Zero-Valent Iron Nanoparticles and Its Combined Process for Diclofenac Degradation under Various Experimental Conditions

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Abstract

The use of nanoscale zero-valent iron (nZVI) for the purification of contaminated water and soil was investigated for its high potential to remove subsurface contaminants. In this study, the mechanism of diclofenac (DCF) degradation by nZVI and the combined process of nZVI and hydrogen peroxide (H₂O₂) are discussed. The results demonstrated that nZVI with acidic conditions had a certain degradation efficiency on DCF, with a removal rate about 30% in a 2-hour reaction at pH 5. The combined process of nZVI and H₂O₂ could obviously remove DCF, with a removal rate greater than 90% in a 2-hour reaction at pH 5. In nZVI system, under acidic and aerobic conditions, Fe²⁺ and H₂O₂ can be generated to form a Fenton-like system. Meanwhile, the release of electrons from nZVI could promote the reductive dechlorination of DCF. In nZVI/H₂O₂ system, the high removal rate of TOC was also showed the DCF mineralization by the Fenton-like oxidation.

Keywords: nanoscale zero-valent iron, hydrogen peroxide, diclofenac, Fenton-like oxidation, reductive dechlorination

Introduction

Trace levels of pharmaceuticals have been reported in natural environments because of their widespread use [1-3]. Diclofenac (DCF), a nonsteroidal anti-inflammatory drug, is widely prescribed as a pain killer and has been one of the most frequently detected pharmaceuticals in surface water and groundwater due to its poor treatability in municipal sewage treatment plants (STPs) [4]. The average concentrations detected are in the low μgL⁻¹ range in the influents and effluents of STPs and surface waters [5-8]. Studies have shown that DCF residues and their metabolites in water bodies can produce biotoxic effects on different living organisms in the water environment, which can lead to microbial resistance and cross-resistance [9]. DCF in effluent from STPs may also affect downstream aquatic and terrestrial ecology. The toxic effects of this drug pose a great threat to the environment and human health [10, 11]. Therefore, DCF removal technologies need to be further examined.
Extensive efforts have been made to develop novel and effective treatment processes for the removal of DCF in natural and engineered environments. Advanced oxidation processes producing reactive oxidants (hydroxyl radicals) have been studied as promising technologies because of their success in removing diverse classes of pollutants. For example, the oxidative degradation of DCF by \( \text{O}_3 \) [12, 13], \( \text{O}_2/\text{H}_2\text{O}_2 \) [14], UV/\( \text{H}_2\text{O}_2 \) [13], and photo-Fenton processes [15] have been studied. However, these advanced treatment techniques, except the photo-Fenton processes, usually suffer from high operational costs and relatively slow removal kinetics. Moreover, limitations have also been encountered in groundwater applications.

Nanoscale zero-valent iron (nZVI) has been investigated as a green in situ tool for the degradation of both organic and inorganic contaminants for more than 10 years [16-19]. The successful application of nZVI in organic contaminant degradation has been explored and reported by many researchers [20-25], such as antibiotics, chlorinated organics, nitroaromatics, and so on. In recent years, nZVI combined with the Fenton process has been studied as a catalyst for Fenton-like reactions. Shen et al. [26] used a combined zero-valent iron reduction and Fenton process of \( \text{H}_2\text{O}_2 \) to treat 2,4-dinitroanisole-producing wastewater. The results showed that the degradation of aromatic organic compounds was as high as 77.2%. Shirazi et al. [27] used nZVI as a Fenton-like catalyst. It was found that this combined process of nZVI and \( \text{H}_2\text{O}_2 \) could degrade carbamazepine rapidly and was well suited for groundwater, with a removal rate of more than 98%. Yao et al. [28] used a nZVI Fenton-like system formed by nZVI and \( \text{H}_2\text{O}_2 \) for nitrobenzene treatment. The removal rate of 91.9% was obtained in 240 min reaction. The possible mechanism of synergetic effects was proposed in the nZVI Fenton-like system.

In this study, DCF removal by a combined nZVI and \( \text{H}_2\text{O}_2 \) was investigated. The objectives of this work were (1) to optimize the operation conditions, including solids loading, pH value and dissolved oxygen (DO), and (2) to discuss the removal mechanism of the combined nZVI and \( \text{H}_2\text{O}_2 \).

Materials and Methods

Chemicals and Materials

\( \text{C}_14\text{H}_{10}\text{Cl}_{10}\text{NNaO}_2 \) (diclofenac sodium), \( \text{FeCl}_3 \) (ferric chloride anhydrous), \( \text{NaBH}_4 \) (sodium borohydride), and \( \text{NaOH} \) (sodium hydroxide) were obtained from Aladdin (Shanghai, China). \( \text{HCl} \) (hydrochloric acid) and \( \text{H}_2\text{O}_2 \) (hydrogen peroxide) were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd (Shanghai, China). Methanol (HPLC grade), acetonitrile (HPLC grade), acetic acid (HPLC grade), and t-butanol (tert-butanol) were obtained from Sigma-Aldrich (St. Louis, Missouri). All chemicals were used without further purification.

Ultrapure water was prepared with a Milli-Q water purification system (Millipore, Bedford, MA, USA). Microporous membranes (0.22 μm \( \times \) 50 mm) were obtained from CNW (Germany).

Synthesis and Characterization of nZVI

The nZVI was synthesized by a liquid-phase reduction method [29]. The prepared \( \text{NaBH}_4 \) of 0.5 M and \( \text{FeCl}_3 \) of 0.1 M were reacted with the volume ratio of 1:1. Then the generated nZVI particles were collected through vacuum filtration and respectively washed with ultrapure water for three times. Finally, fresh nZVI particles were stored in ultrapure water by blowing nitrogen at 4°C.

Fresh nZVI particles were scanned by the high-resolution transmission electron microscopy (TEM, JEOL) and the X-ray diffraction (XRD, Bruker) respectively.

Batch Experiments

The DCF stock solution with concentration of 1.0 g/L was prepared with ultrapure water. Degradation reactions were initiated in 150 mL DCF solution. All experiments followed up were performed in triplicate. Without special explanation, the concentration of DCF solution samples was 1,000 μg/L, the initial pH value was 5. After mixing, the reactors were continuously shaken for 2 hours in an orbital shaker.

In nZVI system, the nZVI loading concentrations in the solution were 0.1, 0.2, 0.5, 0.8, and 1.0 g/L. In nZVI/\( \text{H}_2\text{O}_2 \) system, different proportions of nZVI/\( \text{H}_2\text{O}_2 \), the initial solution pH was adjusted from 3 to 9 by small amounts of \( \text{HCl} \) or \( \text{NaOH} \) solution. In nZVI system, the nZVI loading concentration was 0.5 g/L. In nZVI/\( \text{H}_2\text{O}_2 \) system, the concentration of nZVI/\( \text{H}_2\text{O}_2 \) was 0.2 g/L and 1.0 mmol/L. The effect of oxygen on DCF removal was investigated under DO-limiting condition. The DO-limiting condition was established by blowing nitrogen over the solution with a nitrogen evaporator (Organamation Associates, Inc.). The nitrogen blowing time was maintained for at least 15 minutes to ensure a DO concentration less than 0.5 mg/L. The concentration of DO was monitored by a dissolved oxygen meter (Hach Co.). The initial solution pH value was controlled at 3 and 5 in nZVI system, and at 5 in nZVI/\( \text{H}_2\text{O}_2 \) system. In nZVI system, the nZVI loading concentration was 0.5 g/L. In nZVI/\( \text{H}_2\text{O}_2 \) system, the concentration of nZVI/\( \text{H}_2\text{O}_2 \) was 0.2 g/L and 1.0 mmol/L.
To further study the mineralization degree of DCF, total organic carbon (TOC) and chloride ions (Cl\(^-\)) were detected. In nZVI system, the nZVI loading concentration was 0.5 g/L. In nZVI/H\(_2\)O\(_2\) system, the concentration of nZVI/H\(_2\)O\(_2\) was 0.2 g/L and 1.0 mmol/L. The concentration of TOC was measured by a TOC analyzer (Shimadzu). The concentration of Cl\(^-\) was measured by an ion chromatography (Dionex).

To estimate whether the hydroxyl radical is the main removal factor of DCF, excessive t-butanol was added as the scavenger of the hydroxyl radical, which was produced during the reaction [30, 31]. Appropriate amounts (10:1, 50:1, 100:1, and 1,000:1 molar ratios of scavengers (t-butanol) to DCF) were added to the solutions prior to the addition of H\(_2\)O\(_2\). The concentration of nZVI/H\(_2\)O\(_2\) was 0.2 g/L and 1.0 mmol/L.

All solution samples were filtered with a 0.22 μm membrane after adding t-butanol to stop the further degradation of DCF by residual hydroxyl radicals before analysis. The concentrations of DCF in the sample were determined by high-performance liquid chromatography (HPLC, Agilent 1260) equipped with an EC-C18 packed column (Agilent). The initial mobile phase of the analysis was a mixture of 30% ultrapure water (containing 0.1% CH\(_3\)COOH) and 70% acetonitrile. The final mobile phase ratio was 25%:75%, within 5 min. The samples were measured at a rate of 1.0 mL/min at a wavelength of 275 nm. After measurement, methanol was used to clean the EC-C18 column.

Results and Discussion

Characterization of nZVI

Fresh nZVI particles were analyzed by TEM. The iron particles were typically less than 100 nm in diameter. Fig. 1 showed the smooth sphere surrounded the core structure, indicating that oxidation occurred on the surface. The XRD spectrum of fresh nZVI clearly displayed the characteristic peaks of Fe. As shown in Fig. 2, apparent peaks at the 2θ of 44.7º, 65.0º and 82.3º indicate the presence of nZVI (α-Fe) crystalline phase.

Degradation Efficiency of DCF by nZVI/H\(_2\)O\(_2\)

Effect of nZVI and H\(_2\)O\(_2\) Concentration

Different concentrations of nZVI and H\(_2\)O\(_2\) were discussed for the degradation at a DCF concentration of 1,000 μg/L for 2 hours. The initial pH value of the samples was adjusted to 5. Fig. 3 showed the removal process of DCF under three conditions. In the condition of only nZVI added in, when nZVI loading was higher than 0.5 g/L, the removal efficiency was more than 30%. In the condition of only H\(_2\)O\(_2\) added in, there was almost no removal efficiency on DCF. When DCF was treated by the combined process of nZVI and H\(_2\)O\(_2\), a significant effect in removing DCF was obtained. The degradation reaction of DCF was very rapid, and a large part of the removal process was completed in the first five minutes, whether the nZVI was added alone or as the combined process of nZVI and H\(_2\)O\(_2\).

The results have shown that nZVI can remove DCF. As an effective dechlorination reducing agent, nZVI has been widely applied for chlorinated organics removing. Zhou et al. [32] have proved that dechlorination is one of the pathways for nZVI to remove DCF. Ghauch et al. [33] used commercial iron powders for DCF removal, and dechlorination was also obtained. Meanwhile, under acidic conditions, Fe\(^{2+}\) and H\(_2\)O\(_2\) could be generated by the nZVI corrosion (Equation (1)) [34, 35]. On the one hand, the above two substances can form Fenton-like system (Equation (2-3)) to remove DCF by oxidation [36]. On the other hand, the existing of H\(_2\)O\(_2\) may compete with DCF for electrons, thus affecting the DCF removal effect. So reductive dechlorination and oxidation may both be the way to remove DCF by nZVI.
In the condition of both nZVI and H$_2$O$_2$ added in, with the increasing of the H$_2$O$_2$ concentration, the degradation of DCF increased significantly. During this procedure, nZVI was maintained at a constant dosage of 0.2 g/L. When the H$_2$O$_2$ concentration reached 1 mmol/L, the removal rate of DCF reach more than 90%. With the same concentration of 1 mmol/L H$_2$O$_2$, a higher dosage of 0.5 g/L nZVI resulted in a lower removal rate of DCF compared with the dosage of 0.2 g/L nZVI. H$_2$O$_2$ can remove DCF only in the presence of nZVI, and the removal efficiency is much greater than that of nZVI alone. Studies have shown that nZVI can remove organic matter through Fenton-like reactions. There are two possibilities of homogeneous and heterogeneous Fenton-like systems. Under acidic conditions, Fe$^{2+}$ generated by nZVI corrosion (Equation (4)) reacts directly with the addition of H$_2$O$_2$ (Equation (2)), to form homogeneous Fenton-like reaction system [37]. The nZVI can also directly activate H$_2$O$_2$ to produce hydroxyl radical (Equation (5)), to form heterogeneous Fenton-like reaction system [38]. Under acidic conditions, Fe$^{2+}$ could be continuously generated by nZVI corrosion. However, if the concentration of nZVI is too high, the Fe$^{3+}$ produced by the reaction will consume H$_2$O$_2$ (Equation (3)), which will affect the removal efficiency of DCF. The yellow color of the water sample after the experiment explains that excessive nZVI produced a large amount of Fe$^{3+}$ ions.

\[
  \text{Fe} + \text{O}_2 + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}_2 \quad (1)
\]

\[
  \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^- \quad (2)
\]

\[
  \text{Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{H}_2\text{O}^- + \text{H}^+ \quad (3)
\]

\[
  \text{Fe} + 2\text{H}^+ \rightarrow \text{Fe}^{2+} + \text{H}_2 \quad (4)
\]

\[
  \text{Fe} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{2+} + \text{OH}^- + \text{OH}^- \quad (5)
\]

Different initial pH values were prepared for DCF degradation.

Fresh prepared nZVI particles with a concentration of 0.5 g/L were injected into the solution with a DCF concentration of 1,000 μg/L for 2 hours. The variation of pH in different initial values is shown in Fig. 4a). A small increase in pH was observed under neutral and alkaline conditions. The pH increased relatively under acidic conditions but remained below 7. Fig. 4b) shows the degradation results at various pH conditions. The removal efficiency under acidic conditions was much higher than that under neutral and alkaline conditions. Under acidic conditions, the removal efficiency rapidly reached 30% within 5 min. Under neutral and alkaline conditions, the reaction was carried out relatively slowly. The best removal result was obtained in the initial pH 5 condition. The removal trends were similar in conditions of initial pH 5 and pH 3. When the initial pH was 9, the removal rate was less than 5% after 2 hours of reaction.

The combined process of nZVI and H$_2$O$_2$ for DCF removal at different pH values was also explored. The freshly prepared 0.2 g/L nZVI and 1 mmol/L H$_2$O$_2$ were injected into a 1,000 μg/L DCF sample in turn. The degradation trend of DCF by the combined process was similar to that of nZVI alone. The removal efficiency under acidic conditions was much higher than that under neutral and alkaline conditions. When the reaction lasted for 2 hours, the removal efficiency under
Fig. 4. Variation and effect of pH value during DCF removal by nZVI only.

Fig. 5. Effect of pH value on DCF removal by nZVI and H$_2$O$_2$. 
Acidic conditions could reach more than 85%. The best removal efficiency occurred at the initial pH value of 5, as shown in Fig. 5.

The nZVI particles were corroded by acid and oxygen. During the corrosion of iron by acid, ferrous iron and ferric iron solution could be generated [29]. The presence of H+ inhibited the formation of iron (oxy)hydroxide, providing advantageous environmental conditions for electron transfer. Therefore, when nZVI is added alone under acidic condition, reductive dechlorination and oxidation by Fenton-like reaction induced by Fe^{2+} and H_{2}O_{2} may be the main reasons for the removal of DCF. When nZVI and H_{2}O_{2} are added simultaneously in the solution, the nZVI continuously forms Fe^{2+}, which provides a catalyst for the Fenton-like reaction and promotes hydroxyl radical formation from H_{2}O_{2} to oxidize and degrade DCF, thus realizing the effective removal of DCF.

Under neutral and alkaline conditions, the FeOOH-shell could be formed based on Equations (6-8) [29, 39, 40]. According to the equations, the nZVI particles carry a positive charge in acidic conditions and a negative charge in alkaline conditions. The dissolution ability of Fe^{2+} decreases after the FeOOH-shell formed. Meanwhile, under alkaline conditions, H_{2}O_{2} is unstable and can rapidly decompose into H_{2}O and O_{2}, as shown in Equation (9). In this case, adsorption may be the main reason for the removal of DCF.

\[
2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \quad (6)
\]

\[
4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \quad (7)
\]

\[
4Fe + 3O_2 + 2H_2O \rightarrow 4FeOOH \quad (8)
\]

\[
2H_2O_2 \rightarrow 2H_2O + O_2 \quad (9)
\]

Effect of Solution DO

To further study the DCF degradation mechanism, the effect of DO was also investigated.

Freshly prepared nZVI particles with a concentration of 0.5 g/L were injected into the solution with a DCF concentration of 1,000 μg/L for 2 hours. Under DO-unadjusted conditions, the degradation of DCF by nZVI was maintained at a certain extent, with the DO concentration maintained above 2 mg/L. The DO in the system was reduced to less than 0.5 mg/L by blowing nitrogen. As shown in Fig. 6, under DO-limiting conditions, both in pH 3 and in pH 5, the removal rate of DCF was obviously reduced, resulting in a removal rate of DCF of only approximately 10%. Moreover, the removal rate of DCF also decreased, and the removal rate gradually stabilized after 20 minutes of reaction. The experimental results fully showed that DO limited the removal of DCF by nZVI.

According to Equation (1), in the nZVI system, oxygen was the key factor limiting the production of H_{2}O_{2}. Therefore, under DO-limiting conditions, the production of H_{2}O_{2} was greatly reduced in the samples, and the degradation was restricted.

In the combined process of nZVI and H_{2}O_{2}, the removal efficiency was significant whether under DO-unadjusted or DO-limiting conditions. As shown in Fig. 6, the removal efficiency of DCF rapidly increased to 70% in 5 min and to over 90% in 2 hours. DO was not the limiting factor in the nZVI/H_{2}O_{2} system.

In the nZVI/H_{2}O_{2} system, excessive H_{2}O_{2} existed in the solution to ensure the Fenton-like reaction, maintaining high removal efficiency. However, in the nZVI system, H_{2}O_{2} was produced by the presence of oxygen. In conclusion, the conversion of oxygen into H_{2}O_{2} was the key step for DCF removal in the absence of nitrogen.

Fig. 6. Effect of DO on DCF removal in nZVI and nZVI/H_{2}O_{2} system. The “solid line” represents DCF degradation by nZVI. The “dotted line” represents DCF degradation by nZVI/H_{2}O_{2}.
of H2O2 in the samples. In the nZVI/H2O2 system, Fenton-like system played a leading role.

Degradation Mechanism

TOC and Cl− were detected to further study the mineralization degree of DCF.

As shown in Fig. 7, about 85% of TOC was degraded to CO2 in nZVI/H2O2 system, which was much higher than nZVI system. So was the release of Cl−. Under DO-limiting conditions, both DCF degradation and Cl− concentration were lower than those under DO-unadjusted conditions. All these phenomena indicated that oxygen restricted the DCF removal process. According to Equation (1), under acidic and aerobic conditions, Fenton-like system could be formed by the generation of Fe2+ and H2O2. So, oxidation is the main pathway to remove DCF in nZVI system. Under DO-limiting conditions in nZVI system, there were still 4% of TOC degraded, 13% of DCF removed, and 0.033 mg/L of Cl− released. According to the structure of DCF, 1 mg/L of DCF can be mineralized completely to produce 0.223 mg/L of Cl−. The 0.033 mg/L of Cl− released represented that about 14% of Cl− had released by reductive dechlorination of nZVI. It is suggested that the removal mechanism of DCF under DO-limiting conditions is mainly reductive dechlorination. DCF is not mineralized completely, and the removal of TOC may be Fenton-like oxidation formed in the presence of a small amount of oxygen or surface adsorption of nZVI. Under DO-unadjusted conditions in nZVI system, the removal rates of TOC and DCF were both increased. There were about 21% of TOC degraded, 33% of DCF removed, and 32% of Cl− released. Compared with DO-limiting conditions, the degradation of TOC increased significantly. This indicated that DCF mineralization increased, but reductive dechlorination still happened. Under DO-unadjusted conditions in nZVI/H2O2 system, there were about 85% of TOC degraded, 93% of DCF removed, and 89% of Cl− released. In nZVI/H2O2 system, the dosages of nZVI was lower than that in nZVI system. So, the adsorption sites and available electrons were reduced accordingly. Due to the addition of H2O2, a lot of hydroxyl radicals were generated. The standard redox potential 2.8 V of hydroxyl radical is undifferentiated oxidation to any organic substance [27, 28]. The high removal rate of TOC was also showed the DCF mineralization by the Fenton-like oxidation.

The mechanism of nZVI and its combined process for DCF degradation is complex. Fig. 8 shows the main DCF removal mechanisms by nZVI. (1) In nZVI system, reductive dechlorination and Fenton-like oxidation are the main degradation mechanism. Under acidic conditions, nZVI produces electrons and Fe2+. DCF directly obtains electron from nZVI to release Cl−. Another part of electron is captured by oxygen to produce H2O2. Under neutral and alkaline conditions, the FeOOH-shell could be formed. The formation of core-shell structure will affect the electron transfer. Adsorption may be the main reason for the removal of DCF. (2) In nZVI/H2O2 system, additional H2O2 can generate a lot of hydroxyl radicals with zero valent iron and Fe2+. The Fenton-like oxidation is the main degradation mechanism. (3) There are three ways to realize Fenton-like oxidation. The first way is to form Fenton-like system by H2O2 added and Fe2+ generated by nZVI. The second way is to produce H2O2 from nZVI by reducing oxygen, and then form a Fenton-like system with Fe2+ generated by nZVI. The third way is to directly activate H2O2 added by nZVI to produce hydroxyl radicals.

In conclusion, the Fenton-like reaction is the main driver of DCF removal in the system. H2O2 and Fe2+ are indispensable. To further investigate the mechanism of DCF degradation by the Fenton-like system, appropriate amounts (10:1, 50:1, 100:1, and 1000:1 molar ratios of scavengers (t-butanol) to DCF) were added to the solutions prior to the addition of H2O2 [41]. Then, 0.2 g/L nZVI and 1.0 mmol/L H2O2 were added to the solutions. As shown in Fig. 9, DCF showed effective degradation at ratios of 10:1 and 50:1. The degradation of DCF by nZVI/H2O2 with these two ratios was almost the same as that without t-butanol. At a ratio of 100:1, the degradation of DCF by nZVI/H2O2 was obviously decreased. After two hours of reaction, the removal rate of DCF was still below 70%. When the ratio reached...
1,000:1, the combined process of nZVI and H$_2$O$_2$ had almost no effect on the removal of DCF. Incomplete inhibition of DCF degradation by the addition of t-butanol can be explained by competition second-order rate constants of hydroxyl radicals with t-butanol and DCF. The second-order rate constant of the hydroxyl radical with DCF is $7.5 \times 10^{9}$ M$^{-1}$s$^{-1}$, which is 12.5 times greater than that with t-butanol ($6 \times 10^{8}$ M$^{-1}$s$^{-1}$) [42]. Thus, t-butanol could not completely inhibit the reaction in a lower addition. However, when a 1000-fold higher molar ratio of t-butanol was added, the t-butanol was sufficient to quench the generation of hydroxyl radicals during the Fenton-like reaction. These results clearly showed that DCF was oxidatively degraded by hydroxyl radicals in the enhanced Fenton-like system.

**Conclusions**

The present study demonstrated that nZVI and nZVI/H$_2$O$_2$ system have a certain degradation effect on DCF. The mechanism of nZVI and nZVI/H$_2$O$_2$ system for DCF degradation is complex, including Fenton-like oxidation, reductive dechlorination and adsorption.

(1) With a solids loading of 0.5 g/L nZVI, the degradation of DCF could reach approximately 30% in a 2-hour reaction at pH 5. The pH and DO were the main limiting factors for DCF removal by nZVI. Under acidic and aerobic conditions, Fe$^{2+}$ and H$_2$O$_2$ can be generated to form a Fenton-like system. Meanwhile, the release of electrons from nZVI could promote the reductive dechlorination of DCF. The core-shell structure formed by nZVI corrosion also had a certain adsorption effect.

(2) To enhance the removal efficiency of DCF by a Fenton-like system, the combined process of nZVI and H$_2$O$_2$ was further examined. The nZVI/H$_2$O$_2$ of 0.2 g/L and 1 mmol/L can obviously remove DCF, with a removal rate greater than 90% in a 2-hour reaction at pH 5. Due to the addition of H$_2$O$_2$, a lot of hydroxyl radicals were generated. The high removal rate of TOC was also showed the DCF mineralization by the Fenton-like oxidation.

This study has provided the basis for DCF removal by nZVI and a method for enhancing Fenton-like reactions using the combined process of nZVI and H$_2$O$_2$. A follow-up study can optimize to further study the relationship of Fenton-like oxidation and reductive dechlorination, and the sustainability and stability of the reaction to provide a theoretical basis for wider applications.

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**Conflict of Interest**

The authors declare no conflict of interest.

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