

A kinetic study on the degradation of *p*-nitroaniline by Fenton oxidation process

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Abstract

A detailed kinetic model was developed for the degradation of *p*-nitroaniline (PNA) by Fenton oxidation. Batch experiments were carried out to investigate the role of pH, hydrogen peroxide and Fe²⁺ levels, PNA concentration and the temperature. The kinetic rate constants, k_{ap} , for PNA degradation at different reaction conditions were determined. The test results show that the decomposition of PNA proceeded rapidly only at pH value of 3.0. Increasing the dosage of H₂O₂ and Fe²⁺ enhanced the k_{ap} of PNA degradation. However, higher levels of H₂O₂ also inhibited the reaction kinetics. The k_{ap} of PNA degradation decreased with the increase of initial PNA concentration, but increased with the increase of temperature. Based on the rate constants obtained at different temperatures, the empirical Arrhenius expression of PNA degradation was derived. The derived activation energy for PNA degradation by Fenton oxidation is 53.96 kJ mol⁻¹.

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1. Introduction

In recent years, the so-called advanced oxidation processes (AOPs) have been identified as an attractive option for water treatment, particularly in cases where the contaminant species are difficult to remove using the usual biological or physico-chemical processes. The processes involve the generation of highly reactive hydroxyl radical (•OH), which can oxidize and mineralize almost all the organic molecules owing to its high oxidation potential ($E^0 = +2.8$ V) [1–3]. Among the most promising AOPs for water contaminated by organic molecules, application of the Fenton's reagent (an aqueous mixture of Fe²⁺ and H₂O₂ that produces hydroxyl radicals) stands out due to its high oxidation power, rapid oxidation kinetics, relatively cheap and easily

operated and maintained [4], which has been employed to treat a variety of industrial wastewaters containing aromatic amines, phenols, dyes, pesticides, etc. toxic and biologically refractory organic substances [5–9].

p-Nitroaniline (PNA) is an important compound used as an intermediate or precursor in the manufacture of organic synthesis, such as *p*-phenylenediamine, azo dyes, antioxidants, fuel additives, corrosion inhibitors, pesticides, antiseptic agents, medicines for poultry, pharmaceutical synthesis, etc. Nowadays, PNA has been listed as a priority pollutant by many countries due to its toxicity, potential carcinogenic and mutagenic effects. Because the presence of a nitro group in the aromatic ring enhances the stability to resist chemical and biological oxidation degradation, while the anaerobic degradation produces nitroso and hydroxylamines compounds which are known as carcinogenic [10,11]. So the purification of wastewater polluted with PNA is a very difficult task. AOPs have been investigated for the treatment of wastewater polluted with PNA over the last several years. Gautam et al. [12] investigated the degradation of PNA by photocatalysis. Spacek et al. [13]

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compared the degradation of PNA by photocatalysis and photo-Fenton process and showed that the degradation efficiency by photo-Fenton reaction was higher than that by photocatalysis. However, the information regarding the kinetic study on the degradation of PNA by Fenton oxidation is still limited. Therefore, the principal objective of this work was to propose a detail kinetic modeling, by which to clearly understand the degradation mechanisms and kinetics of PNA by Fenton oxidation process.

2. Materials and methods

2.1. Reagents

p-Nitroaniline was obtained from Beijing Chemical Reagents Co. (Beijing, China). Hydrogen peroxide (30%, w/w), ferrous sulfate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$), sulfuric acid and sodium hydroxide were all obtained from Shanghai Chemical Reagents Co. (Shanghai, China). All chemicals used were of analytical grade and without any further purification. Deionized water was used throughout this study.

2.2. Experimental procedures

All the PNA degradation tests were conducted in a 200 mL double glass cylindrical jacket reactor, allowing cycle water to maintain the temperature of the reactors. Temperature control was realized through a thermostat. A magnetic stirrer was used to stir reaction solutions, and the stirring rate was 280 rpm. To start each test, appropriate volumes of stock PAN and ferrous sulfate solutions were placed into the reactor and then diluted with deionized water to 100 mL. The pH of each reaction solution was adjusted to the desired level by using the prepared 1.0 M sulfuric acid or 1.0 M sodium hydroxide solution, and was measured with a model PHS-3C pH meter. The reactions were initiated by adding predetermined amounts of hydrogen peroxide to the reactor. Samples were taken out from the reactor periodically using a pipette and were analyzed immediately.

2.3. Analytical methods

The UV–vis spectra of PNA were recorded from 200 to 800 nm using a UV–vis spectrophotometer (Lambda 17, Perkin-Elmer) with a spectrometric quartz cell (1 cm path length). The maximum absorbance wavelength (λ_{max}) of PNA can be found at 380 nm from the spectra. Therefore, the concentration of the PNA in the reaction mixture at different reaction times were determined by measuring the absorption intensity at $\lambda_{\text{max}} = 380$ nm and from a calibration curve.

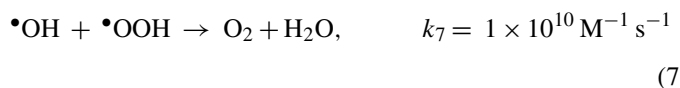
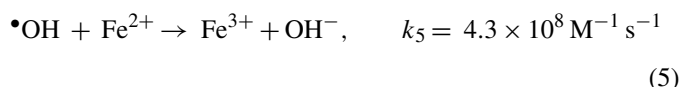
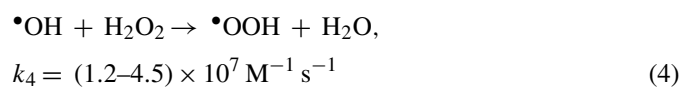
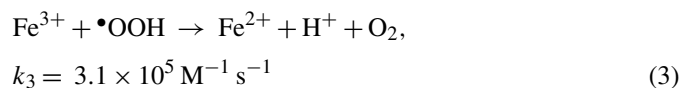
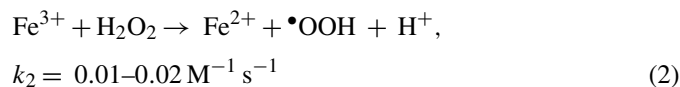
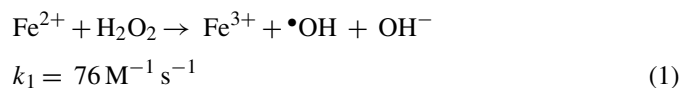
All the Graphics and statistical data analysis were carried out by Origin 6.0 software (Microcal).

3. Results and discussion

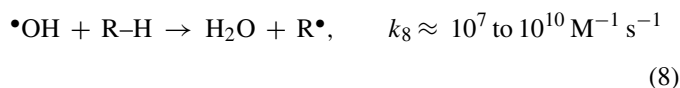
3.1. Kinetic modeling

In classic Fenton's chemistry, it is generally considered that the reactions between hydrogen peroxide and Fe^{2+} in acidic

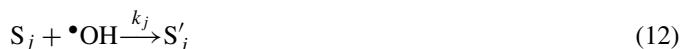
aqueous medium (≈ 3.00) involved the following steps (Eqs. (1)–(7)) [4,14,15]. The rate constants are reported in $\text{M}^{-1} \text{s}^{-1}$ for a second order reaction rate.



Although the degradation of an organic compound by Fenton's reagent is complex, several researchers have offered evidence of the formation of the $\bullet\text{OH}$ radical as the principle active oxidant in the Fenton system by many techniques, such as electron paramagnetic resonance (EPR) spin-tapping technique. The $\bullet\text{OH}$ radical can attack and initiate the oxidation of organic pollutants molecule (R) by several degradation mechanisms as shown below (Eqs. (8)–(10)) [4,16]:



Therefore, the following simplified mechanism may interpret the degradation of PNA by Fenton oxidation process:



where S_j is the scavenger species such as intermediates, excess of H_2O_2 , Fe^{2+} , $\bullet\text{OH}$ radical, $\bullet\text{OOH}$ radical, etc.; k_i and k_j are the global rate coefficients of reactions (11) and (12).

The corresponding kinetic equation for PNA and $\bullet\text{OH}$ radical can be expressed as follows:

$$\frac{d[\text{PNA}]}{dt} = -k_i[\text{PNA}][\bullet\text{OH}] \quad (13)$$

$$\frac{d[\bullet\text{OH}]}{dt} = k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}] - k_i[\text{PNA}][\bullet\text{OH}] - \sum_j k_j[S_j][\bullet\text{OH}] \quad (14)$$

Generally, the pseudo steady state assumption was used when concerning the concentrations of reactive radicals in the kinetics studies. Based on the pseudo steady state assumption, at a certain time, the concentration of reactive $\bullet\text{OH}$ radical will not vary with reaction time, i.e.,

$$\frac{d[\bullet\text{OH}]}{dt} = 0 \quad (15)$$

Thus, the following equation (Eq. (16)) derived from Eqs. (14) and (15) can be obtained,

$$[\bullet\text{OH}] = \frac{k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{k_i[\text{PNA}] + \sum_j k_j[S_j]} \quad (16)$$

Then Eq. (13) can be rewritten as that,

$$\frac{d[\text{PNA}]}{dt} = -\frac{k_i k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{k_i[\text{PNA}] + \sum_j k_j[S_j]}[\text{PNA}] \quad (17)$$

If the concentration of PNA is high, i.e., the condition of insufficient $\bullet\text{OH}$ radical because of insufficient hydrogen peroxide, so $k_i[\text{PNA}] \gg \sum_j k_j[S_j]$, and the Eq. (17) can be simplified to a zero order reaction rate with respect to PNA as follows:

$$\frac{d[\text{PNA}]}{dt} = -k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}] \quad (18)$$

According to Eq. (18), a plot of $[\text{PNA}]$ versus reaction time t will yield a straight line. In this case, the PNA could not be degraded effectively.

However, in the practical application of Fenton process, in order to degrade the pollutants effectively, the dosage of hydrogen peroxide should be sufficient in order to provide sufficient $\bullet\text{OH}$ radical, but at the same time, multi scavenger species are also generated. Indeed, a great deal of $\bullet\text{OH}$ radical was consumed by multi scavenger species in reaction process, which resulted in the dosage of hydrogen peroxide used is commonly much more than the concentrations of pollutants. The same results were also observed in the present study, the concentration of PNA is lower than that of hydrogen peroxide ($[\text{H}_2\text{O}_2]/[\text{PNA}] \approx 55:1$), herein, it can be concluded that $k_i[\text{PNA}]$ is much smaller than $\sum_j k_j[S_j]$, thus

$$k_i[\text{PNA}] + \sum_j k_j[S_j] \approx \sum_j k_j[S_j] \quad (19)$$

Then Eq. (17) can be simplified as

$$\frac{d[\text{PNA}]}{dt} = -\frac{k_i k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]}{\sum_j k_j[S_j]}[\text{PNA}] \quad (20)$$

or

$$\frac{d[\text{PNA}]}{dt} = -k_{\text{ap}}[\text{PNA}] \quad (21)$$

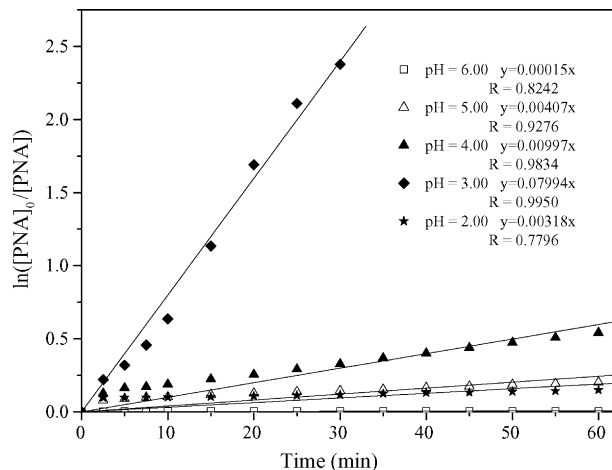


Fig. 1. Plot of $\ln([\text{PNA}]_0/[\text{PNA}]) - t$ at different initial pH values ($[\text{PNA}]_0 = 0.181 \text{ mM}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.05 \text{ mM}$, temperature = $20 \pm 1 \text{ }^\circ\text{C}$).

where k_{ap} represents $(k_i k_1[\text{H}_2\text{O}_2][\text{Fe}^{2+}]) / (\sum_j k_j[S_j])$. k_{ap} is the pseudo-first-order reaction rate with respect to PNA. Obviously, k_{ap} is related to $[\text{Fe}^{2+}]$, $[\text{H}_2\text{O}_2]$ and $[S_j]$. The integrated form of Eq. (21) is

$$\ln\left(\frac{[\text{PNA}]_0}{[\text{PNA}]}\right) = k_{\text{ap}}t \quad (22)$$

Therefore, if the relationship between $\ln([\text{PNA}]_0/[\text{PNA}])$ versus reaction time t is linear then the degradation of PNA will follow a pseudo-first-order reaction and the values of k_{ap} at given test conditions can be obtained from the slopes of plots of $\ln([\text{PNA}]_0/[\text{PNA}]) - t$.

3.2. Kinetic studies

The kinetics of PNA degradation by Fenton oxidation process under various reaction conditions has been investigated. The test range of each factor was chosen according to the reality of Fenton process application and the needs of kinetic studies in this research. The effects of pH, initial concentrations of H_2O_2 , Fe^{2+} and PNA, and temperature on the kinetic rate constants, k_{ap} , for PNA degradation will be separately discussed in the following sections.

3.2.1. The role of pH

The effect of pH on the kinetic rate constants, k_{ap} , for PNA degradation was studied in the range of 2.0–6.0 at the experiment condition of $[\text{PNA}]_0 = 0.181 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.05 \text{ mM}$ and $T = 20 \pm 1 \text{ }^\circ\text{C}$. The plots of $\ln([\text{PNA}]_0/[\text{PNA}]) - t$ at different pH values were shown in Fig. 1. It is obvious that the line is quite linear at pH 3.0 ($R > 0.99$). Therefore, it can be deduced that the PNA degradation fits the pseudo-first-order kinetic model. The results in Fig. 2 showed that the k_{ap} of PNA degradation was significantly influenced by the pH value of solutions and the optimal solution pH was observed at pH 3.0. The values of k_{ap} quickly increase when pH increases from 2.0 to 3.0, suddenly decrease when pH

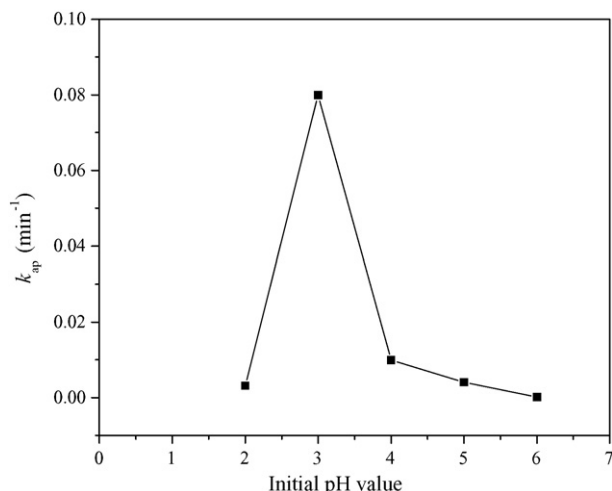


Fig. 2. Effect of the initial pH value on the degradation rate constant of PNA ($[PNA]_0 = 0.181$ mM; $[H_2O_2]_0 = 10$ mM, $[Fe^{2+}]_0 = 0.05$ mM, temperature = 20 ± 1 °C).

is raised from 3.0 to 4.0, and then gradually and slightly drop off with the increase of pH in the range of 4.0–6.0. The contributing factors for the low k_{ap} in lower pH range (<3.0) include the formation of oxonium ion (i. e. $H_3O_2^+$) due to the strong proton solvating ability of H_2O_2 , complex species $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$ [17] and enhanced $\bullet OH$ scavenging by H^+ [18] in low pH range. The poor degradation of PNA at a high pH values (>4.0) was caused by the formation of ferrous and ferric hydroxide complexes with much lower catalytic capability than Fe^{2+} .

3.2.2. The role of H_2O_2

The effect of initial hydrogen peroxide concentration on the kinetic rate constants, k_{ap} , for PNA degradation was performed by varying the $[H_2O_2]_0$ from 2.5 to 40 mM and at the experiment condition of $[PNA]_0 = 0.181$ mM, $[Fe^{2+}]_0 = 0.05$ mM, pH 3.0 and $T = 20 \pm 1$ °C, and the results are shown in Fig. 3. It can be seen the pseudo-first-order kinetic model is applicable

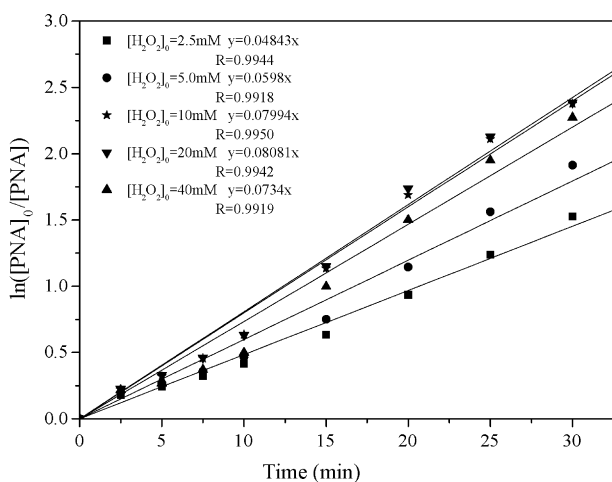


Fig. 3. Plot of $\ln([PNA]_0/[PNA]) - t$ at different initial hydrogen peroxide concentrations ($[PNA]_0 = 0.181$ mM, $[Fe^{2+}]_0 = 0.05$ mM, pH 3.00, temperature = 20 ± 1 °C).

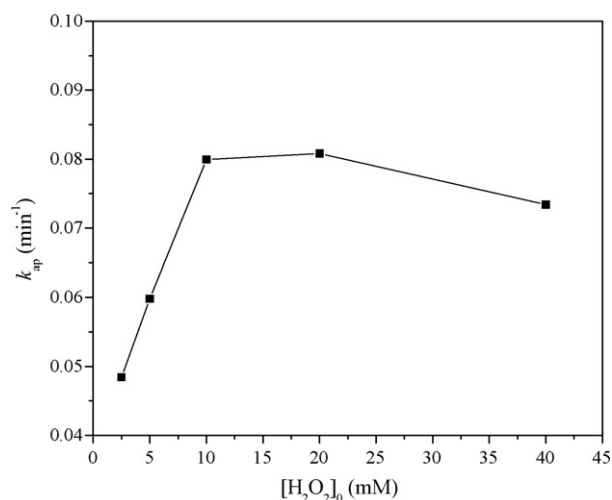


Fig. 4. Effect of initial hydrogen peroxide concentration on the degradation rate constant of PNA ($[PNA]_0 = 0.181$ mM, $[Fe^{2+}]_0 = 0.05$ mM, pH 3.00, temperature = 20 ± 1 °C).

to the PNA degradation quite well under the given test conditions ($R > 0.99$). It can be observed from Fig. 4 that the k_{ap} of PNA degradation increased with the increase $[H_2O_2]_0$ in the range of 2.5–10 mM. However, with continuous increase of $[H_2O_2]_0$ in the range of 10–40 mM, the increasing of $[H_2O_2]_0$ leads to the decline of k_{ap} especially when $[H_2O_2]_0$ is higher than 20 mM. The phenomena could be explained from the perspective of so-called critical concentration of hydrogen peroxide. Generally, under the critical concentrations, the degradation rates of different organic compounds, e.g., PNA in this research, increase with increasing of $[H_2O_2]_0$ due to the increment of $\bullet OH$ radical produced through the decomposition of increasing hydrogen peroxide. Beyond the critical concentrations, the degradation rate of organic compounds decreased with increasing of $[H_2O_2]_0$ due to scavenging of $\bullet OH$ by H_2O_2 and incremental generation of $\bullet OOH$ also consumed $\bullet OH$ [15,18].

3.2.3. The role of Fe^{2+}

The effect of Fe^{2+} concentration on the kinetic rate constants, k_{ap} , for PNA degradation was studied by varying $[Fe^{2+}]_0$ from 0.025 to 0.1 mM and at the experiment condition of $[PNA]_0 = 0.181$ mM, $[H_2O_2]_0 = 10$ mM, pH = 3.0 and $T = 20 \pm 1$ °C and the results are presented in Fig. 5. It indicates the pseudo-first-order kinetic model also fit the PNA degradation at the given test condition. In addition, it can be seen from Fig. 6 that the k_{ap} of PNA degradation was almost increased with the increasing of Fe^{2+} concentration by linear ($R > 0.98$). This is due to Fe^{2+} plays a very important role in initiating the decomposition of H_2O_2 to generate the very reactive $\bullet OH$ in Fenton oxidation process. However, it is not a good idea to use too high concentration of Fe^{2+} . Otherwise a large quantity of ferric based sludge would be generated, which complicates the PNA degradation due to the requirement of separation and disposal of the sludge.

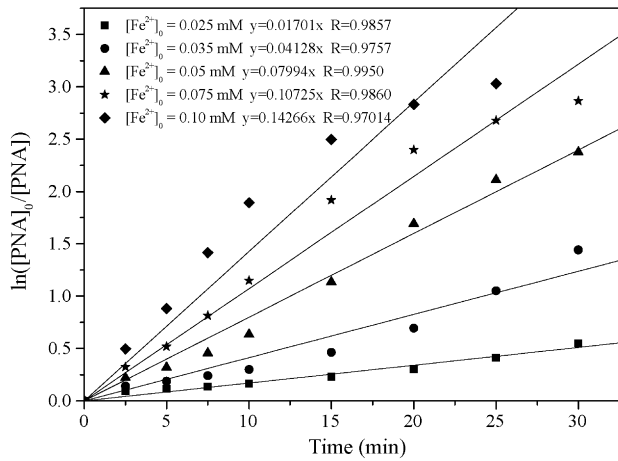


Fig. 5. Plot of $\ln([\text{PNA}]_0/[\text{PNA}])$ – t at different initial Fe^{2+} concentrations ($[\text{PNA}]_0 = 0.181 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $\text{pH} 3.00$, temperature = $20 \pm 1 \text{ }^\circ\text{C}$).

3.2.4. The role of initial PNA concentration

The effect of initial PNA concentration on the kinetic rate constants, k_{ap} , for PNA degradation was studied by varying the $[\text{PNA}]_0$ from 72×10^{-3} to $217 \times 10^{-3} \text{ mM}$ and at the experiment condition of 10 mM $[\text{H}_2\text{O}_2]_0$, 0.05 mM $[\text{Fe}^{2+}]_0$, $\text{pH} 3.0$ and temperature = $20 \pm 1 \text{ }^\circ\text{C}$, and the results are shown in Fig. 7. It can be seen that the PNA degradation kinetics at the given test condition was also fitted the pseudo-first-order kinetic model well. The results from Fig. 8 showed that the relationship between the k_{ap} of PNA degradation and the initial PNA concentration was in a good linear ($R > 0.98$).

3.2.5. The role of temperature

The effect of temperature on the kinetic rate constants, k_{ap} , for PNA degradation was studied at the temperatures of 10 , 20 , 30 , 40 and $50 \text{ }^\circ\text{C}$ with other tests conditions at $[\text{PNA}]_0 = 0.181 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.05 \text{ mM}$ and $\text{pH} 3.0$. The obtained results shown in Fig. 9 with a clear indication that k_{ap} of PNA degradation is significantly affected by reaction temperature and increased with the raising of temperature.

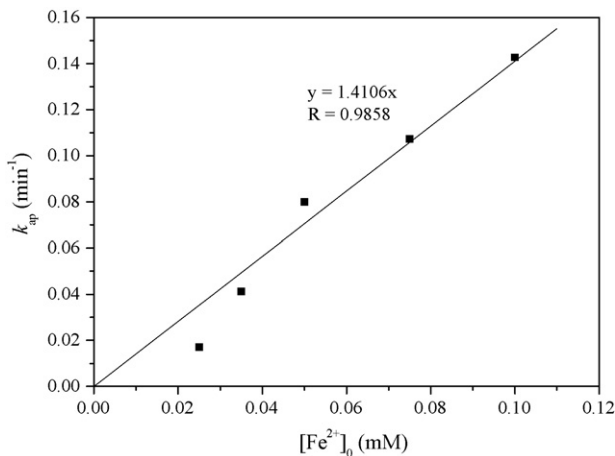


Fig. 6. Effect of initial Fe^{2+} concentration on the degradation rate constant of PNA ($[\text{PNA}]_0 = 0.181 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $\text{pH} 3.00$, temperature = $20 \pm 1 \text{ }^\circ\text{C}$).

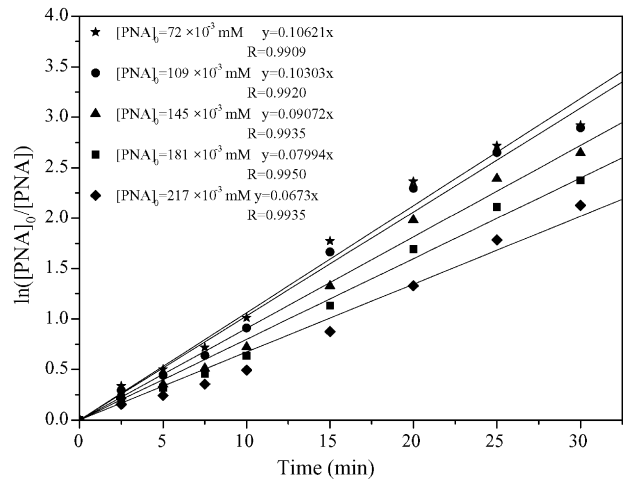


Fig. 7. Plot of $\ln([\text{PNA}]_0/[\text{PNA}])$ – t at different initial PNA concentrations ($[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; $[\text{Fe}^{2+}]_0 = 0.05 \text{ mM}$; $\text{pH} 3.00$ and temperature = $20 \pm 1 \text{ }^\circ\text{C}$).

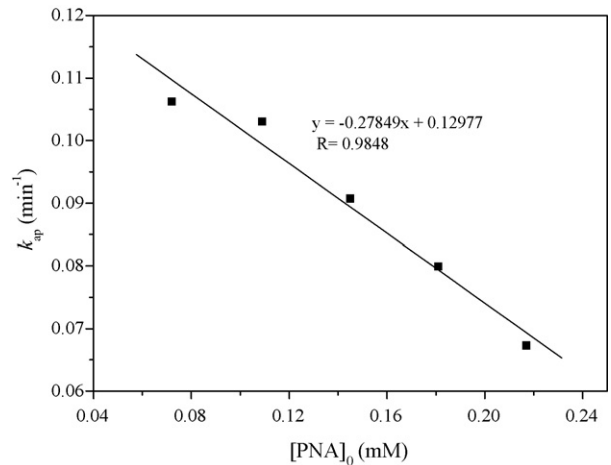


Fig. 8. Effect of initial PNA concentration on the degradation rate constant of PNA ($[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$; $[\text{Fe}^{2+}]_0 = 0.05 \text{ mM}$; $\text{pH} 3.00$ and temperature = $20 \pm 1 \text{ }^\circ\text{C}$).

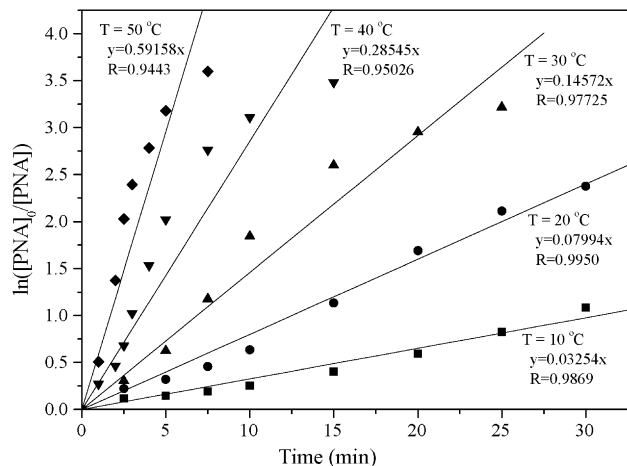


Fig. 9. Plot of $\ln([\text{PNA}]_0/[\text{PNA}])$ – t at different temperatures ($[\text{PNA}]_0 = 0.181 \text{ mM}$, $[\text{H}_2\text{O}_2]_0 = 10 \text{ mM}$, $[\text{Fe}^{2+}]_0 = 0.05 \text{ mM}$, $\text{pH} 3.00$).

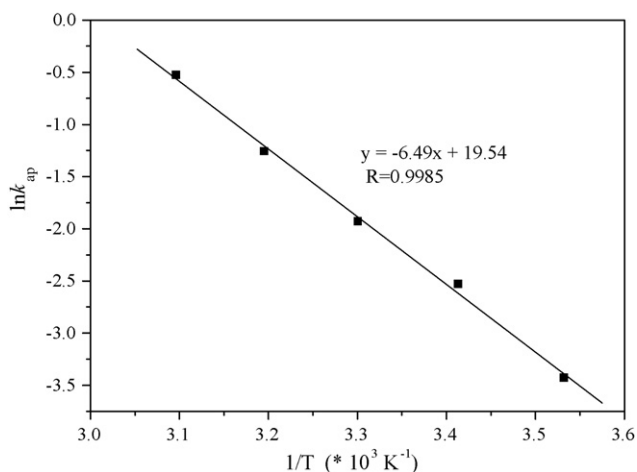


Fig. 10. Plot of $\ln k_{ap}-(1/T)$ for the degradation of PNA by Fenton oxidation process ($[PNA]_0 = 0.181$ mM, $[H_2O_2]_0 = 10$ mM, $[Fe^{2+}]_0 = 0.05$ mM, pH 3.00).

The Arrhenius expression, showing the relationship between the reaction temperature and the specific reaction rate, k , is expressed as follows:

$$k = A \exp\left(-\frac{E}{RT}\right) \quad (23)$$

where A is preexponential (or frequency) factor; E is the activation energy ($J mol^{-1}$); R is the ideal gas constant ($8.314 J mol^{-1} K^{-1}$); T is the reaction absolute temperature (K). Due to the narrow temperature range employed in this study (i.e., 10–50 °C), variations of the preexponential factors and the activation energies of the empirical Arrhenius expressions of the reaction of the degradation of PNA may be neglected.

The relationships of $\ln(k_{ap})$ derived from Fig. 9 versus $1/T$ are plotted in Fig. 10. Good linear relationships exist between the plots of $\ln(k_{ap})$ and $1/T$ because the regression coefficient was higher than 0.99. Based on the slope ($-E/R$) and intercepts ($\ln A$) of the plot in Fig. 10, E and A in Arrhenius form (Eq. (23)) are determined, i.e., $E = 53.96 kJ mol^{-1}$ and $A = 3.06 \times 10^8 min^{-1}$. Therefore, the Arrhenius form of the PNA degradation can be described as:

$$k = 3.06 \times 10^8 \exp\left(-\frac{53.96 \times 10^3}{T(K^{-1})}\right) (min^{-1}) \quad (24)$$

4. Conclusions

A detail kinetic modeling has been developed to understand the degradation mechanisms and kinetics of PNA by Fenton oxidation process. The test results showed that the pH value of solutions, the initial H_2O_2 concentration, the initial Fe^{2+} concentration, initial PNA concentration and the temperature are the main factors that have strong influences on the kinetic rate constants, k_{ap} , for PNA degradation. The k_{ap} of PNA degradation was: (1) increased with the increase of pH in the range of 2.0–3.0 and then decreased with the continuous increase of pH in the range of 3.0–6.0; (2) increased with the increase of initial concentration of H_2O_2 in the range of 2.5–10 mM and then slightly decreased with the further raising of H_2O_2 concentration in the

range of 10–40 mM; (3) increased with the increase of Fe^{2+} concentration in the range of 0.025–0.100 mM; (4) decreased with the increase of initial PNA concentration; (5) also increased with the increase of temperature. Based on the rate constants obtained at different temperatures, the empirical Arrhenius expression of PNA degradation by Fenton oxidation was derived. The derived activation energy for PNA degradation by Fenton oxidation is $53.96 kJ mol^{-1}$.

Acknowledgement

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