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Study of diclofenac removal by the application of combined zero-valent iron and calcium peroxide nanoparticles in groundwater

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Abstract: Diclofenac (DCF) is one of the most frequently detected pharmaceuticals in groundwater, posing a great threat to the environment and human health due to its toxicity. To mitigate the DCF contamination, experiments on DCF degradation by the combined process of zero-valent iron nanoparticles (nZVI) and nano calcium peroxide ($nCaO_2$) were performed. A batch experiment was conducted to examine the influence of the adding dosages of both nZVI and $nCaO_2$ nanoparticles and pH value on the DCF removal. In the meantime, the continuous-flow experiment was done to explore the sustainability of the DCF degradation by jointly adding nZVI/$nCaO_2$ nanoparticles in the reaction system. The results show that the nZVI/$nCaO_2$ can effectively remove the DCF in the batch test with only 0.05 g/L nZVI and 0.2 g/L $nCaO_2$ added, resulting in a removal rate of greater than 90% in a 2-hour reaction with an initial pH of 5. The degradation rate of DCF was positively correlated with the dosage of $nCaO_2$, and negatively correlated with both nZVI dosage and the initial pH value. The order of significance of the three factors is identified as pH value > nZVI dosage > $nCaO_2$ dosage. In the continuous-flow reaction system, the DCF removal rates remained above 75% within 150 minutes at the pH of 5, with the applied dosages of 0.5 g/L for nZVI and 1.0 g/L for $nCaO_2$. These results provide a theoretical basis for the nZVI/$nCaO_2$ application to remove DCF in groundwater.

Keywords: Nanoscale zero-valent iron (nZVI); Nano calcium peroxide ($nCaO_2$); Diclofenac; Fenton-like reaction; Groundwater pollution

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Introduction

Groundwater is an important part of water resources and drinking water sources. However, with the rapid development of society, the pollution of groundwater has become increasingly severe. In China, 60% of the groundwater has been seriously polluted (Bin et al. 2013). In recent years, pharmaceutically active compounds (PhACs) have been continuously detected from groundwater. Diclofenac (DCF), one of the most frequently detected PhACs in groundwater (Mutiyar et al. 2018; Vymazal et al. 2017), is difficult to remove by the traditional treatment process (Vieno et al. 2014). The concentrations of DCF detected in groundwater are in the range of ng/L (Einsiedl et al. 2010; Jurado et al. 2019). Previous studies show that DCF residues and their metabolites in water bodies have biotoxic effects on different living organisms in the water environment, and subsequently lead to microbial resistance and cross-resistance (Schwaiger et al. 2004). Therefore, DCF removal technologies need to be further examined.

Advanced oxidation processes that can produce reactive oxidants such as hydroxyl radicals have been studied for DCF degradation as promising technologies (Forrez et al. 2010; Gomes et al. 2018). Nanoscale zero-valent iron (nZVI), as an environment-friendly in situ material for both organic and inorganic contaminant degradations, has been investigated for more than 10 years (Li et al. 2015; Liang et al. 2014; Stefaniuk et al. 2016). In recent years, a combined nZVI with H_2O_2 has

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been discussed as a catalyst for Fenton-like reactions (Shen et al. 2013; Shirazi et al. 2013). The combined nZVI and H_2O_2 was used to treat 2,4-dinitroanisole-producing wastewater, showing a high removal rate of 77.2% (Shen et al. 2013). Similarly, Shirazi et al. (2013) found that a combined process of nZVI and H_2O_2 can degrade carbamazepine rapidly with a high removal rate of 98%. Previous studies also showed that the nZVI/H_2O_2 system has a good removal effect on phenols, surfactants, antibiotics and other pollutants (Zhang et al. 2017). Although the Fenton-like system of nZVI/H_2O_2 can effectively remove organic pollutants, a recent research conducted by Liang et al. (2020) showed that the nZVI/H_2O_2 was able to remove organic pollutants very quickly, whereas part of H_2O_2 yet could not be utilized by the reaction system. The calcium peroxide (CaO_2), as an environmentally friendly oxygen releasing compound, has been widely used in water pollution remediation (Abraham et al. 2008). More importantly, CaO_2 can slowly release H_2O_2, which can be used in Fenton-like reaction instead of H_2O_2 to prolong reaction time and reduce hydrogen peroxide loss (Qian et al. 2013). Due to the low release rate of H_2O_2 from CaO_2, the content of H_2O_2 in the system remains low but relatively constant, which can effectively offset the disproportionation and decomposition of H_2O_2 and improve the utilization rate (Abraham et al. 2008).

In this study, the DCF removal by the combination of nZVI and nCaO_2 will be investigated. The objective of this work is to (1) optimize the solids loading of nZVI and nCaO_2, and (2) study the removal efficiency of the DCF in continuous-flow experiments by adding nZVI/nCaO_2 in the flow system.

1 Materials and methods

1.1 Chemicals and materials

In order to prepare necessary materials and conduct associated experiments, $C_{14}H_{10}Cl_2NNaO_2$ (diclofenac sodium), $FeCl_3$, $NaBH_4$, NaOH, and $CaCl_2$ were obtained from Aladdin (Shanghai, China). HCl, H_2O_2 and ammonia solution were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd (Shanghai, China). Methanol, acetonitrile, t-butanol and acetic acid were obtained from Sigma-Aldrich (St. Louis, Missouri). All the 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× 50 mm) were obtained from CNW (Germany).

1.2 Synthesis of nZVI and nCaO_2

The nZVI was synthesized according to the method of liquid-phase reduction of $FeCl_3$ by $NaBH_4$ (Sun et al. 2006). The $NaBH_4$ (0.5 M) and $FeCl_3$ (0.1 M) with the volume ratio of 1:1 were vigorously reacted. Then the generated jet-black 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 after blowing nitrogen at 4°C. The fresh nZVI particles need to be consumed within 7 days.

The nCaO_2 was synthesized by adding $CaCl_2$ (3 g) and H_2O_2 (30% m/m, 15 mL) into ammonium solution (1 mol/L). When the solution gradually changed to viscous liquid, the precipitate (NaOH solution at pH 12-13) was titrated to the prepared solution to obtain a white precipitation mixture by increasing the pH to 10-12. The white precipitate was then filtered and washed with diluted ethanol (deionized water: absolute ethanol = 1: 1 by volume). The filter cake was cooled at −80℃ and freeze-vacuum dried, after which the nCaO_2 powder with particle sizes of 20-100 nm was obtained.

The size and distribution of nZVI particles were analyzed by transmission electron microscopy (TEM, JEOL). The TEM was set at 200 kV.

The X-ray diffraction (XRD) measurement was carried out on a Bruker X-ray D8 Advance diffraction instrument (Cu Kα), the diffraction angle (2θ) from 10° to 90° was scanned.

1.2.1 Characterization of nZVI

As shown in Fig. 1, the fresh nZVI particles are agglomerated. The diameter of the particles is less than 100 nm, and most of the particles are in the range of 20-50 nm.

The XRD spectrum of fresh nZVI clearly

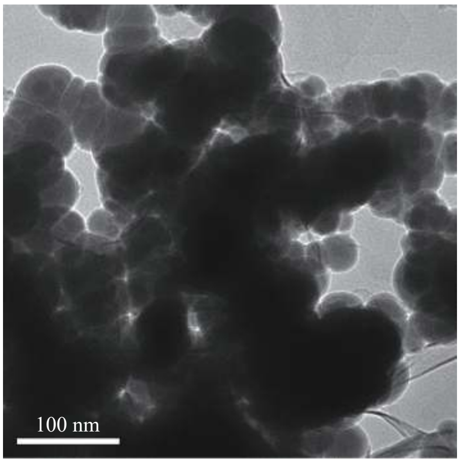


Fig. 1 TEM characterization of fresh nZVI

displayed the characteristic peaks of Fe as shown in Fig. 2. The 2θ peaks at 44.7°, 65.0° and 82.3° indicate the presence of nZVI (α-Fe) crystalline phase (Table 1), compared with the standard PDF card of Fe (card number: 65-4899). Except for three diffraction peaks, no other impurity phase diffraction peaks were detected. Thus, it was found that there were not many impurities in the nZVI particles prepared, and the corresponding purity was high.

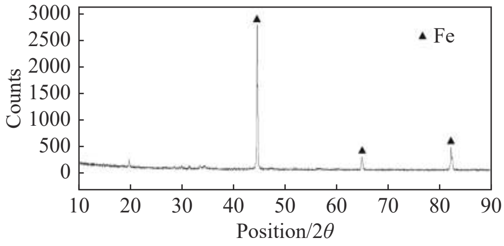


Fig. 2 XRD spectrum of fresh nZVI

Table 1 Crystal plane index of nZVI

Diffraction angle (°)	44.7	65.0	82.3
Crystal plane distance (Å)	2.025 7	1.433 7	1.170 6

1.2.2 Characterization of $nCaO_2$

The XRD spectrum of fresh $nCaO_2$ is shown in Fig. 3, where the 2θ peaks are located at 30.1°, 35.6°, 47.3°, 51.6°, 53.2° and 82.3°, respectively, indicating the presence of CaO_2 (Table 2), compared with the standard PDF card of CaO_2 (card number: 03-0865). At the same time, the spectrum shows that there are other impurity peaks, which may be other substances produced in the preparation process.

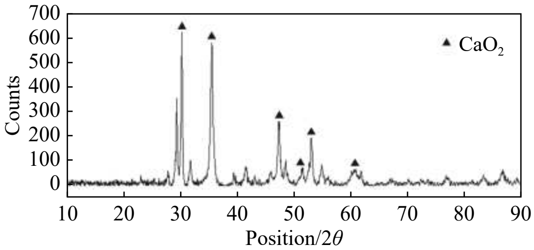


Fig. 3 XRD spectrum of fresh $nCaO_2$

Table 2 Crystal plane index of $nCaO_2$

Diffraction angle (°)	30.1	35.6	47.3	51.6	53.2
Crystal plane distance (Å)	2.966 6	2.519 8	1.920 2	1.769 9	1.720 3

1.3 Batch experiment

The DCF stock solution (1.0 g/L) was prepared with ultrapure water. The degradation reactions were initiated in 150 mL DCF solution at 1.0 mg/L, with different proportions of $nZVI/nCaO_2$ added. After mixing, the reactors were continuously shaken for 2 hours in an orbital shaker. Considering the adaptability of the materials (nZVI and $nCaO_2$) to pH values and the weak acidity of the polluted groundwater, the initial pH value was 5. All experiments were performed in a triplicate manner.

The experiments were started with all samples filtered with a 0.45-μm membrane after adding t-butanol to stop further degradation of the DCF by residual hydroxyl radicals, and followed by relevant data analysis. The concentrations of DCF in the samples 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 A (30% ultrapure water with 0.1% CH_3COOH) and B (70% acetonitrile). The final mobile phase of A was linear decreased to 25% and B was linear increased to 75%, within 5 min. The samples were measured at a rate of 1.0 mL/min at a wave length of 275 nm.

1.4 Continuous-flow experiments

A continuous-flow system of the DCF removal by $nZVI/nCaO_2$ was prepared with different dosages of nZVI and $nCaO_2$ (Table 3) initially added to the reactor (Fig. 4). The samples of 1.0 mg/L DCF at

Table 3 Dosages of nZVI and $nCaO_2$ in continuous-flow experiments

	nZVI (g/L)	**$nCaO_2$ (g/L)**
1	0.05	0.2
2	0.1	1.0
3	0.5	1.0
4	0.75	1.0

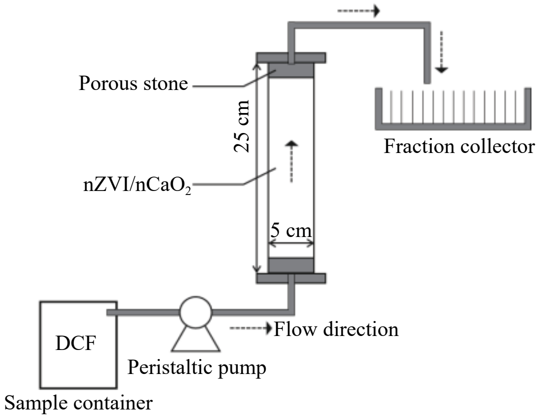


Fig. 4 The continuous-flow reactor

pH 5 were continuously injected for 3 hours at a flow rate of 50 mL/min so that the reaction time was at about 10 min. The inlet direction of the reactor was bottom-up to prevent the aggregation of solid particles from settling. The sampling interval was 15 minutes.

2 Results and discussion

2.1 Degradation efficiency of DCF in batch experiments

2.1.1 Effect of nZVI and $nCaO_2$ dosages

In order to study the degradation effect of the combined process of nZVI and $nCaO_2$ on DCF, the dosage experiments were carried out. Fig. 5 shows the results of batch experiments with different nZVI/$nCaO_2$ dosages. When 0.1 g/L nZVI was added without $nCaO_2$, the removal efficiency was about 17%; when 0.2 g/L $nCaO_2$ was added without nZVI, there was almost no DCF removal; while with the joint addition of only 0.05 g/L nZVI and 0.2 g/L $nCaO_2$, a significant DCF removal was obtained–the removal rates of DCF reached more than 90%. The degradation of DCF by nZVI happened rapidly, with a large part of the removal process completed in the first five minutes, despite whether the added nZVI was combined with $nCaO_2$.

When $nCaO_2$ dosages increased and nZVI content stayed at the same (0.1 g/L) level, the removal of DCF increased first and then decreased. The optimal $nCaO_2$ dosage was 0.2 g/L. Excessive $nCaO_2$ (i.e. >0.2 g/L) has a better DCF removal than that of insufficient addition of the $nCaO_2$ (i.e. <0.2 g/L). At the optimal $nCaO_2$ dosage (0.2 g/L), adding 0.05 g/L nZVI resulted in the optimal DCF removal, while a higher dosage (0.08 g/L) of nZVI brought a lower removal rate than a lower dosage (0.02 g/L). More surprisingly, even when the higher nZVI dosages such as 0.1 g/L and 0.2 g/L were added to the reactor, they both significantly lowered the DCF removal rates. This reflected that the excessive nZVI dosage inhibited the reaction.

Previous study has shown that CaO_2 can decompose in water to release both oxygen and H_2O_2 at the same time, as shown in Equations 1 and 2 (Wang et al. 2016). In the case of acidic and aerobic reaction, Fe^{2+} and H_2O_2 can be generated through the nZVI (Fe) corrosion in acid water (Equations 3 and 4) (Sun et al. 2006; Vilardi et al. 2018). As shown in Equation 5, the existence of Fe^{2+} and H_2O_2 forms a Fenton-like system to remove DCF by oxidation (Mikhailov et al. 2017; Muhammad et al. 2010). However, the Fe^{2+} generated by excessive nZVI further loses electrons to form Fe^{3+} (Equation 6) (Sun et al. 2006). The Fe^{3+} competes with Fe^{2+} for H_2O_2, which affected the Fenton-like reaction (Equations 5 and 7) (Mikhailov et al. 2017; Muhammad et al. 2010). Therefore, the inhibition of Fenton-like reaction may be the main reason of negative effect of the excessive nZVI on the removal of DCF. As regard to the effect of excessive $nCaO_2$, not only O_2 and H_2O_2 can be released, but also hydroxyl ions are generated (Equations 1 and 2). In generally, the Fenton-like system requires sufficient O_2 and H_2O_2, where the H_2O_2 is decomposed to generate O_2. The generated O_2 further enhances the nZVI to produce Fe^{2+} and H_2O_2, which in turn promotes the degradation process of DCF. However, excessive hydroxyl ions will consume hydrogen ions in the water and form oxide layers around the nZVI to affect its activity, thus excessive $nCaO_2$ lowers down the removal rate of DCF, comparing to the optimal dose (0.2 g/L).

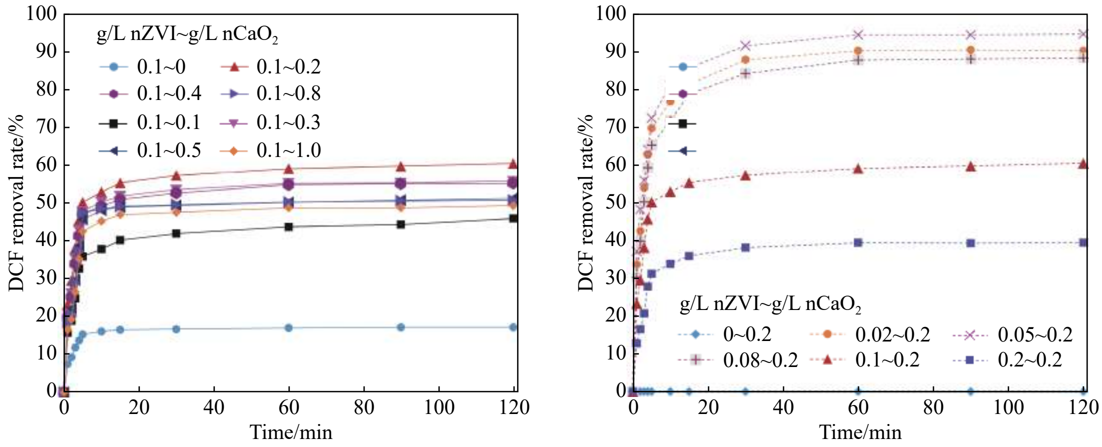


Fig. 5 Effect of nZVI/$nCaO_2$ dosages on DCF removal

$$2CaO_2 + 2H_2O \rightarrow 2Ca(OH)_2 + O_2 \tag{1}$$

$$CaO_2 + 2H_2O \rightarrow Ca(OH)_2 + H_2O_2 \tag{2}$$

$$Fe + O_2 + H^+ \rightarrow Fe^{2+} + H_2O_2 \tag{3}$$

$$2Fe + O_2 + 4H^+ \rightarrow 2Fe^{2+} + 2H_2O \tag{4}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \tag{5}$$

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 2Fe^{3+} + 2H_2O \tag{6}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \tag{7}$$

2.1.2 Effect of initial pH values

The pH value is one of the most important influencing factors on Fenton reaction. The above analysis shows that Fenton-like reaction is one of the effective degradation ways, so that the initial pH value is discussed. Fig. 6 shows the results of batch experiments at various pHs. The removal rates reach about 60% at pH of 5 and around 90% at pH of 3. However, under the neutral or alkaline condition (pH 9), adding nZVI/nCaO_2 does not help remove the DCF. Fig. 6 also shows that the removal patterns are similar in the acidic conditions with the pH of 3 and 5, respectively, where the nZVI particles are corroded by both acid and O_2. During the corrosion of iron in the acid solutions, Fe^{2+} and Fe^{3+} are generated as described by the Equations 3-4 and 6, from which it can be seen that the presence of H^+ inhibits the formation of iron hydroxide. In this study, when nZVI and nCaO_2 were jointly added in the solution, the nZVI continuously formed Fe^{2+}, which provided a catalyst for the Fenton-like reaction and promoted the hydroxyl radical formation through oxidizing H_2O_2 and degrading DCF, thus completing the effective removal of the DCF. Under neutral and alkaline conditions, the FeOOH-shell is usually formed, as indicated in Equation 8-10 (Joo et al. 2004); the core-shell structure decreases the activity of nZVI. Meanwhile, hydroxyl ions consume most of the Fe^{2+} generated from the nZVI reactions. As a result, the Fenton-like oxidation system is hard to form. The 0% DCF removal also indicates that the FeOOH-shell structure of nZVI has limited adsorption capacity to DCF. The $Ca(OH)_2$ generated by the reaction of CaO_2 as indicated in Equation 1-2 could be another shell that coat the nZVI particles, which also decreases the activity of nZVI and competes with DCF for the adsorption sites on the surface of nZVI, reducing the adsorption. Meanwhile, as a slow-release agent of H_2O_2, previous studies (Abraham and Daniel, 2008) have shown that pH also affects the release rate of CaO_2. The lower the pH value, the faster the release rate of H_2O_2 by CaO_2 is. This is also one of the reasons of the efficient DCF removal in acidic conditions.

$$2Fe + O_2 + 2H_2O \rightarrow 2Fe(OH)_2 \tag{8}$$

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \tag{9}$$

$$4Fe + 3O_2 + 2H_2O \rightarrow 4FeOOH \tag{10}$$

The variation of pH with different initial values is shown in Fig. 6. The pHs basically remain unchanged under the neutral and alkaline conditions, which is perhaps due to the decrease of decomposition rate of the nCaO_2 (Wang et al. 2016). According to Equations 1-2, more $Ca(OH)_2$ can be generated over time, resulting in the raise of pH values. In this study, increased pH values were observed under the acidic conditions, but they remained below 7. During the first five minutes of the reaction, the removal rates of DCF increased rapidly at the initial pH values of 3 and 5,

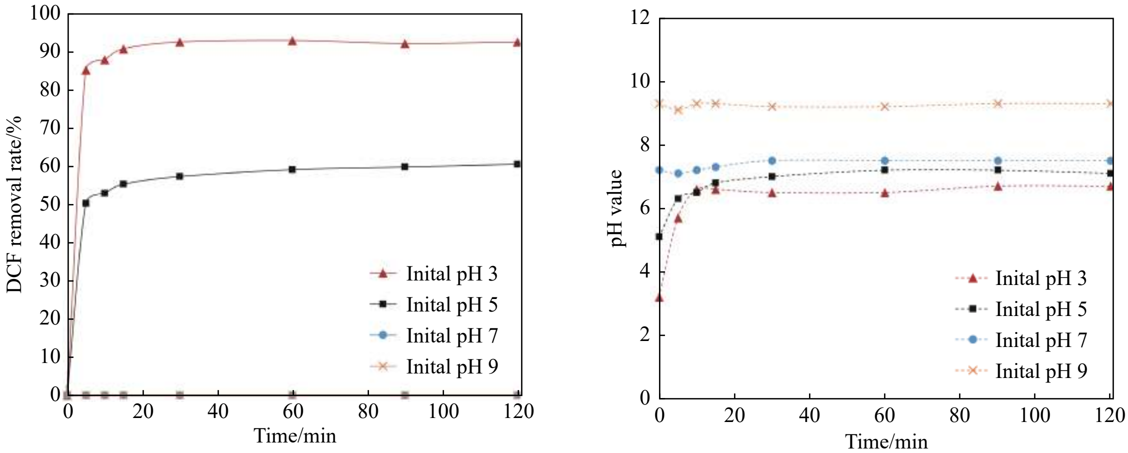


Fig. 6 Effect of initial pH on DCF removal by nZVI/nCaO_2

respectively. At the same time, the pHs increased rapidly, but stabilized later when they reached near-neutral. In the process of Fe^{2+} and Fe^{3+} generations, the H^+ is quickly consumed. Meanwhile, OH^- released from the decomposition of $nCaO_2$ did not make the solution alkaline, which suggests that the OH^- was largely consumed by the iron precipitation and the formation of shell structure around the nZVI particles.

2.1.3 Response surface model equations

Analysis of variance was performed to identify the significant factors such as nZVI dosage (A), $nCaO_2$ dosage (B), and pH value (C) that affect the DCF degradation, by using Design Expert v11.0.

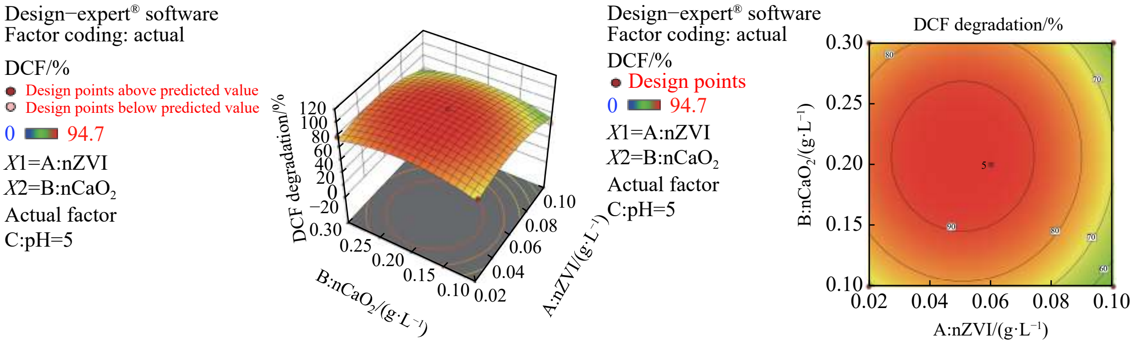
A quadratic model was established on the basis of the experimental data, with the equations shown in Equations 11 and 12, respectively. Moreover, the predictive results based on the equations are presented and visualized by the 3-D surfaces and contour plots shown in Fig. 7.

$$\%DCF\ \deg radation = 94.70 - 7.65A + 2.05B - 42.10C - 16.50A^2 - 14.90B^2 - 36.90C^2 \tag{11}$$

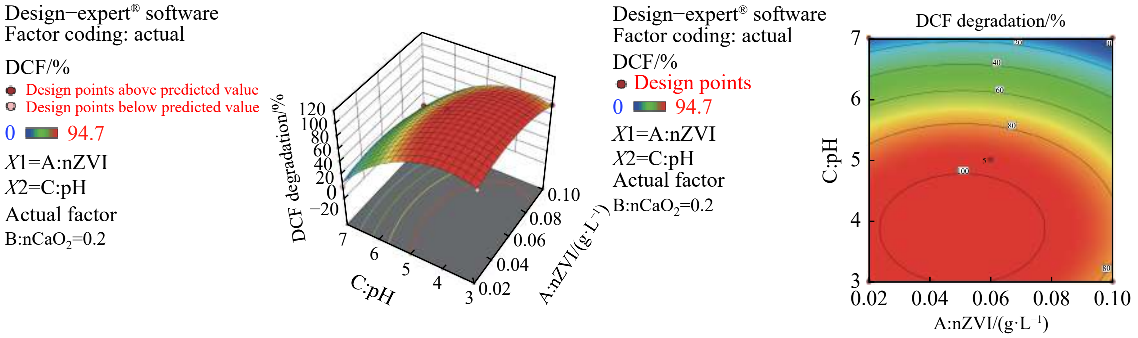
$$\%DCF\ \deg radation = -120.025 + 1046.25(nZVI) + 616.5(nCaO_2) + 71.2(pH) - 10312.5(nZVI)^2 - 1\,490(nCaO_2)^2 - 9.225(pH)^2 \tag{12}$$

The 3-D surfaces and contour plots can reflect the interaction among the variables (i.e. nZVI dosage, $nCaO_2$ dosage, and pH value) that collectively affect the degradation rate of DCF. The results of 3-D surfaces show the impact of two out of the three factors on the degradation rate with the third one as a constant. It can be seen from Fig. 7 that there is a positive correlation between the area of the surface graph and the degradation rate,

(a) nZVI and $nCaO_2$



(b) nZVI and pH



(c) $nCaO_2$ and pH

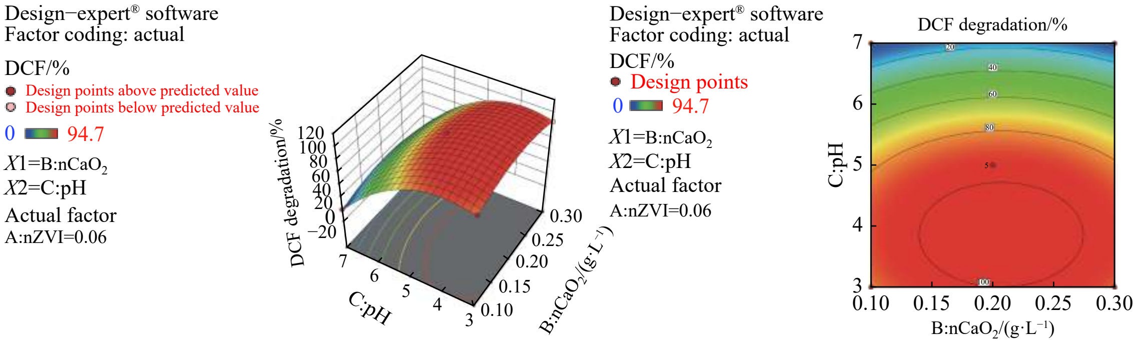


Fig. 7 3-D surfaces and contour plots for the effect of factors on DCF degradation

where the colour of the graph area from blue to red reflects the increase of the degradation rate.

As shown in Fig. 7b and 7c, the effect of pH is negative for both nZVI and $nCaO_2$, indicating that an increase in pH may lower down the degradation of DCF. The DCF degradation increases as the dosages of nZVI and $nCaO_2$ jointly increase and levels off to a certain limit with the further addition of the particles (Fig. 7a). Excess dosages of nZVI and $nCaO_2$ would cause a decrease in DCF removal.

The rationale of DCF degradation rate model is usually verified by the method of variance analysis. The evaluation results of the secondary model are shown in Table 4, in which the regression coefficients are used to measure the significance of the degradation rate model. Among them, the significance level is measured by p value; and if the $p < 0.000\ 1$, it can be judged that the linear correlation between the dependent variable and all independent variables in the correlation equation determined by the model is good. F in Table 4 corresponds to the ratio of the mean square of each variable to the mean square of the residual. The larger the F value, the higher the significance of the variable is (Singh et al. 2012). For this study, the order of significance of three factors is: pH value > nZVI dosage > $nCaO_2$ dosage.

Numerical optimization method was also employed by using Design Expert v11.0. In determining the set of factors (nZVI dosage, $nCaO_2$ dosage and pH value) that would yield the highest DCF removal efficiencies, 29 possible solutions were found. Considering the weakly acid property of groundwater and the effluent pH value, the range of pH value was set between 5 and 6. Table 5 summarizes the optimized conditions and the corresponding predicted DCF degradation.

2.2 Degradation efficiency of DCF in continuous-flow experiments

To further study the application of nZVI/$nCaO_2$ system in the actual groundwater environment, the continuous-flow experiment was conducted to explore the removal effect of DCF. Fig. 8 shows the results from the continuous-flow experiments. As can be seen from Fig. 8, the use of optimal dosage of nZVI/ $nCaO_2$ mixture (i.e. 0.05 g/L for nZVI and 0.2 g/L for $nCaO_2$) yields the removal rate of above 30% in the time length of around 15 minutes to 120 minutes, which is much lower than those of the batch experiments. This suggests that the 0.2 g/L $nCaO_2$ is insufficient to produce H_2O_2 to maintain the Fenton-like system with the addition of nZVI/$nCaO_2$ under the continuous-flow conditions, so that it is not able to fully utilize hydroxyl radicals to degrade the DCF. The dosages of both nZVI and $nCaO_2$ hence need to be appropriately increased.

In order to ensure that there would be enough H_2O_2 in the continuous-flow system, the dosage of $nCaO_2$ was increased to 1.0 g/L. The above study shows that the dosage of nZVI has the most significant impact on the DCF removal, so the nZVI dosage also needs to be further adjusted. The result of continuous flow test shows that the DCF removal rate increases as the adding dosages of nZVI and $nCaO_2$ are increased. However, with the dosage of 0.1 g/L for nZVI and 1.0 g/L for $nCaO_2$, the removal rate is still below 50%. During the continuous-flow tests, increasing the dosage nZVI and $nCaO_2$ to 0.5 g/L and 1.0 g/L, respectively for the nZVI/$nCaO_2$ mixture, the removal rate of DCF reached the highest at a level of about 75% after

Table 4 Analysis of variance of DCF degradation model

Parameter	Square sum	F value	p value
Model	23 202.18	153.88	<0.000 1
A nZVI	468.18	18.63	0.001 5
B $nCaO_2$	33.62	1.34	0.274 3
C pH	14 179.28	564.24	<0.000 1
A^2	1 146.32	45.62	<0.000 1
B^2	934.78	37.20	0.000 1
C^2	5 733.09	228.14	<0.000 1

Table 5 Optimized condition of DCF degradation

nZVI dosage (g/L)	$nCaO_2$ dosage (g/L)	pH value	DCF degradation (%)
0.045-0.055	0.190-0.212	5.0	94.9-95.7

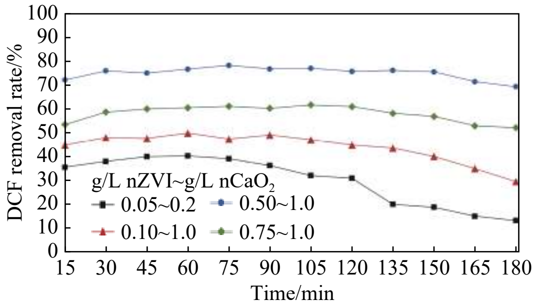


Fig. 8 DCF degradation by nZVI/$nCaO_2$ in continuous-flow experiments

150 min of the reaction commenced and then slightly decreased after 180 min. When the nZVI was increased to 0.75 g/L, the DCF removal rate was lowered to 60%. These results further indicate that when the dosage of $nCaO_2$ in the continuous-flow system is enough to provide H_2O_2 for the reaction, the removal rate of DCF by nZVI/$nCaO_2$ first increases and then decreases with the increase of the dosage of nZVI. This may be due to the fact that the nZVI, as the solid iron source of Fenton-like system, needs to continuously supply Fe^{2+} to the system, resulting in Fenton-like reaction to degrade DCF. This is proved by adding insufficient nZVI (e.g. 0.1 g/L) in the system, which cannot provide enough Fe^{2+} to induce the Fenton-like reaction and results in the low DCF removal rates. On the other hand, as adding an excessive nZVI (e.g. 0.75 g/L) in the system, the produced H_2O_2 will be consumed, which competes with DCF and affects the removal effect of DCF. The optimal dosage of nZVI and $nCaO_2$ combination (0.5 g/L nZVI and 1.0 g/L $nCaO_2$) for the DCF removal in continuous-flow experiment was higher than that in the batch experiment (0.05 g/L nZVI and 0.2 g/L $nCaO_2$), because nZVI and $nCaO_2$ could fully be contacted in batch experiment after full stirring, while in continuous-flow experiment, the contact between nZVI and $nCaO_2$ was formed by hydrodynamic force, which may lead to the uneven distribution of H_2O_2, affecting the removal effect of DCF by the nZVI/$nCaO_2$ combination.

3 Conclusions

The present study demonstrates that nZVI and $nCaO_2$ can form a Fenton-like system under acidic conditions, which has an efficient degradation effect on diclofenac (DCF) in groundwater. The combination of 0.05 g/L nZVI and 0.2 g/L $nCaO_2$ can remove the DCF effectively, with a removal rate greater than 90% in a 2-hour reaction at a pH of 5.

In the nZVI/$nCaO_2$ combination process, the degradation rate of DCF is positively correlated with the dosage of $nCaO_2$, and negatively correlated with both nZVI dosage and initial pH value. The order of significance of the three factors is identified as pH value > nZVI dosage > $nCaO_2$ dosage.

The experimental results by adding nZVI/$nCaO_2$ in the continuous-flow system show that the efficient removal rates remain above 75% within 150 minutes with the dosages of 0.5 g/L for nZVI and 1.0 g/L for $nCaO_2$.

This study has provided the basis for DCF removal by a Fenton-like system using the combined process of nZVI and $nCaO_2$. A follow-up study can focus on optimizing the decomposition of $nCaO_2$, controlling the release rate of H_2O_2, and improving its utilization.

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