. This study extended this application to the field of degradation of high-energy explosives (PA and AP). The effect of H_2O_2 concentration (0.029–0.29 M) on the degradation of explosives was investigated. In Fig. 2, the degradation efficiencies were promoted from 32 to 71% for PA and from 26 to 69% for AP after 120 min.

3.1.3. Effect of UV-light

In Fig. 2, the degradation efficiency was further increased by the exposure to 40 W UV-light for 120 min. This is because the Fe^{3+} was reduced in acidic solution thus more active ferrous ions (Fe^{2+}) were generated [29].

$$FeOH^{2+} + h\nu \rightarrow Fe^{2+} + OH^{\bullet} \tag{3}$$

With the aid of UV-light, the photo-Fenton mechanism was initiated and higher degradation efficiencies (85% for PA and

89% for AP) were obtained. This trend was corresponding with Perez's results [29].

3.2. Oxidation kinetics

3.2.1. Reaction pathway

The apparent rate of a heterogeneous reaction is usually dominated by both the rate of intrinsic chemical reaction on the surface and the rate of diffusion of the solutes to the surface. A two-step process was applied to describe the pathways of explosive degradation. The first step is the adsorption procedure and the second is the Fenton-like reaction. Polynomial kinetic models were employed to illustrate the mechanism of Fenton-like reaction. The overall reaction rate is equal to the summation of individual sub-rate constants for each step:

$$k_t = \sum \chi_i k_i \tag{4}$$

where k_t is the overall reaction rate constant, χ_i the coefficient of sub-rate rate constant in its respective reaction system and k_i is the sub-rate constant for the ith step.
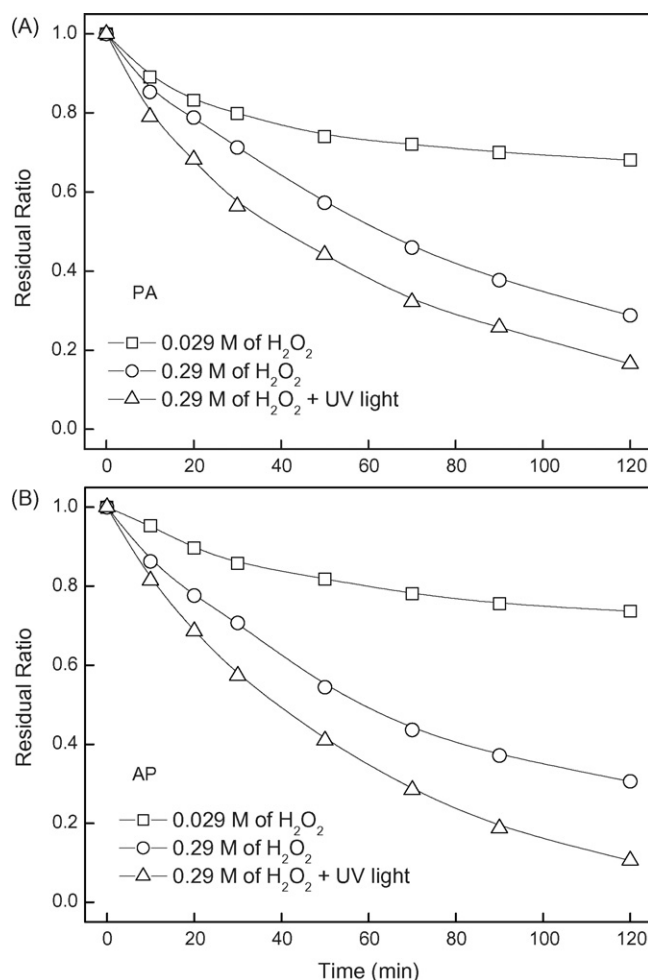

Fig. 2. Effects of H_2O_2 concentration and UV-light on Fenton-like degradation for (A) PA and (B) AP at pH 2.8. Experimental conditions: [H_2O_2] = 0.029 M without UV-light (□); [H_2O_2] = 0.29 M without UV-light (○); [H_2O_2] = 0.29 M with UV-light (△); 0.2 g goethite per 50 mL of solution. Residual ratios (C/C_o) are normalized with the initial concentration (C_o: 2.0×10^{-4} M).

Table 1
Comparisons of rate constants (k), half-lives ($\tau_{1/2}$) and half-lives after correction ($\tau_{1/2}^*$) for PA and AP at different initial concentrations

PA				AP			
Initial concentration ($\times 10^{-4}$ M)	k ($\times 10^{-2}$ min^{-1})	$\tau_{1/2}$ (min)	$\tau_{1/2}^*$ (min)	Initial concentration ($\times 10^{-4}$ M)	k ($\times 10^{-2}$ min^{-1})	$\tau_{1/2}$ (min)	$\tau_{1/2}^*$ (min)
3.11	1.02	67.7	66.8				
2.07	1.01	63.1	57.1	2.16	0.574	126.7	108.5
1.50	1.11	62.3	58.0	1.57	1.15	60.1	65.6
0.986	1.32	52.4	49.1	1.06	1.22	56.6	58.4
0.522	1.66	41.7	43.3	0.514	1.02	59.5	53.8
0.244	1.70	40.8	42.8				

Three possible iron sources (α-FeOOH, Fe^{2+} and Fe^{3+}) participate in the reaction, and thus overall constant rate can be expanded to three divisions:

$$k_t = \chi_{\alpha\text{-FeOOH}} k_{\alpha\text{-FeOOH}} + \chi_{Fe^{3+}} k_{Fe^{3+}} + \chi_{Fe^{2+}} k_{Fe^{2+}} \qquad (5)$$

$$k_t = \chi_{Fe^{2+}} k_{Fe^{2+}}$$
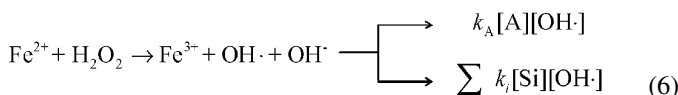
In the previous literatures [30,31], the rate constants of Fe^{3+}-initiated decomposition of H_2O_2 (0.0002 M^{-1} s^{-1}) is much lower than that of Fe^{2+} ($76 \pm 1.9 \times 10^5$ M^{-1} s^{-1}) in the Fenton reaction. Furthermore, the rate constant of the homogeneous reaction is higher than that of the heterogeneous reaction. The rate constants trend is:

$$k_{Fe^{2+}} > k_{Fe^{3+}} \gg k_{\alpha\text{-FeOOH}}$$

From the components of the above expression, the rate constant in the system is similar to that in the Fenton reaction. In other words, ferrous ions (Fe^{2+}) dissolved from goethite still remain as the main catalysts in the Fenton-like reaction.

3.2.2. Kinetic study

The calculation of the model was fundamentally based on the mass balance for hydroxyl radicals ($^\bullet OH$). The reacting routes and consuming stoichiometry for the reaction are listed below.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \longrightarrow \begin{array}{l} k_A[A][OH\cdot] \\ \sum k_i[Si][OH\cdot] \end{array} \qquad (6)$$

By applying mass balance for $OH^\bullet$,

$$\frac{d[OH^\bullet]}{dt} = k_{OH}[Fe^{2+}][H_2O_2]$$
$$- k_A[A][OH^\bullet] - \sum k_i[Si][OH^\bullet] \qquad (7)$$

where [A] is the original concentrations of the nitroaromatic explosive; [Si] the concentration of the intermediate; k_A and k_i are the rate constants, respectively. In the experiment, since excess amount of hydrogen peroxide was provided, $[OH^\bullet]$ should be constant during the reaction. Therefore, we define OH radicals concentration at the steady-state as $[OH^\bullet]_{SS}$. Based on this condition, pseudo-steady-state hypothesis (PSSH) was assumed and $d[OH^\bullet]/dt$ was equal to zero. The Eq. (7) can be transformed to $k_{OH}[Fe^{2+}][H_2O_2] =$

$k_A[A][OH^\bullet]_{SS} + \Sigma k_i[Si][OH^\bullet]_{SS}$ in which the value of $[OH^\bullet]_{SS}$ is given by Eq. (8):

$$[OH^\bullet]_{SS} = \frac{k_{OH}[Fe^{2+}][H_2O_2]}{k_A[A] + \sum k_i[Si]} \qquad (8)$$

The reaction rate (r) for the explosive is proportional to the concentration of explosive [A] and OH radicals $[OH^\bullet]_{SS}$. By substituting the value of $[OH^\bullet]_{SS}$, the pseudo-first-order reaction
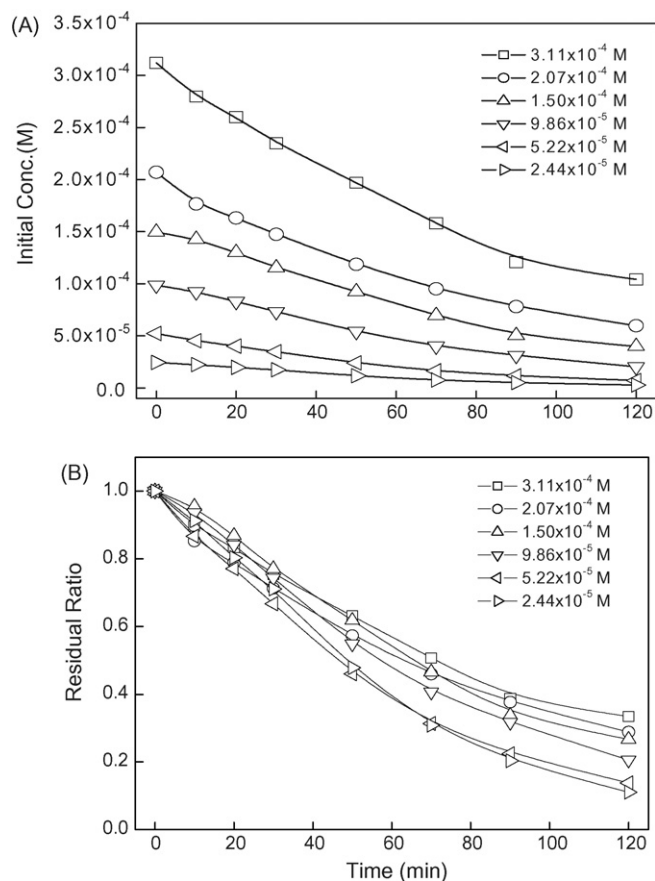

Fig. 3. (A) Dependency of Fenton-like oxidation reaction at the different initial concentration for PA and (B) decay curves of residual ratios are normalized by their respective initial concentrations. Experimental conditions: [PA] = 3.11×10^{-3} M ($\square$); [PA] = 2.07×10^{-3} M ($\bigcirc$); [PA] = 1.50×10^{-3} M ($\triangle$); [PA] = 9.86×10^{-4} M ($\triangledown$); [PA] = 5.22×10^{-4} M ($\triangleleft$); [PA] = 2.44×10^{-4} M ($\triangleright$) with 0.2 g goethite at pH 2.8.

rate obtained is shown by the following equation:

$$r = -\frac{d[A]}{dt} = k_A[A][OH^\bullet]_{SS}$$

$$= \frac{k_A k_{OH}[Fe^{2+}][H_2O_2]}{k_A[A] + \sum k_i[Si]}[A] = k[A] \quad (9)$$

where

$$k = \frac{k_A k_{OH}[Fe^{2+}][H_2O_2]}{k_A[A] + \sum k_i[Si]} \quad (10)$$

Since the concentrations of the explosive [A] and the intermediates [Si] are both variables of the rate constant (k), the intermediate effect will affect the half-life ($\tau_{1/2} = (\ln 2)/k$) of the first-order reaction, especially when $k_A[A] \cong \Sigma k_i[Si]$.

In another case, if $k_A[A] \gg \Sigma k_i[Si]$, where intermediate effect is negligible, the Eq. (9) is changing to a second-order reaction.

$$-\frac{d[A]}{dt} = k_{OH}[Fe^{2+}][H_2O_2] \quad (11)$$

The reciprocal from Eq. (9) gives a linear relationship between $1/r$ and $1/[A]$, as Eq. (12).

$$\frac{1}{r} = \frac{1}{k_{OH}[Fe^{2+}][H_2O_2]} + \frac{\sum k_i[Si]}{k_A k_{OH}[Fe^{2+}][H_2O_2]}\frac{1}{[A]} \quad (12)$$
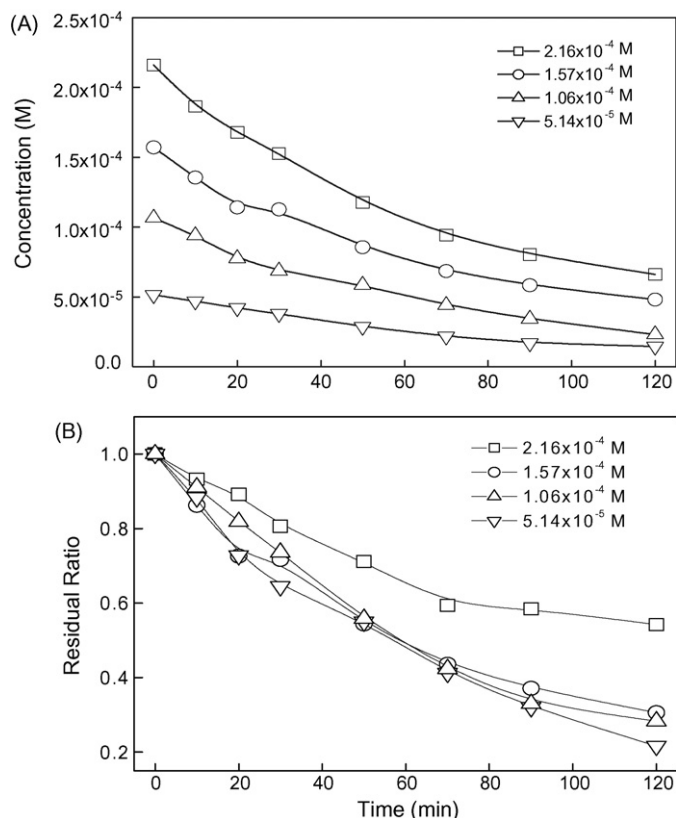

Fig. 4. (A) Dependency of Fenton-like oxidation reaction at the different initial concentration for AP and (B) decay curves of residual ratios are normalized by their respective initial concentrations. Experimental conditions: [AP] = 2.16 × 10⁻³ M (□); [PA] = 1.57 × 10⁻³ M (○); [PA] = 1.06 × 10⁻³ M (△); [PA] = 5.14 × 10⁻⁴ M (▽) with 0.2 g goethite at pH 2.8.

The integration of Eq. (12) gives Eq. (13).

$$t = \frac{\sum k_i[Si]}{k_A k_{OH}[Fe^{2+}][H_2O_2]} \ln\frac{[A]_0}{[A]}$$

$$+ \frac{1}{k_{OH}[Fe^{2+}][H_2O_2]}([A]_0 - [A]) \quad (13)$$

where $[A]_0$ is the initial concentration at $t = 0$. The half-life is given when [A] is equal to $1/2[A]_0$. Therefore, Eq. (7) is obtained.

$$t_{1/2} = \frac{\sum k_i[Si]}{k_A k_{OH}[Fe^{2+}][H_2O_2]} \ln 2 + \frac{[A]_0}{2k_{OH}[Fe^{2+}][H_2O_2]} \quad (14)$$

3.2.3. Effect of initial concentration

The initial concentrations of PA and AP solutions were varied from 2.44×10^{-5} to 3.11×10^{-4} M. The reaction was initiated by adding 0.2 g of goethite with 1.5 mL of 30% H₂O₂. Figs. 3 and 4 show the degradation curves at different initial concentrations. Table 1 lists the rate constants and the half-lives.
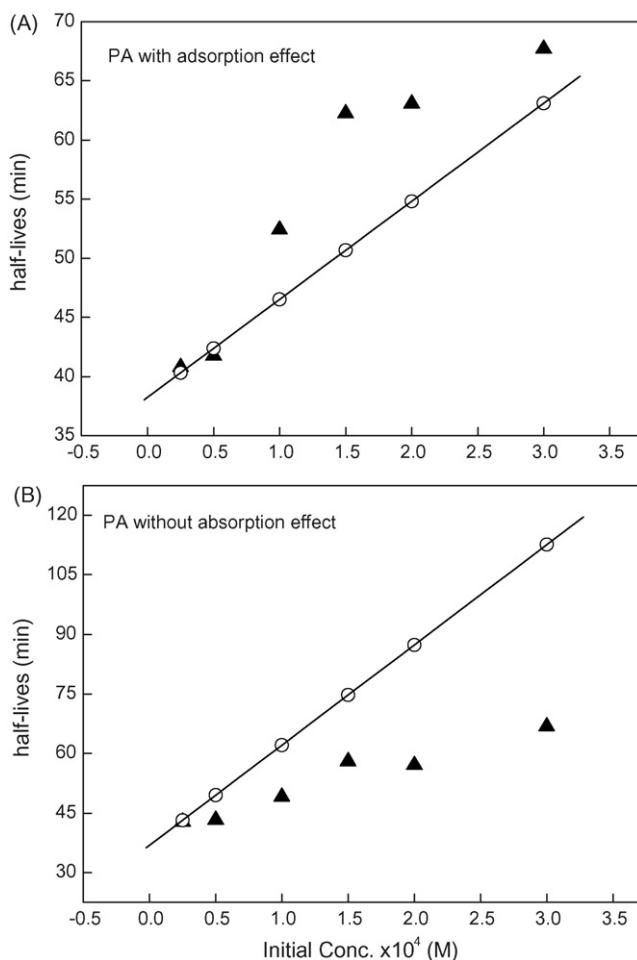

Fig. 5. (A) Comparisons of the expected PA half-lives ($t^*_{1/2}$) (○) from Eq. (12) and the experimental PA half-life ($\tau_{1/2}$) obtained from the proposed pseudo-first-order hypothesis (▲). (B) Comparisons of the expected PA half-lives ($t^*_{1/2}$) after subtraction of absorption effect calculated from Eq. (12) (○) and the experimental PA half-lives ($\tau^*_{1/2}$) obtained from the proposed pseudo-first-order hypothesis (▲).

The actual half-life was directly obtained from the experiments and calculated by PSSH method. The half-life after correction ($\tau_{1/2}^*$) was the value after subtracting the amounts of explosives absorbed on the goethite. It can be found that the fastest degradation rate occurred at the lowest initial concentration. It was because the intermediate effect was neglected and the half-life is determined by the initial concentration of the explosives $[A]_0$. It was suggested that the higher initial concentration produces more meta-stable intermediates, which may compete with the explosives reacting with hydroxyl radicals thus limiting the degradation rate.

The comparisons of these two kinetic models for PA and AP are shown in Figs. 5 and 6. By the regression analysis of the reciprocal reaction rate ($1/r$) and initial concentration ($1/[A]$), the high correlation coefficient ($R_{PA}^2 > 0.99$) for PA was obtained. It indicates that the model was fit properly in the Fenton-like reaction. However, the lower correlation coefficient ($R_{AP}^2 > 0.94$) for AP inferred that other factors were apparently affecting the reaction rate. In order to predict the rate equation properly, the adsorption effect was considered. After subtracting the adsorbed amounts of explosives on the goethite surface, the expected half-lives are more close to the actual values.
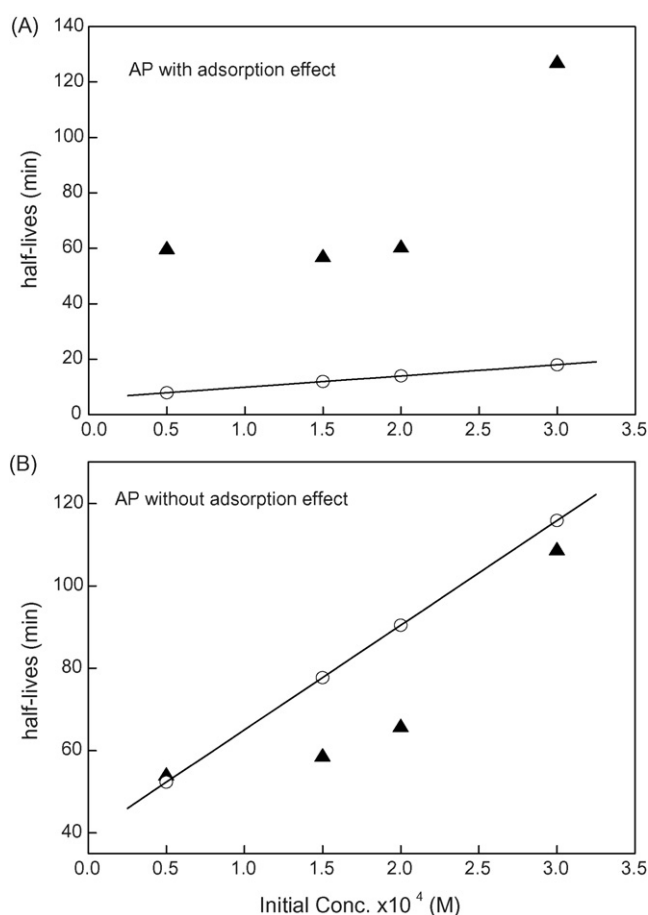
The theoretical rate constants of hydroxyl radicals (k_{OH}) can be obtained from the value of the intercept ($1/(k_{OH}[Fe^{2+}]_0[H_2O_2]_0)$). For $[Fe^{2+}] = 4.4 \times 10^{-6}$ M and $[H_2O_2] = 0.29$ M, k_{OH} was 4.72 min^{-1} for PA and was 9.67 min^{-1} for AP. The higher k_{OH} implied higher degradation rate; however, this does not correspond with our previous results, wherein the degradation rate of PA was larger than that of AP [28]. We supposed that byproducts generated from the decomposition of AP will clog the active sites on the goethite surface due to its structural characteristics and the stronger affinity between AP and goethite. At lower concentration of explosive ($\approx 0.5 \times 10^{-4}$), the adsorption effect is weak and thus these actual and corrected half-lives are within the error-range of 5%. The error-range is acceptable because the few amounts of the intermediates are hard to be quantified and subtracted. Moreover, the faster decomposition rate at lower concentration produced lower intermediates than parent explosives (i.e. $\Sigma k_i[Si] \gg k_A[A]$), thus the competition of intermediate for hydroxyl radicals could be negligible. After taking the adsorption effect into consideration, the corrected rate constants of hydroxyl radicals (k_{OH}^*) are 1.55 for PA and 1.53 for AP, respectively. This modified kinetic model was suitable to describe our previous results.

4. Conclusion

The goethite/H_2O_2 Fenton process can be applied to oxidize nitroaromatic explosives. Effects of catalyst dosage, H_2O_2 concentration and UV-light on the oxidation reaction have been studied. The optimum dosage of goethite at the experimental conditions in this study was 0.4 g/50 mL. It was found that adding more goethite inhibited the degradation but enhanced the adsorption effect of explosives. For increasing the explosive oxidation, hydrogen peroxide governed the reaction rate rather than UV-light.

The kinetic properties of the Fenton-like system can be obtained by the varying concentration of explosives. By the PHHS method, the efficiency of explosive degradation can be evaluated in terms of rate constant (k) and half-lives ($\tau_{1/2}$). After modification with the adsorption effect, we found that the degradation rate of PA is larger than that of AP. This study has successfully proposed a mechanism to compare both the rate constants from theoretical estimation and from the experimental data.

Fig. 6. (A) Comparisons of the expected AP half-lives ($t_{1/2}^*$) (○) from Eq. (12) and the experimental AP half-life ($\tau_{1/2}$) obtained from the proposed pseudo-first-order hypothesis (▲). (B) Comparisons of the expected AP half-lives ($t_{1/2}^*$) after subtraction of absorption effect calculated from Eq. (12) (○) and the experimental AP half-lives ($\tau_{1/2}^*$) obtained from the proposed pseudo-first-order hypothesis (▲).

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