Remediation and Optimisation of Petroleum Hydrocarbon Degradation in Contaminated Water by Persulfate Activated with Bagasse Biochar-Supported Nanoscale Zerovalent Iron

Ronghai Zhang 1,2,3, Yudao Chen 1,2,*, Shudi Li 3, Zhuangmian Wei 3, He Huang 3 and Tian Xie 3

1 College of Environmental Science and Engineering, Guilin University of Technology, Guilin 541006, China; bosscozrh@163.com
2 Collaborative Innovation Center for Water Pollution Control and Water Safety in Karst Area, Guilin University of Technology, Guilin 541006, China
3 National Technology Center, Guangxi Bossco Environmental Protection Technology Co., Ltd., Nanning, 530004, China; lishudi1017@hotmail.com (S.L.); wzmn140312@163.com (Z.W.); river_63@163.com (H.H.); tianckstar@163.com (T.X.)
* Correspondence: cyd0056@vip.sina.com

Abstract: In this study, biochar (BC) was prepared from bagasse and then successfully loaded with nanoscale zerovalent iron (nZVI) to produce BC-supported nZVI, termed nZVI@BC. Satisfactory results were obtained using a nZVI@BC-activated persulfate (PS), termed nZVI@BC/PS, to remediate total petroleum hydrocarbons (TPH)-contaminated water. The effects of three influencing factors—the dosage of nZVI@BC, D_{nZVI@BC}, the concentration of PS, C_{PS}, and the initial pH, pH_{i}—on TPH removal were examined through single-factor and batch tests. The results show the following. Each factor considerably influenced the performance of the prepared nZVI@BC/PS reaction system in removing TPH. The TPH degradation process conformed to a first-order kinetic model. The response surface method (RSM) was used in tandem with a Box–Behnken design to optimise the variables involved in TPH degradation. The three influencing variables (i.e., D_{nZVI@BC}, C_{PS}, and pH_{i}) were set in the range of 0.4–1.0 g/L, 20–160 g/L, and 2.21–9.42, respectively, during the experiment. An optimised quadratic model used to fit the experimental data displayed a high level of significance ($p < 0.0001$) with a very high regression value ($R^2 = 0.9906$; adjusted $R^2 = 0.9786$). Analyses of regression and variance revealed that the quadratic model sufficiently explains the TPH degradation rate. An electron paramagnetic resonance (EPR) spectroscopic analysis of the nZVI@BC/PS system revealed that $SO_4^−$, $·OH$, $O_2^−$, and $1O_2$ participated in the activation and degradation processes. The results of this study show that nZVI@BC-activated PS systems possess great potential for applications in TPH-contaminated wastewater treatment and environmentally sustainable development.

Keywords: nZVI@BC; activated persulfate; petroleum hydrocarbons; response surface method (RSM); electron paramagnetic resonance (EPR)

1. Introduction

The extraction, transportation, storage, and accidental spills of petroleum can lead to serious contamination. Most substances (e.g., alkanes and arenes) contained in petroleum are toxic and harmful [1], while some can even cause cancer, abnormalities, and mutations [2,3]. When released into the environment, total petroleum hydrocarbons (TPH) can disrupt soil and water functions and directly or indirectly endanger human health and trigger a series of problems [4,5]. Biodegradation, enhanced natural attenuation (ENA), and chemical oxidation are used to remove TPH from water; however, the technology has limitations due to the considerable time required for biodegradation and ENA [6,7]. Therefore, searching for effective and environmentally friendly methods to remove TPH from water is a crucial task. Satisfactory progress has been made in recent years in the
development of activated persulfates (PSs) used in advanced oxidation processes (AOPs). Research has shown that PS-based AOPs can be employed to eliminate multiple organic contaminants from water effectively [8–10]. PSs can be activated in the presence of light, heat, transition-metal ions (TMIs) (e.g., ferrous iron [Fe$^{2+}$] ions), strong oxidants (e.g., hydrogen peroxide), or strong alkalis to enhance their oxidation capacity [11–13]. A complex after treatment is required in the TMI-based method to remove the byproducts generated during activation [2,14,15]. In addition, highly concentrated TMIs can capture free radicals (FRs) and therefore affect the continuation and efficiency of the removal of organic contaminants [16]. The pH required for alkali-based activation of PSs may cause corrosion in the remediation equipment [17]. Novel activation techniques have been developed in recent years. Using PSs activated by zerovalent Fe (ZVI), particularly PSs activated by nanoscale ZVI (nZVI), to remove organic contaminants has garnered widespread attention as an effective and environmentally friendly technique [15,18,19].

In real-world applications, nanoscale Fe particles tend to agglomerate in water due to their small size and mutual magnetic attraction, and therefore display reduced mobility and stability [14]. Moreover, nanoscale Fe also tends to undergo secondary oxidation reactions in the presence of air and water that reduce its electron transfer efficiency and slow its reactions with contaminants [18,20]. Therefore, modifying nanoscale Fe to increase the efficiency of its reaction with contaminants has become a topical area of research in recent years [21]. Recently, biochar (BC) has been frequently used as a carrier for nZVI [22,23] to synthesise new low-cost materials used to remediate contaminated sites and to activate PSs to generate FRs capable of degrading organic contaminants [24,25]. According to recent research findings, compared to nZVI alone, a combined nZVI and BC system is appreciably more efficient in removing organic compounds (e.g., 2,4-dichlorophenol [19] and polycyclic aromatic hydrocarbons [26]). Hence, it is necessary to investigate the use of BC-supported nZVI, termed nZVI@BC, to remove TPH from water [27,28].

Guangxi is one of the major sugarcane production areas in China. A large amount of bagasse is abandoned after sugar production [29], which is very wasteful and needs to be recycled. In this study, nZVI was prepared by liquid-phase reduction, while BC was produced from bagasse. On this basis, nZVI@BC was synthesised and used to activate a PS (sodium PS [SPS] was used in this study). The activated PS system, termed nZVI@BC/PS, was used to degrade TPH. This process was examined by single-factor tests and the response surface method (RSM), with a focus placed on the effects of three factors—the dosage of nZVI@BC, D$_{nZVI@BC}$, the concentration of PS, C$_{PS}$, and the initial pH, pH$_i$—on the performance of the nZVI@BC/PS reaction system in removing TPH and the relevant mechanism. Finally, electron paramagnetic resonance (EPR) spectroscopy was used to study the FR system in nZVI@BC/PS responsible for TPH removal and the mechanism behind TPH degradation.

2. Materials and Methods

2.1. Reagents and Chemicals

Fe(II) sulfate (FeSO$_4$), sodium borohydride (NaBH$_4$), ethanol, sodium thiosulfate (STS), SPS, sodium hydroxide (NaOH), hydrochloric acid (HCl), and dichloromethane were purchased from Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China). In addition, 5,5-dimethyl-1-pyrroline-N-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were provided by Sigma Aldrich (Shanghai, China). Deionised (DI) water was prepared in-house using a Milli-Q Ultrapure water purification system (Milli-Q® IQ 7003, Millipore Corporation, Billerica, MA, USA).

2.2. Preparation of nZVI@BC and TPH-Polluted Groundwater

2.2.1. nZVI@BC

(1) BC preparation. Bagasse was crushed and rinsed with DI water to remove dirt and excess sugar, followed by drying in an oven at 105 °C until a constant weight was reached (this process lasted for 8 h). The treated bagasse was then placed in a tube furnace, into
which nitrogen (N\textsubscript{2}) was introduced to displace the air, followed by gradual heating at a rate of 10 °C/min to the carbonisation temperature of 500 °C under an N\textsubscript{2} flow maintained at 100 mL/min. The carbonisation process continued for 2 h, after which the bagasse was allowed to cool to room temperature and then rinsed with DI water until a pH of 7 was attained. Next, the bagasse was dried at 105 °C and then ground into powder. Thus, bagasse-derived BC was produced.

(2) nZVI preparation. nZVI was prepared through liquid-phase reduction. N\textsubscript{2} was delivered into a 1000-mL three-necked flask to displace the air. In the presence of N\textsubscript{2} flow, 100 mL of a 0.18-mol/L FeSO\textsubscript{4} solution was added into the flask, followed by stirring at a rate of 400 r/min, during which 50 mL of a 0.8-mol/L NaBH\textsubscript{4} solution was added dropwise into the flask. Subsequently, the chemicals were allowed to react with each other for 20 min. The product of the reaction (i.e., nZVI) was rinsed three times with deoxygenated (DO) pure water and ethanol, and then separated magnetically, followed by drying under cold vacuum conditions for 24 h. The obtained nZVI was transferred into a small sealed bag, into which N\textsubscript{2} was delivered for 5 s. Finally, the bag was stored in a desiccator.

(3) nZVI@BC synthesis. First, 1 g of BC was added into a 1000-mL three-necked flask, into which N\textsubscript{2} was subsequently introduced to displace the air. Then, in the presence of N\textsubscript{2} flow, 100 mL of a 0.18-mol/L FeSO\textsubscript{4} solution was added into the flask, followed by stirring at a rate of 400 r/min, during which 50 mL of a 0.8-mol/L NaBH\textsubscript{4} solution was added dropwise into the flask. Next, the chemicals were allowed to react with each other for 20 min. The product of the reaction (i.e., nZVI@BC) was rinsed three times with DO pure water and ethanol, and then separated centrifugally, followed by drying under cold vacuum conditions for 24 h.

2.2.2. TPH-Polluted Water

No. 0 diesel was dissolved in ultrapure water at a volume ratio of 1/100. The mixture was oscillated in a shaker at a constant temperature of 20 °C and a rate of 35 r/min for 5 h, followed by filtration through a glass-fibre filter with a pore size of 0.22 µm. The obtained subnatant containing dissolved diesel was used as TPH-contaminated water. Analysis using a gas chromatography (GC) system coupled with a flame ionisation detector (FID) revealed the C\textsubscript{10}–C\textsubscript{40} content (TPH). The TPH concentration, C\textsubscript{TPH}, was measured to be 6 mg/L.

2.3. Degradation Kinetics Experiment

2.3.1. Performance Analysis of TPH Degradation by Different Systems

The effects of each parametric variable on TPH degradation were investigated by comparing the effectiveness of four test systems, namely, PS, BC, nZVI@BC, and a combination of BC and PS (BC/PS). Batch tests were conducted to examine the efficiency of each test system in removing TPH. First, 100 mL of the TPH-contaminated water prepared in Section 2.2.2 was added into a 150-mL brown closed glass bottle. Then, 0.1-mol/L HCl and 0.1-mol/L NaOH were used to adjust the pH\textsubscript{i} of the reaction system.

2.3.2. Effect of Key Impact Factors for TPH Degradation on the nZVI@BC/PS System

D\textsubscript{nZVI@BC}, C\textsubscript{PS}, and pH\textsubscript{i} were principal factors affecting the removal of TPH from water. In single-factor tests, D\textsubscript{nZVI@BC}, C\textsubscript{PS}, and pH\textsubscript{i} were set to 0.4–1.2 g/L, 20–160 g/L, and 2.21–10.99, respectively. Batch tests were performed to investigate the effects of the influencing factors on TPH removal efficiency. First, 100 mL of the TPH-contaminated water prepared in Section 2.2.2 was added into a 150-mL brown closed glass bottle. Then, 0.1-mol/L HCl and 0.1-mol/L NaOH were used to adjust the pH\textsubscript{i} of the reaction system. Consequently, nZVI@BC and PS were added to the bottle. (a) The effects of D\textsubscript{nZVI@BC} on TPH removal efficiency were investigated by varying D\textsubscript{nZVI@BC} from 0.4 to 1.2 g/L while keeping C\textsubscript{PS} and pH\textsubscript{i} constant at 80 g/L and ca. 5.8, respectively. (b) The effects of C\textsubscript{PS} on TPH removal efficiency were investigated by varying C\textsubscript{PS} from 20 to 160 g/L while keeping D\textsubscript{nZVI@BC} and pH\textsubscript{i} constant at 1.0 g/L and ca. 5.8, respectively. (c) The effects of pH\textsubscript{i} on TPH removal
efficiency were investigated by varying pH$_i$ from 2.21 to 10.99 while keeping D$_{nZVI@BC}$ and C$_{PS}$ constant at 1.0 and 80 g/L, respectively. In each single-factor test, samples were collected destructively at different reaction times (30, 60, 120, 180, and 240 min). The oxidation reaction was terminated with 5 mL of a 1-mol/L STS solution, after which the water sample was tested to determine C$_{TPH}$ within 6 h. Three repeats were performed for each test. The mean and standard deviation (SD) of the results were calculated for analysis. The calculation method of petroleum hydrocarbon removal rate is shown in Equation (1).

\[ \eta = \frac{C_0 - C}{C_0} \times 100\% \]  

(1)

\( \eta \) was the petroleum hydrocarbon removal rate, \( C_0 \) was the initial concentration of petroleum hydrocarbon, and \( C \) was the concentration of petroleum hydrocarbon at a certain time during the removal process.

2.4. RSM: The Box–Behnken Experimental Design

Design Expert software (version 13.0, Stat-Ease Corporation, Minneapolis, USA) was used to design the experiments and establish and optimise the mathematical model [30,31]. According to the principle of the Box–Behnken experimental design in RSM, a three-factor, three-level RSM experiment involving a total of 17 experimental points was designed based on the single-factor test results with C$_{PS}$, D$_{nZVI@BC}$, and pH$_i$ as independent variables, and the TPH removal rate as a response value. Table 1 summarises the experimental conditions. The experimental data were fitted to a second-order polynomial model, as shown in Equation (2).

\[ Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 + \sum_{i=1}^{k} \sum_{j=1}^{k} \beta_{ij} X_i X_j + e_0 \]  

(2)

where \( Y \) is the predicted response (i.e., the TPH removal efficiency), \( \beta_0, \beta_i, \beta_{ii}, \) and \( \beta_{ij} \) are the constant term, regression coefficient, quadratic regression coefficient, and interaction coefficient of the model, respectively, \( X_i \) and \( X_j \) are coded coefficients, and \( e_0 \) is the error. The goodness of fit of the polynomial model is expressed in terms of the coefficient of determination, \( R^2 \). The F-value is used to measure the statistical significance of the model. The \( p \)-values of the model coefficients are used to examine the linear, square, and interaction effects of the influencing factors. Experimental data analyses (including analysis of variance [ANOVA]) were completed using Design Expert software (version 13.0).

Table 1. Experimental ranges and levels of the independent test variables.

| Variables                  | Symbol | Unit | Coded Variable Level |
|----------------------------|--------|------|----------------------|
| Persulfate (PS) concentration | A      | g/L  | -1 20 90 160 1       |
| nZVI@BC dose               | B      | g/L  | 0.4 0.7 1.0          |
| Initial pH                 | C      | -    | 2.21 5.81 9.42       |

2.5. Reusability of nZVI@BC

Activator stability is a crucial issue. Hence, the prepared activator—the nZVI@BC nanocomposite—was analysed to determine its reusability and stability. After the reaction was terminated, nZVI@BC was recovered using a high-speed centrifuge, followed by rinsing with DI water and ethanol, and then drying prior to analysis.

2.6. Analytical Methods

A JSM-6360LA scanning electron microscopy (SEM) system (JEOL Ltd., Tokyo, Japan) was used to observe the surface morphology of the samples. A D8 Advance X-ray diffractometer (XRD) (Bruker Corporation, Madison, WI, USA) was used to measure the crystal
structure of the samples. X-ray photoelectron spectroscopy (XPS) (Thermo Corporation, Waltham, MA, USA) was used to analyse BC and nZVI@BC composition and the valence state of sample elements. An IS50 Fourier transforms infrared (FTIR) spectrometer (Thermo Corporation, USA) was used to analyse and identify the surface functional groups of the samples. An A200 EPR spectrometer (Bruker Corporation, USA) was used to determine the reactive oxygen (O) species (ROS) formed during the reaction. During the experiment, DMPO was used to capture hydroxyl, sulfate, and superoxide FRs (OH, SO$_4^{2-}$, and O$_2^{2-}$, respectively), while TEMP was used to capture singlet oxygen ($^1$O$_2$).

A 7890b GC system equipped with a gas sampler, an HP-5 column, and an FID (Agilent Technologies, Inc., Santa Clara, CA, USA) was used to measure the C$_{TPH}$ of the water samples. The maximum inlet temperature and the flow rate in the column were set to 320 °C and 2.0 mL/min, respectively. The following programme was used to heat the column: the column was first heated to and kept at 60 °C for 1 min, followed by further heating to 290 °C at a rate of 7.89 °C/min and then to 320 °C at a rate of 30 °C/min. The column was kept at 320 °C for 7 min. The FID temperature was set to 330 °C. High-purity (99.999%) N$_2$, hydrogen (purity: 99.999%; flow rate: 40 mL/min), and air (flow rate: 350 mL/min) were used as carrier gases. The make-up gas flow was set to 30.0 mL/min. The sample was injected first in splitless mode and, 0.75 min later, in split mode (split ratio: 30:1), with a total volume of 1.0 µL.

3. Results and Discussion

3.1. Characterisation of nZVI@BC

SEM coupled with energy-dispersive X-ray spectroscopy (SEM–EDS) was used to analyse BC and nZVI@BC in terms of their morphology, dimension, and energy spectrum. As shown in Figure 1, nZVI@BC particles ranged from 100 to 500 nm in diameter and were covered with chained aggregates with a spherical core–shell structure on their surface. nZVI was incorporated into the surface and various layers of BC. Fe was detected on the nZVI@BC surface, suggesting that BC was successfully loaded with nZVI, which supports a previous study [32]. Analysis of the XRD patterns in Figure S1 reveals an absence of sharp peaks and a presence of only wide diffraction peaks for BC within the range of 10–35°, which can be ascribed to the aromatisation and graphitisation of the organic compounds formed from BC pyrolysis. The diffraction peaks of nZVI@BC at 2θ of 27° and 44.68° indicate the presence of ZVI. The presence of Fe-associated peaks in the X-ray photoelectron spectroscopy (XPS) patterns of nZVI@BC in Figure S2 lends further credence to the success of loading nZVI onto BC. All the SEM–EDS, XRD, and XPS findings presented above show that BC was successfully loaded with nZVI.

The characteristic FTIR spectra of both BC and nZVI@BC (Figure S3) show the characteristic absorption bands of hydroxyl (–OH) functional groups at high frequencies (3500–3000 cm$^{-1}$), suggesting their presence in the composite material. These bands can be attributed to the stretching vibrations caused by the adsorption of water on the BC surface [33]. The absorption peaks at 1625 and 1605 cm$^{-1}$ are associated with the stretching vibrations of C=O bonds. The skeletal vibrations of aromatic C=C bonds were responsible for the absorption peak associated with C=C bonds at 1437 cm$^{-1}$ in the spectrum of BC [34]. The weakening of the absorption peak of nZVI@BC at 1437 cm$^{-1}$ may indicate the occurrence of the interaction and surface complexation between nZVI and the aromatic C=C bonds on the BC surface during the preparation of nZVI@BC [35,36] that allowed nZVI to be loaded onto BC. The absorption peaks at 1371 and 1349 cm$^{-1}$ cannot be assigned to the stretching vibrations of C–N bonds, while those at 1117–1060 cm$^{-1}$ were caused by the stretching vibrations of carboxyl (C–O) bonds. The presence of these peaks suggests that nZVI@BC contained a large number of heterocyclic compounds. The new absorption peak at 613 cm$^{-1}$ in the spectrum of nZVI@BC should be ascribed to the stretching vibrations of Fe–O bonds [37] and suggests that BC was successfully loaded with nZVI. The large number of O-containing functional groups (e.g., hydroxyl and carboxyl groups) formed on the nZVI@BC surface can be used as electron-transfer sources to activate PS.
3.2. TPH Removal Rate by Different Systems

Figure S4 shows the performance of the PS, BC, nZVI@BC, and BC/PS systems in degrading TPH and reveals the following. The reaction system containing PS alone was inefficient in removing TPH. After 240 min of reaction, the PS system only removed 10.3% of the TPH. The reaction system containing BC alone adsorbed only 13.1% of the TPH. In contrast, nZVI@BC adsorbed a larger proportion (26.0%) of the TPH, which can be ascribed to its larger specific area (7.16 cm$^2$/g), compared with that (3.48 cm$^2$/g) of BC. The BC/PS system removed TPH at an even higher rate (29.0% after 240 min). BC and PS displayed a certain synergistic effect, demonstrating that BC was somewhat effective in activating PS [38]. In the absence of ZVI, the hydroxyl and carboxyl functional groups contained in BC activated PS to generate SO$_4^{2-}$ [39]. This finding is consistent with those reported previously [40,41].

The four abovementioned reaction systems all degraded TPH at low efficiency. In comparison, the nZVI@BC/PS system displayed a higher level of effectiveness in removing TPH. The effects of several principal factors on TPH degradation are analysed as follows. Figure 2A describes the effects of D$_{nZVI@BC}$ on the effectiveness of the PS system in removing TPH. nZVI acted as the activator source of the nZVI@BC/PS system. Increasing the amount of nZVI can accelerate the dissolution of Fe$^{2+}$ [42]. Increasing D$_{nZVI@BC}$ from 0.4 to 1.0 g/L led to a substantial increase in both the TPH removal and reaction rates, the latter of which is evidenced by an increase in the reaction rate constant K from 0.0034 to 0.0066 min$^{-1}$, as shown in Table S1. As D$_{nZVI@BC}$ increased, more Fe$^{2+}$ ions were released, resulting in an increase in the number of active sites in PS. Consequently, more SO$_4^{2-}$ radicals were generated and participated in TPH removal. As D$_{nZVI@BC}$ increased beyond 1.0 g/L, the TPH removal and reaction rates decreased slightly, the latter of which is evidenced by a decrease in K from 0.0066 to 0.0063 min$^{-1}$. Such a decrease can be attributed to the partial
consumption of $\text{SO}_4^{2-}$ and $\text{Fe}^{2+}$ on the nZVI@BC surface during the reaction, as shown in Equation (3). Hence, $D_{\text{nZVI@BC}}$ was set to 1.0 g/L in the subsequent tests.

$$\text{SO}_4^{2-} + \text{Fe}^{2+} \rightarrow \text{SO}_4^{2-} + \text{Fe}^{3+}$$

Figure 2A shows the effects of key factors on the nZVI@BC/PS system for TPH degradation. Experimental conditions: (A) Effect of nZVI@BC dosage: $[\text{nZVI@BC}]_0 = 0.4 \text{–} 1.2 \text{ g/L}$, $[\text{PS concentration}]_0 = 80 \text{ g/L}$ and $\text{pH} \approx 5.80$; (B) Effect of PS concentration: $[\text{nZVI@BC}]_0 = 1.0 \text{ g/L}$, $[\text{PS concentration}]_0 = 20 \text{–} 160 \text{ g/L}$ and $\text{pH} \approx 5.80$; (C) Effect of pH: $[\text{nZVI@BC}]_0 = 1.0 \text{ g/L}$, $[\text{PS concentration}]_0 = 80 \text{ g/L}$ and $\text{pH} = 2.21 \text{–} 10.99$.

Figure 2B shows the effects of $C_{\text{PS}}$ on TPH removal. As $C_{\text{PS}}$ increased, both the TPH removal and degradation rates increased. Specifically, as $C_{\text{PS}}$ increased from 20 to 80 g/L,
the TPH degradation rate increased appreciably, as evidenced by a 2.36-fold increase in K (from 0.0028 to 0.0066 min⁻¹) (Table S2). However, as C$_{PS}$ increased from 80 to 160 g/L, both the extent and rate of TPH degradation decreased slightly. Increasing C$_{PS}$ activated the catalytic reaction and therefore led to the formation of more SO$_4$⁻· radicals that intensified TPH oxidation (Equation (4)). However, further increasing C$_{PS}$ led to an instantaneous formation of a large quantity of SO$_4$⁻· radicals that were subsequently quenched and consumed, and failed to oxidise and degrade TPH. Moreover, an excess of PS can also lead to the quenching of SO$_4$⁻· (Equation (5)) [43]. Therefore, C$_{PS}$ should be controlled within a suitable range. Based on the above test results, C$_{PS}$ was set to 80 g/L in the subsequent tests.

\[
\begin{align*}
S_2O_8^{2-} + Fe^{2+} &\rightarrow SO_4^{2-} + SO_4^{-} + Fe^{3+} \\
S_2O_8^{2-} + SO_4^{-} &\rightarrow SO_4^{2-} + S_2O_8^{-}.
\end{align*}
\]

Figure 2C describes the effects of pH$_i$ on the performance of the nZVI@BC/PS system in degrading TPH. The nZVI@BC/PS-based AOP system was effective in removing TPH at a pH range of 2.21–10.99. Similar to most ZVI-activated PS systems, acidic media are often more favourable for the removal of organic contaminants. As pH$_i$ decreased from 9.42 to 3.80, the first-order kinetic constant associated with TPH removal increased from 0.0051 to 0.0068 min⁻¹ (Table S3). The release of Fe$^{2+}$ (a PS activator) from nZVI is a major pathway by which nZVI@BC activates PS. An acidic medium can promote the dissolution of soluble Fe and therefore increase the rate at which Fe$^{2+}$ ions are generated [44].

Further decreasing the pH$_i$ from 3.80 to 2.21 did not increase TPH removal efficiency, as evidenced by a decrease in K from 0.0068 to 0.0060 min⁻¹. A similar phenomenon has been reported previously [45]. As pH$_i$ decreased to a certain value, the efficiency of removing the organic contaminants began to decrease (Table S3), which can be attributed to the following factor. In a strongly acidic medium, a premature release of an excess of soluble Fe$^{2+}$ leads to rapid consumption of the ROS in the system, thereby reducing the efficiency of degrading the target organic compounds. At a pH$_i$ of 10.99, the nZVI@BC/PS system was also effective in removing the alkaline activation of PS contained in the nZVI@BC/PS system in a strongly alkaline medium [2], which constitutes another major pathway for PS activation. Under this condition, the K for TPH degradation was 0.0064 min⁻¹, which is essentially consistent with that at a pH$_i$ of 6.68.

3.3. Box–Behnken Experimental Design and Optimisation Model

3.3.1. Model Checking and ANOVA

Table 2 summarises the matrix of the complete experimental design with three factors as independent variables and the experimentally measured response values. The results are used as a response variable expressed in terms of an empirical second-order polynomial model, as shown in Equation (6).

\[
\eta = 81.24 + 10.77A + 5.09B - 0.4562C + 5.7AB - 0.9225AC - 4.57BC - 10.55A^2 - 5.01B^2 - 1.57C^2
\]

where $\eta$ is the TPH removal rate at 240 min of reaction and A, B, and C are the coded values of C$_{PS}$, D$_{nZVI@BC}$, and pH$_i$, respectively.

ANOVA was performed to statistically evaluate the quality of the second-order quadratic regression model. Table 3 summarises the results. The obtained F-value of 82.31 suggests that the model is significant, while the obtained p-value less than 0.05 indicates that the selected model is reasonable. The quadratic RSM regression model fits the experimental data well. A lack-of-fit test was performed to determine the variation in the data around the fitting model and examine its adequacy of fit. As shown in Equation (6), A, B, AB, and BC are the significant terms of the model, while C and AC are its nonsignificant terms. The lack-of-fit test yielded an F-value of 1.63 and a p-value greater than 0.05, suggesting that the lack of fit is not significant and that the model can be used to yield valid estimates.
Table 2. Three-factor, three-level Box–Behnken design for the experiment: design matrix, and the measured and predicted responses.

| Run | Independent Variables (Coded) | Measured Responses | Predicted Responses |
|-----|--------------------------------|--------------------|---------------------|
|     | η (%)                          | A                  | B                   | C       |                   |                     |
| 1   | 56.45                          | -1                 | -1                  | 0       | 55.53             |                     |
| 2   | 55.61                          | -1                 | 1                   | 0       | 54.30             |                     |
| 3   | 56.74                          | -1                 | 0                   | -1      | 57.90             |                     |
| 4   | 57.75                          | -1                 | 0                   | 1       | 58.83             |                     |
| 5   | 65.69                          | 0                  | -1                  | -1      | 65.46             |                     |
| 6   | 84.63                          | 0                  | 1                   | -1      | 84.78             |                     |
| 7   | 73.85                          | 0                  | -1                  | 1       | 73.70             |                     |
| 8   | 74.49                          | 0                  | 1                   | 1       | 74.72             |                     |
| 9   | 79.33                          | 0                  | 0                   | 0       | 81.24             |                     |
| 10  | 80.46                          | 0                  | 0                   | 0       | 81.24             |                     |
| 11  | 81.56                          | 0                  | 0                   | 0       | 81.24             |                     |
| 12  | 83.21                          | 0                  | 0                   | 0       | 81.24             |                     |
| 13  | 81.66                          | 0                  | 0                   | 0       | 81.24             |                     |
| 14  | 64.36                          | 1                  | -1                  | 0       | 65.67             |                     |
| 15  | 86.32                          | 1                  | 1                   | 0       | 87.24             |                     |
| 16  | 82.36                          | 1                  | 0                   | -1      | 81.28             |                     |
| 17  | 79.68                          | 1                  | 0                   | 1       | 78.53             |                     |

Table 3. ANOVA results of the response surface quadratic model.

| Source            | Sum of Squares | df | Mean Square | F-Value | p-Value       |
|-------------------|----------------|----|-------------|---------|---------------|
| Model             | 1978.16        | 9  | 219.8       | 82.31   | <0.0001       |
| A—PS concentration| 928.16         | 1  | 928.16      | 347.57  | <0.0001       |
| B—nZVI@BC dose    | 207.06         | 1  | 207.06      | 77.54   | <0.0001       |
| C—pH              | 63.72          | 1  | 63.72       | 23.75   | <0.0001       |
| AB                | 129.96         | 1  | 129.96      | 48.67   | 0.0002        |
| AC                | 3.4            | 1  | 3.4         | 1.27    | 0.2961        |
| BC                | 83.72          | 1  | 83.72       | 31.35   | 0.0008        |
| A^2               | 468.26         | 1  | 468.26      | 175.35  | <0.0001       |
| B^2               | 105.82         | 1  | 105.82      | 39.63   | 0.0004        |
| C^2               | 10.32          | 1  | 10.32       | 3.87    | 0.09          |
| Residual          | 18.69          | 7  | 2.67        | 1.63    | 0.3171        |
| Lack of Fit       | 10.28          | 3  | 3.43        | 1.63    | 0.3171        |
| Pure Error        | 8.42           | 4  | 2.1         |         |               |
| Cor Total         | 1996.85        | 16 |             |         |               |

Table S4 summarises the ANOVA results for the regression of the model. \(R^2\) refers to the proportion of the total variability that can be explained by a model and is a measure of the goodness of fit of a model. Models with an \(R^2\) value close to 1 can better fit experimental data. A low \(R^2\) value means a low goodness of fit between a model and the experimental data. In this study, the \(R^2\) value for the TPH removal rate is 0.9906, suggesting that the model can explain 99.06% of the variation in the response value and satisfactorily fit the experimental data. In addition, the adjusted \(R^2\) value (0.9786) is close to the \(R^2\) value, indicating that the model can satisfactorily explain the results within the experimental range and can also be successfully used to predict the TPH removal rate within the experimental range. Figure 3 compares the experimentally measured and model-predicted response values. The coefficient of variation (CV) measures the reproducibility of a model and is expressed in terms of the ratio (in percentage) of the SD to the mean observed response. A model with a CV lower than 10% can be deemed reasonable. As seen in Table S4, the model has a CV of 2.23% (<10%) and is therefore applicable. Moreover, a signal-to-noise ratio of 26.28 (>4) suggests that the resolution of the model is adequate. The above analytical
results collectively show that the model can reflect the effects of C_{PS}, D_{nZVI@BC}, and pH_i on the TPH removal rate.

![Comparison between experimental values and model-predicted response.](image)

**Figure 3.** Comparison between experimental values and model-predicted response.

### 3.3.2. RSM Analysis

Three-dimensional (3D) RSM plots are the graphical representations of regression models and are used to determine the optimum values of the variables within the examined range. A steep-sloped surface and oval contours indicate a strong interaction between the two factors, while a gentle-sloped surface and circular contours suggest a weak interaction between the two factors. These RSM plots are functions of two variables at a fixed value of another variable at the central level. Figure 4 shows the comprehensive effects of the independent variables on the TPH removal rate at 240 min of reaction (A, B, and C are used to denote C_{PS}, D_{nZVI@BC}, and pH_i, respectively). Figure 4A describes the effects of the interaction between C_{PS} and D_{nZVI@BC} on TPH removal. At a constant pH_i of 5.81 and a constant D_{nZVI@BC}, the predicted response value of the TPH removal rate first increases and then decreases as C_{PS} increases. Figure 4B shows the effects of the interaction between C_{PS} and pH_i on TPH removal. Similarly, at a constant D_{nZVI@BC} of 0.7 g/L, the predicted response value of the TPH removal rate first increases and then decreases as C_{PS} increases. However, the surface slope is gentler in Figure 4B than in Figure 4A, suggesting that the interaction between C_{PS} and pH_i is less impactful than that between C_{PS} and D_{nZVI@BC}, as also demonstrated by the correlation coefficient. Figure 4C shows the effects of the interaction between D_{nZVI@BC} and pH_i on TPH removal at a C_{PS} of 90 g/L. At a pH_i < 7, the TPH removal rate increases as D_{nZVI@BC} increases. Acidic conditions are more favourable for the dissolution of Fe^{2+} and activation of PS. In alkaline conditions, the TPH removal rate generally remains at a high level, which may be ascribed to the synergistic role of ·OH and SO_4^{2-} in the degradation of organic contaminants. The curvature of the response surface and contour can distinctly reflect the importance and interaction of the process variables.
Figure 4. The 3-dimensional surface plots of the effect of (A) PS concentration and nZVI@BC dose, (B) PS concentration and initial pH, and (C) nZVI@BC dose and initial pH of the solution on the degradation (%) efficiency of TPH in the nZVI@BC/PS system.

3.4. Model Validation and Reusability of nZVI@BC

The catalytic performance of nZVI@BC was evaluated after repeated recovery and reuse processes. A TPH removal rate of 91.56% was obtained under the optimum parametric conditions derived from combined RSM and single-factor test results. A TPH removal
rate of 65.9% was achieved when the same nZVI@BC sample was used for the third time (Figure 5). This finding shows a high level of reusability for the nZVI@BC composite, which is likely due to its structure. A stable interaction has been reported to exist between C particles and the low-valent Fe on their surface [45]. The large number of Fe–O–C chemical bonds formed between Fe and C are responsible for the improved overall stability of the activator. In nZVI@BC, the encapsulation of nZVI within C particles appreciably reduces the loss of total Fe. In short, under optimum reaction conditions, nZVI@BC displays exceptional catalytic activity, and good recoverability and stability in the nZVI@BC/PS system. As a result, the nZVI@BC/PS system can be used to remediate TPH-contaminated waters.

Figure 5. Under optimized conditions, nZVI@BC Stability test results (Initial pH = 5.81, nZVI@BC Dose = 1.0 g/L, PS concentration = 80 g/L).

3.5. Catalytic Mechanism of nZVI@BC

Generally, contaminants can be degraded using chemical AOPs by two pathways that involve and do not involve FRs [46]. The FRs (SO$_4^-$ · and ·OH) involved in metal-catalysed reactions usually dominate the degradation process [47–49]. The latest findings show the presence of a 1O$_2$-dominated non-FR pathway when using a nonmetallic C-based catalyst to activate PS [50]. Therefore, it is inferred that SO$_4^-$ ·, ·OH, and 1O$_2$ are participants in the catalytic process of the nZVI@BC/PS system. The PS-based catalytic process may generate some FRs or non-FR oxides that can oxidise contaminants, as shown in Equations (7)–(11).

$$\text{S}_2\text{O}_8^{2-} + 2\text{OH}^- \rightarrow 2\text{SO}_4^{2-} + \text{HO}_2^- + \text{H}^+ \quad (7)$$
$$\text{S}_2\text{O}_8^{2-} + \text{HO}_2^- \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} + \text{O}_2^- + \text{H}^+ \quad (8)$$
$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \cdot \text{OH} + \text{H}^+ \quad (9)$$
$$2\text{S}_2\text{O}_8^{2-} + 2\text{OH}^- \rightarrow 2\text{SO}_4^{2-} + 2\text{SO}_4^{2-} + \text{O}_2 + 2\text{H}^+ \quad (10)$$
$$2\text{O}_2^- + 2\text{H}^+ \rightarrow 1\text{O}_2 + \text{H}_2\text{O}_2 \quad (11)$$

To validate this inference, an EPR analysis was performed with DMPO and TEMP as spin-trapping agents (STAs) (Figure 6). The characteristic peaks of the DMPO-SO$_4$ and DMPO-OH conjugates (DMPO-SO$_4$: a$_{H}$ = 12.3 G; a$_{N}$ = 9.6 G; a$_{L}$ = 1.48 G; a$_{LL}$ = 0.78 G; DMPO-OH: a$_{N}$ = 15.05 G; a$_{NN}$ = 14.21 G; quartet intensity ratio: 1:2:2:1) are evident in the 5-min EPR spectrum obtained with DMPO as an STA [51,52]. These results perspicuously demonstrate that SO$_4^{2-}$ · and ·OH participated in the catalytic reaction.
Further analysis of the EPR spectra of the nZVI@BC/PS system reveals the trend of change in the characteristic peaks of the DMPO-SO₄²⁻ and DMPO-OH conjugates. The peaks of these conjugates intensified as the reaction progressed. The formation of DMPO-SO₄²⁻ is usually accompanied by that of DMPO-OH. Two factors preclude the sole presence of DMPO-SO₄²⁻: (1) SO₄²⁻ radicals are partially transformed to ·OH radicals (Equations (9)) and (2) the DMPO-SO₄²⁻ conjugate is susceptible to transformation to DMPO-OH through nucleophilic substitution [53]. O₂⁻· radicals were also identified in the studied system (Figure S5). Moreover, representative triplet EPR spectra (1:1:1; α = 17.2 G) were obtained with TEMP as an STA [19,44]. The peak intensity increased sharply within 60 min, suggesting a continuous formation of ¹O₂. These FRs could be released and diffuse onto the surface of the liquid.
and solid phases of the solution. The intermediate products in the degradation process of TPH were identified by GC–MS, including epoxides and esters (Figure S6, Table S5).

The mechanism by which PS is activated by the nZVI@BC composite to degrade TPH can be inferred from the results presented above (Figure 7). nZVI is the main source of Fe$^{2+}$ in the solution. The activation of PS by Fe$^{2+}$ on the nZVI@BC surface is primarily responsible for the generation of SO$_4^{−}$ [26]. The Fe$^{2+}$ release rate depends on the corrosion rate of the nZVI surface. Acidic conditions can accelerate the release of Fe$^{2+}$. Fe$^{2+}$ can be regenerated inside the pores of the nZVI@BC system through the reaction between Fe$^{3+}$ and the nZVI surface. ·OH and O$_2^{−}$· are other important types of FRs that can degrade TPH [54]. The carboxylic (C–OOH) and alcoholic (C–OH) groups on the BC surface can also produce SO$_4^{−}$· by releasing organic groups, as shown in Equations (12) and (13). In the nZVI@BC system, nZVI is well dispersed on the BC surface, reducing the formation of aggregates. Therefore, the nZVI@BC can enhance the capacity of the nZVI@BC/PS system to yield SO$_4^{−}$·. A $^{1}$O$_2$-dominated non-FR pathway is partially responsible for TPH degradation in the presence of the nZVI@BC/PS system. This pathway improves the catalytic performance of nZVI@BC, thereby further increasing the TPH degradation rate. In the nZVI@BC/PS system, under the oxidation of SO$_4^{−}$·, ·OH, O$_2^{−}$·, and $^{1}$O$_2$, taking long-chain alkanes as an example, long-chain alkanes may degrade into short-chain alkanes, epoxides and esters, and finally mineralise into carbon dioxide and water under the condition of sufficient oxidants.

\[
\begin{align*}
\text{BC-OH} + S_2O_8^{2−} & \rightarrow SO_4^{−}· + HSO_4^{−} + \text{BC-O} \quad (12) \\
\text{BC-OOH} + S_2O_8^{2−} & \rightarrow SO_4^{−}· + HSO_4^{−} + \text{BC-OO} \quad (13)
\end{align*}
\]

Figure 7. Potential mechanism of TPH degradation by the nZVI@BC/PS system.

4. Conclusions

In this study, nZVI was loaded onto bagasse-derived BC to produce nZVI@BC, which was subsequently used to activate a PS. The activated PS, termed nZVI@BC/PS, was found to be highly effective in removing TPH from water. The relevant reaction followed first-order kinetics. $D_{nZVI@BC}$, $C_{PS}$, and pH were the key factors influencing the performance of the nZVI@BC/PS system. Analysis of the single-factor test results and RSM-based optimisation results revealed a TPH removal rate of 91.56% under $pH = 5.81$, $D_{nZVI@BC} = 1.0 \text{ g/L}$, and $C_{PS} = 80 \text{ g/L}$. nZVI@BC displayed good stability with a TPH removal rate of 65.9% when the same nZVI@BC sample was used for the third time. EPR spectroscopic analysis of the nZVI@BC/PS system revealed that SO$_4^{−}$·, ·OH, O$_2^{−}$·, and $^{1}$O$_2$ participated in the activation and degradation processes. The results of this study show that nZVI@BC-
activated PS systems possess enormous potential for applications in wastewater treatment and environmentally sustainable development.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/su14159324/s1, Figure S1. XRD. Figure S2. XPS. Figure S3. FTIR. Figure S4. PS, BC nZVI@BC and BC/PS system on the degradation of TPH. Figure S5. O2-· in nZVI@BC/PS system. Figure S6. GC-MS of TPH in nZVI@BC/PS system. Table S1. First-order kinetic parameters for removing TPH at different nZVI@BC dose. Table S2. First-order kinetic parameters for removing TPH at different Persulfate (PS) conc. Table S3. First-order kinetic parameters for removing TPH at different initial pH values. Table S4. Analysis of variance of quadratic regression equation. Table S5. Retention time and qualitative information of organic compounds during degradation of TPH.

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