Activating peroxymonosulfate using carbon from cyanobacteria as support for zero-valent iron

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Abstract
In the present study, the cyanobacterial char (ACC) prepared from Chaohu cyanobacteria was used as a nanoscale carrier for zero-valent iron (NZVI) to synthesize a highly efficient activation material designated as cyanobacterial char-supported nanoscale zero-valent iron (NZVI@ACC), which was subsequently used for activating peroxymonosulfate (PMS) to degrade the orange II (OII) dye. The XRD and XPS results revealed that NZVI was anchored onto the ACC through coordination bonding, forming a stable structure. The SEM and TEM observations revealed that the NZVI was embedded in the sheet structure of the ACC. The NZVI@ACC had a larger specific surface area (42.249 m²/g) and also magnetism, due to which its components could be separated through an externally applied magnetic field. Using this NZVI@ACC/PMS system, the rate of degradation of OII (100 mg/L) reached 98.32% within 14 min. The OII degradation reaction using the NZVI@ACC/PMS system followed first-order kinetics. The activation energy of this degradation reaction was 17.34 kJ/(mol·K). Quenching and EPR experiments revealed that various free radicals (SO₄·−, ·OH) were produced, with SO₄·− playing the major role in the reaction. The theoretical calculations revealed that SO₄·− attacked the 12 (N) of OII, thereby destroying and degrading both azo and hydrogenated azo structures of OII. The presence of halogen ions in the actual dye-containing wastewater samples inhibited the OII degradation by the NZVI@ACC system to different degrees, and the inhibition effect followed the order I− > Br− > Cl−.

Keywords Cyanobacterial carbon · NZVI@ACC · PMS activation

Introduction
Advanced oxidation processes (AOPs) based on sulfate radicals are gaining increasing attention recently. In comparison to the hydroxyl radical (-OH)-based advanced oxidation, the sulfate radical (SO₄·−)-based AOPs have a higher redox potential (2.5 ~ 3.1 V) and a longer half-life (T₁/₂(SO₄·−) = 30 ~ 40 µs, T₁/₂(OH) = 10⁻³ µs), which becomes a contributing factor in the effective and sustainable degradation of refractory organic matter in water (Yang et al. 2011; Sun et al. 2019). In a typical AOP, peroxymonosulfate (PMS) may be activated to generate SO₄·− using various activation methods, including those based on the ultraviolet light, electricity, heat, alkali, and transition metal ions such as Cu²⁺, Co²⁺, and Fe²⁺ (Xu et al. 2020). Light-based and thermal activation methods are expensive and energy-consuming, rendering it difficult to achieve effective PMS activation in dark and low-temperature environments. Moreover, the commonly available transition metals, such as Ag⁺, Co²⁺, and Cu²⁺, are biotoxic and prone to secondary pollution (Zha et al. 2016; Czech et al. 2015; Soubh and Mokhtarani 2016; Lin et al. 2011).

Nanoscale zero-valent iron (NZVI), reduced iron powder, and other kinds of NZVI have been used for catalyzing the PMS degradation of organic pollutants in the environment. NZVI refers to particles with sizes ranging from 1 to 100 nm, large specific surface area, and strong reducibility, properties that confer NZVI with high reactivity and excellent performance. However, the small size and the high reactivity of these nanoparticles lead to easy agglomeration,
poor dispersion, and no ideal reactivity, all of which seriously impact their performance during the actual usage (Li et al. 2019; Yan et al. 2015). Therefore, various methods for preventing agglomeration during practical application have been studied, including adding a dispersant or carrier to the reaction system to disperse the nanoparticles (Zhong et al. 2019; Song et al. 2015). The modification methods that have been explored to overcome the defects of NZVI mainly include doping NZVI with other elements, surface modification by organic matter, and embedding NZVI to support and stabilize NZVI on carbon or other porous materials (Li et al. 2021).

With environment-friendly materials receiving increasing attention in the past few years, environment-friendly carrier materials and biochar exhibiting ideal immobilization and several economic and environmental advantages have gradually emerged (Wu et al. 2018; Lee et al. 2020; Zhou et al. 2014; Kwon et al. 2015). The materials come from various biomasses, especially some waste biomass, such as straw, animal manure, and wastewater sludges. As is well-known, the phenomenon of eutrophication in several water bodies has caused cyanobacteria to accumulate and occupy a large area of the water surface, leading to a series of ecological and environmental problems, including infesting on livestock, fish, and humans, and directly inducing liver cancer. The domestic measures for cyanobacteria control are implemented mostly after the outbreak of water blooms. The commonly used emergency control measures include salvage and ashore treatment and disposal by manpower, ships, tools, or other physical methods. However, the disposal of algae sludge does not happen in time, leading to various environmental problems that are being now being focused on by the management departments and all sectors of human society. Cyanobacteria are characterized by low ash, high moisture, and high volatility, with levels of C, H, O, fixed carbon, and volatility similar to the straw. These characteristics of cyanobacteria allow their application in synthesizing materials with developed pore structures (Zhang et al. 2020a, b; Gong et al. 2017). These materials can be made of carbon-rich solid products or synthesized using biochar-based composite materials. Researchers are also attempting to design and modify biochar using various physical and chemical methods to improve its performance further. Since different modification methods have different effects on biochar, it is essential to improve the characteristics of biochar specific to the requirements (Lian et al. 2020; Ma et al. 2018; Liu et al. 2018). This approach not only improves the physicochemical properties but also results in new composite material. The products could be used in environmental treatment and in realizing the recycling of resources (Liang et al. 2021; Li et al. 2021; Hao et al. 2021).

In the present study, cyanobacterial char (ACC) supported nanoscale zero-valent iron (NZVI@ACC) was prepared and then used to activate PMS to remove a typical refractory organic dye named OII from water samples. The study included the following aspects: (1) characterization of the prepared NZVI@ACC, (2) evaluation of the factors associated with the NZVI@ACC/PMS system influencing the OII degradation, (3) determination of the active species of the reaction system and analyzing the underlying activation mechanism, and (4) explore the effect of the NZVI@ACC/PMS system on different halogens and dyes.

**Materials and methods**

**Materials**

Cyanobacteria collected from Chaohu lake were used as the raw material for obtaining biochar. The element ratios of cyanobacteria were C (46.68%), H (7.36%), N (7.02%), and O (38.94%), respectively. PMS (KHSO₅·0.5KHSO₄·0.5K₂SO₄), FeSO₄·7H₂O, NaBH₄, HCl, NaOH, ethanol (C₂H₅OH), methanol (CH₃OH, MeOH), tert-butyl alcohol (CH₂₂COH, TBA), and furfuryl alcohol (C₅H₆O₂, FFA) were purchased from Aladdin Reagent Co. Ltd. Congo red (C₁₃H₁₂N₂Na₂O₅S, CR), methylene blue (C₁₈H₂₂ClN₃S, MB), and rhodamine B (C₂₈H₃₁ClN₂O₂, RB) were purchased from Sinopharm Chemical Reagent Co. Ltd. All reagents used in the present study were analytical grade.

**Preparation of NZVI@ACC**

An appropriate amount of dry cyanobacteria powder was placed in a crucible. The tube furnace was programmed to heat at 500 °C for 6 h at a heating rate of 10 °C/min under N₂ protection. The carbonization temperature was maintained for the stated duration, and then the furnace was cooled. The carbonized powder was ground through a 100-mesh sieve and then soaked in 1 mol/L of HCl for 12 h. After removing ash, the powder was washed with deionized water, neutral dried, and preserved. An amount of 3.754 g of FeSO₄·7H₂O was dissolved in 250 mL deionized water (0.054 mol/L) followed by the addition of 250 mL of anhydrous ethanol as the dispersant. ACC was added to this solution followed by magnetic stirring (200 r/min) for 10 h. The solution was then dried and ground, and the obtained dry mixture was dissolved in 100 mL of deoxidized and deionized water to obtain a solution. Subsequently, intermediate products and 50 mL (1~2 drops/s) of 0.135 mol/L of freshly prepared NaBH₄ solution were added to this solution under the N₂ protection. After aging for 1 h, black particles were generated, which were first washed three times with deoxidized and deionized water three times and then with ethanol. Finally, after vacuum drying in an oven, NZVI@ACC was obtained and stored in a sealed container for preservation.
Experimental procedure

The batch test was performed in a glass conical flask (250 mL) containing 100 mL of the reaction solution. NZVI@ACC was added to 100 mL of OII (100 mg/L) at the initial pH of 6. Subsequently, the flask was placed in an oscillation box at a constant temperature of 25 °C and an oscillation frequency of 110 times/min. PMS (1 mmol/L) was added, and the duration was measured after dissolution. The effects of the following parameters on the degradation of OII were studied: the dosage of NZVI@ACC, the ratio of iron to carbon (Fe/C) in NZVI@ACC, the reaction temperature, and the reaction pH. At each measurement time point, a volume of 5 mL was sampled and filtered through a 0.45 µm filter membrane. The absorbance of the filtered sample was measured at 484 nm in an ultraviolet spectrophotometer.

Analytical methods

The elements were determined using a Vario SL cube elemental analyzer (Elementar, Germany). TD-3500 X-ray diffractometer (Tongda, China) was employed to radiate the samples to obtain their X-ray diffraction (XRD) patterns. The XPS spectra were obtained by scanning the samples using Thermo Fisher K-Alpha X-ray photoelectron spectroscopic instrument (Thermo Field). In addition, the samples were gold-plated and observed under an S-4800 cold-field emission (Hitachi, Japan) scanning electron microscope (SEM). Transmission electron microscopy (TEM) observation of the samples was performed using FEI-TALOS-F200X (Fei, America). The radicals in the samples were detected using electron paramagnetic resonance with DMPO and TEMP (EPR, Bruker A300, Germany). A vibrating sample magnetometer (VSM) was used at 7040 ± 2 T (Lake Shore, America). The specific surface area and the pore size of the particles in the sample were determined based on the N2 adsorption/desorption curves using a fully automated surface and porosity tester (Quantachrome, America). The samples were measured by the Nicolet IS 50 + Continuum (Thermo Fisher, America) Fourier transform infrared spectrometer (FTIR). The zeta potential was tested by a zeta analyzer at different pH (Zetasizer Nano-ZS 90, Malvern, America). TOC measured by TOC-L analyzer (Shimadzu, Japan). The concentration of iron ion was analyzed by a AA-7000 atomic absorption spectrometer (Shimadzu, Japan).

Results and discussion

Material characterization

XRD and XPS analyses

The XRD pattern, the XPS survey, and XPS analysis of C 1 s, O 1 s, and Fe 2p binding states in NZVI@ACC was depicted in Fig. 1. A sharp diffraction peak was observed at 44.7°, as depicted in Fig. 1a, while a weak diffraction peak was observed at 64.8°. When compared to the standard PDF card (06–0696) of iron, these two peaks corresponded precisely to the 110 crystal plane diffraction (44.7°) and 200 crystal plane diffraction (65.0°), respectively. According to Bragg’s equation, the crystal spacing was 0.203 nm. In addition, a sharp diffraction peak was observed at 26.6°, as depicted in Fig. 1a. It was comparable to the standard PDF card (26–1077) of carbon. The chemical composition of NZVI@ACC was revealed in the XPS analysis (Fig. 1b–e). The binding energies of C 1 s at 284.7 eV and 286.0 eV were classified as those of C–C and C-O, respectively. In the Fe 2p spectra, the binding energy of the characteristic peaks at 707.00 eV, 710.70 eV, and 712.50 eV were attributed to Fe0, Fe2+, and Fe3+, respectively (Li et al. 2019). After loading the NZVI onto NZVI@ACC, the Fe peak (peak C depicted in Fig. 1c) was formed at 288.7 eV, while the characteristic peak of C-O exhibited a redshift (Fig. 1d, e) indicating the loss of electrons of C and O corresponding to the gain of electrons of Fe. According to the hybrid orbital theory, it may be observed in Fig. 1f, g, and h that the lone pair electrons from C sp3 and O sp3 hybrid orbital could occupy the Fe2+ sp3d2 orbital, a strong force can be established between active groups (C-O, -OH) and metal ion (Fe2+), which suggested that a coordinate bond (Fe–C and Fe–O) could be established between the NZVI and the active group on the surface of ACC (Huang et al. 2022).

SEM and TEM

The morphology of the catalysts was observed using SEM and TEM. As depicted in Fig. 2, the NZVI@ACC material had a loose structure and a flat lamellar organization, attributed to the aggregation of NZVI during its formation process. The TEM images were depicted in Fig. 2c and d. The TEM results revealed that the iron particles (black spots in the depicted images) were highly dispersed throughout ACC. The lattice spacing was determined to be 0.203 nm, and the crystal plane was (110). The images depicted in Fig. 2e and f together confirmed the successful preparation of NZVI@ACC with an even distribution.
of NZVI over the ACC surface. The prepared NZVI@ACC had an increased surface area; it also contained an increased number of edges and defects. The TEM mappings of NZVI@ACC were shown in Fig. 2f; the results revealed the chemical element (N, O, Si) in the NZVI@ACC.

BET, magnetic detection, FTIR, and zeta potential

The Brunauer–Emmett–Teller (BET) surface area ($S_{\text{BET}}$) and the pore volume of NZVI@ACC, determined according to the $N_2$ adsorption–desorption isotherm, and BJH desorption pore size distribution were 49.249 m$^2$/g and 0.104 cm$^3$/g, respectively (Fig. 3a). According to the IUPAC classification, the adsorption isotherms of NZVI@ACC were of the characteristic type IV, with P/P$_0$ having an H4 hysteresis loop between 0.4 and 1.0. The prepared NZVI@ACC contained both micropores and mesoporous pores, most with sizes of approximately 19.096 nm.

Figure 3b depicted the hysteresis loop of NZVI@ACC. The symmetric loop shape of the origin indicated good ferromagnetism and sub-ferromagnetism of the prepared NZVI@ACC, due to which its components could be separated using an external magnetic field during a practical
Fig. 2  a, b SEM; c, d TEM; and e, f TEM mapping of NZVI@ ACC
application, thereby allowing material recycling. This was also verified in experimental operation. The coercivity and magnetization of NZVI@ACC were 233.16 Oe and 0.67 emu/g, respectively. The low saturation magnetization of NZVI@ACC indicated that the particle size of NZVI@ACC was in the micron range, which was consistent with the SEM results.

The FTIR spectra of NZVI@ACC (Fig. 3c) indicated the presence of a large number of carbon and oxygen functional groups in the material. The peak at 812 cm\(^{-1}\) corresponded to the symmetrical stretching peak of Si–O–Si. The peak at 1102 cm\(^{-1}\) was the C-O symmetrical stretching peak. The peak at 1520 cm\(^{-1}\) was the C=C telescopic vibration peak. The peak 1710 cm\(^{-1}\) was the C=O carboxylic acid carbonyl stretching vibration peak. The functional group corresponding to the peak value of 3678 cm\(^{-1}\) and 1398 cm\(^{-1}\) was -OH. Due to its hydrophilicity, it was conducive to the material to play a role in dye wastewater. The XPS results of NZVI@ACC confirmed the surface functional groups of the material.

In Fig. 3d, under the different pH, the zeta potential values of NZVI@ACC were measured; the point of zero charge (pHpzc) value of NZVI@ACC was 6.7, which was shown in Fig. 3d.

**Effects of reaction conditions on OII degradation**

The effects of activator dosage, ratio of Fe/C, reaction temperature, and reaction pH on the activation of PMS using NZVI@ACC were analyzed. The results were presented in Fig. 4.

The effects of different dosages of activator and kinetics on the degradation of OII were presented in Fig. 4a and e. Since NZVI@ACC provided the active sites, its dosage affected the degradation effect of OII. PMS had a high redox potential (2.01 V), and due to its low activity, the rate of OII removal could only reach 4.62% within 14 min. When 0.1 g of NZVI@ACC was added to the system, the rate of OII removal reached 98.32% within 14 min. With the increase in the dosage of NZVI, the oxygen-containing functional groups on the surface of NZVI@ACC also increased, thereby increasing the activation of PMS (Li et al. 2016). The simulation results presented in Fig. 4e revealed that the reaction process conformed to the first-order kinetics under the influence of dosage. Both kinetic constant \(k\) and the reaction rate increased within a certain range. According to origin fitting analysis, the reaction rate constant increased linearly with increasing dosage, which was consistent with \(y = 2.89x - 0.0108\); the correlation index \(R^2\) was 0.973. As
the dosage increased, a greater NZVI@ACC surface area was available for the reaction, which increased the reaction rate. However, when the activator was in excess, no significant change was observed in the effect of OII removal as the excessive activator led to wasted active sites and decreased utilization rate of the material.

As visible in Fig. 4b, ACC alone had almost no catalytic effect on PMS, and the rate of OII removal achieved using the ACC/PMS system (Fe/C = 0:1) was only 9.43% within 14 min. After the addition of NZVI, which was a strong reducing agent, to the system, the OII removal effect of the system was significantly improved. When added the NZVI alone, the OII removal rate reached 86.64% within 14 min in the NZVI/PMS system (Fe/C = 1:0). The ratio of Fe/C in the NZVI@ACC/PMS system was 1:1; the OII removal rate reached 98.32% within 14 min, which was almost complete removal. Therefore, the NZVI@ACC/PMS system exhibited the best OII removal effect.

The influence of reaction temperature and kinetic on the OII degradation effect was depicted in Fig. 4c and f. When the reaction temperature was 10 °C, the OII degradation rate of 93.09% was reached within 14 min. When the reaction temperature was increased to 25 °C and 40 °C, the OII removal rate increased to over 98.32%. It could be observed that an increase in the reaction temperature could accelerate the molecular movement and improve the reaction speed within a certain range. Figure 4f illustrated the kinetic simulation of the OII degradation effects at different temperatures, which conformed to quasi-first-order kinetics. The degradation rate increased with the increase in the reaction temperature from 10 to 40 °C. The increase in the temperature improved the energy absorbed by the molecules during the reaction and accelerated the decomposition to produce free radicals (Zrinyi and Pham 2017). Meanwhile, the molecular motion was accelerated, which increased the probability and the rate of molecular collision, thereby accelerating the reaction.
process (Hori et al. 2005). According to the Arrhenius’ law, the relationship between the reaction rate and the temperature followed the equation lnk = lnk° − Ea/RT. After linear fitting lnk and 1/T, the following fitting equation was obtained: y = −2086.2x + 5.7156, and the activation energy of NZVI@ACC/PMS degradation of OII was calculated to be 17.34 kJ/(mol·K).

Furthermore, the pH of the reaction system affects the charge of NZVI@ACC and the free radicals in the system, which, in turn, has a significant influence on the PMS-based degradation of pollutants in wastewater. The results presented in Fig. 4d revealed that at the initial reaction pH of 4, the OII removal rate was 99.01% within 14 min. At the pH of 6 and 8, the OII removal rates were 98.32% and 93.09%, respectively. Therefore, while a high degradation rate was maintained, the degradation rates were various at different pH values. In the acidic environment, under the pHpzc values (6.7) of NZVI@ACC, the surface of NZVI@ACC was positively charged; it was easy to absorb the anionic dyes of OII and increase the possibility of degradation in the reaction system. In addition, NZVI@ACC was more likely to precipitate Fe²⁺, SO₄²⁻, ·OH, and Fe³⁺ produced upon the activation of PMS by Fe²⁺ (Eq. 1 and 2), thereby generating more ·OH as an electron from H₂O (Eq. 3) (Du et al. 2016; Fuller et al. 2013; Hussain et al. 2017; Lin et al. 2013). However, in alkaline conditions, SO₄²⁻ and OH⁻ could generate ·OH with a slightly lower oxidation activity (Eq. 4), thereby decelerating the degradation rate, although the organic compounds could nonetheless be degraded by ·OH ultimately. When the pH increased to 10, the OII degradation rate of only 67.55% remained. With the increase of pH, a passivation layer was formed on the surface of NZVI, which inhibited the generation of free radicals, thereby decreasing the OII degradation rate (Gao et al. 2019; Zhang et al. 2020a, b).

\[
\begin{align*}
Fe^{2+} + HSO_5^- &\rightarrow Fe^{3+} + OH + SO_4^{2-} \\
Fe^{2+} + HSO_5^- &\rightarrow Fe^{3+} + HO^- + SO_4^{-}
\end{align*}
\] (1) (2)

\[
SO_4^{2-} + H_2O \rightarrow SO_4^{2-} + OH + H^+ \quad (3)
\]

\[
SO_4^{2-} + OH^- \rightarrow SO_4^{2-} + OH \quad (4)
\]

**Mechanism underlying the effect of OII degradation by NZVI@ACC activated PMS**

MeOH reacts rapidly with both SO₄²⁻ (9.7 × 10⁸ L/mol·s) and ·OH (3.2 × 10⁸ L/mol·s) (Huang et al. 2014); TBA is a well-recognized efficient scavenger of ·OH that is not sensitive to SO₄²⁻ because of its higher reaction rate constant for ·OH (3.8 × 7.6 × 10⁸ L/mol·s) compared to that for SO₄²⁻ (4.0 × 9.1 × 10⁵ L/mol·s). Therefore, TBA serves as the probe specifically for ·OH (Pham et al. 2009; Tsai et al. 2008; Anipsitakis and Dionysiou 2004). The singlet oxygen (¹O₂), as a potential reactive oxygen species, could be inhibited by FFA in a non-radical pathway. The MeOH, TBA, and FAA inhibitors were utilized to determine the contribution of SO₄²⁻, ·OH, and ¹O₂ in the reaction process. The results of the analysis were presented in Fig. 5a. The OII degradation rate of 98.32% was achieved in the no scavenger group, which decreased to 74.54%, 84.49%, and 95.47% after the addition of MeOH, TBA, and FAA, respectively. MeOH inhibited a greater inhibition effect than TBA and FAA. It was speculated that SO₄²⁻ played a major role in the reaction, the second was ·OH, and the last was ¹O₂. The radicals generated in the NZVI@ACC/PMS system remained concentrated on the surface of the activator, the reaction could occur on the surface of the activator (Dong et al. 2019).

In order to determine the types of active radicals generated in the reaction process, the trapping agent DMPO and TEMP was used for EPR detection during the degradation process. The results were presented in Fig. 5b. No evident signal peak appeared for the reaction system with only PMS, and the degradation rate achieved was only 4.62% without NZVI@ACC, which indicated that PMS was relatively stable, and no active radicals were generated in the system.
In the DMPO capture results for the NZVI@ACC/PMS system, the characteristic peaks of DMPO-OH and DMPO-SO$_4^{2-}$ were detected within 2 min; an obvious typical peak signal was observed as the reaction of DMPO-SO$_4^{2-}$, which suggested that SO$_4^{2-}$ might be the dominant reactive species responsible for OII degradation. In addition, the TEMP capture result shown that there was no obvious typical peak of $^{1}$O$_2$ in the NZVI@ACC/PMS system. The results of trapping agent DMPO and TEMP test agreed with the inhibitor, indicating the presence of SO$_4^{2-}$, ·OH, and $^{1}$O$_2$ in the reaction system, and that SO$_4^{2-}$ played a major role.

Theoretical calculations were performed to provide deeper insights into the OII degradation by NZVI@ACC activated PMS. Numerous free radicals were generated in the NZVI@ACC/PMS reaction system. The main types of reactions were the free radical and the nucleophilic reactions. The calculations for the local descriptor and Fukui function were performed to identify the most vulnerable sites of OII. The optimized OII molecule was depicted in Fig. 6. The CDD values calculated using Gaussian 09 were listed in Table 1. The highest CDD value of 12 (N) atom indicated that 12 (N) was the site most vulnerable to the attack of oxidative species. The proposed degradation mechanism underlying the reaction for OII degradation by NZVI@ACC/PMS was presented in Fig. 7. First, there was a contact among OII, NZVI@ACC, and PMS, and the reaction occurred under agitation. Next, the free radicals produced in the reaction attacked the 12 (N), thereby breaking down the OII structure; both azo and hydrogenated azo structures were effectively degraded, producing smaller organic molecules, such as phenylamine and naphthalene. Finally, OII was degraded completely into small molecules (CO$_2$ and H$_2$O) (Yin et al. 2017).

**Applications**

Halogen ions are the common anions present in dye wastewater and may react with SO$_4^{2-}$ and OH (Zhang and Parker 2018) according to the following reaction formula:

$$SO_4^{2-} + X^- + OH^- \rightarrow SO_4^{2-} + OH^- + X$$  \hspace{1cm} (5)

Here, $X$ denotes the halogen ion, such as Cl$^-$, Br$^-$, and I$^-$. According to the steady-state approximation, the degradation rate of OII may be expressed as follows:

![Fig. 6 Optimized structure of OII and the numbering system (gray, carbon; red, oxygen; blue, nitrogen; white, hydrogen; yellow, sulfur; and purple, sodium)](image_url)

![Table 1 CCD values of atoms in OII molecule](image_url)

| Atoms | CCD   | Atoms | CCD   | Atoms | CCD   | Atoms | CCD   | Atoms | CCD   |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1 (C) | -0.0404 | 8 (C) | -0.0035 | 15 (C) | -0.0038 | 22 (O) | -0.0063 | 29 (H) | 0.0061 |
| 2 (C) | 0.0029 | 9 (C) | -0.0047 | 16 (C) | -0.0083 | 23 (H) | -0.0101 | 30 (H) | -0.0000 |
| 3 (C) | -0.0078 | 10 (C) | -0.0559 | 17 (C) | -0.0115 | 24 (H) | -0.0079 | 31 (H) | 0.0001 |
| 4 (C) | -0.0268 | 11 (O) | -0.0189 | 18 (C) | -0.0039 | 25 (H) | -0.0081 | 32 (H) | 0.0034 |
| 5 (C) | -0.0305 | 12 (N) | 0.0581 | 19 (C) | -0.0100 | 26 (H) | -0.0046 | 33 (H) | -0.0038 |
| 6 (C) | -0.0073 | 13 (N) | 0.0114 | 20 (S) | 0.0004 | 27 (H) | 0.0012 | 34 (O) | -0.0256 |
| 7 (C) | 0.0016 | 14 (C) | -0.0154 | 21 (O) | -0.0164 | 28 (H) | -0.0019 | 35 (Na) | 0.2446 |

![Fig. 7 The proposed mechanism underlying the reaction for OII degradation by NZVI@ACC/PMS.](image_url)
The degradation rate of OII decreased significantly when the concentration of Cl− was increased to 2.0 mmol/L. According to these data, it could be concluded that halogen ions exerted an evident inhibition effect on the OII degradation by the NZVI@ACC/PMS system, and the inhibition effect followed the order I− > Br− > Cl−.

Since the addition of the halogen ions reduced the OII degradation efficiency of the NZVI@ACC/PMS system, it was inferred that in the NZVI@ACC/PMS OII degradation system, halogen ions competed for active radicals with the substrates and degradation intermediates, for electron transfer with SO4·−, ·OH, SO5·−, and SO·−, and for other active radicals, resulting in the formation of less active radicals.

Owing to the variety of dyes available and the complexity of the actual dye composition, the degradation experiments were conducted using different cationic and anion dyes to evaluate the treatment effect of the NZVI@ACC/PMS system. The results were presented in Fig. 8d. The rates of degradation of CR, OII, RB, and MB at 100 mg/L achieved by the optimal dosage of the NZVI@ACC/PMS system within 14 min were 99.39%, 98.32%, 64.61%, and 52.55% under, respectively. It could be observed that the removal rate achieved by the NZVI@ACC/PMS system for anionic dyes was significantly higher than that achieved by this system for cationic dyes, because the anionic dyes might be easy to contact NZVI@ACC and promote the generation of active free radicals such as SO4·−. Moreover, the NZVI@ACC could be recycled, basing on the magnetism, the rates of degradation of OII in the NZVI@ACC/PMS system within 14 min were 85.23% after recycling three times, the NZVI@ACC may lose part of activity after prolonged use, it was probably
because of surface passivation by precipitates, and it could regenerate by high temperature (Chen et al. 2016). The TOC removal rate was 51.77% in the NZVI@ACC/PMS system within 42 min; the result indicated that the reaction system could not only degrade OII, but also decompose and oxidize organic matter. The concentration of iron ion was detected in the solution. NZVI@ACC dissolved out iron ion was low, the concentration of iron ion was 0.828 mg/L within 14 min, and the combination of the NZNI and ACC was relatively stable. These results showed that activators of NZVI@ACC could maintain high activity and stability.

**Conclusions**

NZVI@ACC was successfully synthesized, and it was revealed that NZVI combined with ACC through coordination bonding, thereby forming a stable structure. NZVI@ACC exhibited high efficiency and stability in activating PMS to degrade OII. The rate of OII degradation achieved using the NZVI@ACC/PMS system reached 98.32% within 14 min. The reaction system produced a mass of $SO_4^{2-}$, which attacked the 12 (N) of OII, thereby destroying and degrading both azo and hydrogenated azo structures of OII. Since the NZVI@ACC used in the present study was prepared using ACC from cyanobacteria and NZVI, it allows realizing the effective utilization of the cyanobacteria reserves and NZVI.

**Author contribution**  Jun Chen: validation, investigation, visualization, resources, writing, and review and editing 
Layun Zhu: investigation, methodology, visualization, writing—original draft, and writing—review & editing 
Sisi Cao: validation, visualization, investigation, and review and editing 
Zihui Song: investigation and review and editing 
Jie Jin: validation, resources, writing, and review and editing 
Zhaoming Chen: investigation and review and editing

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**Data availability**  The datasets used and/or analyzed during the current study are available from the corresponding author on reasonable request.

**Declarations**

**Ethics approval and consent to participate**  Not applicable.

**Consent for publication**  Not applicable.

**Competing interests**  The authors declare no competing interests.

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