Degradation of high-concentration p-nitrophenol by Fenton oxidation
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ABSTRACT

This work aimed to degrade high-concentration p-nitrophenol (PNP) by Fenton oxidation. We studied various reaction parameters during Fenton oxidation, such as the iron dosage (as Fe\(^{2+}\)), the initial concentration and temperature of PNP, and the dosage of hydrogen peroxide (H\(_2\)O\(_2\)), especially the influence of temperature on the PNP degradation rate and degree. Under the addition of the same molar ratio of H\(_2\)O\(_2\)/Fe\(^{2+}\) and H\(_2\)O\(_2\) dosage according to the theoretical stoichiometry, the PNP degradation rate and the removal rate of total organic carbon (TOC) increased significantly with the increase in the initial PNP concentration. Moreover, the oxidative degradation effect was significantly affected by temperature. The increased reaction temperature not only significantly reduced the Fe\(^{2+}\) dosage, but also greatly promoted the removal rate of chemical oxygen demand (COD) and TOC, and improved the utilization efficiency of H\(_2\)O\(_2\). For example, when the initial concentration of PNP was 4,000 mg·L\(^{-1}\), and the dosage of Fe\(^{2+}\) was 109 mg·L\(^{-1}\) (H\(_2\)O\(_2\)/Fe\(^{2+}\) = 200), the removal rates of COD and TOC at 85 °C reached 95% and 71% respectively. Both were higher than the 93% COD removal rate and 44% TOC removal rate when the dosage of Fe\(^{2+}\) was 1,092 mg·L\(^{-1}\) (H\(_2\)O\(_2\)/Fe\(^{2+}\) = 20) at room temperature.

Key words | advanced oxidation processes, Fenton oxidation, high concentration, p-nitrophenol, wastewater treatment

HIGHLIGHTS

- The increased reaction temperature not only significantly reduced the Fe\(^{2+}\) dosage, but also greatly promoted the removal rate of COD and TOC, and improved the utilization efficiency of H\(_2\)O\(_2\).
- Fenton oxidation is both an economical and an environmentally beneficial method to treat high-concentration harmful wastewater.
- The conclusion can provide theoretical guidance for high-concentration actual wastewater treatment.

INTRODUCTION

The production of dyes, medicines and explosives produces a large amount of high-concentration and high-color nitrophenol wastewater (Xue et al. 2013; Wu et al. 2016). Nitrophenol is one of a number of organic compounds that are difficult to biodegrade, as they have stable chemical properties and high toxicity to humans and microorganisms. Meanwhile, increasing the number of nitro groups on the benzene ring enhances the concentration of nitrophenol wastewater and leads to greater dangers. For example, a COD\(_{\text{Cr}}\) and concentration of nitrophenol of wastewater of about 50,000 mg·L\(^{-1}\) and 42,000 mg·L\(^{-1}\) respectively were produced in the production of dye intermediate dinitrobenzene in a chemical plant in China. Nitrophenol is an explosive and dangerous product. Due to the increasingly strict environmental regulations, traditional combustion (Kim & Ihm 2011), zero-iron reduction and the biological methods...
suitable for the treatment of low-concentration wastewater. However, it is only effective method for wastewater treatment. However, it is only suitable for the treatment of low-concentration wastewater (Sharma 2012; Bouabidi et al. 2019), while the above-mentioned high-concentration wastewater containing biotoxic compounds cannot be directly treated by the biological method (Jemaat et al. 2015; Arora et al. 2014). Instead, such wastewater is typically pre-treated by advanced oxidation processes (AOPs) to reduce the organic load or toxicity of organic wastewater from different sources, decrease the effluent toxicity to a safe level, and improve biodegradability, so as to meet the conditions for further biological treatment (Gogate & Pandit 2004; Paździort et al. 2019). The combination of biological method and AOPs is both an economical and an environmentally beneficial method to treat high-concentration harmful wastewater (Kong et al. 2019).

AOPs make use of the high oxidizing ability of the hydroxyl radicals (Neyens & Baeyens 2005) of the main active species produced by reaction processes. In recent years, the effect of nanoparticles with photocatalytic activity on textile wastewater and organic pollutants has been extensively studied (Handojo et al. 2020; Samuel et al. 2020). However Fenton oxidation is still the most common method, as it can degrade many types of organic pollutants in various types of sewage. Therefore, it has been successfully used in the degradation of different industrial wastewaters in various fields, including pharmaceuticals, textiles, softwood processing, and pulp (Tambosi et al. 2006; Tekin et al. 2006; Bautista et al. 2008; Munoz et al. 2014).

In addition, in-depth studies have been conducted on the treatment of low-concentration aromatic compounds, including phenol, p-nitrophenol (PNP), and chlorophenol by Fenton oxidation (Chamarro et al. 2001; Zazo et al. 2005; Singh & Garg 2017; Rodrigues et al. 2018). There are many factors affecting the total efficiency of Fenton oxidation, among which the most important factors are the dosage of hydrogen peroxide (H₂O₂) and iron (as Fe²⁺), and the molar ratio of H₂O₂/Fe²⁺ (Sharma 2012). However, there are few reports on the relationship between high-concentration aromatic compounds, the initial concentration of organic matter and the Fenton oxidation conditions (Babuponnusami & Muthukumar 2014).

Fenton oxidation degrades organic pollutants through a large number of hydroxyl radicals produced by the reaction of Fe²⁺ and H₂O₂. It is a simple, stable and reliable operation with high efficiency, and can be performed at room temperature and atmospheric pressure. However, its current application in actual wastewater treatment has been limited, mainly due to the high cost of H₂O₂ and the large amount of Fe(OH)₃ sludge produced (Santos et al. 2007; Canizares et al. 2009). Zazo et al. (2011) took 100 mg·L⁻¹ phenol as the target compound, and found that at low doses of H₂O₂ and Fe²⁺, an increase in the reaction temperature can significantly enhance the oxidation rate and the degree of mineralization. Munoz et al. (2014) studied the impact of temperature on the treatment of saw-mill waste (COD = 3 g·L⁻¹) and obtained the same results. However, less attention has been paid to the fact that increasing the reaction temperature can reduce the amount of iron, thereby producing less Fe(OH)₃ sludge and improving the efficiency of H₂O₂ by reducing the competitive trapping reaction, that is, the influence of reaction temperature on the Fenton oxidation effect (Lopez et al. 2005).

The purpose of this work is to treat high-concentration PNP using Fenton oxidation, and systematically study the effect of different reaction factors on the removal rates of chemical oxygen demand (COD) and total organic carbon (TOC) and the kinetics of PNP degradation. This study focuses on the relationship between the reaction temperature and the Fenton oxidation effect, with the aim of reducing the amount of Fe²⁺ and improving the utilization efficiency of H₂O₂.

**EXPERIMENTS**

**Reagents and instruments**

Reagents: p-nitrophenol (AR); 30% hydrogen peroxide (AR); FeSO₄·7H₂O (AR).

Instruments: electronic balance (PG-603S, METTLER TOLEDO); magnetic stirrer (ZNCL-GS, Shanghai Yushen Instrument Co., Ltd); high performance liquid chromatograph (HPLC 1100 Series, Agilent Technologies Co., Ltd); COD detector (DR 3900, Hach Company, USA); TOC analyzer (Sievers Innovox ES, General Electric Company); pH meter (HI 2211, HANNA Instruments Company, Italy).

**Experimental methods**

The 150 mL of simulated PNP wastewater with a concentration of 4,000 mg·L⁻¹ was added to a three-necked flask, and the pH was adjusted to 5 with pre-configured 1 mol·L⁻¹ sulfuric acid and sodium hydroxide solutions. Unless...
otherwise specified, the concentration of PNP was 4,000 mg·L⁻¹, the pH of the reaction solution was 3, the temperature was room temperature (25 °C), and the reaction time was 60 min. The doses of Fe²⁺ and H₂O₂ required for the experiment were added in order according to the experimental design. In addition, to prevent the solution from volatilizing at high temperature, a condensation reflux device was installed. Then the Fenton oxidation experiment was performed at a constant temperature in a water bath during the reaction time. Finally, sampling and analysis were conducted within a certain time interval, and the reaction was ended after 60 min.

Analysis methods

The sample was taken and analyzed during the given reaction time interval. The phenolic compounds and their intermediates were analyzed by an Agilent 1100 HPLC with a reversed-phase C18 column and a UV detector. A gradient elution method was used with 0.1% formic acid (A) and acetonitrile (B) as the mobile phases, with a flow rate of 1.0 ml·min⁻¹ and a sample injection volume of 25 μl. The 0.5 ml of methanol was added to the sample to prevent the potential reaction of hydroxyl radicals on the target. The TOC of the water sample after the reaction was measured by the combustion oxidation non-dispersive infrared absorption method (HJ 501-2009), and the pH was adjusted to about 11 with sodium hydroxide to stop the reaction, followed by the removal of excess H₂O₂. COD was determined according to potassium dichromate method (GB/T 11914-1989), and the H₂O₂ concentration was measured by the oxalate titanium salt method (Sellers 1980).

RESULTS AND DISCUSSION

Impact of the Fe²⁺ concentration

Figure 1(a) shows the influence of the molar ratio of H₂O₂/Fe²⁺ on the degradation of 4,000 mg·L⁻¹ PNP. The dosage of H₂O₂ is the theoretical dosage of 13,260 mg·L⁻¹ (1 Qth, the theoretical stoichiometric value of PNP completely oxidized to H₂O and CO₂), and the molar ratio ranges from 50 to 400. The impact of Fe²⁺ concentration on the degradation of PNP was studied. It can be seen from Figure 1(a) that under all conditions, PNP is basically completely degraded within 30 min. As the molar ratio of H₂O₂/Fe²⁺ decreases, the reaction rate of the oxidation system increases continuously. When the molar ratio of H₂O₂/Fe²⁺ is 50 and the reaction time is 2 min, PNP is completely degraded. Obviously, the smaller the molar ratio of H₂O₂/Fe²⁺, the greater the dosage of Fe²⁺, and the high concentration of Fe²⁺ will effectively enhance the reaction rate of Fenton oxidation. When the molar ratio is reduced to 20, the reaction is more rapid, and PNP cannot be detected after 1 min (not shown in the figure).

The kinetic fit of changes in PNP concentration during oxidation is shown in Figure 1(b). The fitting results follow the pseudo-first-order reaction kinetics equation, which is the same process as the degradation of 200 mg·L⁻¹ PNP and other aromatic compounds by Fenton oxidation. (Kwon et al. 1999; Kavitha & Palanivelu 2005). Figure 1(b) indicates that the first few data points of ln(C/C₀) have a linear relationship with t when the molar ratio of H₂O₂/Fe²⁺ is 50–400. The slope k of the line represents the rate constant of the rapid reaction stage. When the molar

Figure 1 | Effect of H₂O₂/Fe²⁺ molar ratio on PNP degradation ([PNP]₀: 4,000 mg/L, [H₂O₂]₀: 13,260 mg/L, pH: 3).
ratio of H₂O₂/Fe²⁺ is 50 and 100, only the first few data points exist, and they have a linear relationship with t, indicating that the reaction is faster. When the molar ratio is 50 (437 mg·L⁻¹ Fe²⁺), the degradation rate of PNP is the fastest, and the k value is 11.53 min⁻¹; when the molar ratio is 400, the degradation rate is the slowest, and the k value is 0.36 min⁻¹. When the ratio is large, the actual iron ion concentration is only 55 mg·L⁻¹, thus H₂O₂ cannot be catalyzed within a short time to produce a large number of hydroxyl radicals, which reduces the oxidation reaction rate.

Figure 2 shows the variation curves of COD and TOC with Fe²⁺ concentration during PNP oxidation. It can be seen that when the molar ratio of H₂O₂/Fe²⁺ changes from 400 to 20, the COD removal rate increases from 69% to 93%, an increase of about 0.4 times; the removal rate of TOC also increases from 12% to 44%, an increase of about 2.7 times. When H₂O₂ is fixed to a theoretical value, as the dosage of Fe²⁺ increases, the decomposition reaction of H₂O₂ gradually accelerates, and the number of hydroxyl radicals per unit time increases to further react with the intermediate products in the solution, which gradually enhances the removal rate of COD and TOC. When the molar ratio of H₂O₂/Fe²⁺ is 20 (1.092 mg·L⁻¹ Fe²⁺), the removal rate of TOC reaches 44%, which is higher than in low-concentration aromatic compounds (Zazo et al. 2013).

The concentration of Fe²⁺ determines the Fenton oxidation reaction rate, and the dosage of H₂O₂ determines the depth of oxidation. The molar ratio of H₂O₂/Fe²⁺ is a key factor for the removal rate of organic matter in Fenton oxidation. Both low and high ratios will inhibit the degree of oxidation reaction (Sellers 1980; Wang et al. 2016). The excess Fe²⁺ in the reaction medium may also scavenge the OH free radicals, thereby reducing the removal efficiency (Kang & Hwang 2000). It has been reported in a previous study that the best molar ratios of H₂O₂/Fe²⁺ for the Fenton oxidation of low-concentration aromatic compounds are: 10–25 (PNP), 10–100 (phenol), and 5–15 (chlorophenol) (Du et al. 2006). When the molar ratio of H₂O₂/Fe²⁺ is 20, the result of the oxidation of the above-mentioned high-concentration PNP is that not only is the PNP degradation rate fast, but also the TOC removal rate is high, which may be ascribed to the significant reduction of side reactions during the Fenton oxidation of high-concentration PNP solution. The result is different from the Fenton oxidation of low-concentration solutions.

**Influence of initial PNP concentration**

Under the condition that the molar ratio of H₂O₂/Fe²⁺ is 100 and dosage of H₂O₂ is the theoretical dosage, the experimental results of Fenton oxidation of the PNP solution at the initial concentration of 100–6,000 mg·L⁻¹ are shown in Figure 3(a). It can be seen that PNP at all concentrations is completely degraded within 15 min. With the increase of concentration, the oxidation reaction rate becomes faster, and PNP at the concentration of 6,000 mg·L⁻¹ has the best degradation effect.

During the oxidation at different initial concentrations, the changes in PNP concentration also follow the kinetic equation of the pseudo-first-order reaction (as shown in Figure 3(b)). It can be seen from the figure that when the concentration of PNP is 100 mg·L⁻¹, the reaction is slow then speeds up, and the rate constant at the early stage of reaction is 0.57 min⁻¹. The concentration of 500 mg·L⁻¹ seems to be a turning point, where the rate is the same during the whole process with a rate constant of 1.3 min⁻¹. When the concentration is greater than 500 mg·L⁻¹, the reaction is fast then slows down. At the same time, all rate constants increase with the rise in concentration. When the concentration is 6,000 mg·L⁻¹, the rate constant is 6.38 min⁻¹, which is about 11 times larger than that of PNP with the concentration 100 mg·L⁻¹.

Figure 4 displays the curves of COD and TOC with the changes in initial PNP concentration in the oxidation experiment. It can be seen that when the initial concentration of the target changes from 100 mg·L⁻¹ to 6,000 mg·L⁻¹, the removal rates of COD and TOC increase from 68% and 21% to 81% and 30% respectively, indicating that the
removal rates of COD and TOC increase with the increased PNP concentration, which is similar to the pattern of changes in PNP concentration described previously. The changes of both are stable and are not much affected by the increase in concentration until the concentration of 4,000 mg·L\(^{-1}\) is reached, which may be ascribed to the fact that the higher the concentration of PNP, the higher the probability of reaction with the rapidly generated hydroxyl radicals, which is shown in the increase of the removal rates of COD and TOC. However, as the concentration increases, more acids with low molecular weight that are difficult to oxidize are generated in the reaction, which makes the further removal of COD and TOC difficult. Due to the formation of large amount of acid, the pH measured after the reaction will steadily decrease, which may hinder further reaction.

When the molar ratio is fixed, as the concentration of PNP increases, the dosage of H\(_2\)O\(_2\) and iron also increases simultaneously, thus more hydroxyl radicals are generated. On the other hand, the probability of collision of high-concentration PNP with hydroxyl radicals is increased, which will significantly reduce the side reactions. Therefore, the greater the oxidation rate and/or the removal rate of TOC, the more obvious the degradation effect. The oxidability of hydroxyl radicals is not related to the initial concentration of organic matter, while the removal efficiency of organic matter is related to the number of hydroxyl radicals. If the concentration of organic matter relative to the number of hydroxyl radicals is reduced, the removal efficiency will inevitably decrease. Therefore, the optimal concentration of the reagent should be determined according to the initial concentration of organic pollutant to ensure effective degradation (Titouhi & Belgaied 2016; Mirzaei et al. 2017).

The influence of temperature

In the experiment, 109 mg·L\(^{-1}\) Fe\(^{2+}\) and the theoretical dosage of H\(_2\)O\(_2\) were selected. The impact of temperature on the degradation of 4,000 mg·L\(^{-1}\) PNP is shown in Figure 5(a), from which it can be seen that only 0.7 mg·L\(^{-1}\) PNP remained after the reaction at 25 °C for 10 min. With the increase in temperature, the reaction rate further accelerated, so that the lines in the latter part almost coincide. In the reaction at 85 °C for 1.5 min, no PNP was detected, suggesting that at high temperature and
low Fe$^{2+}$ concentration, the Fenton method is effective for the oxidative degradation of high-concentration PNP. In order to better illustrate the influence of temperature on the reaction rate, the kinetic fitting results of changes in PNP concentration are shown in Figure 5(b). It is obvious that the reaction rate accelerated with the increase in temperature, and the oxidative reaction at high temperature was almost instant. The reaction rate constant at 85 °C (20.80 min$^{-1}$) was over 10 times greater than that at 25 °C (1.56 min$^{-1}$).

The impact of temperature on the removal rate of COD is shown in Figure 6. It can be observed that the removal rate of COD also increased with the rise in temperature, from 72% at 25 °C to 88% at 85 °C. At the same time, the influence of temperature on the removal rate of TOC was more prominent (as shown in Figure 7): it increased from 24% at 25 °C to 54% at 85 °C. The rise in temperature significantly improved the conversion of TOC. Moreover, Figure 7 also shows that this effect decreased with the increase in the initial Fe$^{2+}$ concentration, and at the high Fe$^{2+}$ concentration, the increased temperature was not conducive to the efficiency of the process.

To further study the effect of high temperature on Fenton oxidation, the following experiment was performed: at a temperature of 85 °C, H$_2$O$_2$ was added at the theoretical value, and at low dose (109 mg·L$^{-1}$) and high dose (1,092 mg·L$^{-1}$) of Fe$^{2+}$, the changes of H$_2$O$_2$ and TOC with time were measured. The results are shown in Figure 8. It can
be seen that when Fe$^{2+}$ is 109 mg·L$^{-1}$ (Figure 8(a)), H$_2$O$_2$ decreased by 73% and TOC decreased by 52% within 30 min of the initial reaction, then H$_2$O$_2$ gradually decomposed, and TOC continued to decrease. After 4 hours of reaction, the removal rate of TOC was 71% and the COD removal rate was as high as 95%.

By contrast, the combination of high-temperature and high-concentration Fe$^{2+}$ will have a negative impact on the efficiency of the Fenton process (Figure 8(b)). H$_2$O$_2$ was basically completely consumed within 5 min of the initial reaction, and the corresponding removal rate of TOC was about 50%, which no longer changed with time. A large number of hydroxyl radicals generated in a short period of time increased the probability of the destruction of free radicals and other side reactions, which ultimately resulted in a reduced TOC removal rate. The reaction process was the same as that at room temperature and with a high dose of Fe$^{2+}$ (Du et al. 2006).

Multivariate analysis is an important tool for conducting valuable and statistically significant model studies on a phenomenon through a minimum number of carefully selected experiments (Torrades et al. 2003). In this experiment, a three-factor Box-Behnken Design (BBD) coupled with response surface methodology (RSM) was applied to optimize the important variables. Design Expert software was also used to build the response surfaces, with the variable parameters represented in the removal percentage of COD after reaction shown in the ordinate. As shown in Figure 9, it reflected the influence of temperature and Fe$^{2+}$ on the COD removal rate of the response value. When H$_2$O$_2$ was 13,260 mg·L$^{-1}$, the Fe$^{2+}$ concentration was in a low range. As the temperature rose the COD removal rate increased significantly. At the lowest Fe$^{2+}$ dosage, the COD removal rate increased from 50% at 25°C to 84% at 85°C, an increase of 34%. With the increase in iron ion concentration, the impact of temperature on the removal rate of COD became less obvious, thus the Fe$^{2+}$ dosage could be appropriately reduced. This experimental model was good for predicting the changing trend of COD under the corresponding conditions, and the predicted value of COD showed a good correlation with the measured value (Figure 10).

The above experimental results demonstrate that the increase of operating temperature not only significantly reduces the dosage of Fe$^{2+}$, resulting in less Fe(OH)$_3$ sludge, but it also reduces side reactions to significantly improve the utilization efficiency of H$_2$O$_2$. However, the influence of reaction temperature on the Fenton oxidation effect has never received much attention. On the one hand, operation at room temperature is considered to be
one of the advantages of Fenton oxidation. On the other hand, heating low-concentration wastewater will increase costs. However, the temperature of high-concentration nitrified wastewater was much higher than room temperature, making the high-temperature Fenton process a possible method for the pre-treatment of such high-concentration wastewater.

**Influence of H$_2$O$_2$ dosage**

Figure 11 shows the effect of H$_2$O$_2$ dosage on the removal of TOC at different temperatures. The Fe$^{2+}$ concentration was maintained at 437 mg·L$^{-1}$. It can be seen from the figure that at 25 °C, TOC increased rapidly with the increase in the dosage of H$_2$O$_2$, exceeding 80% of the stoichiometric stoichiometry value (4/5 Qth), and the removal of TOC did not increase significantly; at 55 °C, the TOC removal effect is more obvious than that at low temperature. At 85 °C, the TOC removal rate was the highest, showing almost a straight upward trend. The experimental results suggest that when the Fe$^{2+}$ concentration had a certain value, the increase in the dosage of H$_2$O$_2$ promoted the formation of ·OH and the mineralization effect; the increase in the temperature enhanced the consumption efficiency of H$_2$O$_2$, thereby significantly improving the oxidation rate and degree of mineralization. In the evaluation of reagent consumption, the removal amount of TOC at decomposition ($\eta$) and fed ($\epsilon$) per gram of H$_2$O$_2$ was considered (as shown in Table 1). The second variable is more representative because the remaining H$_2$O$_2$ cannot be recycled.

Table 1 shows the values of $\eta$ and $\epsilon$ at different doses of H$_2$O$_2$ and at different temperatures. At 25 °C and 55 °C, the $\epsilon$ values increased first with the increase in H$_2$O$_2$ dosage, from 8 mg·L$^{-1}$ and 30 mg·L$^{-1}$ at 2/5 Qth to 66 mg·L$^{-1}$ and 79 mg·L$^{-1}$ at 4/5 Qth respectively. However, the values decreased when H$_2$O$_2$ was added at the stoichiometric ratio. Because the amount of H$_2$O$_2$ could still be detected at the end of the reaction, the $\epsilon$ values were small, only 55 mg·L$^{-1}$ and 78 mg·L$^{-1}$, and their $\eta$ values were increasing. At 85 °C, the values of $\eta$ and $\epsilon$ showed an increasing trend, indicating that the increase in temperature significantly boosted the utilization efficiency of H$_2$O$_2$.

The influence of the dosage of H$_2$O$_2$ on the removal of PNP and intermediate compounds at 85 °C is shown in Figure 12. The main intermediate compounds detected

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*a*mg TOC/g H$_2$O$_2$ converted.

*b*mg TOC/g H$_2$O$_2$ fed.
During the oxidation process, hydroquinone (HQ) and 4-nitrocatechol (4-NC), which are the same as the results of oxidation of low-concentration PNP. The possible reaction mechanism for 4,000 mg·L⁻¹ PNP has been proposed during Fenton processes and is shown in Figure S1 (Supplementary Material). Figure 12 shows that with the increase in the dosage of H₂O₂ the number of hydroxyl radicals generated in the reaction increased, and the amount of PNP and intermediate products were reduced. When 7/10 Qth of H₂O₂ was added at 85 °C, there was only 0.4 mg·L⁻¹ 4-NC and 0.1 mg·L⁻¹ PNP. Typically, the degradation efficiency of organic pollutants increases with the rise of the H₂O₂ dosage, but the dosage of H₂O₂ is a major factor determining the economic efficiency of Fenton oxidation. Therefore, determining the dosage of H₂O₂ according to the concentration limit of highly toxic aromatic organic substances that can be treated in a biochemical pond, as well as according to other indicators, can further reduce the cost of pre-treating high-concentration wastewater by high-temperature Fenton oxidation.

**CONCLUSION**

The experimental results demonstrate the effectiveness and efficiency of the advanced treatment of 4,000 mg·L⁻¹ PNP by Fenton oxidation. In this work, the Fenton oxidation kinetics analysis under different conditions was performed with PNP degradation, and it was found there are certain changes in COD and TOC during the reaction. The degradation rate of high-concentration PNP and the TOC removal rate were higher than the degradation of low-concentration PNP. The increased temperature greatly increased the removal efficiency of TOC and COD, improved the utilization efficiency of H₂O₂, and significantly reduced the dosage of Fe²⁺. The optimal parameters of Fenton oxidation for 4,000 mg·L⁻¹ PNP were pH of 3, H₂O₂ dosage of 13,260 mg·L⁻¹, Fe²⁺ concentration of 109 mg·L⁻¹ and temperature of 85 °C. Under these conditions, the removal rates of COD and TOC were 95% and 71%, respectively. Since the temperature of high-concentration nitrified wastewater is much higher than room temperature, the high-temperature Fenton process may be a suitable method for the pre-treatment of such high-concentration wastewater.

**SUPPLEMENTARY MATERIAL**

The Supplementary Material for this paper is available online at https://dx.doi.org/10.2166/wst.2020.284.

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