Oxidative decomposition of *p*-nitroaniline in water by solar photo-Fenton advanced oxidation process

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Abstract

The degradation of *p*-nitroaniline (PNA) in water by solar photo-Fenton advanced oxidation process was investigated in this study. The effects of different reaction parameters including pH value of solutions, dosages of hydrogen peroxide and ferrous ion, initial PNA concentration and temperature on the degradation of PNA have been studied. The optimum conditions for the degradation of PNA in water were considered to be: the pH value at 3.0, 10 mmol L^{-1} H$_2$O$_2$, 0.05 mmol L^{-1} Fe^{2+}, 0.072–0.217 mmol L^{-1} PNA and temperature at 20 °C. Under the optimum conditions, the degradation efficiencies of PNA were more than 98% within 30 min reaction. The degradation characteristic of PNA showed that the conjugated π systems of the aromatic ring in PNA molecules were effectively destructed. The experimental results indicated solar photo-Fenton process has more advantages compared with classical Fenton process, such as higher oxidation power, wider working pH range, lower ferrous ion usage, etc. Furthermore, the present study showed the potential use of solar photo-Fenton process for PNA containing wastewater treatment.
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Keywords: *p*-Nitroaniline; Solar photo-Fenton; Advanced oxidation processes (AOPs); Hydroxyl radical; UV–vis spectra

1. Introduction

p-Nitroaniline (PNA), one of the nitroaniline derivatives, 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 and pharmaceutical synthesis. The release of PNA directly through PNA production or utilization process will cause many serious eco-environmental problems due to its toxicity, carcinogenic and mutagenic effects. It has been listed as one of the major priority contaminants in water for removal by the National Environmental Protection Agency (NEPA) of the People's Republic of China.

Nowadays, a variety of physical, chemical, and biological methods have been used for the treatment of wastewater discharged from various industries. However, it is not cost-effective and environmental friendly to treat PNA containing wastewater with traditional physical and chemical methods, because they are usually non-destructive, inefficient, costly and usually result in the generation of secondary pollution. In addition, its high toxicity and inhibition to biodegradation make it also difficult to remove PNA from water by biological approaches. Therefore, the removal/degradation of PNA from wastewater is a great challenge to environmental scientists and engineers and the novel and cost-effective PNA removal technologies have to be developed.

In recent years, the so-called advanced oxidation processes (AOPs) have been widely investigated for the destruction and

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mineralization of hazardous materials in wastewater. In principle, the AOPs are innovative technologies that rely on the generation of very reactive hydroxyl radical ($\bullet$OH) to oxidize a broad range of organic pollutants to CO_2 and H_2O rapidly and non-selectively. O_3/H_2O_2, O_3/UV, H_2O_2/UV, TiO_2/UV, Fenton, Fenton-like, and some oxidant (such as H_2O_2 or O_3) combined with ultrasonic irradiation, etc. are the main types of AOPs that have been widely studied [1–7]. The degradation of PNA by Fenton process has been studied in detail in our previous work, and the results showed that the Fenton process has many advantages in the degradation of PNA, such as rapid degradation kinetics, relatively inexpensive, easily operate and maintain and so on [8].

Many studies have shown that the oxidizing power of Fenton process can be greatly enhanced by combination with the irradiation of UV or UV–vis, i.e. photo-Fenton process. The photo-Fenton process has been proved to be powerful in destroying persistent organic pollutants such as aniline, phenol, pentachlorophenol, nitrophenols, etc [9–12]. However, artificial UV/UV–vis light source was mainly employed in the most studies, which is uneconomical for practical application. Indeed, the solar irradiation offers an inexpensive and environmental friendly source of energy, and it will be particularly advantageous if it could be introduced to wastewater treatment processes. Furthermore, the main disadvantage of the photo-Fenton process, high-energy consumption of electrical lamps, might be overcome by solar irradiation. Although some studies have been reported on solar photo-Fenton process for the degradation of hazardous materials in water [13–18], the data on the solar photo-Fenton process's investigation are still very scarce. To the best of our knowledge, there are no reliable data on the degradation of PNA in water by solar photo-Fenton process at present.

The intent of this work, therefore, was to explore the application of the solar photo-Fenton process to the degradation of PNA in water. Influence of operating conditions, such as the pH value, the dosages of hydrogen peroxide and ferrous ion, initial concentration of PNA and temperature, were all evaluated in detail. In addition, the degradation characteristic of PNA was also analyzed.

2. Materials and methods

2.1. Chemicals

PNA was obtained from Beijing Chemical Reagents Co. (Beijing, China). Hydrogen peroxide (30%, w/w), ferrous sulfate ($FeSO_4 \cdot 7H_2O$), sulfuric acid and sodium hydroxide were all supplied by 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 methods

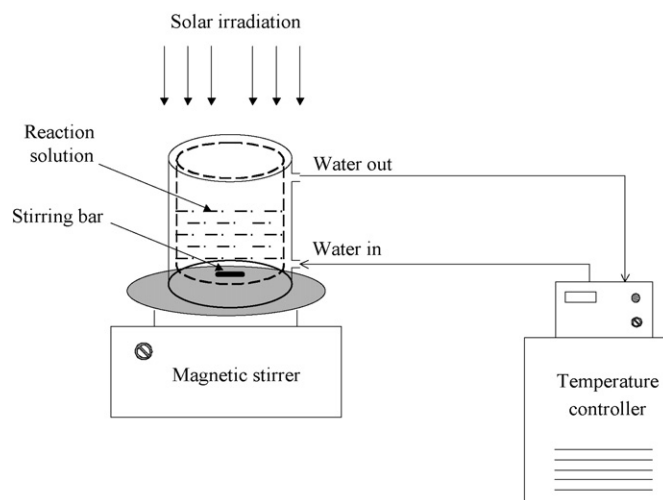The solar photo-Fenton experiments were performed at the College of Chemistry and Environmental Sciences, Henan Nor-

Fig. 1. The schematic illustration of experimental devices used in this study.

mal University, at the city of Xinxiang, China ($35°19'$ N; $113°54'$ E). All batch tests were conducted between 12:00 a.m. and 14:00 p.m. on the sunny days from March to May 2006.

The schematic illustration of experimental devices used in this study was shown in Fig. 1. All experiments were carried out in a 200 mL double glass cylindrical jacket reactor, allowing cycle water to maintain the temperature of the reactions. Temperature control was realized through a thermostat, and a magnetic stirrer was used to stir reaction solutions (stirring rate was 280 rpm). To start each experiment, 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 value of each reaction solutions was adjusted to the desired level using the prepared $1.0 \, mol \, L^{-1}$ sulfuric acid or $1.0 \, mol \, L^{-1}$ sodium hydroxide solutions. The reactions were initiated by adding pre-determined amounts of hydrogen peroxide to the reactor. Samples were taken out from the reactor periodically using a pipette, and which were immediately analyzed and returned back to the reactor. Because the reaction continued after sampling, sampling and measurement of the absorbance of reaction solutions were finished within 1 min.

2.3. Analytical methods

The pH value of the solutions was measured using a PHS-3C digital pH meter. Before the measurement, the pH meter was calibrated with standard buffers (pH 4.0, 7.0 and 10.0) at 25 °C.

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

The degradation efficiency of PNA was defined as follows:

$$\text{Degradation efficiency} (\%) = \left(1 - \frac{C_t}{C_0}\right) \times 100\% \qquad (1)$$

where C_0 is the initial concentration of PNA and C_t is the concentration of PNA at reaction time t (min).

The intensity of solar irradiation in experimental process was measured every 10 min by a JD-3 digital Lux meter (Shanghai, China). The average solar irradiation intensity was about 5.50×10^4 lx and that kept nearly constant in the whole study.

3. Results and discussion

3.1. Degradation of PNA by different processes

The different processes, solar + H_2O_2 + PNA, Fenton + PNA and solar photo-Fenton + PNA, were carried out as the control experiments for the degradation of PNA in water and the results were shown in Fig. 2. It can be seen that PNA in water could hardly be decomposed by the process of solar + H_2O_2. However, in both Fenton process and solar photo-Fenton process, PNA could be degraded effectively and the degradation efficiency achieved 90.72% and 99.59% within 30 min reaction, respectively. This can be explained from the fact that: In Fenton's reaction, active species such as $^\bullet OH/^\bullet OOH$ can be fast generated by the inter-reaction of hydrogen peroxide with ferrous and ferric ions in acid solution (Eqs. (2)–(4)). The generated $^\bullet OH$ can react with PNA by abstracting the π-electrons of the aromatic ring and resulting in the degradation of PNA (Eq. (5)). In addition, ferric ion generated in Eq. (2) can react with $^\bullet OOH$ or decomposed radical ($^\bullet R$) to regenerate ferrous ion, so the Fenton's reactions could be continued (Eqs. (6) and (7)) [19].

$$Fe^{2+} + H_2O_2 + H^+ \rightarrow Fe^{3+} + {}^\bullet OH + H_2O \qquad (2)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe\text{–}O_2H^{2+} + H^+ \qquad (3)$$

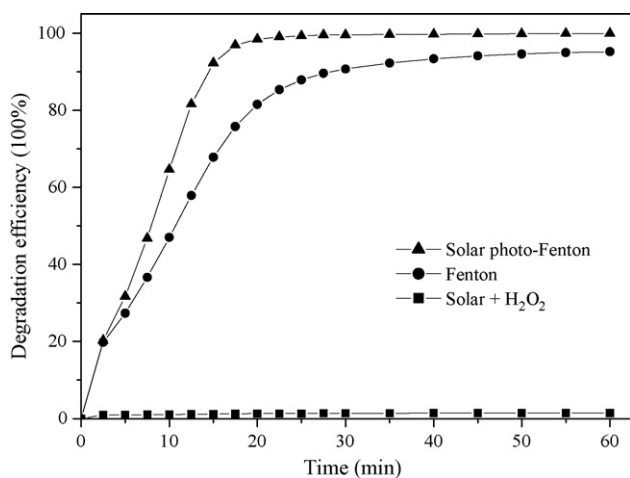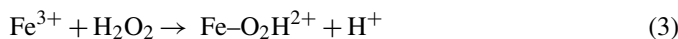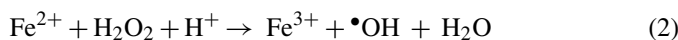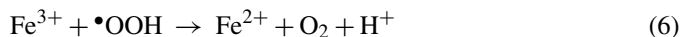$$Fe\text{–}O_2H^{2+} \rightarrow Fe^{2+} + {}^\bullet OOH \qquad (4)$$

Fig. 2. Degradation of PNA by different processes. Experimental conditions: $[PNA]_0 = 181 \times 10^{-3}$ mmol L^{-1}; $[H_2O_2]_0 = 10$ mmol L^{-1}; $[Fe^{2+}]_0 = 0.05$ mmol L^{-1}; pH 3.0 and temperature = 20 ± 1°C.
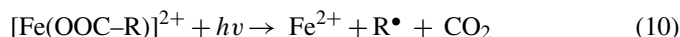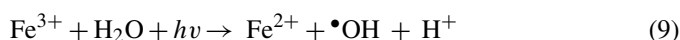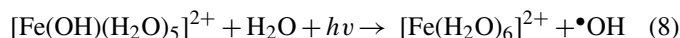
Table 1
The predominant ferric iron species in aqueous solutions at different pH ranges

Ferric iron species	pH ranges
$[Fe(H_2O)_6]^{3+}$	1–2
$[Fe(OH)(H_2O)_5]^{2+}$	2–3
$[Fe(OH)_2(H_2O)_4]^{+}$	3–4

$$PNA + {}^\bullet OH \rightarrow \text{oxidized products} \qquad (5)$$

$$Fe^{3+} + {}^\bullet OOH \rightarrow Fe^{2+} + O_2 + H^+ \qquad (6)$$

$$Fe^{3+} + R^\bullet \rightarrow Fe^{2+} + R^+ \qquad (7)$$

It is worth noting that a higher degradation rate of PNA was observed by solar photo-Fenton process from Fig. 2. This is due to that besides of $^\bullet OH$ generated by Fenton's reactions, more $^\bullet OH$ could be generated by the other reactions in this process. Firstly, it is known that the existing form of ferric iron in aqueous solutions was closely related with the acidity of solution (the predominant ferric iron species in aqueous solutions at different pH ranges were shown in Table 1) [20], and it mainly exists as $[Fe(OH)(H_2O)_5]^{2+}$ complex and ferric ion at pH 3.0. Both $[Fe(OH)(H_2O)_5]^{2+}$ complex and ferric ion could be reduced to generate $^\bullet OH$ and ferrous ion with the irradiation of solar light (Eqs. (8) and (9)) [21,22]. Secondly, ferric species can react with some degradation products (specially organic acids) to form iron-organic complexes (such as $[Fe(OOC\text{–}R)]^{2+}$), which are photochemically active and can also be decomposed to form ferrous ion and $R^\bullet$ by solar irradiation (Eq. (10)) [23]. In addition, ferrous ion generated in Eqs. (8)–(10) can continually participate in further Fenton's reactions to generate more $^\bullet OH$. All of above presentation contributed to the solar photo-Fenton process' stronger oxidizing power and resulted in the more PNA being degraded.

$$[Fe(OH)(H_2O)_5]^{2+} + H_2O + h\nu \rightarrow [Fe(H_2O)_6]^{2+} + {}^\bullet OH \quad (8)$$

$$Fe^{3+} + H_2O + h\nu \rightarrow Fe^{2+} + {}^\bullet OH + H^+ \qquad (9)$$

$$[Fe(OOC\text{–}R)]^{2+} + h\nu \rightarrow Fe^{2+} + R^\bullet + CO_2 \qquad (10)$$

3.2. Effect of pH on the degradation of PNA by solar photo-Fenton

The pH value of solutions is an important parameter for Fenton's reactions, which controls the production rate of $^\bullet OH$ and the concentration of ferrous ion. The effect of pH value of solutions on the degradation of PNA in water by solar photo-Fenton process was investigated and the results were shown in Fig. 3. It can be seen that when decreasing the pH value of solutions from 6.0 to 3.0, the degradation efficiency of PNA increased from 3.83% to 99.92% within 60 min reaction. However, when pH value of PNA solutions were continued to decrease from 3.0 to 2.0, the degradation efficiency of PNA declined from 99.92% to 17.66%. This can be explained from the following aspects: In conditions of pH > 4.0, the deactivation of ferrous ion catalyst caused the reduction of $^\bullet OH$ due to the formation of ferrous/ferric hydroxide complexes; In addition, the decreasing oxidation potential of $^\bullet OH$ in the higher pH conditions was
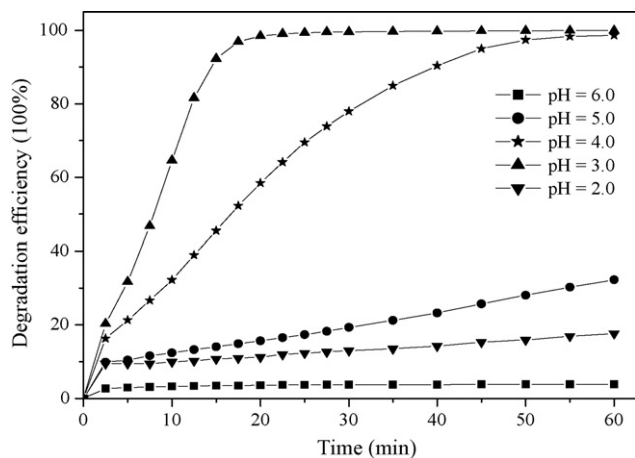
Fig. 3. Effect of pH on the degradation of PNA by solar photo-Fenton process. Experimental conditions: $[PNA]_0 = 181 \times 10^{-3}$ mmol L^{-1}; $[H_2O_2]_0 = 10$ mmol L^{-1}; $[Fe^{2+}]_0 = 0.05$ mmol L^{-1} and temperature $= 20 \pm 1\,^{\circ}C$.

Fig. 4. Effect of H_2O_2 dosage on the degradation of PNA by solar photo-Fenton process. Experimental conditions: $[PNA]_0 = 181 \times 10^{-3}$ mmol L^{-1}; $[Fe^{2+}]_0 = 0.05$ mmol L^{-1}; pH 3.0 and temperature $= 20 \pm 1\,^{\circ}C$.

another reason for lower degradation efficiency of PNA in this pH range (the oxidation potential of the redox couple $^{\bullet}OH/H_2O$ is 2.59 V at pH 0 and that of $^{\bullet}OH/OH^-$ decrease to 1.64 V at pH 14) [24]. In lower pH conditions (pH < 3.0), hydrogen peroxide become stable due to it solvated a proton and formed an oxonium ion (e.g., $H_3O_2^+$), which severely reduce its reactivity with ferrous ion; some complex species, such as $[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$, formed in this pH range also slowed the Fenton's reactions; and the scavenging effect of the $^{\bullet}OH$ by H^+ enhanced in this pH range [25,26]; all the above facets result in reducing the generation of $^{\bullet}OH$ and consequently lower the degradation efficiency of PNA.

Compared with the degradation of PNA by Fenton process, the resemblance of PNA degradation trend changed with pH value between Fenton process and solar photo-Fenton process was observed. However, it is worth noting that the solar photo-Fenton process had a wider working pH range than Fenton process. For example, in conditions of pH 4.0 and the same of other operating parameters (temperature, volume, H_2O_2 and Fe^{2+} dosage, reaction time, etc.), there only 41.80% of PNA was degraded by Fenton process within 60 min, but 98.65% degradation efficiency of PNA was achieved by solar photo-Fenton process.

3.3. Effect of H_2O_2 dosage on the degradation of PNA by solar photo-Fenton

The effect of H_2O_2 dosage on the degradation of PNA in this process was studied and the results were shown in Fig. 4. When H_2O_2 concentration was increased from 2.5 to 10 mmol L^{-1}, the degradation efficiency of PNA went up from 74.60% to 92.27% within 15 min reaction. Further increase of H_2O_2 concentration from 10 to 20 mmol L^{-1} resulted in the degradation efficiency of PNA also increased but not obvious. However, when H_2O_2 concentration was continued to increase from 20 to 40 mmol L^{-1}, the degradation efficiencies of PNA started to decrease. The fact is due to the oxidizing agent role that H_2O_2 played in Fenton's reactions. At first, the increase of H_2O_2 concentration resulted
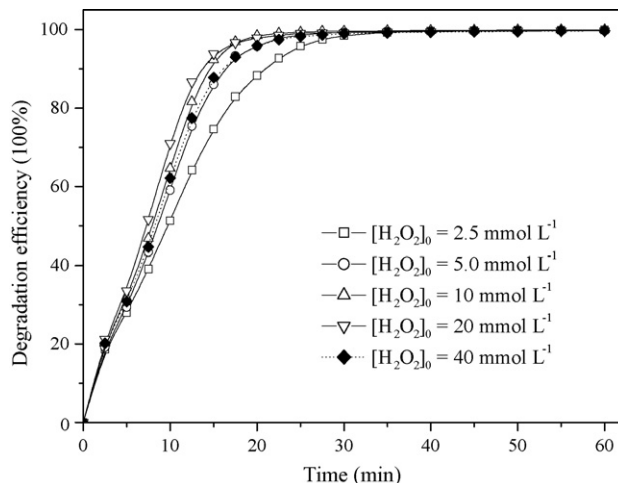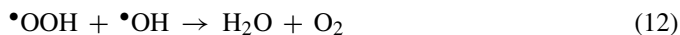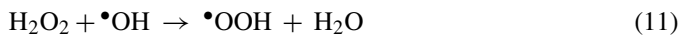
in increasing production of $^{\bullet}OH$ and consequently enhanced the degradation of PNA. However, with an excessive H_2O_2 load ($[H_2O_2]_0 > 20$ mmol L^{-1}), the scavenging effect of the $^{\bullet}OH$ by H_2O_2 and the recombination of $^{\bullet}OH$ were enhanced greatly (Eqs. (11)–(13)) [19,27].

$$H_2O_2 + {}^{\bullet}OH \rightarrow {}^{\bullet}OOH + H_2O \tag{11}$$

$${}^{\bullet}OOH + {}^{\bullet}OH \rightarrow H_2O + O_2 \tag{12}$$

$${}^{\bullet}OH + {}^{\bullet}OH \rightarrow H_2O_2 \tag{13}$$

The above results indicated that it is important to control the H_2O_2 concentration in solar photo-Fenton process and the optimum H_2O_2 dosage for the degradation of PNA experimentally selected was 10 mmol L^{-1}.

3.4. Effect of Fe^{2+} dosage on the degradation of PNA by solar photo-Fenton

Ferrous ion acts as a catalyst in Fenton's reactions. To choose the optimal amount of Fe^{2+} added in the reaction solution, a set of tests was performed. Fig. 5 illustrates the percent removal of PNA as a function of Fe^{2+} concentration. As can be seen from Fig. 5, Fe^{2+} dosage has a significant effect on the degradation of PNA. The degradation efficiency increased from 42.62% to 99.10% within 15 min reaction as a consequence of raising the initial concentration of Fe^{2+} from 0.025 to 0.100 mmol L^{-1}. As a catalyst, ferrous ion initiates the decomposition of hydrogen peroxide to generate the very reactive $^{\bullet}OH$ in Fenton's reactions. Therefore, higher initial Fe^{2+} concentration lead to higher generation of $^{\bullet}OH$ and better degradation of PNA. However, it can be seen that there was no significant distinction in the degradation efficiency of PNA within 30 min reaction when Fe^{2+} concentration at 0.05, 0.075 and 0.10 mmol L^{-1}. In addition, higher dosage of Fe^{2+} might produce a larger quantity of Fe^{3+} sludge. The removal/treatment of the sludge-containing Fe^{3+} at the end of the wastewater treatment is expensive and needs large amount of chemicals and manpower. Therefore,
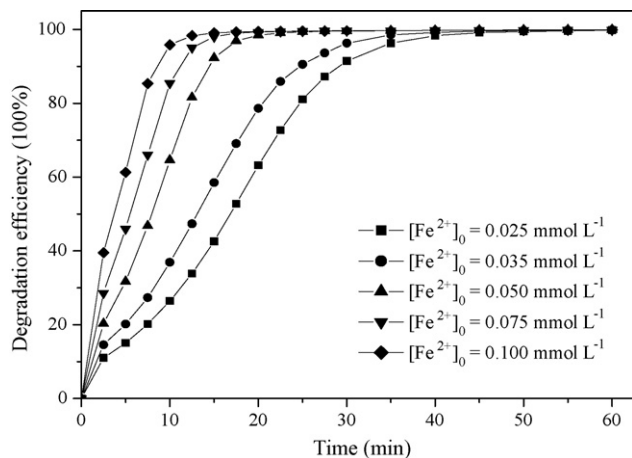
Fig. 5. Effect of Fe^{2+} dosage on the degradation of PNA by solar photo-Fenton process. Experimental conditions: $[PNA]_0 = 181 \times 10^{-3}$ mmol L^{-1}; $[H_2O_2]_0 = 10$ mmol L^{-1}; pH 3.0 and temperature = 20 ± 1 °C.

0.05 mmol L^{-1} was selected as the optimum Fe^{2+} dosage in this work.

Compared with the degradation of PNA by Fenton process, it is interesting to note that the solar photo-Fenton process has a lower Fe^{2+} usage. For example, in conditions of Fe^{2+} dosage with 0.025 mmol L^{-1} and the same operating parameters (temperature, volume, pH, H_2O_2 dosage, reaction time, etc.), there only 82.94% PNA was degraded by Fenton process within 60 min reaction, but 99.80% degradation efficiency of PNA was achieved by solar photo-Fenton process.

3.5. Effect of PNA concentration on the degradation of PNA by solar photo-Fenton

The effect of initial PNA concentration in this process was studied and the results were shown in Fig. 6. It can be seen that the degradation of PNA was inversely proportional to the initial PNA concentration. For example, the degradation efficiency
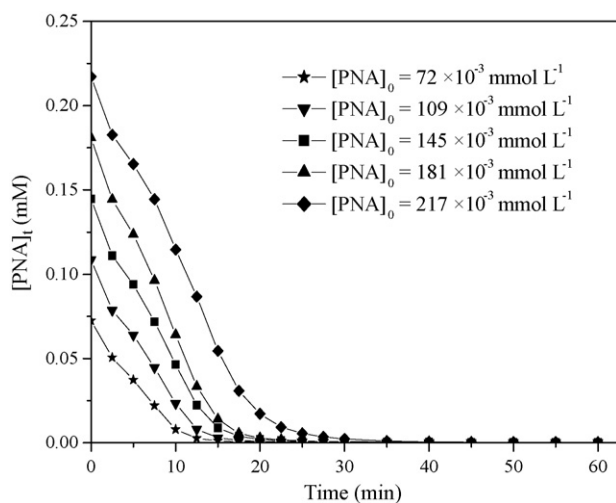
of PNA decreased from 89.01% to 47.20% within 10 min of reaction time as a consequence of increasing PNA concentration from 0.072 to 0.217 mmol L^{-1}. This is due to that when the initial concentration of PNA is increased but the generation of $^\bullet$OH is not increased correspondingly, so a relative lower $^\bullet$OH concentration resulted in the decrease of degradation efficiency of PNA. However, it can be observed that when the initial concentration of PNA in the range of 0.072–0.217 mmol L^{-1}, the degradation efficiencies of PNA were all more than 98% within 30 min reaction and nearly complete degradations of PNA were achieved within 60 min reaction.

3.6. Effect of temperature on the degradation of PNA by solar photo-Fenton

The effect of temperature on the degradation of PNA in water by solar photo-Fenton was studied and the results were shown in Fig. 7. It can be seen that temperature has a significant effect on the degradation of PNA. For instance, the degradation efficiency increased from 64.62% to 99.55% within 10 min reaction when the reaction temperature increased from 20 to 50 °C. The time required for the degradation of PNA was about five times shorter at 50 °C than that at room temperature. This is due to the temperature is critical to the reaction rate and it influences the product yield and distribution greatly. Increasing the temperature could enhance the rate of the redox reaction, so a higher temperature resulted in the reaction rate increased between hydrogen peroxide and any form of ferrous/ferric iron (chelated or not), and an increasing rate of generation of $^\bullet$OH as well as the degradation rate of PNA were obtained.

3.7. Degradation characteristic of PNA by solar photo-Fenton

To clarify the degradation characteristic of PNA by solar photo-Fenton process, representative UV–vis spectra changes of the PNA in water as a function of reaction time were depicted
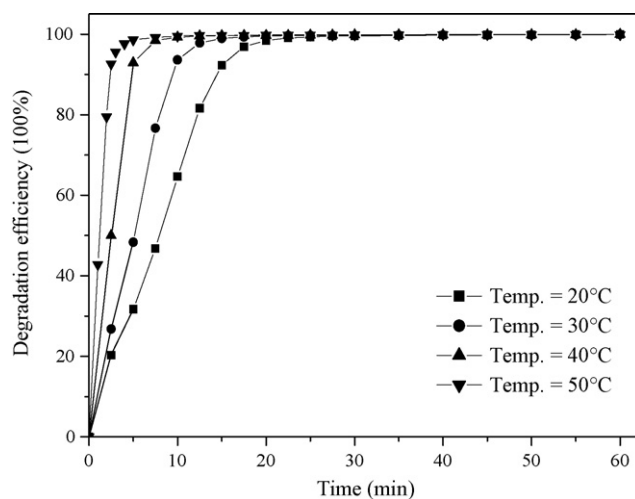

Fig. 6. Effect of initial PNA concentration on the degradation of PNA by solar photo-Fenton process. Experimental conditions: $[H_2O_2]_0 = 10$ mmol L^{-1}; $[Fe^{2+}]_0 = 0.05$ mmol L^{-1}; pH 3.0 and temperature = 20 ± 1 °C.

Fig. 7. Effect of temperature on the degradation of PNA by solar photo-Fenton process. Experimental conditions: $[PNA]_0 = 181 \times 10^{-3}$ mmol L^{-1}; $[H_2O_2]_0 = 10$ mmol L^{-1}; $[Fe^{2+}]_0 = 0.05$ mmol L^{-1}; pH 3.0.
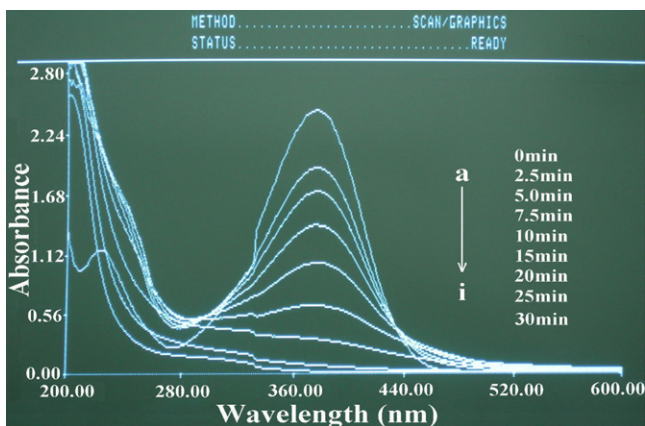
Fig. 8. UV–vis spectra changes of the PNA aqueous solutions as a function of reaction time under solar photo-Fenton process. Experimental conditions: $[PNA]_0 = 181 \times 10^{-3}$ mmol L^{-1}; $[H_2O_2]_0 = 10$ mmol L^{-1}; $[Fe^{2+}]_0 = 0.05$ mmol L^{-1}; pH 3.0 and temperature = $20 \pm 1°C$.

in Fig. 8. As can be observed from the spectra, before it was treated, the absorption spectrum of the PNA in water was characterized by one main band with a maximum absorption at 380 nm. This absorbance peak is attributed to the absorption of the $\pi \rightarrow \pi^*$ transition related to the benzene ring bonded to $-NO_2$ and $-NH_2$ groups in PNA molecule [28]. The peak at 380 nm diminished very fast and nearly completely disappeared within 30 min reaction, which indicated that the conjugated π systems of the benzene ring in PNA molecule has been destructed in this process. The results showed that PNA in water could be degraded efficiently by solar photo-Fenton process.

4. Conclusion

The degradation of PNA by solar photo-Fenton process was significantly influenced by pH value of the solutions, hydrogen peroxide and ferrous ion dosage, initial PNA concentration and the reaction temperature. The optimum conditions for the degradation of PNA in water were considered to be: the pH value at 3.0, 10 mmol L^{-1} H_2O_2, 0.05 mmol L^{-1} Fe^{2+}, and temperature at 20 °C. Under the optimum conditions, the degradation efficiencies of PNA (initial concentration of PNA was 0.072–0.217 mmol L^{-1}) were more than 98% within 30 min reaction. The experimental results indicated that solar photo-Fenton process has more advantages for the treatment PNA in water than that by classical Fenton process, such as higher degradation efficiency, wider working pH range, lower ferrous ion usage, etc. The present study also provides an effective approach to the treatment PNA containing wastewater to some extent.

Acknowledgement

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