Removal of norfloxacin using coupled synthesized nanoscale zero-valent iron (nZVI) with H₂O₂ system: Optimization of operating conditions and degradation pathway

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ABSTRACT

In this study, nanoscale zero-valent iron (nZVI) was synthesized in the laboratory by the borohydride reduction method. nZVI was characterized by transmission electron microscopy (TEM), scan electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). In addition, the degradation performance of norfloxacin (NOR) in nZVI/H₂O₂ Fenton-like system was investigated in detail under various experimental conditions. It was found that the removal of NOR depended on its initial concentration, initial pH, temperature, H₂O₂ concentration and nZVI dose. At the ambient temperature, the degradation rate of NOR by nZVI/H₂O₂ Fenton-like reaction under the acidic medium (pH = 3–4) was more than 95% within 40 min of the reaction time, and the mineralization degree was around 50% in terms of total organic carbon (TOC) measurement. Optimal temperature for NOR removal was 308 K, and higher temperature would cause useless decomposition of H₂O₂ and consequently reduction of NOR degradation. The degradation rate and total removal efficiency of NOR were favored by increasing the nZVI and H₂O₂ dosages. The optimal conditions for NOR degradation were: initial pH = 4.0, H₂O₂ concentration = 20 mmol/L, nZVI dose = 100 mg/L, temperature = 308 K. The rate constants (*K*_{obs}) of NOR degradation could be fitted well with a pseudo-second-order kinetic equation. Several degradation intermediates of NOR were detected and confirmed, including C₁₅H₂₀FN₃O (*m/z* 278), C₉H₁₁FN₂ (*m/z* 167), C₇H₇FN₂ (*m/z* 139), and C₇H₈FN (*m/z* 126), respectively. Based on the identified intermediates and the Gaussian quantum statistics molecular bonding energy calculation, the possible pathway for NOR degradation under nZVI/H₂O₂ Fenton-like reaction was discussed.

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1. Introduction

Antibiotics are widely used in both disease therapy and epidemic prevention of human being and animals. However, more than 75% of them were released into the environment because of low metabolic rate and poor biodegradability. They would pose a great threat to human health since the pathogens become more and more resistant to the drugs due to the common existence of antibiotic residues in the aquatic environment [1]. Therefore, it is of particular importance to develop efficient technologies for removal of antibiotics in water bodies.

Now, traditional Fenton process has been widely used in the treatment of antibiotics wastewater and other industrial wastewaters. The main drawback of this technology is related to the high amount of ferrous iron salts needed (usually FeSO₄), which must be separated from the treated effluent (generally by precipitation), thus leading to considerable loads of exhausted iron sludge that required further management (usually disposed as hazardous solid waste) [2].

Recently, heterogeneous Fenton oxidation was developed to overcome the disadvantage of sludge production in traditional Fenton process [3–5]. This alternative Fenton system involved the oxidation of zero-valent iron (ZVI) at acidic conditions and in-situ generation of ferrous iron, which promoted the production of hydroxyl radicals. Nanoparticles have shown excellent performance in removal or toxicity mitigation of all kinds of hazardous pollutants. They are characterized by high removal capacity, fast

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kinetics and high reactivity for contaminant removal due to their extremely small particle size and high surface-area-to-volume ratio [6]. Among the most widely used nanoparticles, increasing attention has been paid to magnetic nZVI for engineering applications in treatment of polluted water or remediation of ground water [6]. A number of studies have shown that nZVI was an effective water treatment material due to strong reducing property. It was proven to be much more reactive than conventional iron powders. Zhang et al. [7] investigated the application of nanosized (1–100 nm) ZVI particles for the removal of organic contaminants. It exhibited high reactivity due to a large specific surface area with average of 33.5 m²/g for the nanosized particles (the specific surface area of commonly used microscaled particles was 0.9 m²/g), so the reaction rate was also much faster (by up to 100 times) than traditional iron powders [7]. Previous researches have reported that some refractory compounds, such as trichloroethylene, polycyclic aromatic hydrocarbons (PAHs) and pesticides could be effectively degraded with highly reactive nZVI [8–16]. Chen et al. reported that metronidazole was almost completely removed within 90 min by using nZVI particles treatment [17]. Furthermore, nZVI was used as a heterogeneous Fenton catalyst for degradation of organic contaminants. The removal efficiency of organic contaminants was influenced by its initial concentration, solution pH, H₂O₂ and nZVI doses. Wang and his co-workers investigated the removal of chlorpheniramine in nZVI catalyzed Fenton system. Chlorpheniramine (≤ 15 g/L) was completely oxidized after 60 min when the initial pH was 3.0, H₂O₂ concentration was 0.1 mM, and the dosage of nZVI was 22.4 mg/L [18]. The pentachlorophenol (PCP) degradation process in the nZVI/H₂O₂ system was also examined, and the degradation process was completed within 1 h. Moreover, magnetite (Fe₃O₄) was found to be the main corrosion product of nZVI in the nZVI/H₂O₂ system, it also performed well as an adsorbent and/or catalyst [19]. Both used nZVI and Fe₃O₄ could be effectively recycled with magnetic separation.

In this study, nZVI was prepared in the laboratory by liquid phase reducing method. And the synthesized nZVI was characterized by using transmission electron microscopy (TEM), scan electronic microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX). Additionally, the degradation performance of Norfloxacin (NOR) antibiotics with nZVI/H₂O₂ Fenton-like reaction was investigated under various experimental conditions. The intermediate products of NOR were determined with high performance liquid chromatography (HPLC) and high performance liquid chromatography-tandem quadrupole time of flight mass spectrometry (HPLC/Q-TOF/MS). Finally, the pathways of NOR degradation were discussed based on chemical analysis and Gaussian quantum statistics calculation.

2. Materials and methods

2.1. Preparation and characterization of nZVI

nZVI particles were prepared freshly each day by adding 0.1 mol/L KBH₄ NaBH₄ aqueous solution dropwise to 0.025 mol/L FeCl₃ aqueous solution at ambient temperature as described by previous studies [20,21]. The preparation was performed under vigorous magnetic stirring, rapid formation of fine black precipitates was observed as the ferric iron reduced to nZVI. Then, the black iron particles were separated with magnetic field and washed using milli-Q water several times. The synthesized nZVI was stored in N₂ environment to avoid oxidation for later use. Particle size, size distribution and surface composition were characterized by transmission electron microscopy (TEM, S-570, Japan), X-ray diffraction (XRD, PANalytical, Netherlands), high-resolution X-ray photoelectron spectroscopy (HR-XPS, Rigaku, Japan) according to

procedure described by Sun et al. [22]. Brunauer Emmett Teller (BET) surface area was also measured with ASAP 2000 (Micromeritics, USA).

2.2. NOR removal

The catalytic oxidation of NOR was carried out in a 500 mL glass batch reactor under vigorous stirring. The pH of this solution was adjusted by adding NaOH (1 mol/L) or H₂SO₄ (1 mol/L). An appropriate amount of H₂O₂ was added into the stirred NOR solution. Then, nZVI was dispersed in deionized water (5 mL) under low-intensity ultrasound for 20 min before the mixture was added to the reaction solution. The samples were taken at different time periods, and the oxidation reaction was stopped by raising the solution pH to above 9 with NaOH solution. Finally, the concentration of NOR was detected with high performance liquid chromatography (HPLC) after the nZVI particles were separated with magnetic field.

2.3. Analytical methods

2.3.1. Analysis of norfloxacin and degradation intermediates

NOR concentration was measured by HPLC system equipped with a Waters C-18 column. A two solvent gradient elution consisting of 0.025% phosphoric acid and acetonitrile (87:13, v/v%) at a flow rate of 1.0 mL/min was used. The NOR was measured at 278 nm. All standard curves were linear with regression coefficients above 0.999 in all cases. In addition, the degradation products were initially separated using HPLC. Afterwards, ion spectra of all byproducts were collected by running selected high performance liquid chromatography-tandem quadrupole time of flight mass spectrometry (HPLC/Q-TOF/MS, micromass Q-TOF micro Waters, USA) experiments. In order to protect chromatographic column in HPLC/Q-TOF/MS, phosphoric acid could not be used as mobile phase. So formic acid with pH of 3 was used. Due to prevent the messy mass spectrum and keep the sensitivity of mass spectrometer, no reagents was added in mobile phase.

2.3.2. Other analytical methods

Scan electronic microscopy (SEM, S-3000N, Japan) analysis was carried out to observe the surface of the experimental samples. Total organic carbon (TOC) analyzer (Teledyne Tekmar, USA) was used for TOC determination. pH was measured by pH meter (pHS-3C, Shanghai, China). Ferric iron was determined with inductively coupled plasma atomic emission spectrometry (ICP-OES, Leeman, USA) after HNO₃ and microwave digestion [23].

3. Results and discussion

3.1. Characterization of synthesized nZVI

As Fig. S1 shown, the morphology of nZVI was observed by TEM. It presented a typical chain structure. The single particle was spherical and uniform (Fig. S1a). Moreover, analysis of the freeze-dried particles by TEM revealed that the primary particle size of nZVI ranged from 2 to 50 nm with an average size of approximately 20 nm. The presence of a strong diffraction pattern during TEM analysis confirmed that the particles were crystalline. The surface area of the particle was 39.2 m²/g (see in Table 1). After particles were nanocrystallized, the surface of particle tended to accumulate a great deal of charges and produce high surface energy, which making the particles aggregate to keep them stable. The results of the particle sizing and surface area measurements were similar to the results found by other researchers for nZVI. Due to large specific surface area, it can be inferred that nZVI

Table 1
Basic properties of synthesized nZVI.

Items	Physical properties				Surface chemical composition (wt%)		
	Pore volume (cm ³ g ⁻¹)	Pore size (nm)	Particle size (nm)	Specific surface area (m ² /g ⁻¹)	C	O	Fe
Value	0.19	9.84	20–40	39.16	5.1	1.0	93.9

had more active sites on the surface, which might show a high reactivity in the solid-liquid interface. The XRD analysis indicated that no other minerals, such as magnetite or maghemite, were identified in the freshly prepared samples (Table 1). The element of oxygen was likely to be caused by slow oxidation in the surface of nZVI due to high activity. Before XRD analysis, carbon was coated to the sample. Therefore, a small amount of carbon was detected. In order to avoid oxidation, nZVI must be used immediately. Therefore, nZVI were prepared freshly each day.

3.2. NOR degradation in nZVI and nZVI/H₂O₂ system

The NOR degradation performances in nZVI and nZVI/H₂O₂ system were compared in this study. The colors of the solution had big difference after reaction under the same initial conditions (pH = 3). The color of the solution become yellow and the upper had obvious bubbles using nZVI alone in the experiment (Fig. S2b). However, it remained the same color throughout the reaction in the nZVI/H₂O₂ system (Fig. S2a). This observation indicated that the reaction mechanisms of nano iron particles might differ. Nano-iron particles were not completely oxidized in nZVI/H₂O₂ system, while a large amount of iron oxide was generated in nZVI system.

In order to understand the changes in morphology and surface elements, the solids were detected by SEM and EDX after centrifugation and sufficient washing. As displayed in Fig. 1, the morphologies of nano iron were significantly different compared to that of

nano-iron. nZVI remained the original typical features in presence of hydrogen peroxide. Otherwise, no obvious porous structure was observed in nZVI system, which meant that iron had lost its original morphology in absent of hydrogen peroxide.

The element composition of centrifugal materials after degradation was shown in Fig. 2. The amounts of C and O in nano iron were 5.11% and 1.02%, respectively. After NOR degradation in nZVI/H₂O₂, the amounts of C and O in centrifugal material were slight increased by 6.28% and 5.77%. And the amounts of C and O increased markedly, up to 39.03% and 12.40% after NOR degradation in nZVI system alone. It showed that the oxidation took place in nZVI solution.

The changes of the surface elements of iron could be attributed to their chemical reaction or the adsorption of other matters. The variations of surface elements were different after reaction. It was indirect evidence that there were different reaction pathways of iron in different systems. As shown in Fig. 3, no new organic compounds was detected with HPLC after 24 h, indicating that the NOR was resistant to nZVI treatment alone. However, degradation products were detected in nZVI/H₂O₂ system. In combination related literatures with results of present experiments, the reaction process in nZVI/H₂O₂ system could be deduced as the following reactions [24–26]:

Firstly, nZVI was oxidized by dissolved oxygen (DO) under acid condition via a two-electron transfer from the particle surface to oxygen to generate ferrous ions and hydrogen peroxide. Moreover, hydrogen peroxide reacted with nZVI and ferrous ions were produced. Finally, Fenton reaction was initiated to produce the ferric ions and hydroxyl radicals.

According to the results above, oxidation happened between nZVI and dissolved oxygen in nZVI system alone. There was no free

Fig. 1. SEM images of (a) nano-iron (100 X); (b) nano-iron (20 kX); (c) iron in the nZVI/H₂O₂ system (5 kX); and (d) iron in the nZVI system (5 kX).

Fig. 2. The surface element composition of centrifugal materials after treatment.

radical generated, accordingly organics were degraded. The process [27] could be described as follows:

The production of hydrogen caused air bubbles in this process, as Fig. 1(b) shown. The whole process was a self oxidation reaction of nZVI, degradation of organic matter was not involved. According

to the EDX analysis, the increased C element content in nZVI system alone was higher than that in nZVI/H₂O₂ system after reaction. It was likely to be related to the high adsorption ability of iron oxides such as FeOOH produced on organics in the reaction [28].

The hydroxyl radicals participated into the oxidative degradation of NOR in nZVI/H₂O₂ system. During this process, the effects of adsorption nZVI on NOR was very limited, since it was easy to desorb through physical interactions. In addition, it can be seen from HPLC analysis that there was no new matter was detected in nZVI system, revealing that NOR was not oxidized. Hence, H₂O₂ was an indispensable reagent in degradation of NOR during the Fenton-like reaction.

3.3. Effect of reaction conditions on removal efficiency of NOR

3.3.1. pH

As depicted in Fig. 4, the removal efficiency of NOR was strongly related to solution pH. Lower solution pH was favored to degradation of NOR. It was evident that degradation rate of NOR was much faster at pH of 3–4, more than 90% of NOR was removed within 10 min. The NOR degradation efficiency was significantly reduced to 15% in 40 min when the solution pH was raised to around 6. Firstly, the surface of nZVI was easy to protonate and then formed complexes with NOR under acidic condition [29]. It increased the contact rate between reaction substrates and nZVI, which accelerated the oxidative reaction. Iron ion in alkaline solution reacted with hydroxyl quickly and deposited on the surface of nZVI, consequently preventing the degradation of NOR. Secondly, oxidation potential of hydroxyl radicals was strongly influenced by solution pH. A high pH value always led to a low oxidation potential of $\cdot\text{HO}$, thus its ability to attack NOR molecules was weakened [30]. Then $\cdot\text{HO}$ was easy to react with OH^- and Fe^{3+} generated in the process as shown in Eqs. (3)–(11). Finally, H₂O₂ was extremely unstable and quickly decomposed into water and oxygen in alkaline condition.

The degradation efficiency of NOR was more than 90% at pH of 3 or 4 after 40 min of reaction time. But iron dissolution was high at low pH, which would be discussed later. So the optimum pH value was 4.

Fig. 3. HPLC spectra of the NOR in nZVI and nZVI/H₂O₂ system after 24 h reaction ([NOR]₀ = 100 mg/L; [nZVI]₀ = 100 mg/L; [H₂O₂]₀ = 10 mmol/L; pH = 3; T = 25 °C).

Fig. 4. The degradation of NOR in nZVI/H₂O₂ system at different initial pHs ([NOR]₀ = 100 mg/L; [nZVI]₀ = 100 mg/L; [H₂O₂]₀ = 10 mmol/L; T = 25 °C).

3.3.2. H₂O₂ dosage

As Fig. 5 displayed, the degradation rate of NOR increased with the increasing dosage of H₂O₂. The degradation efficiency of NOR was about 20% after 40 min, when the concentration of H₂O₂ was 5 mmol/L. And the degradation efficiency could be increased to 90% after 10 min by raising the H₂O₂ concentration to 20 mmol/L. However, no obvious change of the degradation rate was observed with the continual increasing in H₂O₂ dosage.

At the higher concentration, H₂O₂ could contact more efficiently with the catalyst (nZVI) and consequently produced more ·HO, improving the degradation rate of substrate (NOR). Nevertheless, excessive amount of H₂O₂ (80 mmol/L) could induce useless consumption of hydroxyl radicals (·HO), which caused conversion from ·HO to H₂O as Eqs. (3)–(11) shown. The optimal dose of H₂O₂ was 20 mmol/L, which didn't only exhibit higher removal rate of NOR but also a slower reaction rate. Previous studies have reported that the consumption of H₂O₂ was decreased sharply as the dosage of H₂O₂ was increased to above 20 mmol/L in nZVI/H₂O₂ system [31]. It just required nearly half H₂O₂ concentration compared to that of light-assisted Fenton. Thus, nZVI had a very highly catalytic activity on H₂O₂ in heterogeneous Fenton, which performed well in the removal of NOR.

Fig. 5. Influence of H₂O₂ dose on NOR degradation ([NOR]₀ = 100 mg/L; [nZVI]₀ = 100 mg/L; pH = 3; T = 25 °C).

3.3.3. Dosage of nZVI

The increasing concentration of nZVI can improve the NOR degradation as Fig. 6 depicted. Only about 40% of NOR was removed, when the dosage of nZVI was 10 mg/L. The removal efficiency of NOR had reached more than 90% by raising the dosage of catalyst to 100 mg/L. The increased catalyst dose enhanced hydrogen peroxide decomposition and production of hydroxyl radicals, consequently improved the degradation efficiency of organics. However, excessive dosage of nZVI caused particles aggregation, leading to reduction of NOR degradation rate. Moreover, overdosed nZVI could participate in reaction as a reductant which consume ·HO to be used for NOR degradation. Thus, the optimal dosing of nZVI was 100 mg/L in the study.

3.3.4. Temperature and reaction rate

A chemical reaction is able to proceed when activation energy (E_a) reaches a fixed value. Previous researches have shown that a high reaction temperature can cause a high E_a , which is benefit to chemical reaction. The relationship among E_a , reaction rate (k) and temperature (T) can be quantified by Arrhenius equation [32].

As depicted in Fig. 7, the reaction conformed to the Arrhenius equation at the temperature from 288 K to 308 K. The degradation rate of NOR was improved with the elevated temperature. The

Fig. 6. Removal rate of NOR in varying nZVI doses ([NOR]₀ = 100 mg/L; [H₂O₂]₀ = 10 mmol/L; pH = 3; T = 25 °C).

Fig. 7. Effects of NOR removal with different initial temperatures ([NOR]₀ = 100 mg/L; [nZVI]₀ = 100 mg/L; [H₂O₂]₀ = 10 mmol/L; pH = 3).

degradation was completed after 20 min, when the reaction temperature was increased to 308 K. However, it subsequently dropped significantly with further increase in temperature. Meanwhile, the solution system turned tawny, and the degradation was unable to proceed. It might be caused by the $\cdot\text{HO}$ scavenging effect of nZVI. That is to say, hydrogen peroxide in nZVI/ H_2O_2 system reacted rapidly with nZVI and decomposed into O_2 rather than $\cdot\text{HO}$ with the increasing of temperature.

The NOR degradation in nZVI/ H_2O_2 system showed a typical characteristic of catalytic reaction. A heterogeneous Fenton reaction was accompanied by the phase interface diffusion, adsorption followed by oxidation. As mentioned above, the contribution of adsorption to NOR removal was very limited based on TOC analysis in nZVI system alone. It could be inferred that adsorption and degradation occurred simultaneously on the interface of nanoparticles. The small molecules produced by degradation could diffuse to lower concentration region and desorb from particle surfaces. Then, they continued to be degraded and completely mineralized finally.

It showed that the degradation of NOR could be generally divided into two stages: initial slow stage followed by fast stage in nZVI/ H_2O_2 system at varying reaction conditions. The NOR removal rate was very low within 0–10 min, and it increased sharply later in 10–20 min under different conditions. The observation demonstrated that heterogeneous reaction was dominant on the surface of nZVI in the early stage. And a quickly increasing rate was a combined result of $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ homogeneous Fenton reaction and nZVI/ H_2O_2 heterogeneous reaction. At the same time, this stage also followed the chain reactions of free radicals. The activation energy was very small between free radicals and saturated molecules, which meant chemical reaction was easy to take place. The chemical form of substrate was changed during this process, and new free radicals could participate in chain reactions. It should be noted that there were significant differences between non-chain reactions and chain reactions. Under condition of the high

concentration of reactants, reaction rate reached the maximum in the initial stage and then decreased with time in non-chain reaction. However, it was not observed in chain reactions, since the production of free radical was difficult in the initial stage. There was induction period in the chain reactions, and then the reaction rate accelerated significantly after that [33–35].

3.3.5. Kinetic fitting

In order to understand the degradation process of NOR, the several kinetic models were calculated and given in Table S1 depicted. The rate constants (k) increased with the decreasing pH values according to the result of kinetic models. And the pseudo second-order kinetic model perfectly fitted the degradation of NOR at different pHs. The reaction rate constants (k) was $9.1 \times 10^{-2} \text{ (min}^{-1}\text{)}$, $3.38 \times 10^{-3} \text{ (min}^{-1}\text{)}$, $2.04 \times 10^{-3} \text{ (min}^{-1}\text{)}$ and $7.4 \times 10^{-5} \text{ (min}^{-1}\text{)}$, respectively. The result revealed that the removal efficiency of NOR was reduced with the increasing pH value, while its degradation rate accelerated with increasing dosages of H_2O_2 and nZVI. Obviously, the rate constants increased initially and then decreased by elevating temperature, which was consistent with the removal efficiency of NOR.

3.4. Degradation pathway of NOR

3.4.1. Products analysis based on HPLC

Fig. 8 displayed the results of HPLC at pH 4 in different time. It was noticeable that the standard molecular peak of NOR was appeared at about 12 min. There were three main products generated due to oxidative degradation with the peak time of 2.4 min, 3.9 min and 4.3 min, respectively. The chromatographic peak of NOR was extremely weak after nZVI/ H_2O_2 treatment, which demonstrated that NOR was degraded completely after 40 min. In addition, a new chromatographic peak appeared in 8 min, and it disappeared after further reaction.

Fig. 8. The HPLC spectra in nZVI/ H_2O_2 at different time ($[\text{NOR}]_0 = 100 \text{ mg/L}$; $[\text{nZVI}]_0 = 100 \text{ mg/L}$; $[\text{H}_2\text{O}_2]_0 = 10 \text{ mmol/L}$; pH = 3; T = 25 °C).

The HPLC chromatograms after 15 min of oxidative reaction under different initial pHs and dosages of H_2O_2 were shown in Figs. 9 and 10. It was obvious that the similar patterns were observed in nZVI/ H_2O_2 systems. This result indicated that the mechanisms were the same under these conditions. The vast majority of initial degradation intermediates were product 2. After NOR was degraded completely, the amount of product 1 increased, and the content of product 2 decreased as Figs. 9 and 10 displayed.

3.4.2. The degradation pathway

In order to clarify the products from NOR degradation, the mass spectrums of products and NOR standard sample in different time were analyzed by HPLC/Q-TOF/MS. Fig. 11 displayed the total ion chromatography before and after NOR degradation, it was found that there were three main kinds of degradation products. The spectrum peaks of HPLC approximately in 2.4 min, 3.9 min, 4.3 min were accordant to the results of LC/MS with peak time at 2.1 min, 3.1 min and 4.1 min. The spectrum peak intensities of products decreased significantly compared to the standard substance (100 mg/L), as Fig. 12 shown. It was observed that a part of the degradation products had been mineralized.

According to the mass-to-charge ratio of molecular ion peak, a relative molecular mass can be gained. Mass spectrometry can give the relative molecular mass of unknown material. The molecular weight of degradation products can be obtained by the result of HPLC/Q-TOF/MS. The mass-to-charge ratio (m/z) of the main NOR degradation products were 278, 167, 139, 126 respectively. In order to verify the molecular structures of degradation products, it was necessary to analyze the possible degradation pathways according to the knowledge of substance structure and bond energy. The information including interatomic cohesive energy, molecular structure and charge distribution could be obtained through quantum chemical calculation, which was based on theoretical calculation and analysis of the extranuclear electrons movement of atoms or molecules. Therefore, the NOR stable structure

Fig. 11. The spectrogram of the NOR degradation product TOF-MS ES⁺ (120:400).

was obtained according to energy optimization calculation by quantum chemistry method. The structure of NOR was displayed in Fig. 12. The values of natural bond orbitals (NBO) by quantum chemistry calculation were indicated the relative size of bond energy, which represented the stability of chemical bond. The NBO values of all chemical bonds of NOR were listed in Table S2. The bond energies of C_9-O_{21} , $C_{11}-C_{12}$, $N_{10}-C_{12}$, $N_{27}-C_{28}$ were low. Therefore, the possible chemical structures of the degradation products were predicted as shown in Table 2. It could be inferred that the degradation of NOR primarily occurred in the major structures of piperazine and nalidixic rings suffered the attack of hydroxyl free radical.

One of the chemical bond energy of double bond was relatively low according to the result of quantitative calculation. Thus, it was easy to be attacked by free radical and then break down [36]. The value of chemical bond energy was correlated with the binding energy between different atoms. Consequently, due to these

Fig. 9. The HPLC result of different pH at 15 min ($[NOR]_0 = 100$ mg/L; $[nZVI]_0 = 100$ mg/L; $[H_2O_2]_0 = 10$ mmol/L; $T = 25$ °C).

Fig. 10. The HPLC with different H_2O_2 doses at 15 min ($[NOR]_0 = 100$ mg/L; $[nZVI]_0 = 100$ mg/L; pH = 3; $T = 25$ °C).

Fig. 12. (a) The reaction in nalidixic ring and the cleavage of the chemical bonds in piperazine ring; and (b) the degradation pathway of NOR in nZVI/H₂O₂ Fenton-like reaction.

Table 2

The possible degradation products of NOR.

Compound	<i>m/z</i>	MW	Molecular structure	Molecular structure
NOR	320.14	319.33	C ₁₆ H ₁₈ FN ₃ O ₃
Compound 1	126.07	125.14	C ₇ H ₈ FN
Compound 2	167.09	166.20	C ₉ H ₁₁ FN ₂
Compound 3	278.16	277.12	C ₁₅ H ₂₀ FN ₃ O
Other compounds	Organic acids			

characteristics, the possibility of the double bond and bond rupture between different atoms should be considered firstly.

Subjected to the effects of electron-withdrawing on benzene ring, the carboxyl of nalidixic ring was more prone to decarboxylated. Therefore, the decarboxylation reaction occurred firstly and generated the product 1. Secondly, the hydroxyl radicals continued to attack the double bonds of nalidixic ring, then leading to electron transferring. It then resulted in increasing density of electron cloud between C₁₁–C₁₂ and formation of repulsive interaction between C₉–O₂₁. Simultaneously, the electron cloud density of C₃ was increased due to electron transfer, making it become electronegative. Then, the positively charged N₁₀ might combine with the negatively charged C₃, producing new bond C–N. As a result, product 3 was generated. Finally, because of the influence of electron-withdrawing of adjacent benzene ring, the electrons could transfer to benzene ring. It caused a high activity of electrons between N₁₀–C₁₄. And the electrons were able to combine with hydroxyl radicals, leading to rupture of the chemical bond between N₁₀–C₁₄. As a result, product 4 was generated. The whole process was given in Fig. 12(a).

The reaction of chemical bond rupture on piperazine ring (product a) was displayed in Fig. 12(a). The bonding energy between N₂₇–C₂₈ was around 0.033 (hartree) according to the result of quantitative calculation. It might be a result of the connection between N₂₇ and benzene ring and the effects of fluorine atoms nearby, which led to a high activity of N₂₇–C₂₈ electrons. Thus, they were easy to be attacked by hydroxyl radicals. Thus, product b was formed due to the chemical bond rupture and the ring-opening reactions. The C₃₁–C₃₇ bond of product b was influenced by symmetrical N atoms which had a high reactivity. As a result, the hydroxyl free radicals could attack the C₃₁–C₃₇ bond easily, and product c was generated. Finally, the degradation pathway of NOR in nZVI/H₂O₂ system was summarized in Fig. 12(b).

4. Conclusions

In this study, the degradation process of NOR with nZVI/H₂O₂ Fenton-like reaction was investigated under various experimental conditions. According to the results, some conclusions could be drawn as follows:

- (1) nZVI synthesized in the laboratory by the borohydride reduction method presented a typical chain structure and the single particle, which was spherical and uniform. The average size of particle size was approximately 20 nm with specific surface area of 39.2 m²/g.

- (2) NOR could not be degraded with nanoscale-iron alone at room temperature. However, it was effectively removed in a coupled nZVI and H₂O₂ system.
- (3) The solution pH value had significant effects on NOR degradation in nZVI/H₂O₂ system. At the ambient temperature, the degradation rate of NOR under the acidic medium (pH 3–4) was more than 95% within 40 min of the reaction time, and the mineralization degree was around 50%. Elevating temperature was conducive to removal of NOR, excessively high temperature caused the formation of iron oxide and useless decomposition of H₂O₂. In addition, increasing the dosages of H₂O₂ and nZVI were favored to improving NOR degradation rate and efficiency. The NOR removal followed two-staged process with time under different conditions.
- (4) NOR degradation was mainly resulted from the bonding breakage in piperazine and pyrimidine rings. The intermediate products included 4 species: C₁₅H₂₀FN₃O (*m/z* 278), C₉H₁₁FN₂ (*m/z* 167), C₇H₇FN₂ (*m/z* 139), and C₇H₈FN (*m/z* 126), respectively.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.seppur.2016.08.008>.

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