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Degradation of 2-Chlorophenol in Aqueous Solutions Using Persulfate Activated by Biochar Supported Sulfide-Modified Nanoscale Zero-Valent Iron: Performance and Mechanisms

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Abstract: In this work, soybean biochar-supported sulfide-modified nanoscale zero-valent iron (BC@S-nZVI) was synthesized and used to activate persulfate (PS) to degrade 2-chlorophenol (2-CP) in aqueous solutions. Batch experiments were carried out to investigate the degradation effects under different conditions, including initial mass ratios among 2-CP, PS, and BC@S-nZVI, initial pH values, temperature, and anions. The results showed that the mass ratio of PS to 2-CP equal to 70 and the mass ratio of BC@S-nZVI to PS equal to 0.4 were the optimum mass ratios in the degradation system. The degradation efficiency of 2-CP was higher under acidic and alkaline conditions than the neutral condition, and the effect was best at a pH of 3; meanwhile, it increased with the increase in temperature. Moreover, the degradation rate was restrained with the addition of Cl^- , promoted with the addition of NO_3^- and CO_3^{2-} . Both free radical and material functions played leading roles in the degradation of 2-CP, and the stability of BC@S-nZVI was better than nZVI and S-nZVI. The experimental results showed that it was promising to remove 2-CP and other organic pollutants from groundwater by PS activated with BC@S-nZVI.

Keywords: biochar-supported sulfide-modified nanoscale zero-valent iron; persulfate; 2-chlorophenol; degradation effect; free radical

1. Introduction

Chlorophenols are widely used in the pesticides and manufacturing industries, and their contamination of groundwater has been a concern because of their toxicity and carcinogenicity [1]. Among them, 2-CP is regarded as one of the most typical chlorophenols in soil and groundwater and has been included as a priority pollutant by the United States Environmental Protection Agency and the Ministry of Ecology and Environment of the People's Republic of China [2,3]. In some paper mills or pesticide-contaminated groundwater, the concentration of 2-CP is as high as 12 mg/L, but Chinese urban water quality standards stipulate that the total amount of chlorophenols must not exceed 0.01 mg/L [3]. Therefore, it is urgently necessary to explore efficient methods for 2-CP degradation in the remediation of groundwater.

The traditional methods of chlorophenols removal include biological filtration, photocatalytic processes, membrane filtration, and adsorption processes [4,5]. However, the biodegradability of chlorophenol is very low, and the removal of chlorophenol by adsorption could induce second pollution [4]. The advanced oxidation processes (AOPs), including ozone (O₃), persulfate (PS) activation, hydrogen peroxide activation, and peracetic acid activation, have been confirmed as highly promising methods for degrading toxic and recalcitrant organic compounds [6–9]. Compared to H_2O_2 , peracetic acid, and



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). O₃, persulfate is more stable and persisted during transport in the subsurface [10] and has been widely applied to remove organic contaminants in wastewater and in situ chemical oxidation (ISCO) remediation of groundwater [11,12]. Under mild conditions, PS can be activated via photolysis (UV and visible), alkali, heat, electron beam, and transition metals, forming the hydroxyl radical (HO•) and sulfate radical anion (SO₄•⁻) [13–16]. SO₄•⁻ has a high reduction potential (E₀ = 2.5–3.1 V), and is nonselective compared with HO•, and it can quickly mineralize most of the organic pollutants into inorganic compounds [17,18].

Transition metals have been widely applied to activate PS because of their effectiveness and cost-effectiveness [19]. Nanoscale zero-valent iron (nZVI) has also been used to activate PS for the removal of refractory organic pollutants such as antibiotics and organophosphorus pesticides [20,21]. To overcome the agglomeration effect of nanomaterials, various porous media such as coal fly ash [22], clay minerals [23], and carbon-based materials [24] have been applied as supports of nZVI or S-nZVI to boost their reactivity. Biochar (BC) is considered one of the best carriers for nZVI due to its low cost, porous structure, and high surface area [7,25]. However, the BC would lower the degradation efficiency of nZVI due to the slow electron transfer rate and passivation induced by biochar [26,27], and different kinds of carbon matrices also have significant performance differences [28]. Therefore, the sulfide-modified method has been used to improve the removal efficiency, which ascribes to the enhancements of hydrophobicity of nZVI, the production of HO•, and salt resistance [29,30]. The presence of sulfur could also regulate the morphology of S-mZVI (sulfide-modified millimeter-scale zero-valent iron) with a dispersed and spherical shape, and it could improve the activation performance of PS [31]. The feasibility and mechanism of sulfide-modified nanoscale zero-valent iron supported on biochar (BC@S-nZVI) for the removal of trichloroethylene (TCE) in groundwater remediation is investigated, and the results showed that BC@S-nZVI, combining the high adsorption capacity of BC and the high reductive capacity of S-nZVI, had much better performance than the single S-nZVI or BC [32].

Li et al. [33] found that the removal efficiency of 2,4-dichlorophenol using the nZVI/PS system was better than those of the Fe²⁺/PS and nFe₃O₄/PS; however, nZVI catalysis has low PDS activation efficiency in the process of 2-CP degradation because of its aggregation, passivation, and poor electron transfer [34]. The research on the efficiency and mechanism of 2-CP removal in the aqueous solutions using persulfate activated by biochar-supported sulfide-modified nanoscale zero-valent iron is also limited. Hence, soybean residue biocharsupported S-nZVI (BC@S-nZVI) synthesized in a two-step method has been developed to activate PS for the degradation of 2-CP in an aqueous solution in this study. Soybean residue was chosen as a raw material for the synthesis of biochar because it is a very common agricultural waste in Hefei City, it is produced along with soybean products processing. According to statistics, in 2019, the cultivation areas for soybean in the Hefei area reached 85,000 hectares, and the soybean residue produced in the production of soybean products accounted for 16~25% of the whole bean quality [35,36]. The effects of initial concentration values of 2-CP and PS, BC@S-nZVI doses, pH values, reaction temperature, and some anion concentration values on the degradation efficiency were also investigated. Furthermore, the scavengers of radical and electron spin resonance (ESR) have been used to explore the degradation mechanism and the contribution of each chemical factor in the reaction system under optimum mass ratios of PS and BC@S-nZVI.

2. Materials and Methods

2.1. Chemicals and Reagents

2-chlorophenol (2-CP, C₆H₅OCl \geq 98.5%), iron nitrate nonahydrate (Fe(NO₃)₃•9H₂O \geq 98.5%), sodium sulfide (Na₂S•9H₂O \geq 98.5%), and tert-butyl alcohol (TBA, C₄H₁₀O \geq 98.0%) were chemically pure reagents, purchased from Sinopharm Chemical Reagent Co., Ltd., Shanghai, China. Sodium persulfate (PS, Na₂S₂O₈ \geq 99.0%) and potassium borohydride (PBH, KBH₄ \geq 99.0%) were analytical reagents, bought from Shanghai Macklin Biochemical Co., Ltd., Shanghai, China. Hydrochloric acid (HCl, 36.0~38.0%), sodium hydroxide (NaOH \geq 99.0%),

sodium chloride (NaCl \geq 99.5%), sodium carbonate (Na₂CO₃ \geq 99.5%), and sodium nitrate (NaNO₃ \geq 99.5%) were analytical reagents, obtained from Tianjin Kermel Chemical Reagent Co., Ltd., Tianjin, China. Methanol (MeOH, CH₄O \geq 99.9%) and dichloromethane (DCM, CH₂Cl₂ \geq 99.9%) were guarantee reagents, purchased from Shanghai Weston Trading Co., Ltd., Shanghai, China. The ultra-pure water for the preparation of aqueous solutions in all experiments of this study was produced by Merck Millipore Synergy UV, Shanghai, China.

2.2. Synthesis of BC@S-nZVI

Soybean residue was chosen as the material for preparing biochar because it is a common waste in Hefei. It was collected from a soybean processing factory and dried under 105 °C in the air-dry oven for 24 h before being used. The dried soybean residue was then placed in a tube-heating furnace with the model OTF-1200X. The temperature was raised from 0 to 800 °C in one hour at a heating rate of 14 °C/min, maintained for half an hour, and dropped to room temperature in four hours with nitrogen flushing in the whole process. After cooling down, the obtained BC was ground and passed through a 50-mesh sieve.

BC@S-nZVI was synthesized in a two-step method. First, 3.472 g BC was added to a 0.31 M Fe(NO₃)₃ solution of 200 mL, stirring constantly for 30 min with the injection of nitrogen into the solution, and then 200 mL of a 3.1 M PBH solution was added to the suspension liquid dropwise. After stirring for 10 min, 110 mL of a 0.14 M Na₂S solution was added to the mixed solution and treated by ultrasound for 30 min. The solution was separated from the solid and liquid, and the filter residue was cleaned with ultra-pure water until the conductivity dropped below 50 μ S/cm. Lastly, the material was dried in a freeze dryer and obtained BC@S-nZVI with mass ratios of C and Fe, and S and Fe of 1:1 and 1:7, respectively.

2.3. Experimental Process

All reaction systems were carried out in 40 mL vials with the same volume of initial 2-CP solution with 20 mL. Then, BC@S-nZVI and PS solutions were added to the solution with different dosages but kept the total volume the same for all batches by adding ultrapure water. The vials were shaken under different setting reaction temperatures (10 °C, 30 °C, and 50 °C) at 180 rpm in the thermostatic reciprocating shaker (model of SHA-B). The samples were collected at different reaction times (10 min, 30 min, 1 h, 2 h, 4 h, 8 h, 16 h, 24 h, 48 h, and 72 h) and filtered through 0.22 mm membranes after being extracted by DCM to determine the 2-CP concentration by Gas Chromatography. The extraction process was as follows: 5 mL of the reaction solution was taken from the sample bottle and 0.2 mL of the MeOH reagent was added to stop the reaction. Then 2 drops of concentrated HCl were added to the bottle to make the solution pH value less than 2, followed by 0.5 g NaCl and 5 mL DCM reagent. The bottle was shaken at 180 rpm for 20 min, then stood for 10 min under headstand conditions. Finally, the solution of 1 mL from the lower layer was collected and transferred into a sample vial with a syringe and capped for determination.

To explore the optimal reaction conditions, the mass ratios of PS to 2-CP were 0, 10, 20, 30, 40, 50, 60, 70, and 80, the mass ratios of BC@S-nZVI to PS were 0, 0.1, 0.2, 0.3, 0.4, 0.8, 1.0, and 1.5, and the 2-CP concentration values were 20, 50, and 100 mg/L in this study. pH values were designed as 3.0, 5.0, 7.0, 9.0, and 11.0, temperature values were designed as $10 \,^{\circ}$ C, $30 \,^{\circ}$ C, and $50 \,^{\circ}$ C, and anion (including chloride ions, nitrate ions, and carbonate ions) concentrations were designed as 0, 50, 100, 200, and $500 \,$ mg/L to identify their influence on the 2-CP removal in the aqueous solutions using persulfate activated by BC@S-nZVI. Each experiment was duplicated, and the result was reported as the average of the measurements.

2.4. Analytical Methods

The surface features of the BC@S-nZVI before and after reactions were observed using a scanning electron microscope (SEM) with Energy-Dispersive Spectroscopy (EDS) (TESCAN MIRA 3 LMH FE-SEM, Oberkochen, Germany) at the University of Science and Technology of China. The concentration of 2-CP was determined by Gas Chromatography (Shimadzu Nexis GC-2030, Kyoto, Japan) in the Hefei Engineering Research Center for Soil and Groundwater Remediation. Chromatographic conditions were as follows: Column: SH-RTX-5 (30 m \times 0.32 mm \times 0.25 mm), FID detector, detector temperature: 300 °C, injection volume: 1 µL, inlet temperature: 250 °C, splitter ratio: 2:1, column flow rate: 1.5 mL /min, heating procedure: keeping 50 °C for 5 min, then increased to 140 °C by a heating rate of 10 °C/min, the detection limit of 2-CP was 5 µg/L, and the recovery of 2-CP was better than 92%. The pH and the conductivity of the aqueous solution were measured by PHBJ-260 pH and DDS-307 conductivity meter.

The active substances HO• and SO4•[–] generated in the systems were identified by electron spin resonance (ESR; JES-FA200, JEOL, Beijing, China) at the University of Science and Technology of China. The ESR spectra were recorded at 20 °C equipped with a circulating water system to maintain the temperature, and the ESR spectrometer was operated at an X band frequency of 9.84 GHz, while the radical trapping agent was 5, 5-Dimethyl-1-pyrrolin-N-oxide (DMPO). Spectrometer parameters were as follows: Sweep width of 100 G, center field of 3505 G, sweep time of 30 or 60 s, modulation amplitude of 1 G, modulation frequency of 100 kHz, receiver gain of 30 dB, microwave attention of 25 dB, convention time of 12.64 ms, and time constant of 5.12 ms.

3. Results and Discussion

3.1. Characteristic of BC@S-nZVI Composite

The morphology, shape, and elementary composition of BC and BC@S-nZVI before and after the reaction were analyzed using SEM with Energy-Dispersive Spectroscopy (EDS), the results of which are shown in Figure 1. Carbon and oxygen are the most abundant elements in biochar (Figure 1a), and it has a smooth loading surface and provides a framework for the S-nZVI (Figure 1d). The iron and sulfur elements were loaded onto the surface of biochar during the preparation of BC@S-nZVI (Figure 1b), and the S-nZVI nanoparticles were tightly packed together on the BC and almost covered its surface completely (Figure 1e). Moreover, the proportion of iron and sulfur elements decreased after the reaction with PS (Figure 1c), indicating that iron and sulfur could be dissolved during the activation reaction of PS. It was verified by the appearance of the honeycomb structure of the BC surface (Figure 1f). This illustrated that BC provided vast binding sites and effectively prevented the agglomeration of S-nZVI and was more conducive to the S-nZVI activation of PS to produce free radicals.



Figure 1. EDS and SEM images of BC (**a**,**d**), BC@S-nZVI before reaction (**b**,**e**), and BC@S-nZVI after reaction (**c**,**f**). The magnifications of the SEM images are all 10.00 k×.

3.2. Degradation Analyses of 2-CP in Different Conditions and Systems

The dosages of oxidant and catalyst were the basis of the research on the degradation of 2-CP in the BC@S-nZVI-activated PS system [13,20,29–31]. The effect results with different mass ratios of PS to 2-CP and BC@S-nZVI to PS on the degradation of 2-CP are shown in Figure 2. The influence of the mass ratio of PS to 2-CP is shown in Figure 2a. With the same catalyst mass, as the mass ratio of PS to 2-CP changes from 0 to 70, the removal rate of 2-CP increases from 9.2% to 100.0% within 72 h, indicating that a higher PS dosage was beneficial to the degradation of 2-CP. The radical was generated due to the activation of PS by BC@S-nZVI (see Equations (1)–(3)), which means that increasing the dosage of PS would promote the production of oxidative species, leading to higher 2-CP removal rates. However, with the continued increase in the PS dose, the removal rate of 2-CP decreased with a PS-to-2-CP mass ratio of 80. This can be attributed to the consumption of SO₄•⁻ by the reaction with each other or PS (see Equations (4) and (5)) [37]. Therefore, a PS-to-2-CP mass ratio of 70 was selected as the optimum dosage of PS for further experimentation.



Figure 2. Effect of different activation systems on the degradation of 2-CP: (a) Different mass concentrations of PS, (b) different mass concentrations of BC@S-nZVI. Reaction conditions: [2-CP] = 20 mg/L of 20 mL, T = 30 °C, pH = 5 ± 0.2.

The influence of the BC@S-nZVI-to-PS mass ratio on the degradation of 2-CP is shown in Figure 2b. With the same PS concentration, as the mass ratio of BC@S-nZVI to PS varied

from 0 to 0.4, the removal rate of 2-CP increased from 22.3% to 100.0% within 72 h, and when continuously increasing the mass ratio of BC@S-nZVI to PS to 1.5, the complete degradation time of 2-CP was reduced to less than 24 h. To explore the influence factors of BC@S-nZVI-activated PS, the initial efficiency of the reaction system should not be set too high; therefore, the mass ratio of BC@S-nZVI to PS was set to 0.4 in this study.

$$Fe^{0} + S_{2}O_{8}^{2-} + 2H_{2}O \rightarrow Fe^{2+} + 2HO \bullet + 2SO_{4}^{2-} + 2H^{+}$$
 (1)

$$2Fe^{0} + O_{2} + 2H_{2}O \rightarrow 2Fe^{2+} + 4OH^{-}$$
⁽²⁾

$$Fe^{2+} + S_2O_8^{2-} \to Fe^{3+} + SO_4^{2-} + SO_4^{-} \bullet^-$$
 (3)

$$SO_4 \bullet^- + SO_4 \bullet^- \to S_2 O_8^{2-} \tag{4}$$

$$SO_4 \bullet^- + S_2 O_8^{2-} \to SO_4^{2-} + S_2 O_8 \bullet^-$$
 (5)

The degradation effects of eight various reaction systems with the same condition are compared in Figure 3. Within 48 h, the 2-CP removal rates of the BC@S-nZVI/PS, BC@S-nZVI, BC@nZVI/PS, BC@nZVI, S-nZVI/PS, S-nZVI, nZVI/PS, and nZVI systems were 99.2%, 8.6%, 54.0%, 4.4%, 97.8%, 3.5%, 27.6%, and 6.6%, respectively. Almost no 2-CP was removed within 72 h under the pure BC@S-nZVI, BC@nZVI, S-nZVI, and nZVI system, and the 2-CP removal rates are less than 66.3% and 50.5% within 72 h under the BC@nZVI/PS and nZVI/PS system. Compared to the previous reaction system, the degradation efficiency of 2-CP was significantly improved by the BC@S-nZVI/PS and S-nZVI/PS and BC@S-nZVI/PS has a higher reaction efficiency in which 2-CP was completely removed in 48 h. The above results show that the introduction of S and BC to nZVI considerably activated PS, possibly due to the increased electron transfer capacity of the BC@nZVI/PS system by the surface sulfide treatment [29,30]. Therefore, the BC@S-nZVI/PS system could be used as an advanced oxidation system to remove 2-CP for wastewater or groundwater remediation.



Figure 3. Degradation effects of various reaction systems. Reaction conditions: The mass ratio of PS to 2-CP was 70 and the mass ratio of BC@S-nZVI to PS was 0.4, T = $30 \degree$ C, pH = 5 ± 0.2 .

3.3. Factors Affecting the 2-CP Degradation in the BC@S-nZVI-Activated PS System 3.3.1. Initial Concentration

The degradation effects of different initial 2-CP concentrations are shown in Figure 4. Under the reaction conditions previously set, when the initial concentration of 2-CP increases from 20 to 100 mg/L, the concentration of PS increases from 1400 to 7000 mg/L, and the concentration of BC@S-nZVI increases from 560 to 2800 mg/L, respectively. The removal efficiency of 2-CP increases at 50 mg/L and then decreases at 100 mg/L. The possible reason is that during the process of increasing the initial concentration of 2-CP from 20 to 50 mg/L, the concentrations of the BC@S-nZVI-activated PS system also increase correspondingly, and the contact area between 2-CP and the degradation system in the unit volume of the solution increases, resulting in an increase in the degradation rate [32,33]. When the initial concentration of 2-CP continues to increase from 50 to 100 mg/L, the concentrations of the degradation system become excessive and PS consumes each other (see Equations (4) and (5)) [37], resulting in a decrease in the degradation rate. Moreover, it is evident that the BC@S-nZVI-activated PS system set in this study could be applicable even at the varied initial concentration value of 2-CP.



Figure 4. Degradation effects of different initial concentration values of 2-CP. Reaction conditions: The mass ratio of PS to 2-CP was 70 and the mass ratio of BC@S-nZVI to PS was 0.4, T = 30 °C, $pH = 5 \pm 0.2$.

3.3.2. pH and Temperature

The pH and temperature were essential factors of the chemical reaction, and batch experiments of varied pH and temperature values were carried out to explore their influence, the results of which are shown in Figure 5. The removal rate of 2-CP could achieve 100.0% at 16 h, 48 h, and 72 h with pH values of 3, 5, and 11, respectively. However, the degradation rate of 2-CP was only 64.5% for the pH value of 7. This demonstrated that the degradation of 2-CP decreased by the BC@S-nZVI-activated PS system is more efficient in acidic and alkaline conditions compared to neutral conditions. Furthermore, compared with the alkaline condition, it is obvious that the acidic condition had a more positive effect on removing 2-CP. This may indicate that acidic conditions are favorable for the transformation of PS to form $SO_4 \bullet^-$ (see Equation (6)), but under alkaline conditions, iron oxides and iron hydroxides formed on the surface of BC@S-nZVI would impede the activate reaction between BC@S-nZVI and PS via inhabited the release of Fe²⁺ and the reaction (see Equations (7) and (8)). Moreover, the activation energy required to activate PS could be

reduced under acidic conditions, resulting in the activation process being accelerated and the 2-CP degradation being enhanced [38].

$$S_2O_8^{2-} + H^+ \to SO_4 \bullet^- + SO_4^{2-} + H^+$$
 (6)

$$Fe^{3+} + 3OH^- \rightarrow Fe(OH)_3 \downarrow$$
 (7)

$$SO_4 \bullet^- + OH^- \to SO_4^{2-} + HO \bullet$$
 (8)



Figure 5. Effect of pH and temperature on the degradation of 2-CP: (a) Different values of pH. Reaction conditions: [2-CP] = 20 mg/L of 20 mL, PS = 1400 mg/L, BC@S-nZVI = 560 mg/L, T = 30 °C; (b) different values of temperature. Reaction conditions: [2-CP] = 20 mg/L of 20 mL, PS = 1400 mg/L, BC@S-nZVI = 560 mg/L, pH = 5 \pm 0.2.

The results of the influence on the degradation of 2-CP in the BC@S-nZVI/PS system of different temperatures are shown in Figure 5b, and the degradation rate of 2-CP significantly decreased when the temperature decreased from 50 °C to 10 °C. The 2-CP removal achieved 100.0% within 16 h at 50 °C, whereas the removal rate was only 23.7% at 10 °C within

72 h. This was consistent with previous reports that higher temperatures had a positive effect on the activation of PS and the degradation of contaminants [39]. The relatively low temperature of natural groundwater could limit the application of the BC@S-nZVI/PS system in the ISCO of groundwater [5].

3.3.3. Inorganic Anions of Chloride, Nitrate and Carbonate

The composition of actual wastewater was quite complex, and inorganic anions may coexist and could affect the degradation efficiency of contaminants [40]. The effect of inorganic anions Cl⁻, NO₃⁻, and CO₃²⁻ on the degradation of 2-CP in the BC@S-nZVI/PS system is shown in Figure 6. The degradation of 2-CP could achieve 100.0% without Cl⁻ in the aqueous solution within 48 h, while it was slightly restrained with the addition of Cl⁻. The 2-CP removal rate decreased to 93.0% within 72 h at a chloride concentration of 50 mg/L, while the degradation rate of 2-CP was 90.3% within 72 h with a chloride concentration of 500 mg/L. The degradation rate of 2-CP decreased with the increase in the chloride concentration. On one hand, the chloride could quench radicals acted as radical scavengers and decrease the degradation rate of 2-CP [40], and on the other hand, chlorine radicals could be generated due to the chain reaction of Cl⁻ and SO₄•⁻, which likely involves the degradation of organic contaminant as even its activity was slightly weaker than that of SO₄•⁻ (see Equation (9)).



$$SO_4 \bullet^- + Cl^- \to SO_4^{2-} + Cl \bullet$$
 (9)

Figure 6. Cont.



Figure 6. Effect of inorganic anions on the degradation of 2-CP (a) Cl⁻, (b) NO₃⁻, and (c) CO₃²⁻. Reaction conditions: [2-CP] = 20 mg/L of 20 mL, PS = 1400 mg/L, BC@S-nZVI = 560 mg/L, T = 30 °C, pH = 5 \pm 0.2.

The effects of NO₃⁻ and CO₃²⁻ on 2-CP degradation by the BC@S-nZVI/PS system are shown in Figure 6b,c. The degradation of 2-CP slightly increased within 72 h after the NO₃⁻ and CO₃²⁻ addition into the aqueous solution. The 2-CP removal rate increased from 86.9% to 91.0% and 87.7% within 48 h at nitrate and carbonate concentrations of 50 mg/L, respectively. Meanwhile, the degradation rate of 2-CP was 95.6% and 93.8% within 48 h at the nitrate and carbonate concentration of 500 mg/L. The 2-CP removal rates were all 100% within 72 h. The C/C₀ is not close to 1 at the beginning reaction time in Figure 6b, while this is different from Figure 6c. There are two possible reasons for this phenomenon: Nitrate can enhance the absorption of 2-CP to the surface of BC@S-nZVI on the one hand, and nitrate reacts with SO₄•⁻ to generate a reactive radical on the other hand (see Equation (10)), which may promote the degradation of 2-CP, and the degradation rate increased with the increase in the nitrate concentration [21]. Wang and Lin [41] found that a carbonate radical could be generated due to the reaction of CO₃²⁻ and SO₄•⁻ (see Equation (11)), which may react rapidly with phenol substances at high concentrations and showed a positive effect with constant consumption.

$$SO_4 \bullet^- + NO_3^- \to SO_4^{2-} + NO_3 \bullet \tag{10}$$

$$SO_4 \bullet^- + CO_3^{2-} \to SO_4^{2-} + CO_3 \bullet^-$$
 (11)

3.4. The Degradation Mechanism of 2-CP in the BC@S-nZVI/PS System

Tertiary butyl alcohol (TBA) and methanol (MeOH) had been used to explore the contributions of different chemical species during the 2-CP degradation in the BC@S-nZVI/PS system through free-radicals quenching experiments. There are likely four main contributors in the BC@S-nZVI/PS system, such as PS, BC@S-nZVI, and the HO• and $SO_4\bullet^-$ free radicals identified by the ESR (Figure 7). During the degradation of 2-CP via the BC@S-nZVI/PS system, the pre-addition of tertiary butyl alcohol (TBA) could inhibit the contribution of HO•, while the pre-addition of methanol (MeOH) could inhibit the contribution of HO• and $SO_4\bullet^-$, respectively. The addition of PS alone or BC@S-nZVI alone could exhibit the contribution of oxidation of PS and the function of BC@S-nZVI, respectively. The removal rates of 2-CP with reaction time are shown in Figure 8, and the contribution rates of the four chemical factors could be calculated by the difference in removal rates of 2-CP at different time points. Taking the reaction time point of 24 h as an example, the C/C₀ is 0.172 in the BC@S-nZVI/PS system, which means the removal rate of 2-CP in the reaction system is 82.8% by the function of the four chemical factors.

Furthermore, the C/C₀ is 0.963 in the PS-only system, which means the removal rate of 2-CP is 3.7% by the oxidation of PS. The C/C₀ is 0.929 in the BC@S-nZVI-only system, which means the removal rate of 2-CP is 7.1% by the function of BC@S-nZVI. The C/C₀ is 0.770 when adding MeOH to the BC@S-nZVI/PS system and the C/C₀ is 0.617 when adding TBA to the BC@S-nZVI/PS system, which means the removal rate of 2-CP in the reaction system is 15.3% by the oxidation of SO₄•⁻ according to the difference between 0.770 and 0.617, and the removal rate of 2-CP in the reaction system is 56.7% by the oxidation of HO• according to the difference between 82.8% and the sum of the other three chemical factors. The contribution rates of HO• and SO₄•⁻, the oxidation of PS, and the function of BC@S-nZVI could be calculated as the ratio of 56.7%, 15.3%, 3.7%, 7.1%, and 82.8%, respectively. The contribution rates of chemical factors at other reaction time points could also be calculated like this, and the results are shown in Figure 9.



Figure 7. ESR spectra of DMPO-HO• and DMPO-SO4•⁻ adduct. Reaction conditions: [2-CP] = 20 mg/L of 20 mL, PS = 1400 mg/L, BC@S-nZVI = 560 mg/L, DMPO = 2800 mg/L, T = 30 °C, pH = 5 \pm 0.2.



Figure 8. The removal rates of 2-CP in different reaction systems. Reaction conditions: [2-CP] = 20 mg/L of 20 mL, T = 30 °C, pH = 5 ± 0.2.



Figure 9. Contribution rate of chemical factors at different reaction times. Reaction conditions: $[2-CP] = 20 \text{ mg/L of } 20 \text{ mL}, \text{ T} = 30 \degree \text{C}, \text{ pH} = 5 \pm 0.2.$

The function of BC@S-nZVI had the largest contribution rate (45.2%) at 0.5 h, which includes the adsorption and reductive de-chlorination of 2-CP [19,20,32,34]. The reason was that there were enough reaction sites on the BC to promote degradation in the initial reaction stage. The contribution rate of HO• from 2 h was higher than the other three factors and reached the maximum (68.5%) at 24 h, which can be attributed to PS being rapidly activated by nZVI to form HO• at this stage (see Equation (1)), which was superior to the formation of SO₄•⁻ (see Equations (2) and (3)). In the later stage, stable precipitation of ferric hydroxide was formed by the consumption of OH⁻ (see Equation (7)). The concentration of HO• decreases, and the contribution rate of SO₄•⁻ was higher than the other three other three factors at 72 h (46.6%).

3.5. Stability of BC@S-nZVI

Stability and reusability are important factors when evaluating a catalyst's properties. To assess the reusability of the BC@S-nZVI/PS system, the contrast tests of nZVI, S-nZVI, and BC@S-nZVI were conducted with three cycles. As shown in Figure 10, the degradation rate of 2-CP decreased from 67.9% to 40.5% and from 100.0% to 80.1% in three cycles, respectively, in the nZVI/PS system and S-nZVI/PS system, while the degradation rate of 2-CP only decreased from 100.0% to 96.3% in three cycles in the BC@S-nZVI/PS system. This implies BC@S-nZVI still retained high catalytic activity after three cycles. The decrease in efficiency could be caused by the S-nZVI release or consumption on the surface of BC (Figure 1). It could also be due to the precipitation of iron species [42], which would reduce the released ferrous ion from the catalyst and prevent contact between the catalyst and the persulfate. Therefore, BC@S-nZVI was assessed as suitable for activating PS for 2-CP degradation with high stability.



Figure 10. Reusability of catalysts in three cycles: (a) nZVI/PS, (b) S-nZVI/PS, and (c) BC@S-nZVI/PS. Reaction conditions: [2-CP] = 20 mg/L, PS = 1400 mg/L, BC@S-nZVI = 560 mg/L, T = 30 °C, pH = 5 \pm 0.2.

4. Conclusions

In this study, soybean residue biochar-supported S-nZVI (BC@S-nZVI) was synthesized in a two-step method and was used as an activator of persulfate (PS) to remove 2-CP in the aqueous solution. The dosage of PS and BC@S-nZVI, the influences of pH, temperature, and anions, and the degradation mechanism of 2-CP were explored and discussed. The soybean residue biochar-supported S-nZVI could be used to activate the PS for 2-CP degradation, and the degradation rate of 2-CP could achieve 100.0% less in than 72 h with mass ratios of PS to 2-CP and BC@S-nZVI to PS of 70 and 0.4, respectively. The degradation of 2-CP was more efficient in acidic and alkaline conditions compared to neutral conditions, and it significantly increased as the temperature increased from 10 °C to 50 °C. The addition of Cl⁻ had a negative effect on the degradation of 2-CP, while the addition of NO₃⁻ and CO_3^{2-} had positive effects. There were several contributions including HO• and SO₄•⁻, and the function of BC@S-nZVI was dominant in 2-CP degradation in the different stages of the reaction.

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References

- 1. Decker, S. Ullmann's encyclopedia of industrial chemistry. Mater. Manuf. Process. 1999, 14, 626. [CrossRef]
- 2. Keith, L.H.; Telliard, W.A. Priority pollutants: I-a perspective view. Environ. Sci. Technol. 1979, 13, 416–423. [CrossRef]
- 3. Ge, F.; Zhang, Z.X.; Fu, H.; Tang, S.Y.; Xu, K.K.; Song, X.; Wang, Q.; Luo, Y.M. Current situation analysis and prospect of organic contaminated sites in China. *Soil* **2021**, *53*, 1132–1141.
- 4. Huang, J.Y.; Yi, S.P.; Zheng, C.M.; Lo, I.M.C. Persulfate activation by natural zeolite supported nanoscale zero-valent iron for trichloroethylene degradation in groundwater. *Sci. Total Environ.* **2019**, *684*, 351–359. [CrossRef]
- Zhu, F.; Wu, Y.; Liang, Y.; Liang, H.L. Degradation mechanism of Norfloxacin in Water using Persulfate Activated by BC@nZVI/Ni. Chem. Eng. J. 2020, 389, 124276. [CrossRef]
- Liu, P.; Guo, Z.P.; Wang, Y.D.; Zhang, L.; Xue, G. Enhanced decolorization of methyl orange in aqueous solution using iron-carbon micro-electrolysis activation of sodium persulfate. *Chemosphere* 2017, 180, 100–107. [CrossRef]
- Xu, H.; Gao, M.X.; Hu, X.; Chen, Y.H.; Li, Y.; Xu, X.Y.; Zhang, R.Q.; Yang, X.; Tang, C.F.; Hu, X.J. A novel preparation of S-nZVI and its high efficient removal of Cr(VI) in aqueous solution. J. Hazard. Mater. 2021, 416, 125924. [CrossRef]
- Zhou, Y.; Zhang, Y.; Hu, X. Enhanced activation of peroxymonosulfate using oxygen vacancy-enriched FeCo₂O₄x spinel for 2,4-dichlorophenol removal: Singlet oxygen-dominated nonradical process. *Colloids Surf. A* 2020, 597, 124568. [CrossRef]
- 9. Yao, K.Y.; Fang, L.; Liao, P.B.; Chen, H.S. Ultrasound-activated peracetic acid to degrade tetracycline hydrochloride: Efficiency and mechanism. *Sep. Purif. Technol.* **2023**, *306*, 122635. [CrossRef]
- Huang, K.C.; Couttenye, R.A.; Hoag, G.E. Kinetics of heat-assisted persulfate oxidation of methyl tert-butyl ether (MTBE). J. Soil Contam. 2002, 11, 447–448. [CrossRef]
- 11. Chen, C.Y.; Cho, Y.C.; Lin, Y.P. Activation of peroxydisulfate by carbon nanotube for the degradation of 2,4-dichlorophenol: Contributions of surface-bound radicals and direct electron transfer. *Chemosphere* **2021**, *283*, 131282. [CrossRef] [PubMed]
- 12. Liu, Y.; Zhao, Y.; Wang, J. Activation of peroxydisulfate by a novel Cu⁰-Cu₂O@CNTs composite for 2, 4-dichlorophenol degradation. *Sci. Total Environ.* **2020**, 754, 141883. [CrossRef]
- Matzek, L.W.; Carter, K.E. Activated persulfate for organic chemical degradation: A review. *Chemosphere* 2016, 151, 178–188. [CrossRef] [PubMed]
- 14. Muhammad, A.; Klu, P.K.; Wang, C.; Zhang, W.; Luo, R.; Zhang, M.; Qi, J.; Sun, X.; Wang, L.; Li, J. Metal-organic frameworkderived Hollow Co₃O₄/Carbon as Efficient Catalyst for Peroxymonosulfate Activation. *Chem. Eng. J.* **2019**, *363*, 234–246.
- 15. Peng, L.; Deng, D.; Guan, M.; Fang, X.; Zhu, Q. Remediation HCHs POPs-contaminated soil by activated persulfate technologies: Feasibility, impact of activation methods and mechanistic implications. *Sep. Purif. Technol.* **2015**, *150*, 215–222. [CrossRef]
- 16. Wang, J.; Wang, S. Activation of persulfate (PS) and peroxymonosulfate (PMS) and application for the degradation of emerging contaminants. *Chem. Eng. J.* **2018**, *334*, 1502–1517. [CrossRef]

- 17. Devi, P.; Das, U.; Dalai, A.K. In-situ chemical oxidation: Principle and applications of peroxide and persulfate treatments in wastewater systems. *Sci. Total Environ.* **2016**, *571*, 643–657. [CrossRef]
- Gao, Y.Q.; Gao, N.Y.; Deng, Y.; Yang, Y.Q.; Ma, Y. Ultraviolet (UV) light-activated persulfate oxidation of sulfamethazine in water. *Chem. Eng. J.* 2012, 195, 248–253. [CrossRef]
- 19. Wang, Y.; Wang, L.; Zhang, Y.; Mao, X.; Xi, B. Perdisulfate-Assisted Advanced Oxidation of 2,4-Dichlorophenol by Bio-inspired Iron Encapsulated Biochar Catalyst. *J. Colloid Interf. Sci.* **2021**, *592*, 358–370. [CrossRef]
- 20. Kim, C.L.; Ahn, J.Y.; Kim, T.Y.; Shin, W.S.; Hwang, I. Activation of Persulfate by Nanosized Zero-Valent Iron (NZVI): Mechanisms and Transformation Products of NZVI. *Environ. Sci. Technol.* **2018**, *52*, 3625–3633. [CrossRef]
- Gao, Y.Q.; Gao, N.Y.; Wei, W.; Kang, S.F.; Xu, J.H.; Xiang, H.M.; Yin, D.Q. Ultrasound-assisted heterogeneous activation of persulfate by nano zero-valent iron (nZVI) for the propranolol degradation in water. *Ultrason. Sonochem.* 2018, 49, 33–40. [CrossRef] [PubMed]
- 22. Chen, Z.; Xing, J.; Pu, Z.; Wang, X.; Yang, S.; Wei, B.; Ai, Y.; Xiang, L.; Chen, D.; Wang, X. Preparation of nano-Fe⁰ modified coal fly-ash composite and its application for U(VI) sequestration. *J. Mol. Liq.* **2018**, *266*, 824–833. [CrossRef]
- Li, X.; Zhao, Y.; Xi, B.; Mao, X.; Gong, B.; Li, R.; Peng, X.; Liu, H. Removal of nitrobenzene by immobilized nanoscale zero-valent iron: Effect of clay support and efficiency optimization. *Appl. Surf. Sci.* 2016, 370, 260–269. [CrossRef]
- 24. Pirsaheb, M.; Moradi, S.; Shahlaei, M.; Wang, X.; Farhadian, N. A new composite of nano zero-valent iron encapsulated in carbon dots for oxidative removal of bio-refractory antibiotics from water. J. Clean. Prod. 2018, 209, 1523–1532. [CrossRef]
- 25. Kumar, N.S.; Shaikh, H.M.; Asif, M.; Al-Ghurabi, E.H. Engineered biochar from wood apple shell waste for high-efficient removal of toxic phenolic compounds in wastewater. *Sci. Rep.* **2021**, *11*, 2586. [CrossRef] [PubMed]
- Dong, H.R.; Zhang, C.; Deng, J.M.; Jiang, Z.; Zhang, L.H.; Cheng, Y.J.; Hou, K.J.; Tang, L.; Zeng, G.M. Factors influencing degradation of trichloroethylene by sulfide-modified nanoscale zero-valent iron in aqueous solution. *Water Res.* 2018, 135, 1–10. [CrossRef]
- Vogel, M.; Georgi, A.; Kopinke, F.D.; Mackenzie, K. Sulfidation of ZVI/AC composite leads to highly corrosion-resistant nanoremediation particles with extended life-time. *Sci. Total Environ.* 2019, 665, 235–245. [CrossRef]
- Xu, J.; Cao, Z.; Wang, Y.; Zhang, Y.L.; Gao, X.Y.; Ahmed, M.B.; Zhang, J.; Yang, Y.; Zhou, J.L.; Lowry, G.V. Distributing sulfidized nanoscale zerovalent iron onto phosphorus-functionalized biochar for enhanced removal of antibiotic florfenicol. *Chem. Eng. J.* 2019, 359, 713–722. [CrossRef]
- 29. Cai, J.; Zhang, Y. Enhanced degradation of bisphenol S by persulfate activated with sulfide-modified nanoscale zero-valent iron. *Environ. Sci. Pollut. Res.* 2022, 29, 8281–8293. [CrossRef]
- Wu, G.C.; Kong, W.J.; Gao, Y.; Kong, Y.; Dai, Z.G.; Dan, H.B.; Shang, Y.N.; Wang, S.Q.; Yin, F.J.; Yue, Q.Y.; et al. Removal of chloramphenicol by sulfide-modified nanoscale zero-valent iron activated persulfate: Performance, salt resistance, and reaction mechanisms. *Chemosphere* 2021, 286, 131876. [CrossRef]
- Zhang, P.; Song, D.; Xu, X.J.; Hao, Y.; Sun, H. Sulfidated zero valent iron as a persulfate activator for oxidizing organophosphorus pesticides (OPPs) in aqueous solution and aged contaminated soil columns. *Chemosphere* 2021, 281, 130760. [CrossRef] [PubMed]
- 32. Chen, J.; Dong, H.R.; Tian, R.; Li, R.; Xie, Q.Q. Remediation of Trichloroethylene-Contaminated Groundwater by Sulfide-Modified Nanoscale Zero-Valent Iron Supported on Biochar: Investigation of Critical Factors. *Water Air Soil Poll.* 2020, 231, 432. [CrossRef]
- 33. Li, R.C.; Jin, X.Y.; Megharaj, M.; Naidu, R.; Chen, Z.L. Heterogeneous Fenton oxidation of 2,4-dichlorophenol using iron-based nanoparticles and persulfate system. *Chem. Eng. J.* 2015, 264, 587–594. [CrossRef]
- Zhao, M.; Zhou, M.; Li, Y.C.; Wang, J.; Gao, B.; Sato, S.; Feng, K.; Yin, W.; Igalavithana, A.D. Biochar-supported nZVI (nZVI/BC) for contaminant removal from soil and water: A critical review. J. Hazard. Mater. 2019, 373, 820–834.
- 35. China Rural Statistical Yearbook; N. B. S. China Statistics Press: Beijing, China, 2020.
- 36. Li, H. Low fat and high fiber soybean food. Farm Prod. Process. 2011, 8, 28–29.
- Yousefi, N.; Pourfadakari, S.; Esmaeili, S.; Babaei, A.A. Mineralization of high saline petrochemical wastewater using Sonoelectroactivated persulfate: Degradation mechanisms and reaction kinetics. *Microchem. J.* 2019, 147, 1075–1082. [CrossRef]
- Manz, K.E.; Carter, K.E. Investigating the effects of heat activated persulfate on the degradation of furfural, a component of hydraulic fracturing fluid chemical additives. *Chem. Eng. J.* 2017, 327, 1021–1032. [CrossRef]
- 39. Zhao, J.; Zhang, B.T.; Li, J.; Shi, Y.; Yang, Z. Oxidative degradation of chloroxylenol in aqueous solution by thermally activated persulfate: Kinetics, mechanisms and toxicities. *Chem. Eng. J.* **2019**, *368*, 553–563.
- 40. Wang, Y.R.; Tian, D.F.; Chu, W.; Li, M.R.; Lu, X.W. Nanoscaled magnetic CuFe₂O₄ as an activator of peroxymonosulfate for the degradation of antibiotics norfloxacin. *Sep. Purif. Technol.* **2019**, *212*, 536–544. [CrossRef]
- 41. Wang, X.H.; Lin, Y.C. Phototransformation of Cephalosporin Antibiotics in an Aqueous Environment Results in Higher Toxicity. *Environ. Sci. Technol.* **2012**, *46*, 12417–12426. [CrossRef]
- Luo, X.W.; Shen, M.X.; Liu, J.H.; Ma, Y.J.; Gong, B.N.; Liu, H.Q.; Huang, Z.J. Resource utilization of piggery sludge to prepare recyclable magnetic biochar for highly efficient degradation of tetracycline through peroxymonosulfate activation. *J. Clean. Prod.* 2021, 294, 126372. [CrossRef]

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