Highly efficient UV/H$_2$O$_2$ technology for the removal of nifedipine antibiotics: Kinetics, co-existing anions and degradation pathways

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Abstract

This study investigates the degradation of nifedipine (NIF) by using a novel and highly efficient ultraviolet light combined with hydrogen peroxide (UV/H$_2$O$_2$). The degradation rate and degradation kinetics of NIF first increased and then remained constant as the H$_2$O$_2$ dose increased, and the quasi-percolation threshold was an H$_2$O$_2$ dose of 0.378 mmol/L. An increase in the initial pH and divalent anions (SO$_4^{2-}$ and CO$_3^{2-}$) resulted in a linear decrease of NIF (the $R^2$ of the initial pH, SO$_4^{2-}$ and CO$_3^{2-}$ was 0.6884, 0.9939 and 0.8589, respectively). The effect of monovalent anions was complex; Cl$^-$ and NO$_3^-$ had opposite effects: low Cl$^-$ or high NO$_3^-$ promoted degradation, and high Cl$^-$ or low NO$_3^-$ inhibited the degradation of NIF. The degradation rate and kinetics constant of NIF via UV/H$_2$O$_2$ were 99.94% and 1.45569 min$^{-1}$, respectively, and the NIF concentration = 5 mg/L, pH = 7, the H$_2$O$_2$ dose = 0.52 mmol/L, T = 20 °C and the reaction time = 5 min. The OH$^-$ was the primary key reactive oxygen species (ROS) and O$_2^-$ was the secondary key ROS. There were 11 intermediate products (P345, P329, P329-2, P315, P301, P274, P271, P241, P200, P181 and P158) and 2 degradation pathways (dehydrogenation of NIF $\rightarrow$ P345 $\rightarrow$ P274 and dehydration of NIF $\rightarrow$ P329 $\rightarrow$ P315).

1 Introduction

Water pollution is a major environmental problem the world is facing today, mainly due to modernization [1]. The removal of toxic organic pollutants discharged from the ever-increasing number of industries is a major environmental goal [2,3]. Nifedipine (NIF, Fig 1), 3,5-dimethyl 2,6-dimethyl-4-(2-nitrophenyl)-1,4-dihydropyridine-3,5-dicarboxylate, belongs to the dihydropyridine class of calcium channel antagonists and is one of the most useful pharmaceuticals for the treatment of hypertension, angina pectoris and other cardiovascular...
disorders [4,5]. As a large portion of each administered dose is excreted from medical applications and the pharmaceutical industry, and a substantial amount of NIF is released to the environment [6]. It has been demonstrated that NIF residues in the environment can result in the evolution of novel antibiotic-resistant bacteria that ultimately pose a threat to the aquatic ecosystem and human health through human organ lesions and increased bacterial resistance [7,8]. Hence, the efficient removal of NIF from water is significant and essential to reducing environmental and ecological risks.

The removal of antibiotics from aqueous solutions has been widely researched, including removal by physical methods, chemical methods and biological methods [9–12]. Adsorption and advanced oxidation processes (AOPs, such as photocatalysis, Fenton, Fenton-like, photo-Fenton and catalytic ozonation) are the most promising wastewater treatment technologies for the removal of antibiotics from water environments and reduction of the resulting environmental risks because they are fast, efficient, low cost and convenient [13–16]. Many adsorbents have been employed for the eradication of antibiotics [17]. However, there are some drawbacks, such as incomplete removal, high energy requirements and the generation of toxic sludge and other waste products that entail further disposal [18]. Solar light-driven photocatalysis involves the photoinduced generation of holes (h\(^+\)) in the valence band (VB) and electrons (e\(^-\)) in the conduction band (CB) via light absorption by a semiconductor (TiO\(_2\), ZnO and CdS). Sequential interfacial charge transfers release various reactive oxygen species (ROS), such as superoxide, peroxyde, and hydroxyl radicals, which participate in the degradation of organic and inorganic pollutants [19–22]. However, the limitations of a wide bandgap, the rapid recombination rate of photogenerated electron-hole pairs, low solar light energy utilization efficiency, photocorrosion, and poor recyclability reduce the photocatalytic efficiency.

**Fig 1. Structural formula of NIF.**

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[23–25]. It is imperative to develop a novel Z-scheme system or heterojunction photocatalyst with broad photocatalytic applications [26,27]. However, limited research has focused on the photo-degradation kinetics constants for the zero-order and first-order regions. When the reaction was more than 50% complete, the kinetics of the reaction changed to a first-order mechanism. The photo-degradation kinetics constants for the zero-order and first-order regions were (4.96 ± 0.10) × 10\(^{-9}\) M\(^{-1}\) s\(^{-1}\) and (6.22±0.10) × 10\(^{-5}\) s\(^{-1}\), respectively. This was the first study on the degradation of NIF, but the low degradation rate (65%) and kinetics limited the application of NIF removal via a photo-degradation system.

A novel method of UV light combined with hydrogen peroxide (UV/H\(_2\)O\(_2\)) is highly efficient, fast, and has a strong oxidizing ability; these advantages are attributed to the synergistic ability of UV light and H\(_2\)O\(_2\) to generate ROS [30]. However, in UV/H\(_2\)O\(_2\) AOPs, other constituents in water matrices may significantly affect the removal of target contaminants by competitively interacting with photons and ROS. In our previous study, the degradation of norfloxacin by using UV/H\(_2\)O\(_2\) was investigated [31]. The degradation rate and apparent first-order kinetics constant of norfloxacin via UV/H\(_2\)O\(_2\) were 98.8% and 0.22248 min\(^{-1}\), respectively, and the norfloxacin concentration = 20 mg/L, the H\(_2\)O\(_2\) dose = 1.2 mmol/L, the pH = 7, T = 20˚C and the reaction time = 20 min. The kinetics were low, and the formation mechanism of ROS was controversial, but it provided a novel research direction for the degradation of NIF via a UV/H\(_2\)O\(_2\) system. Therefore, it should be noted that the degree of research to date on the degradation of NIF via UV/H\(_2\)O\(_2\) oxidation processes is insufficient to thoroughly understand the fundamentals of -OH generation, intermediate products, and degradation pathways, which are important processes that must be considered in the design of wastewater treatment technology [32]. Furthermore, the effect of co-existing anions in the UV/H\(_2\)O\(_2\) system may significantly affect the removal of NIF by competitively quenching with ROS [33]. Thus, it is still challenging to design a UV/H\(_2\)O\(_2\) wastewater treatment technology with high efficiency.

On the one hand, the oxidizability of UV/H\(_2\)O\(_2\) AOPs and removal rate of NIF were enhanced due to the combination between UV and H\(_2\)O\(_2\) [30]. On the other hand, the anion (such as NO\(_3^−\)) was generated due to the degradation reaction between NIF and ROS. However, impacts of NO\(_3^−\) showed duality: it promotes the generation of ROS under irradiation, and also quenches the ROS of UV/H\(_2\)O\(_2\) [32,33]. Hence, it is significant and meaningful to study the effect of co-existing anions on the degradation of NIF via UV/H\(_2\)O\(_2\) AOPs. To better understand the removal efficacy of a target compound by UV/H\(_2\)O\(_2\) AOPs in different real water environments, the divalent anions (SO\(_4^{2−}\) and CO\(_3^{2−}\)) and monovalent anions (Cl\(^−\) and NO\(_3^−\)) have been developed to model the impact of water constituents on the reaction kinetics.

The aims of this study were to demonstrate the application of NIF degradation and to evaluate the performance and mechanism of UV/H\(_2\)O\(_2\) AOPs. The specific objectives were (1) to assess the effect of the H\(_2\)O\(_2\) dose, initial pH, and co-existing anions (SO\(_4^{2−}\), CO\(_3^{2−}\), Cl\(^−\) and NO\(_3^−\)) on the degradation of UV/H\(_2\)O\(_2\), (2) to predict the key ROS of the UV/H\(_2\)O\(_2\) method, and (3) to propose the degradation pathway of NIF.
2 Materials and methods

2.1 Chemicals

NIF was purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd. (Shanghai, China). Hydrogen peroxide (H$_2$O$_2$), hydrochloric acid (HCl), sodium hydroxide (NaOH), sodium sulfate (Na$_2$SO$_4$), sodium carbonate (Na$_2$CO$_3$), sodium nitrate (NaNO$_3$) and sodium chloride (NaCl) were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Methyl alcohol (CH$_3$OH) was purchased from Thermo Fisher Scientific (Shanghai, China). All chemicals and reagents used were of analytical grade or higher and directly used without further purification. All solutions were prepared with deionized water.

2.2 Experimental setup

The UV/H$_2$O$_2$ degradation experiments (Fig 2) were conducted in deionized water with the addition of H$_2$O$_2$ to the sample prior to 25 W UV light source exposure (254 nm). The initial NIF concentration was 5 mg/L, the temperature was 20˚C, the H$_2$O$_2$ dose was 0–1.04 mmol/L and the pH was 4–10. To understand the effect of co-existing anions, different sources of SO$_4^{2-}$, CO$_3^{2-}$, Cl$^-$ and NO$_3^-$ (from 5 to 50 mg/L) were added to the NIF degradation experiments to evaluate the removal rate and degradation kinetics.

2.3 Removal rate and degradation kinetics

The removal rate ($\eta$) of NIF under UV/H$_2$O$_2$ was calculated using Eq 1 (Eq 1):

$$ \eta = \frac{C_0 - C_t}{C_0} \times 100\% $$

where $C_0$ is the initial concentration of NIF and $C_t$ is the concentration of NIF at a certain degradation time, which was determined from the liquid chromatogram (S1 and S2 Figs).

The degradation kinetics of NIF via UV/H$_2$O$_2$ followed the apparent first-order kinetic law, and the apparent first-order kinetic constant ($k_{app}$) was described by Eq 2 (Eq 2):

$$ -\ln \frac{C_t}{C_0} = k_{app}t $$

where $t$ is the reaction time.

2.4 Organics analysis

NIF and its intermediate products in the UV/H$_2$O$_2$ degradation reaction solutions were analyzed by an Agilent 1260 series liquid chromatogram mass spectrometry (LC-Q-TOF-MS)
system (Agilent, USA) with a C18 column (100 mm × 2.1 mm, 3.5 mm). The wavelength was 237 nm according to ultraviolet and visible spectrophotometry (S1 Fig). The mobile phase was methyl alcohol and deionized water at 63:35 (v/v). The drying gas of N₂ was 8.0 mL/min, and the testing time was 30 min.

2.5 Electron spin resonance (ESR) measurements

ESR measurements were performed with a JES-FA200 electron spin resonance spectrometer and used to measure the hydroxide radical (·OH) and superoxide radical (·O₂⁻) during the degradation of NIF under UV/H₂O₂ using 5,5-dimethyl-1-pyrroline N-oxide (DMPO) as the spin trapping reagent.

3 Results and discussion

3.1 Effect of H₂O₂ dose

In general, the H₂O₂ dose significantly affects the oxidative degradation of antibiotics by controlling the generation rate of ROS, and the effect of H₂O₂ dose has been shown to have a dual nature. The specific degradation performance of NIF was enhanced by increasing the dose of H₂O₂ when it was low; however, the degradation performance of NIF increased slowly, remained constant or decreased when the H₂O₂ dose was high. As shown in Fig 3A and 3B and S1 Table, the degradation rates of NIF under UV/H₂O₂ were 72.81% (0 mmol/L) < 95.97% (0.13 mmol/L) < 99.31% (0.26 mmol/L) < 99.94% (0.52 mmol/L) < 99.95% (1.04 mmol/L), the kinetics constants k'_{app} were 0.2560 min⁻¹ (0 mmol/L) < 0.6752 min⁻¹ (0.13 mmol/L) < 1.03947 min⁻¹ (0.26 mmol/L) < 1.45569 min⁻¹ (0.52 mmol/L) < 1.59404 min⁻¹ (1.04 mmol/L), and the \( t_{1/2} \) (time of NIF degradation rate = 50%) were 0.4 min (0.52 mmol/L) < 0.6 min (1.04 mmol/L) < 1.0 min (0.26 mmol/L) < 1.5 min (0.13 mmol/L) < 2.8 min (0 mmol/L) when the NIF concentration = 5 mg/L, the H₂O₂ dose = 0–1.04 mmol/L, the pH = 7, \( T = 20 \) °C and the reaction time = 5 min. As shown in Fig 3C, the effect of the H₂O₂ dose on the degradation of NIF via UV/H₂O₂ system had a dual nature. The degradation kinetics constant noticeably increased as the H₂O₂ dose increased and then remained constant at 1.5±0.1 min⁻¹. When the H₂O₂ dose was < 0.52 mmol/L, the slope was 3.013 (min⁻¹)/(mmol/L), but it decreased to 0.266 (min⁻¹)/(mmol/L) when the H₂O₂ dose was > 0.52 mmol/L; hence, the quasi-percolation threshold (QPT) of the H₂O₂ dose was 0.378 mmol/L [34]. This trend was based on the generation and quenching of ·OH described by (Eq 3) to (Eq 6) [35]:

(a) H₂O₂ dose < QPT:

\[
\text{H}_2\text{O}_2 \rightarrow 2 \cdot \text{OH}
\]  
(Eq 3)

(b) H₂O₂ dose > QPT:

\[
\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \cdot \text{HO}_2 + \text{H}_2\text{O}
\]  
(Eq 4)

\[
\cdot \text{HO}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2
\]  
(Eq 5)

\[
2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2
\]  
(Eq 6)
3.2 Effect of initial pH

The pH is another key parameter of the UV/H$_2$O$_2$ system. It significantly affects the oxidative degradation of antibiotics by transforming the protonation states and changing the redox potential at different pH values. As shown in Fig 4A and 4B and S2 Table, the degradation rates of NIF under UV/H$_2$O$_2$ was 97.54% (pH = 10) < 98.69% (pH = 8) < 99.77% (pH = 5) < 99.94% (pH = 4 and 7), the kinetics constant $k_{\text{app}}$ was 0.75217 min$^{-1}$ (pH = 10) < 0.91269 min$^{-1}$ (pH = 8) < 1.21831 min$^{-1}$ (pH = 5) < 1.45569 min$^{-1}$ (pH = 7) < 1.51175 min$^{-1}$ (pH = 4), and the $t_{1/2}$ was 0.4 min (pH = 7) < 0.7 min (pH = 4) < 0.8 min (pH = 5) < 0.9 min (pH = 8) < 1.1 min (pH = 10) when the NIF concentration = 5 mg/L, pH = 4–10, H$_2$O$_2$ dose = 0.52 mmol/L, T = 20 °C and reaction time = 5 min. As shown in Fig 4C, the degradation kinetics of NIF via UV/H$_2$O$_2$ system exhibited a poor linear decrease as the pH increased ($y = -0.1155x + 1.95533$, $R^2 = 0.6884$). The results indicated that acidic solution (pH = 4) was more favorable for degrading NIF than basic solution (pH = 10) under UV/H$_2$O$_2$. The possible reasons were in accord with the redox potential, generation rate of ROS and reaction rate between ROS and NIF. The inhibiting effect of the basic solution was due to the quenching reaction between OH$^-$ and -OH, which is shown in (Eq 7) to (Eq 11) [36]:

\[
\text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}^+ \quad \text{(Eq 7)}
\]

\[
\text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \text{(Eq 8)}
\]
H₂O₂ + HO₂⁻ → H₂O + OH⁻ + O₂  \hspace{1cm} (Eq 9)

·OH + HO₂⁻ → OH⁻ + ·HO₂  \hspace{1cm} (Eq 10)

·OH + HO₂⁻ → H₂O + ·O₂⁻  \hspace{1cm} (Eq 11)

3.3 Effect of SO₄²⁻

It is important to evaluate the effect of co-existing anions (such as SO₄²⁻, CO₃²⁻, Cl⁻ and NO₃⁻) because the co-existing anions in wastewater impact the degradation capacity and the oxidation mechanism of ROS.

As shown in Fig 5A and 5B and S3 Table, the degradation rates of NIF under UV/H₂O₂ with different SO₄²⁻ concentrations were 99.26% (SO₄²⁻ concentration = 50 mg/L) < 99.81% (SO₄²⁻ concentration = 20 mg/L) < 99.93% (SO₄²⁻ concentration = 5 mg/L) < 99.94% (SO₄²⁻ concentration = 0 mg/L), the kinetics constant k'ₜₚ was 1.00154 min⁻¹ (SO₄²⁻ concentration = 50 mg/L) < 1.24540 min⁻¹ (SO₄²⁻ concentration = 20 mg/L) < 1.38175 min⁻¹ (SO₄²⁻ concentration = 5 mg/L) < 1.45569 min⁻¹ (SO₄²⁻ concentration = 0 mg/L), and the t₁/₂ was 0.4 min (SO₄²⁻ concentration = 0 mg/L and 5 mg/L) < 0.6 min (SO₄²⁻ concentration = 20 mg/L) < 0.8 min (SO₄²⁻ concentration = 50 mg/L) when the NIF concentration = 5 mg/L, SO₄²⁻
concentration = 0–50 mg/L, pH = 7, H$_2$O$_2$ dose = 0.52 mmol/L, T = 20 °C and reaction time = 5 min. As shown in Fig 5C, the degradation kinetics of NIF via UV/H$_2$O$_2$ system exhibited a good linear decrease as the SO$_4^{2-}$ concentration increased (y = -0.0088x + 1.437, R$^2$ = 0.9939). The inhibition effect was 5.08% (SO$_4^{2-}$ concentration = 5 mg/L) < 14.45% (SO$_4^{2-}$ concentration = 20 mg/L) < 31.20% (SO$_4^{2-}$ concentration = 50 mg/L), which was in keeping with the trend of the kinetics constants: 1.00154 min$^{-1}$ (SO$_4^{2-}$ concentration = 50 mg/L) < 1.24540 min$^{-1}$ (SO$_4^{2-}$ concentration = 20 mg/L) < 1.38175 min$^{-1}$ (SO$_4^{2-}$ concentration = 5 mg/L). The degradation rate of NIF decreased with increasing SO$_4^{2-}$ concentration, and the quenching mechanism of ROS via SO$_4^{2-}$ is shown in (Eq 12) to (Eq 17) [37]:

$$H^+ + SO_4^{2-} \rightarrow HSO_4^- \quad \text{(Eq 12)}$$

$$HSO_4^- + \cdot OH \rightarrow SO_4^{2-} + H_2O \quad \text{(Eq 13)}$$

$$SO_4^{2-} + H_2O \rightarrow H^+ + SO_4^{2-} + \cdot OH \quad \text{(Eq 14)}$$

$$SO_4^{2-} + H_2O_2 \rightarrow H^+ + SO_4^{2-} + H_2O \quad \text{(Eq 15)}$$

$$SO_4^{2-} + H_2O \rightarrow H^+ + SO_4^{2-} + O_2 \quad \text{(Eq 16)}$$

![Fig 5. Effect of SO$_4^{2-}$ on the removal rate (a), kinetics constant (b) and linear fitting between kinetics constant and concentration of SO$_4^{2-}$ on the degradation of NIF via UV/H$_2$O$_2$. The error bars represent the standard deviation (n = 3).](https://doi.org/10.1371/journal.pone.0258483.g005)
3.4 Effect of CO$_3^{2-}$

As shown in Fig 6A and 6B and S4 Table, the degradation rates of NIF under UV/H$_2$O$_2$ with different CO$_3^{2-}$ concentrations was 99.41% (CO$_3^{2-}$ concentration = 50 mg/L) < 99.71% (CO$_3^{2-}$ concentration = 20 mg/L) < 99.85% (CO$_3^{2-}$ concentration = 5 mg/L) < 99.94% (CO$_3^{2-}$ concentration = 0 mg/L), the kinetics constant k’$_{app}$ was 1.04447 min$^{-1}$ (CO$_3^{2-}$ concentration = 50 mg/L) < 1.16907 min$^{-1}$ (CO$_3^{2-}$ concentration = 20 mg/L) < 1.29550 min$^{-1}$ (CO$_3^{2-}$ concentration = 5 mg/L) < 1.45569 min$^{-1}$ (CO$_3^{2-}$ concentration = 0 mg/L), and the t$_{1/2}$ was 0.4 min (CO$_3^{2-}$ concentration = 0 mg/L) < 0.5 min (CO$_3^{2-}$ concentration = 5 mg/L) < 0.6 min (CO$_3^{2-}$ concentration = 20 mg/L) < 0.7 min (CO$_3^{2-}$ concentration = 50 mg/L) when the NIF concentration = 5 mg/L, CO$_3^{2-}$ concentration = 0–50 mg/L, pH = 7, H$_2$O$_2$ dose = 0.52 mmol/L, T = 20 °C and reaction time = 5 min. As shown in Fig 6C, the degradation kinetics of NIF via the UV/H$_2$O$_2$ system exhibited a good linear decrease as the CO$_3^{2-}$ concentration increased (y = -0.0072x + 1.3771, R$^2$ = 0.8589). The inhibition trend was 11.00% (CO$_3^{2-}$ concentration = 5 mg/L). The degradation rate of NIF decreased with increasing CO$_3^{2-}$ concentration, and the quenching mechanism of the ROS via CO$_3^{2-}$ is shown in (Eq 18) to (Eq 22) [38]:

\[
\text{SO}_4^{2-} + e^- \rightarrow \text{SO}_4^{2-}
\]  

(Eq 17)

\[
\text{CO}_3^{2-} + \text{H}^+ \rightarrow \text{HCO}_3^{-}
\]  

(Eq 18)

\[
\text{HCO}_3^{-} \rightarrow \text{CO}_3^{2-} + \text{H}^+
\]  

(Eq 19)

\[
\text{CO}_3^{2-} + \cdot\text{OH} \rightarrow \text{CO}_3^{-} + \cdot\text{OH}
\]  

(Eq 20)

\[
\text{HCO}_3^{-} + \cdot\text{OH} \rightarrow \text{CO}_3^{-} + \text{H}_2\text{O}
\]  

(Eq 21)

\[
\text{CO}_3^{-} + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{HCO}_3^{-}
\]  

(Eq 22)

3.5 Effect of Cl$^-$

As shown in Fig 7A and 7B and S5 Table, the degradation rates of NIF under UV/H$_2$O$_2$ with different Cl$^-$ concentrations was 99.57% (Cl$^-$ concentration = 50 mg/L) < 99.94% (Cl$^-$ concentration = 0 mg/L) < 99.98% (Cl$^-$ concentration = 20 mg/L) < 100% (Cl$^-$ concentration = 5 mg/L), the kinetics constant k’$_{app}$ was 1.09588 min$^{-1}$ (Cl$^-$ concentration = 50 mg/L) < 1.45569 min$^{-1}$ (Cl$^-$ concentration = 0 mg/L) < 1.72666 min$^{-1}$ (Cl$^-$ concentration = 20 mg/L) < 1.98350 min$^{-1}$ (Cl$^-$ concentration = 5 mg/L), and the t$_{1/2}$ was 0.3 min (Cl$^-$ concentration = 5 mg/L and 20 mg/L) < 0.4 min (Cl$^-$ concentration = 0 mg/L) < 0.9 min (Cl$^-$ concentration = 50 mg/L) when the NIF concentration = 5 mg/L, Cl$^-$ concentration = 0–50 mg/L, pH = 7, H$_2$O$_2$ dosage = 0.52 mmol/L, T = 20 °C and reaction time = 5 min. As shown in Fig 7C, although the degradation kinetics of NIF via UV/H$_2$O$_2$ system decreased with increasing Cl$^-$ concentration, the effect of Cl$^-$ on the degradation of NIF had a dual nature: low Cl$^-$ concentrations promoted the degradation of NIF, while high Cl$^-$ concentrations inhibited the degradation of NIF. The degradation kinetics of NIF via UV/H$_2$O$_2$ system exhibited a poor linear decrease as the Cl$^-$ concentration increased (y = -0.012x + 1.7897, R$^2$ = 0.5013). The trend of inhibition was
-36.25% (Cl⁻ concentration = 5 mg/L) < -18.61% (Cl⁻ concentration = 20 mg/L) < 24.71% (Cl⁻ concentration = 50 mg/L), which was in keeping with the trend of kinetics constant: 1.09588 min⁻¹ (Cl⁻ concentration = 50 mg/L) < 1.72666 min⁻¹ (Cl⁻ concentration = 20 mg/L) < 1.98350 min⁻¹ (Cl⁻ concentration = 5 mg/L). The reaction mechanism between Cl⁻ and ·OH is shown in (Eq 23) to (Eq 27) [39]:

\[
\text{Cl}^- + \text{OH} \rightarrow \text{Cl} \cdot + \text{OH}^- \quad \text{(Eq 23)}
\]

\[
\text{Cl} \cdot + \text{Cl}^- \rightarrow \text{Cl}_2^- \quad \text{(Eq 24)}
\]

\[
\text{Cl}_2^- + \text{H}_2\text{O}_2 \rightarrow \text{H}^+ + 2\text{Cl}^- + \text{H}_2\text{O} \cdot \quad \text{(Eq 25)}
\]

\[
\text{·OH} + \text{Cl}^- \rightarrow \text{HOCl}^- \quad \text{(Eq 26)}
\]

\[
\text{HOCl}^- + \text{H}^+ \rightarrow \text{H}_2\text{O} + \text{Cl}^- \quad \text{(Eq 27)}
\]
3.6 Effect of NO\textsuperscript{3-}

As shown in Fig 8A and 8B and S6 Table, the degradation rates of NIF under UV/H\textsubscript{2}O\textsubscript{2} with different NO\textsuperscript{3-} concentrations was 99.45% (NO\textsuperscript{3-} concentration = 5 mg/L) < 99.94% (NO\textsuperscript{3-} concentration = 20 mg/L) < 99.94% (NO\textsuperscript{3-} concentration = 0 mg/L) < 99.97% (NO\textsuperscript{3-} concentration = 50 mg/L), the kinetics constant \( k'_{\text{app}} \) was 1.03215 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 5 mg/L) < 1.29801 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 20 mg/L) < 1.45569 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 0 mg/L) < 1.55295 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 50 mg/L), and the \( t_{1/2} \) was 0.3 min (NO\textsuperscript{3-} concentration 50 mg/L) < 0.4 min (NO\textsuperscript{3-} concentration = 0 mg/L and 20 mg/L) < 0.6 min (NO\textsuperscript{3-} concentration = 5 mg/L) when the NIF concentration = 5 mg/L, NO\textsuperscript{3-} concentration = 0–50 mg/L, pH = 7, H\textsubscript{2}O\textsubscript{2} dose = 0.52 mmol/L, T = 20˚C and reaction time = 5 min. As shown in Fig 8C, NO\textsuperscript{3-} had the opposite effect on the degradation of NIF via the UV/H\textsubscript{2}O\textsubscript{2} system compared to Cl\textsuperscript{-}. The effect of NO\textsuperscript{3-} on the degradation of NIF had a dual nature: low NO\textsuperscript{3-} concentrations inhibited the degradation of NIF, but high NO\textsuperscript{3-} concentrations promoted the degradation of NIF. The degradation kinetics of NIF via the UV/H\textsubscript{2}O\textsubscript{2} system showed a poor linear decrease with increasing NO\textsuperscript{3-} concentration (\( y = -0.005377x + 1.31881, R^2 = 0.4514 \)). The inhibition effect was -6.68% (NO\textsuperscript{3-} concentration = 50 mg/L) < 10.83% (NO\textsuperscript{3-} concentration = 20 mg/L) < 29.10% (NO\textsuperscript{3-} concentration = 5 mg/L), which was in keeping with the trend of the kinetics constant: 1.03215 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 5 mg/L) < 1.29801 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 20 mg/L) < 1.55295 min\textsuperscript{-1} (NO\textsuperscript{3-} concentration = 50 mg/L). The mechanism of the reaction between
NO$_3^-$ and ·OH is shown in (Eq 28) to (Eq 32) [40]:

$$\text{NO}_3^- + \text{hv} \rightarrow \text{NO}_2^- + \text{O}$$  \hspace{1cm} (Eq 28)

$$\text{NO}_3^- + \text{hv} \rightarrow \text{NO}_2^- + \text{O}^-$$  \hspace{1cm} (Eq 29)

$$2 \text{NO}_2^- + \text{H}_2\text{O} \rightarrow \text{NO}_2^- + \text{NO}^- + 2 \text{H}^+$$  \hspace{1cm} (Eq 30)

$$\text{O} + \text{H}_2\text{O} \rightarrow 2 \cdot \text{OH}$$  \hspace{1cm} (Eq 31)

$$\text{O}^- + \text{H}_2\text{O} \rightarrow \cdot \text{OH} + \text{OH}^-$$  \hspace{1cm} (Eq 32)

In summary, the effect of co-existing anions was as follows: The divalent anions (SO$_4^{2-}$ and CO$_3^{2-}$) caused a good linear decrease with increasing initial pH and concentration of divalent anions ($R^2$ of SO$_4^{2-}$ and CO$_3^{2-}$ was 0.9939 and 0.8589, respectively). The monovalent anions had a complex effect; Cl$^-$ and NO$_3^-$ had opposite effects on NIF degradation: low Cl$^-$ and high NO$_3^-$ promoted degradation, while high Cl$^-$ and low NO$_3^-$ inhibited degradation. The degradation kinetics of NIF via the UV/H$_2$O$_2$ system showed a poor linear decrease with increasing Cl$^-$/NO$_3^-$ concentration ($R^2$ of Cl$^-$ and NO$_3^-$ was 0.5013 and 0.4514, respectively).
3.7 Oxidation mechanism and degradation pathway of NIF via UV/H$_2$O$_2$

In recent advances in UV/H$_2$O$_2$ systems, the degradation of organic pollutants has been due to the generation of ROS, especially -OH and -O$_2$-. The oxidation mechanism of NIF degradation via the UV/H$_2$O$_2$ system was measured by ESR measurements, and the ESR spectra are shown in Fig 9A and 9B. The significant -OH signal (Fig 9A) showed four peaks at 321.8 mT (P$_A$), 323.3 mT (P$_B$), 324.8 mT (P$_C$) and 326.3 mT (P$_D$). The interspaces of P$_A$-P$_B$, P$_B$-P$_C$ and P$_C$-P$_D$ were constant of 1.5 mT, and the intensity ratio of P$_A$, P$_B$, P$_C$ and P$_D$ was 1:2:2:1 [41]. The significant -O$_2$- signal (Fig 9B) showed four peaks at 322.1 mT (P’$_A$), 323.2 mT (P’$_B$), 324.4 mT (P’$_C$) and 325.8 mT (P’$_D$). The interspaces of P’$_A$-P’$_B$, P’$_B$-P’$_C$ and P’$_C$-P’$_D$ were constant within the range of 1.0 mT from 1.5 mT, and the intensity ratio of P’$_A$, P’$_B$, P’$_C$ and P’$_D$ was 1:1:1:1 [42]. However, the intensity of the -OH signal was stronger than that of the -O$_2$- signal, which means that -OH was the primary key ROS and -O$_2$- was the secondary key ROS. The oxidation mechanism of NIF degradation via the UV/H$_2$O$_2$ system is shown in (Eq 33) to (Eq 41) [43].

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \quad \text{(Eq 33)}
\]

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \cdot\text{HO}_2 + \text{H}_2\text{O} \quad \text{(Eq 34)}
\]

\[
\cdot\text{HO}_2 \rightarrow \cdot\text{O}_2^- + \text{H}^+ \quad \text{(Eq 35)}
\]

\[
2 \cdot \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 \quad \text{(Eq 36)}
\]

\[
\cdot\text{HO}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \text{(Eq 37)}
\]

\[
\text{O}_2 + e^- \rightarrow \cdot\text{O}_2^- \quad \text{(Eq 38)}
\]

\[
2 \cdot \cdot\text{O}_2^- \rightarrow \cdot\text{O}_2^+ + \cdot\text{O}_2 + 2e^- \quad \text{(Eq 39)}
\]

\[
2 \cdot \text{OH} \rightarrow \text{H}_2\text{O}_2 \quad \text{(Eq 40)}
\]

\[
\text{NIF} + \text{ROS} \rightarrow \text{Intermediate Products} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \text{(Eq 41)}
\]

The identification of intermediate NIF products via UV/H$_2$O$_2$ was performed using an Agilent 1260 series liquid chromatogram mass spectrometry (LC-Q-TOF-MS) system. The reaction conditions were: NIF concentration = 5 mg/L, pH = 7, H$_2$O$_2$ dose = 0.52 mmol/L, $T = 20^\circ$C and reaction time = 30 min. Preliminary analyses were conducted to evaluate the intermediate products of NIF produced by the UV/H$_2$O$_2$ method, and four kinds of NIF degradation intermediate products were observed in the mass spectrum based on the mass-to-charge ($m/z$) ratio. Four intermediate products were present: P345 ($m/z = 345$), P329 ($m/z = 329$), P315 ($m/z = 315$) and P274 ($m/z = 274$). The structures of P345, P329, P315 and P274 are shown in S3A–S3D Fig, respectively.

As shown in Fig 10A and 10B, the peak areas of all the observed products first increased and then decreased within 30 min. The peak areas of P345 and P274 at different reaction times...
are shown in Fig 10A, and the results indicated that the maximum peak area of P345 appeared at 5 min, the maximum peak area of P274 appeared at 20 min, and the peak intensity of P345 was stronger than that of P274. The first degradation pathway of NIF via the UV/H$_2$O$_2$ method was proposed as follows: protonated NIF ($C_{17}H_{19}N_2O_6^+$, $m/z = 347$) first lost H$_2$ to generate P345 ($C_{17}H_{17}N_2O_5^+$, $m/z = 345$) via dehydrogenation reaction, and then P345 lost C$_3$H$_5$NO to generate P274 ($C_{14}H_{12}NO_5^+$, $m/z = 274$), as shown in Fig 11A [45,46]. The peak areas of P329 and P315 at different reaction times are shown in Fig 10B, and the results indicated that the maximum peak area of P329 appeared at 0.5 min, the maximum peak area of P315 appeared at 7 min, and the peak intensity of P329 was stronger than that of P315. The second degradation pathway of NIF via the UV/H$_2$O$_2$ method was proposed as follows: protonated NIF ($C_{17}H_{19}N_2O_6^+$, $m/z = 347$) first lost H$_2$O to generate P329 ($C_{17}H_{17}N_2O_5^+$, $m/z = 329$) via dehydration reaction, and then P329 lost CH$_2$ to generate P315 ($C_{16}H_{14}N_2O_3^+$, $m/z = 274$), as shown in Fig 11B [45,46].

P315 was degraded with the attack of ROS. The intermediate products of P271 ($m/z = 271$), P241 ($m/z = 241$) and P181 ($m/z = 181$) are shown in S7 Table, and its possible degradation pathway is shown in S4A Fig. P315 first lost CO$_2$ to generate P271 ($C_{15}H_{16}N_2O_3^+$, $m/z = 271$), P271 lost CH$_2$O to generate P241 ($C_{14}H_{14}N_2O_3^+$, $m/z = 241$), and finally, P241 lost C$_2$H$_4$O$_2$ to generate P181 ($C_{12}H_9N_2^+$, $m/z = 181$) [46]. P329 was present as an isomeride that was named P329-2 ($m/z = 329$). The intermediate products, P329-2, P301 ($m/z = 301$), P200 ($m/z = 200$)

![Fig 9. ESR measurements of -OH (a) and -O$_2$ (b).](https://doi.org/10.1371/journal.pone.0258483.g009)

![Fig 10. Chromatography of the intermediate products of NIF via UV/H$_2$O$_2$.](https://doi.org/10.1371/journal.pone.0258483.g010)
and P158 ($m/z = 158$), are shown in S7 Table, and their possible degradation pathways are shown in S4B Fig. P329-2 first lost CO to generate P301 (C$_{16}$H$_{17}$N$_2$O$_5^+$, $m/z = 301$), P301 lost C$_4$H$_7$NO to generate P200 (C$_{12}$H$_{16}$NO$_2^+$, $m/z = 200$), and finally, P200 lost C$_2$H$_2$O to generate P158 (C$_{10}$H$_8$NO$^+$, $m/z = 158$) [46].
3.8 Environmental significance

In this paper, fast, effective and low-cost UV/H$_2$O$_2$ was used in the degradation of the antibiotic NIF, and this work contributed to the sustainable development of new methods for applications in hospital and aquaculture wastewater treatment for sustainable development, cleaner production and an environmentally friendly society, as shown in Table 1. The maximum degradation rate (99.94%), degradation kinetics constant (1.45569 min$^{-1}$) and minimum degradation time (5 min) indicated that the UV/H$_2$O$_2$ system is a promising AOP treatment for organic and medical wastewater. In addition, the cost of the UV/H$_2$O$_2$ system was approximately $0.447 for 1 m^3 wastewater (S8 Table), which was lower than that of related systems (ranging from $0.53 to $0.85 for 1 m^3 wastewater) [47]. During the catalytic oxidation process, all the molecular mechanisms of ROS generation under the UV/H$_2$O$_2$ system, the effects of co-existing anions in an actual water environment, the analysis of intermediate products and the degradation pathways were the basis of the efficient AOP design. Furthermore, intermediate products and the degradation pathways of pollutants should also be studied through theoretical simulation technologies such as density functional theory (DFT) and molecular dynamics (MD) [48].

4 Conclusions

The degradation rate and degradation kinetics of NIF first increased and then remained constant as the H$_2$O$_2$ dose increased, and the quasi-percolation threshold was an H$_2$O$_2$ dose of 0.378 mmol/L. The effect of the initial pH, divalent anions (SO$_4^{2-}$ and CO$_3^{2-}$) and monovalent anions (Cl$^-$ and NO$_3^-$) decreased linearly with increasing initial pH and co-existing anions (the $R^2$ values of the initial pH, SO$_4^{2-}$, CO$_3^{2-}$ Cl$^-$ and NO$_3^-$ were 0.6884, 0.9939, 0.8589, 0.5013 and 0.4514, respectively). ·OH was the primary key ROS, and ·O$_2^-$ was the secondary key ROS. There were 11 intermediate products (P345, P329, P329–2, P315, P301, P274, P271, P241, P200, P181 and P158) and 2 degradation pathways (dehydrogenation reaction of NIF → P345 → P274 and dehydration reaction of NIF → P329 → P315).

Supporting information

S1 Fig. UV-Vis absorption spectra of NIF.
(DOCX)

S2 Fig. Chromatography and standard curve of NIF.
(DOCX)
S3 Fig. Mass spectrum of intermediate products of NIF via UV/H$_2$O$_2$.
(DOCX)

S4 Fig. Possible degradation pathways of P315 and P329-2 in the UV/H$_2$O$_2$ system.
(DOCX)

S1 Table. Effect of H$_2$O$_2$ dose on the degradation of NIF via UV/H$_2$O$_2$. Reaction conditions: NIF concentration = 5 mg/L, H$_2$O$_2$ dose = 0–1.04 mmol/L, pH = 7, T = 20 °C and reaction time = 5 min.
(DOCX)

S2 Table. Effect of initial pH on the degradation of NIF via UV/H$_2$O$_2$.
(DOCX)

S3 Table. Effect of SO$_4^{2-}$ on the degradation of NIF via UV/H$_2$O$_2$.
(DOCX)

S4 Table. Effect of CO$_3^{2-}$ on the degradation of NIF via UV/H$_2$O$_2$.
(DOCX)

S5 Table. Effect of Cl$^-$ on the degradation of NIF via UV/H$_2$O$_2$.
(DOCX)

S6 Table. Effect of NO$_3^-$ on the degradation of NIF via UV/H$_2$O$_2$.
(DOCX)

S7 Table. Molecular weight, molecular formula, structural formula and m/z of intermediate products.
(DOCX)

S8 Table. Cost analysis of UV/H$_2$O$_2$ treatment.
(DOCX)

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