Enhanced Fenton-like Degradation of Trichloroethylene by Hydrogen Peroxide Activated with Nanoscale Zero Valent Iron Loaded on Biochar

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Composite of nanoscale Zero Valent Iron (nZVI) loaded on Biochar (BC) was prepared and characterized as hydrogen peroxide (H₂O₂) activator for the degradation of trichloroethylene (TCE). nZVI is homogeneously loaded on lamellary structured BC surfaces to form nZVI/BC with specific surface area (S_{BE}) of 184.91 m² g⁻¹, which can efficiently activate H₂O₂ to achieve TCE degradation efficiency of 98.9% with TOC removal of 78.2% within 30 min under the conditions of 0.10 mmol L⁻¹ TCE, 1.13 g L⁻¹ nZVI/BC and 1.50 mmol L⁻¹ H₂O₂. Test results from the Electron Spin Resonance (ESR) measurement and coumarin based fluorescent probe technology indicated that ∙OH radicals were the dominant species responsible for the degradation of TCE within the nZVI/BC-H₂O₂ system. Activation mechanism of the redox action of Fe²⁺/Fe³⁺ generated under both aerobic and anaerobic conditions from nZVI and single electron transfer process from BC surface bound C–OH to H₂O₂ promoted decomposition of H₂O₂ into ∙OH radicals was proposed.

As one of the most commonly used chemicals in industry, chlorinated solvents such as trichloroethylene (TCE) has been frequently encountered in subsurface environments as dense non-aqueous phase liquids (DNAPLs) at many industrial sites¹,². Due to its high toxicity and adverse effects on liver and kidney, TCE has been classified as a potential human carcinogen and listed as a priority pollutant by the United States Environmental Protection Agency (U.S. EPA)³, and the Safe Drinking Water Act in the USA defines the maximum contaminant level of TCE at 5 μg L⁻¹ for drinking water⁴. Therefore, effective remediation and complete mineralization of TCE in aquifers is urgently required to reduce its adverse effects on the environment and human health.

Advanced oxidation processes (AOPs) have been emerged as the most efficient alternative to degrade various organic pollutants for the generation of reactive radicals⁵. Among AOPs, Fenton (i.e., the reaction between Fe²⁺ and H₂O₂) is a powerful oxidant generating the hydroxyl radicals (∙OH, E₀ = 2.80 V), which react with various organic compounds at the near-diffusion controlled rates⁶,⁷, leading to an effective degradation and mineralization of organic pollutants⁸. However, it should to be operated at pH < 3.0 and the generated iron sludge limited the wide application of the homogeneous Fenton process⁹. Heterogeneous Fenton-like activator of zero valent iron (ZVI) was developed, which could be used over a wide pH range to decompose H₂O₂ instead of homogeneous ferrous iron¹⁰,¹¹. In addition, nanoscale zero valent iron (nZVI) could enhance H₂O₂ activation due to the small particle size and high reactivity. Xu et al.¹² reported that the heterogeneous Fenton-like system using nZVI as catalyst was effective for the removal of biocide 4-chloro-3-methyl phenol in the presence of H₂O₂, and the reaction was induced through following reactions in the heterogeneous system of nZVI/H₂O₂:

\[
2\text{Fe}^0 + \text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{Fe}^{2+} + 4\text{OH}^- \tag{1}
\]

\[
\text{Fe}^0 + 2\text{H}_2\text{O} \rightarrow \text{Fe}^{3+} + 2\text{OH}^- + \text{H}_2 \tag{2}
\]
Fe^{2+} + H_{2}O_{2} \rightarrow Fe^{3+} + OH + OH^{-} \quad (3)

Though nZVI has performance for H_{2}O_{2} activation, it tends to aggregate into forming microscale particles due to its high surface energy and strong magnetic interaction, leading to the reduced reactivity\(^{13}\). To overcome the problem, granular activated carbon\(^{14}\), bentonite\(^{15}\), and rectorite\(^{16}\) were introduced as a support for nZVI to gain better distribution.Biochar (BC) is a promising environmental friendly material pyrolyzed under low oxygen conditions. It possesses large surface area with porous structure and has oxygen containing functional groups\(^{17}\). Thus, it is anticipated that nZVI loaded uniformly on BC surface to form nZVI/BC composite will effectively prevent the aggregation of nZVI with significantly enhanced performance.

In this study, the composite of nZVI loaded on BC sheets was synthesized and characterized as H_{2}O_{2} activator for the degradation of TCE. The presence of C=O groups on BC surface could be used to activate H_{2}O_{2} through electron transfer process\(^{18}\). Thus, both the dispersive nature and H_{2}O_{2} activator of BC will be simultaneously achieved for nZVI/BC. The present work aims to (1) synthesize a novel composite of nZVI/BC, where nZVI was loaded on BC surface uniformly and the aggregation of nZVI was prevented effectively, (2) characterize nZVI/BC activation ability for H_{2}O_{2} to degrade TCE in aqueous solution, and (3) explore the activation mechanisms of H_{2}O_{2} in the presence of nZVI/BC.

**Results and Discussion**

**Characterization of nZVI/BC.**  SEM analyses were firstly conducted to observe the morphologies of the prepared nZVI, BC and nZVI/BC, respectively. As illustrated in Fig. 1a, nZVI was spherical with diameters of about 30 nm, and the agglomeration of nZVI was observed due to the nanometer effect and magnetic properties of nZVI. In addition, lamellarly structured BC of rough surface morphologies was obtained, and nZVI was homogeneously loaded on BC surface from the SEM image of nZVI/BC composite. XRD was also conducted, and the data were shown in Fig. 1d. It can be seen that the XRD pattern of nZVI revealed a highly crystalline and single phase structure by diffraction peaks at 45.0° (ICPD 01-087-0721)\(^{19}\). The crystallite size of nZVI was estimated to be 29.7 nm derived from the Debye-Sherrer equation (D = Kλ/βcosθ)\(^{20}\), where K is the Sherrer constant (0.89), λ is the X-ray wavelength (0.15418 nm), β is the full peak width at half maximum and θ is the Bragg diffraction angle), which was in accordance with the SEM image. The broad reflection peak of BC in XRD indicated the amorphous BC, suggesting that nZVI was successfully loaded on BC surface from XRD spectrum of nZVI/BC (Fig. 1d).

The BET surface areas were measured by using N\(_2\) adsorption as shown in Fig. 1e. The \(S_{BET}\) values were calculated according to the BET equation: \(S_{BET} = \frac{1}{V_{m}P_{b}} \frac{V_{m}}{P_{b}} + \frac{1}{V_{m}^{2}}\), where \(V\) is the volume of nitrogen adsorbed per gram, \(V_{m}\) is the monolayer capacity and \(C\) is related to the heat of adsorption. From the results, the \(S_{BET}\) value of bare nZVI was 26.61 m\(^2\) g\(^{-1}\), and was increased to 184.91 m\(^2\) g\(^{-1}\) for the nZVI/BC composite after nZVI was loaded onto BC surface (\(S_{BET}\) value of 205.35 m\(^2\) g\(^{-1}\)) in the FTIR spectrum, the band at about 3400 cm\(^{-1}\) was belonged to the vibration of hydroxyl groups (\(-OH\)). The signal at 1590 cm\(^{-1}\) was ascribed to C=O stretching vibration, the peak at 1100 cm\(^{-1}\) was corresponded to the vibration of aromatic C=H\(^{11}\). The weak adsorption in nZVI/BC spectrum at 561 cm\(^{-1}\) was observed in the Fig. 1f, indicating the Fe−O bond formed between BC and nZVI\(^{21}\).

**Heterogeneous fenton-like degradation of TCE in nZVI/BC-H\(_2\)O\(_2\) system.**  The performances of TCE degradation by H\(_2\)O\(_2\) activated with nZVI, BC and nZVI/BC were investigated and presented in Fig. 2a. The control test suggested the TCE (0.10 mmol L\(^{-1}\)) loss was less than 2% due to the volatilization during the experimental period under all the tested conditions. With the effect of 1.50 mmol L\(^{-1}\) H\(_2\)O\(_2\), TCE was hardly degraded in the absence of any activators within 30 min, but its degradation efficiencies were enhanced to 39.1%, 6.5% and 98.9% with H\(_2\)O\(_2\) in the presence of nZVI, BC and nZVI/BC, respectively. Under all the tested conditions, the apparent k value was increased from 0.0128 to 0.136 min\(^{-1}\), the k value for TCE degradation was almost linearly increased for the nZVI/BC composite after nZVI was loaded onto BC surface (k\(_{BET}\) value of 29.7 nm derived from the Debye-Sherrer equation (D = Kλ/βcosθ), where K is the Sherrer constant (0.89), λ is the X-ray wavelength (0.15418 nm), β is the full peak width at half maximum and θ is the Bragg diffraction angle), which was in accordance with the SEM image. The broad reflection peak of BC in XRD indicated the amorphous BC, suggesting that nZVI was successfully loaded on BC surface from XRD spectrum of nZVI/BC (Fig. 1d). The BET surface areas were measured by using N\(_2\) adsorption as shown in Fig. 1e. The \(S_{BET}\) values were calculated according to the BET equation: \(S_{BET} = \frac{1}{V_{m}P_{b}} \frac{V_{m}}{P_{b}} + \frac{1}{V_{m}^{2}}\), where \(V\) is the volume of nitrogen adsorbed per gram, \(V_{m}\) is the monolayer capacity and \(C\) is related to the heat of adsorption. From the results, the \(S_{BET}\) value of bare nZVI was 26.61 m\(^2\) g\(^{-1}\), and was increased to 184.91 m\(^2\) g\(^{-1}\) for the nZVI/BC composite after nZVI was loaded onto BC surface (\(S_{BET}\) value of 205.35 m\(^2\) g\(^{-1}\)). In the FTIR spectrum, the band at about 3400 cm\(^{-1}\) was belonged to the vibration of hydroxyl groups (\(-OH\)). The signal at 1590 cm\(^{-1}\) was ascribed to C=O stretching vibration, the peak at 1100 cm\(^{-1}\) was corresponded to the vibration of aromatic C=H\(^{11}\). The weak adsorption in nZVI/BC spectrum at 561 cm\(^{-1}\) was observed in the Fig. 1f, indicating the Fe−O bond formed between BC and nZVI\(^{21}\).

\[
Fe^{2+} + OH^{-} \rightarrow Fe^{3+} + OH^{-} \quad (4)
\]
In consideration of the effect of H$_2$O$_2$ concentration, the $k$ values were increased quickly from 0.033 min$^{-1}$ to 0.136 min$^{-1}$ as H$_2$O$_2$ concentrations were increased from 0.33 mmol L$^{-1}$ to 1.50 mmol L$^{-1}$. H$_2$O$_2$ is the precursor for -OH generation, relative high H$_2$O$_2$ concentration induced more -OH radicals accounted for TCE degradation, and hence the increased $k$ value was obtained. When the concentration of H$_2$O$_2$ exceeded 1.50 mmol L$^{-1}$, the $k$ value was decreased due to the reaction between -OH and excessive H$_2$O$_2$ (Eq. 5)$^{8,25}$. Therefore, the nZVI/BC dosage and the initial H$_2$O$_2$ concentration were fixed to be 1.13 g L$^{-1}$ and 1.50 mmol L$^{-1}$ respectively for the degradation of 0.10 mmol L$^{-1}$ TCE.

Figure 2d showed the effect of the initial solution pH on TCE degradation in the presence of nZVI/BC and H$_2$O$_2$. The ability of nZVI/BC to activate H$_2$O$_2$ was decreased with the increase of the initial solution pH. However, the $k$ value of 0.059 min$^{-1}$ was observed when the solution pH was as high as 10.0, which indicated that the nZVI/BC-H$_2$O$_2$ system could be effective even in alkaline pH conditions with no adjustment of the pH value being needed for the effective TCE degradation.

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

(5)
TCE mineralization and the stoichiometry efficiency of utilization of H$_2$O$_2$. TOC analyzer was used to evaluate the mineralization of TCE in the presence of H$_2$O$_2$ activated by nZVI/BC. The degradation of TCE was monitored, and the stoichiometry efficiency of utilization of H$_2$O$_2$ was calculated. In accordance with Eq. 6, three moles H$_2$O$_2$ will be consumed to obtain the complete mineralization of one mole TCE in theory. The stoichiometry efficiency of utilization of H$_2$O$_2$ ($\eta$) was the ratio of the amount of H$_2$O$_2$ consumed for the TCE degradation ($\Delta[D[H_2O_2]]_{\text{degradation}}$) to the total amount of the H$_2$O$_2$ decomposed in the reaction ($\Delta[D[H_2O_2]]_{\text{decomposition}}$) in accordance with Eq. 7. The value of $\Delta[D[H_2O_2]]_{\text{degradation}}$ was calculated by measuring the TOC change in the TCE solution. The amount of $\Delta[D[H_2O_2]]_{\text{decomposition}}$ at different reaction time was measured as shown in Fig. 3a.

$$C_2HCl_3 + 3H_2O_2 \rightarrow 2CO_2 + 2H_2O + 3HCl$$ (6)

$$\eta = \frac{\Delta[D[H_2O_2]]_{\text{degradation}}}{\Delta[D[H_2O_2]]_{\text{decomposition}}}$$ (7)

As shown in Fig. 3b in the presence of 1.50 mmol L$^{-1}$ H$_2$O$_2$, the TOC removal after 30 min was 5.1%, 32.6% and 78.2% with the addition of BC, nZVI and nZVI/BC, corresponding to the TCE degradation efficiencies of 6.5%, 39.0% and 98.9% respectively from GC results (Fig. 2a), respectively. The total amount of the H$_2$O$_2$ decomposed in the reaction in BC-H$_2$O$_2$-TCE, nZVI-H$_2$O$_2$-TCE and nZVI/BC-H$_2$O$_2$-TCE systems were 1.76, 12.91 and 15.84 $\mu$mol respectively. Therefore, the calculated efficiencies for the utilization of H$_2$O$_2$ was 48.7%, 33.3% and 65.2% in the above three systems, respectively. The TOC removal and the efficiency for the utilization of H$_2$O$_2$ in nZVI/BC-H$_2$O$_2$-TCE system were consistently higher than those for BC-H$_2$O$_2$-TCE and nZVI-H$_2$O$_2$-TCE systems indicating the superior activation property of nZVI/BC for H$_2$O$_2$ after nZVI was loaded on BC surface.

Determination of free radicals. Based on previous studies, reactive oxygen species (ROSs, such as $\cdot$OH radicals and O$_2$-$\cdot$/HO$_2$ radicals) were generated from the decomposition of H$_2$O$_2$ in homogeneous Fenton reactions at acidic and neutral conditions. In addition, high valent iron (Fe$^{IV}=O$) was also proposed in heterogeneous Fenton-like reaction during the activation of H$_2$O$_2$ by zero-valent iron under alkaline conditions. To ascertain the H$_2$O$_2$ activation mechanism, the involved ROSs in nZVI-H$_2$O$_2$, BC-H$_2$O$_2$, and nZVI/BC-H$_2$O$_2$ systems were monitored by using both DMPO spin trap ESR measurement and coumarin based fluorescent probe technology.
As shown in Fig. 4a, no signals were observed in the presence of H$_2$O$_2$. The measured ESR spectra in the three systems mentioned above illustrated the four-fold characteristic peak with an intensity ratio of 1:2:2:1, which were in accordance with the pattern of typical DMPO-∙OH adduct\textsuperscript{33}. Possibly due to the weak activation ability of BC and high adsorption of DMPO-∙OH adduct by BC in BC-H$_2$O$_2$ system\textsuperscript{17}, relative low concentration of DMPO-∙OH adduct was detected in aqueous solution.

The intensity of DMPO-∙OH adduct in the nZVI/BC-H$_2$O$_2$ system was much higher than that in the nZVI-H$_2$O$_2$ system, indicating more ∙OH radicals being generated. In addition, due to the instability of the O$_2$∙−/HO$_2$∙ radicals in the solution, six-fold characteristic peak of the O$_2$∙−/HO$_2$∙ radicals adduct by using dimethyl sulfoxide as solvent was measured\textsuperscript{34}, with no signal being detected (data were not shown). These results suggested that ∙OH radicals were the main ROSs generated from the decomposition of H$_2$O$_2$ responsible for TCE degradation. Coumarin based fluorescent probe technology was used to measure the generation of ∙OH radicals. As illustrated in Fig. 4b, the fluorescence intensities were increased quickly in the first few minutes in both nZVI/BC-H$_2$O$_2$ and nZVI-H$_2$O$_2$ systems, indicating the fast generation of ∙OH radicals. The fluorescence intensity in the nZVI/BC-H$_2$O$_2$ system was consistently higher than that in the nZVI-H$_2$O$_2$ system, hinting the excellent property of nZVI/BC for H$_2$O$_2$ activation. The data obtained here was well coincided with ESR results.

**Discussion on reaction mechanism.** nZVI particles could be oxidized to Fe$^{2+}$ under anaerobic or aerobic conditions, and it is known that homogeneous Fe$^{2+}$ plays a critical role in the activation of H$_2$O$_2$ to generate ∙OH radicals\textsuperscript{35,36}. Thus, the dissolved Fe$^{2+}$ and Fe$^{3+}$ concentrations in the presence of nZVI/BC with and without H$_2$O$_2$ were measured after reaction, respectively. As shown in Fig. 5a, the concentrations of Fe$^{2+}$ and Fe$^{3+}$ were 0.73 and 3.15 mg L$^{-1}$ respectively with only the nZVI/BC in aqueous solution. However, in the nZVI/BC-H$_2$O$_2$ system, the concentrations of Fe$^{2+}$ and Fe$^{3+}$ were 7.70 and 45.59 mg L$^{-1}$ respectively, being much higher than those in the

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**Figure 3.** (a) H$_2$O$_2$ consumption and (b) TOC removal in nZVI-H$_2$O$_2$, BC-H$_2$O$_2$ and nZVI/BC-H$_2$O$_2$ systems.

**Figure 4.** (a) DMPO spin-trapping ESR spectra of ∙OH radicals and (b) emission spectra intensity of coumarin adduct (excited at 346 nm, and detected at 456 nm) in the systems of H$_2$O$_2$, nZVI-H$_2$O$_2$, BC-H$_2$O$_2$ and nZVI/BC-H$_2$O$_2$. Reaction conditions: the concentration of nZVI itself or in nZVI/BC composite was 0.19 g L$^{-1}$, the concentration of nZVI/BC was 1.13 g L$^{-1}$, the dosage of BC was 0.94 g L$^{-1}$, the concentration of H$_2$O$_2$ was 1.50 mmol L$^{-1}$, the concentration of TCE was 0.10 mmol L$^{-1}$, and the initial pH was 6.2.
The results indicated that the oxidation of nZVI to Fe$^{2+}$ was occurred initially, and the dissolved Fe$^{2+}$ directly activated H$_2$O$_2$ to generate ∙OH radicals subsequently. The consumption of Fe$^{2+}$ for H$_2$O$_2$ activation accelerated nZVI transformation and Fe$^{3+}$ formation in accordance with Eq. 3.

In the BC-H$_2$O$_2$ system, the degradation efficiency of TCE was 6.5%, indicating that BC has also acted as an electron-transfer mediator to activate H$_2$O$_2$. BC characteristics of porosity, specific surface area, surface inertness and surface functional groups might significantly affect the catalytic activity for H$_2$O$_2$ decomposition$^{37,38}$. XPS spectra of nZVI/BC were measured to better understand the roles of BC in the activation of H$_2$O$_2$ before and after the reaction. As illustrated in Fig. 5b, the peaks of C (1 s) at 284.5, 286.5 and 289.0 eV were attributed to C–C, C–OH and COOH, respectively. From the spectra, the proportion of C–C, C–OH and COOH peaks were 71.8%, 21.7% and 6.5% respectively for fresh nZVI/BC before the reaction. However, the proportion of the three peaks mentioned above were 70.0%, 17.3% and 12.7% after the H$_2$O$_2$ activation. The decrease in surface bound C–OH proportion of BC after the reaction suggested that BC might act as an electron transfer medium participated in the H$_2$O$_2$ activation$^{39,40}$, and the increase in COOH was due to the reaction between C–OH and H$_2$O$_2$ in accordance with Eq. 8. By releasing organic radicals of CO$^\cdot$ from C–OH through single electron transfer process, ∙OH radicals were generated (Eq. 9).

$$C{\text{–OH}} + H_2O_2 \rightarrow COOH + H_2O \quad (8)$$

$$C{\text{–OH}} + H_2O_2 \rightarrow CO^\cdot + ∙OH + H_2O \quad (9)$$

As derived from the above discussions, the activation mechanism of H$_2$O$_2$ in the presence of nZVI/BC was proposed in Fig. 6. Firstly, nZVI particles were oxidized to Fe$^{2+}$, and the redox reaction of Fe$^{2+}$/Fe$^{3+}$ was accounted for the generation of ∙OH radicals. Secondly, as an electron transfer mediator to H$_2$O$_2$, BC surface bound C–OH decomposed H$_2$O$_2$ into ∙OH radicals by releasing CO$^\cdot$ radicals. Once ∙OH radicals having been
produced, it would rapidly react with TCE. GC-MS was utilized to monitor the process of TCE degradation, however, no intermediate products was detected except for the undegraded TCE. Though TCE would be transformed into low molecule weight organic acids with the effect of ∙OH radicals initially, only CO₂ and Cl⁻ were measured during the oxidative process in the nZVI/BC-H₂O₂-TCE system.

Conclusions
The nZVI/BC composite was successfully synthesized and characterized as an efficient H₂O₂ activator for the degradation of TCE. nZVI loaded on lamellarly structured BC surface prevented its agglomeration behaviour, which significantly enhanced the generation of ∙OH radicals. The redox effect of Fe²⁺/Fe³⁺ and the single electron transfer process from BC surface bound C–OH to H₂O₂ were accounted for the promoted generation of ∙OH radicals, leading to rapid TCE degradation. The enhanced Fenton-like activation of H₂O₂ using nZVI/BC presents the great potential for TCE degradation in aqueous solution.

Materials and Methods
Chemicals and materials. FeSO₄·7H₂O, NaBH₄, H₂O₂ (30%, w/w), 5,5-Dimethyl-1-pyrrolidine N-oxide (DMPO) and trichloroethylene (TCE, 99.0%) were purchased from Sinopharm Chemical Reagent Co. Ltd. HCl and NaOH were obtained from Shanghai Lingfeng Chemical Reagent Co. Ltd. All chemicals used in this work were used as received without further purification.

Synthesis of nZVI/BC composite. Biochars were prepared by the pyrolysis of rice hull collected locally. Firstly, the rice hull was washed with ultrapure water and dried in oven at 80 °C. Secondly, the dried rice hull was pyrolyzed in muffle furnace under oxygen limited condition at a temperature of 350 °C for 6 h. Finally, the BC were obtained after treating with 1.0 mol L⁻¹ HCl and washed with ultrapure water.

For the synthesis of nZVI/BC composite, 3.78 g biochar was dispersed in 250 mL oxygen free ultrapure water. Then, 0.0135 mol FeSO₄·7H₂O was added at pH 5.0. With mechanical stirring and ultrasonic, nZVI was formed and loaded on the surface of BC by addition of 100 mL 0.27 mol L⁻¹ NaBH₄ at a velocity of 20 mL min⁻¹. Following 2 h reaction, the nZVI/BC composite were separated and washed with deoxygenized ultrapure water, and finally vacuum dried. The preparation of nZVI was described as Eq. 10, and the schematic for the preparation of nZVI/BC composite was shown in Fig. 7.

![Figure 7. The schematic for the preparation of nZVI/BC composite.](image)

Characterization. X-ray diffraction (XRD, X’TRA, Swiss) analysis was conducted to determine the crystal structure and crystallinity of the prepared composites using Cu Kα radiation with 2θ collection range from 10° to 80°. X-ray photoelectron spectra (XPS) were recorded on Axis Ultra spectrometer (Kratos) using Al Kα radiation excitation source. The infrared spectrum was recorded on Fourier transform infrared spectroscopy (FT-IR) spectra from 400 to 4000 cm⁻¹ (NICOLET iN10 MX, Thermo Scientific, USA). The morphology of the composites were observed using scanning electron microscope (SEM, Hitachi S-4800, Japan) with 10 kV accelerating voltage, and the Brunauer-Emmett-Teller (BET) specific surface areas (S_BET) were measured with ASAP 2020M+C (Micromeritics, USA) from N₂ adsorption method.
Procedures and analysis. In a typical sacrificial batch experiment, a 20 mL cylindrical glass vessel was fully filled with 0.10 mmol L\(^{-1}\) TCE, appropriate amounts of H\(_2\)O\(_2\) and activators (i.e., nZVI, BC or nZVI/BC), and the vessel was tightly sealed with Teflon reaction head successively. Then, the reaction was initiated in a rotary shaker at 298 K and 150 rpm. Control test was also carried out under the same condition without H\(_2\)O\(_2\) and activators. Samples were taken at the desired reaction time intervals and filtered through 0.2 \(\mu\)m membrane prior to the analysis. Samples were conducted in triplicate and the mean value was obtained.

The concentration of TCE was analyzed by headspace Gas Chromatograph Mass Spectrometer (GC-MS, Agilent 7890A and 5975C) using DB-624 chromatographic column (30.0 m × 0.25 mm × 1.4μm). Dissolved ferrous ion was quantified through 1,10-Phenanthroline monohydrate Spectrophotometry by using a Cary 50 UV-vis spectrophotometer (Varian Cary 50, USA). The concentration of H\(_2\)O\(_2\) was measured with the DPD method using UV-vis spectrophotometer (Varian Cary 50, USA). The generated radical species was detected with electron spin resonance spectrometer (Bruker ESR 300E, Germany) with microwave bridge (receiver gain, 1 × 10\(^5\)); modulation amplitude, 2 Gauss; microwave power, 10 mW; modulation frequency, 100 kHz) using DMPO as radical spin-trapping reagent, and fluorescence spectra were measured on fluorescence spectrophotometer (Jasco FP-6200, Japan). Total organic carbon (TOC) was recorded with a multi N/C model TOC analyzer (Analytik Jena, multi N/C 2100, Germany).

References
1. Lu, R. et al. Determination of chlorinated hydrocarbons in water using highly sensitive mid-infrared sensor technology. *Scientific Reports* 3, 2525 (2013).
2. Yan, J. C. et al. Degradation of trichloroethylene by activated persulfate using a reduced graphene oxide supported magnetite nanoparticle. *Chem. Eng. J.* 295, 309–316 (2016).
3. Lee, Y. & Lee, W. Degradation of trichloroethylene by Fe(II) chelated with cross-linked chitosan in a modified Fenton reaction. *J. Hazard. Mater.* 178, 187–193 (2010).
4. US Environmental Protection Agency. *Edition of the Drinking Water Standards and Health Advisories. EPA 822-R-09-011.* EPA Office of Water: Washington DC (2009).
5. Yan, J. C. et al. Degradation of sulfamonomethoxine with Fe\(_3\)O\(_4\) magnetic nanoparticles as heterogeneous activator of persulfate. *J. Hazard. Mater.* 186, 1398–1404 (2011).
6. Andreozzi, R. et al. Advanced oxidation processes (AOP) for water purification and recovery. *Catal. Today* 53, 51–59 (1999).
7. Pestorsky, O. & Bakac, A. Aqueous ferryl(IV) ion: kinetics of oxygen atom transfer to substrates and o xo exchange with solvent water. *Inorg. Chem.* 45, 814–820 (2006).
8. Yan, J. C. et al. Efficient degradation of organic pollutants with ferrous hydroxide colloids as heterogeneous Fenton-like activator of hydrogen peroxide. *Chemosphere* 87, 111–117 (2012).
9. Nie, Y. et al. Enhanced Fenton-like degradation of refractory organic compounds by surface complex formation of LaFeO\(_3\) and H\(_2\)O\(_2\). *J. Hazard. Mater.* 294, 195–200 (2015).
10. Bremner, D. H. et al. Phenol degradation using hydroxyl radicals generated from zero-valent iron and hydrogen peroxide. *Appl. Catal. B-Environ.* 63, 15–19 (2006).
11. Segura, Y., Martínez, F. & Melero, J. A. Effective pharmaceutical wastewater degradation by Fenton oxidation with zero-valent iron. *Appl. Catal. B-Environ.* 136–137, 64–69 (2013).
12. Xu, L. J. & Wang, J. L. A heterogeneous Fenton-like system with nanoparticulate zero-valent iron for removal of 4-chloro-3-methyl phenol. *J. Hazard. Mater.* 186, 250–264 (2011).
13. Fu, P., Dionysiou, D. D. & Liu, H. The use of zero-valent iron for groundwater remediation and wastewater treatment: a review. *J. Hazard. Mater.* 267, 194–205 (2014).
14. Mackenzie, K. et al. Carbo-Iron - An Fe/AC composite - As alternative to nano-iron for groundwater treatment. *Water Res.* 46, 3817–3826 (2012).
15. González-Bahamón, L. F. et al. New Fe-immobilized natural bentonite plate used as photo-Fenton catalyst for organic pollutant degradation. *Chemosphere* 82, 1185–1189 (2011).
16. Luo, S. et al. Synthesis of reactive nanoscale zero valent iron using rectorite supports and its application for Orange II removal. *Chem. Eng. J.* 223, 1–7 (2013).
17. Yan, J. C. et al. Biocatal supported nanoscale zerovalent iron composite used as persulfate activator for removing trichloroethylene. *Bioresour. Technol.* 175, 269–274 (2015).
18. Fang, G. D. et al. New Insights into the mechanism of the catalytic decomposition of hydrogen peroxide by activated carbon: implications for degradation of diethyl phthalate. *Ind. Eng. Chem. Res.* 53, 19925–19933 (2014).
19. Hoch, L. B. et al. Carbothermal synthesis of carbon-supported nanoscale zero-valent iron particles for the remediation of hexavalent chromium. *Environ. Sci. Technol.* 42, 2600–2605 (2008).
20. Liu, Z. G., Zhang, F. S. & Wu, J. Z. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. *Fuel* 89, 510–514 (2010).
21. Kan, E. & Huling, S. G. Effects of temperature and acidic pretreatment on Fenton-driven oxidation of MTBE-spent Granular activated carbon. *Environ. Sci. Technol.* 43, 1493–1499 (2009).
22. Duarte, F., Maldonado-Hódar, F. J. & Madera, L. M. New insight about orange II elimination by characterization of spent activated carbon/Fe-Fenton-like catalysts. *Appl. Catal. B-Environ.* 129, 264–272 (2013).
23. Moro, J. M. R. et al. Kinetics of the chemical reduction of nitrate by zero valent iron. *Chemosphere* 74, 804–809 (2009).
24. Zhou, T. et al. Oxidation of 4-chlorophenol in a heterogeneous zero valent iron/H\(_2\)O\(_2\) Fenton system: kinetic, pathway and effect factors. *Sep. Purif. Technol.* 62, 551–558 (2008).
25. Xu, L. J. & Wang, J. L. Magnetic nanoscaled Fe\(_3\)O\(_4\)/CeO\(_2\) composite as an efficient Fenton-like heterogeneous catalyst for degradation of 4-chlorophenol. *Environ. Sci. Technol.* 46, 10145–10153 (2012).
26. Zhang, X. Y. et al. Degradation of bisphenol A by hydrogen peroxide activated with CuFeO\(_2\) microparticles as a heterogeneous Fenton-like catalyst: Efficiency, stability and mechanism. *Chem. Eng. J.* 236, 251–262 (2014).
27. Haber, F. & Weiss, J. The catalytic decomposition of hydrogen peroxide by ferrous salts. *Proc. R. Soc. Lond. Ser. A.* 147, 332–351 (1934).
28. Zhang, X. et al. Degradation of trichloroethylene in aqueous solution by calcium peroxide activated with ferrous ion. *J. Hazard. Mater.* 184, 253–260 (2010).
29. Duesterberg, C. K. & Waite, T. D. Process optimization of Fenton oxidation using kinetic modeling. *Environ. Sci. Technol.* 40, 4189–4195 (2006).
30. Song, K. et al. Role of oxidants in enhancing dewaterability of anaerobically digested sludge through Fe (II) activated oxidation processes: hydrogen peroxide versus persulfate. *Scientific Reports* 6, 24800 (2016).
31. Keenan, C. R. & Sedlak, D. L. Factors affecting the yields of oxidants from the reaction of nanoparticulate zero-valent iron and oxygen. *Environ. Sci. Technol.* **42**, 1262–1267 (2008).
32. Keenan, C. R. & Sedlak, D. L. Ligand-enhanced reactive oxidant generation by nanoparticulate zero-valent iron and oxygen. *Environ. Sci. Technol.* **42**, 6936–6941 (2008).
33. Ma, W. et al. Efficient degradation of organic pollutants by using dioxygen activated by resin-exchanged iron(II) bipyridine under visible irradiation. *Angew. Chem. Int. Ed.* **115**, 1059–1062 (2003).
34. Chen, C. et al. Effect of transition metal ions on the TiO₂-assisted photodegradation of dyes under visible irradiation: A probe for the interfacial electron transfer process and reaction mechanism. *J. Phys. Chem. B* **106**, 318–324 (2001).
35. Kim, J. Y. et al. Inactivation of MS2 coliphage by Fenton’s reagent. *Water Res.* **44**, 2647–2653 (2010).
36. Nieto-Juarez, J. I. et al. Inactivation of MS2 coliphage in Fenton and Fenton-like systems: role of transition metals, hydrogen peroxide and sunlight. *Environ. Sci. Technol.* **44**, 3351–3356 (2010).
37. Rey, A. et al. Influence of the structural and surface characteristics of activated carbon on the catalytic decomposition of hydrogen peroxide. *Appl. Catal. A: Gen.* **402**, 146–155 (2011).
38. Ribeiro, R. S. et al. The influence of structure and surface chemistry of carbon materials on the decomposition of hydrogen peroxide. *Carbon* **62**, 97–108 (2013).
39. Domínguez, C. M. et al. Highly efficient application of activated carbon as catalyst for wet peroxide oxidation. *Appl. Catal. B-Environ.* **140-141**, 663–670 (2013).
40. Domínguez, C. M. et al. The use of cyclic voltammetry to assess the activity of carbon materials for hydrogen peroxide decomposition. *Carbon* **60**, 76–83 (2013).
41. Fang, G. D. et al. Key role of persistent free radicals in hydrogen peroxide activation by biochar: Implications to organic contaminant degradation. *Environ. Sci. Technol.* **48**, 1902–1910 (2014).

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**Author Contributions**
J.Y. conceived and conducted the experiments, as well as wrote the manuscript. L.Q. and W.G. analyzed the data, Y.C. and D.O. discussed the results, and M.C. reviewed and commented on the manuscript.

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