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Fast peroxydisulfate oxidation of the antibiotic norfloxacin catalyzed by cyanobacterial biochar

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HIGHLIGHTS

- Reactivity of Cyanobacterial biochar (CB) rises at high pyrolysis temperature (PT).
- CB pyrolyzed at 950 °C obtains the fastest NOR degradation and can be recycled.
- CBs are active at pH 3–10, with double rates under alkaline conditions.
- Organic, *OH, SO4• radicals and Mn II degrade NOR in presence of low PT CB.
- Electron transfer with radicals involved dominates in presence of high PT CB.

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GRAPHICAL ABSTRACT

A BSTRACT

Peroxidisulfate (PDS) is a common oxidant for organic contaminant remediation. PDS is typically activated by metal catalysts to generate reactive radicals. Unfortunately, as radicals are non-selective and metal catalysts may cause secondary contamination, alternative selective non-radical pathways and non-metal catalysts need attention. Here we investigated PDS oxidation of commonly detected antibiotic Norfloxacin (NOR) using cyanobacterial nitrogen rich biochars (CBs) as catalysts. NOR was fully degraded by CB pyrolysed at 950 °C (CB950) within 120 min. CB950 caused threefold faster degradation than low pyrolysis temperature (PT) CBs and achieved a maximum surface area normalized rate constant of 4.38 × 10⁻² min⁻¹ m⁻² L compared to widely used metal catalysts. CB950 maintained full reactivity after four repeated uses. High defluorination (82%) and mineralization (>82%) were observed for CB950/PDS. CBs were active over a broad pH range (3–10), but with twice as high rates under alkaline compared with neutral conditions. NOR is degraded by organic, *OH and SO4• radicals in low PT CBs/PDS systems, where the presence of Mn II promotes radical generation. Electron transfer reactions with radicals supplemented dominate high PT CBs/PDS systems. This study demonstrates high PT biochars from algal bloom biomass may find use as catalysts for organic contaminant oxidation.

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1. Statement of Environmental Implication

Antibiotics like Norfloxacin are hazardous contaminants of major concern due to their persistence, high production volumes and bacterial resistance development. They are difficult to remove due to their polar and recalcitrant nature resulting in dispersion of antibiotics to the environment. Antibiotics may be degraded by radicals formed via metal catalyst activated peroxysulfate (PDS). However, radicals are non-selective and metal catalysts may cause secondary contamination. Therefore, this study explores the possibility of hazardous algal bloom resource recovery to produce cyanobacterial nitrogen-rich biochars to provide a green and easy-to-manufacture PDS catalyst for organic contaminant degradation by both radical and electron transfer pathways.

2. Introduction

Norfloxacin (NOR) is the most commonly detected fluoroquinolone antibiotic in drinking water (Wang et al., 2019a). The molecular structure, physical, and chemical properties and ionic form of NOR are shown in Fig. S1. NOR has high polarity and water solubility. At low pH, NOR is mainly present as a cation whereas NOR is in the zwiterionic form at neutral pH. Approximately 60% of NOR remains unchanged during human passage and is directly excreted from the body (Zhang et al., 2015). It is detected in aquatic environmental systems at concentrations ranging from ng L$^{-1}$ to μg L$^{-1}$. Its continued input can be harmful to humans, aquatic organisms, and wildlife, impairing species interactions and temporarily reduce the stability of planktonic ecosystems even at NOR concentrations below 0.5 mg L$^{-1}$ (Pan et al., 2020). In addition, antibiotic resistance genes (ARGs) have been recognized as emerging contaminants that accumulate in most water bodies (Li et al., 2021). In conventional wastewater treatment, NOR is not effectively removed due to its persistence and high water solubility, while the formation of disinfection by-products is frequently observed in water treatment processes (Sincero and Sincero, 2002). Furthermore, NOR chlorination by-products have been found to be more toxic than NOR itself (Médic et al., 2021). Therefore, the toxicity of NOR intermediates decreases during direct degradation (Pan et al., 2021) and the final product is non-toxic (Shah et al., 2018). Therefore, a complete approach to remove antibiotic contaminants such as NOR is becoming increasingly urgent.

Advanced oxidation processes (AOPs) such as photo-oxidation and oxidation by strong oxidants are efficient processes for the degradation of organic recalcitrant contaminants such as antibiotics in water and soil (Lee et al., 2020). Among these AOPs, persulfates, which include peroxydisulfate (S$_2$O$_8^2^-$, PDS) and peroxymonosulfate (HSO$_5^-$, PMS) have attracted attention due to their versatility, and low storage and transportation costs. Persulfates can be activated to generate highly reactive structural deterioration of the catalyst (Oh and Lim, 2019). Unlike hydrogen peroxide, which decompose to produce $\cdot$OH radicals, persulfate can be stimulated or enhanced by methods unrelated to other radicals (Yu et al., 2020) to directly oxidize organic contaminants (Wang et al., 2020a).

To date, two dominant non-radical pathways have been reported electron transfer and singlet oxygen (S$_{1g}$) oxidation (Wang et al., 2020b). The mechanism of electron transfer can be summarized as PDS attached to the catalyst surface to form a catalyst-PDS complex, which increases the overall redox potential of the catalyst. When the catalyst exceeds the oxidation potential of the pollutant, the complex will withdraw electrons from the pollutant (Ren et al., 2022), the catalyst acts as an electron mediator.

Due to the slow oxidation of recalcitrant organic pollutants with peroxulfate, various methods have been developed to activate persulfate, including the use of catalysts (Ho et al., 2019), alkaline conditions (Matzek and Carter, 2016), external energy input (microwave irradiation, ultraviolet light and heat) (Chen et al., 2019), and electrochemical methods (e.g. mixed metal oxide anodes) (Li et al., 2019). Compared to other methods, solid catalysts are preferred for wastewater treatment because they are inexpensive, do not require external energy, their production can be easily scaled up, and they can be easily recycled for reuse. Both metal-based and carbon-based materials have been applied to activate persulfates. Metal-based materials consist of one or more multivalent transition metals, such as iron or copper (Zhang et al., 2020) and iron oxides (Yin et al., 2019), which facilitate the PDS reaction via a radical pathway. For example, activation of PMS to produce SO$_4^-$ by zero-valent copper can be effective, but the copper material cannot be recycled because it is consumed during the reaction (Anipitsakis and Dionysiou, 2004) causing a risk of contamination by copper ions.

Carbon-based catalysts such as graphene, carbon nanotubes, activated carbon, and biochar are intensively studied as alternative materials for facilitating contaminant degradation by PDS/PMS. These carbon-based catalysts help to reduce chemical usage and avoid the formation of halogenated intermediates (Wan et al., 2021; Wei et al., 2018). In addition to the radical pathway, carbon-based catalysts, which are known to be good electrical conductors, can also facilitate non-radical pathways. Table S1 compares different methods for facilitating PDS/PMS oxidation of NOR, indicating that carbon-based catalysts are more reusable and can be applied under extreme pH. For example, in two different works by Liwei and co-workers using similar Co/Fe bimetallic oxides (Chen et al., 2018a, 2018b), the oxidation of NOR by CoFe$_2$O$_4$ alone catalyzed PMS via the radical pathway but limited to the pH range 6–8.5 and with the efficiency reduced by 20% after the first recycling run. In contrast, the combination of CoFe$_2$O$_4$ and graphene oxide (GO) catalyzed PMS oxidation of NOR by rapid electron transfer and over a wide pH range of 4–11, with NOR degradation still complete after four cycles.

Considering the high cost of graphene and carbon nanotubes in practical applications (Bhuyan et al., 2016), other carbon materials such as biochar made from wastes or biomaterials are attractive alternatives (Zhu et al., 2018). Nitrogen enrichment of biochar is often used to improve the reaction efficiency, which can be achieved by adding organic/inorganic nitrogen precursors during pyrolysis. Shang and co-workers calculated the adsorption energies ($\Delta E_{ads}$) of the PDS molecule on different carbon structures using Density Functional Theory (DFT) (Shang et al., 2019). The results showed that biochars with graphitic N had the lowest $\Delta E_{ads}$ (–0.437 eV) for PDS, followed by biochars with pyrrolic N (–0.304 eV), pristine graphene (–0.146 eV) and biochars with pyridinic N (–0.072 eV). Therefore, biochars containing graphitic N formed at high PT is favorable for binding PDS and...
facilitating non-radical oxidation (Duan et al., 2018b). The aforementioned N modification can be directly achieved by using high protein and thus nitrogen rich microalgae as feedstocks for biochar. On a wider perspective, nitrogen-rich biochars can also produced from microalgal blooms (Bi and Pan, 2017). The exploration of algal biochar not only provides an opportunity to reuse biowastes, but also an opportunity to explore algal biochars as redox catalysts.

The overall objective of this study was to prepare algal biochars and evaluate the biochar facilitated oxidative degradation of the antibiotic NOR by PDS, and to elucidate the pathway via either radical and/or electron exchange reactions. The specific objectives were (1) to evaluate the performance of different biochars for NOR oxidation by PDS, especially, by comparing photosynthetic cyanobacteria with heterotrophic Chlorella to evaluate the effects of different culture conditions, (2) to compare photosynthetic cyanobacteria with heterotrophic Chlorella to evaluate the effects of different culture conditions, (2) to investigate the effects of key variables such as biochar and PDS concentration, pH and water matrix on the kinetics of the tested process, (3) to identify transformation intermediates of NOR formed in the oxidation process, and (4) to elucidate the reaction mechanism of PDS with emphasis on the determining factors for the electron exchange reaction. These results may help to optimize the properties of algal biochars to favor the electron transfer pathway for the degradation of organic pollutants.

3. Materials and methods

3.1. Materials

Norfloxacin (NOR, analytical standard, ≥98% (TLC)), potassium persulfate (K$_2$SO$_4$, ACS reagent, ≥99.0%), and potassium peroxymonosulfate (KHSO$_5$0.5KHSO$_4$0.5 K$_2$SO$_4$, free-flowing, RediDril™) were purchased from Sigma-Aldrich. Dibasic sodium phosphate (Na$_2$HPO$_4$, ≥99.0%, Sigma-Aldrich) and monobasic sodium phosphate (NaH$_2$PO$_4$, ≥99.0%, Sigma-Aldrich) were used to make pH buffered solutions. Magnesium chloride (MgCl$_2$, 6H$_2$O, ACS reagent, ≥98%, Sigma-Aldrich), sodium nitrate (NaNO$_3$, ACS reagent, ≥99.0%, Sigma-Aldrich), calcium sulfate (CaSO$_4$, 2H$_2$O, ACS reagent, ≥99.99%, Sigma-Aldrich), potassium bicarbonate (KHCO$_3$, ACS reagent, ≥97.7%, Sigma-Aldrich) and humic acid (HA, technical grade, Sigma-Aldrich) were used for natural water simulation. Sodium thiosulfate (Na$_2$S$_2$O$_3$, ≥99.99% trace metals basis, Sigma-Aldrich) was used to quench the oxidation of NOR by PDS followed by analysis of NOR and transformation products. Acetonitrile (High performance liquid chromatography (HPLC) grade), phosphoric acid (H$_3$PO$_4$, 85 wt% in H$_2$O, FCG, FG, Sigma-Aldrich) and triethylamine ((C$_2$H$_5$)$_3$N, bioultra, ≥99.5%, Sigma-Aldrich) were used for preparation of HPLC mobile phase. Formic acid (HCOOH, ACS reagent, ≥98%, Sigma-Aldrich) and ammonium hydroxide solution (NH$_4$OH, ACS reagent, 28.0–30.0% NH$_3$ basis, Sigma-Aldrich) were used for preparation of the Ultra Performance Liquid Chromatography - tandem Mass Spectrometer (UPLC-MS/MS) mobile phase. Methanol (CH$_3$OH, suitable for HPLC, ≥99.9%, Sigma-Aldrich), chloroform (CHCl$_3$, suitable for HPLC, ≥99.8%, Sigma-Aldrich), β-carotene (≥93% (UV), Sigma-Aldrich) were used in radical quenching experiments. 5,5-dimethylpyrroline-N-oxide (DMPO, for ESR-spectroscopy, Sigma-Aldrich) and 2,2,6,6-tetramethylpiperidine (TEMP, ≥99%, Sigma-Aldrich) were used for radical detection. Sodium fluoride (for analysis ESURE, ≥99.5%, Sigma-Aldrich) was used to prepare standard solutions for ion Chromatography. Ammonium bicarbonate (≥99.0%, Sigma-Aldrich) and potassium iodide (KI, ACS reagent, ≥99.0%, Sigma-Aldrich) were used for determining PDS concentrations. Ultrapure water prepared with PURELAB Chorus 1 was used throughout the experiments. All chemicals were analytical grade or better and used without further purification.

3.2. Preparation of algal biochar

Two different types of microalgae harvested from different culture conditions (phototrophic vs heterotrophic) were tested in this study (Text S1). Microalgal powder (2 g) was dried overnight (24 h) at 80 °C, then heated to 200, 500, and 950 °C at a rate of 150 °C h$^{-1}$, and then held there for 1 h in a muffle furnace (LT3/11, Nabhertherm), under N$_2$ atmosphere (≥99.9% N$_2$) at a flow rate of 0.5 L min$^{-1}$. After cooling to room temperature, the pyrolysis products were sieved (200 μm) to obtain the final biochar products. These products are named according to the PT at which they were produced, i.e., CB200, CB500 and CB950 for the cyanobacterial biochars (CBs), and CL200, CL500, and CL950 for the Chlorella sp. biochars (ClAs). We made a comparison with the PDS catalytic effect of Chlorella vulgaris (hereafter Chlorella) because it is another common species in algal blooms (Bi and Pan, 2014). More importantly, Chlorella can be grown on a carbon source such as glucose, which suppresses the development of the photosynthetic apparatus allowing comparison between photosynthetic cyanobacteria (Synechocystis sp. 6803) and heterotrophic Chlorella, which are expected to differ greatly in their elemental composition. The yield of biochars after pyrolysis varied with PT from 17% for PT950 to 91% for PT200 (Table S2).

3.3. Characterisation of biochar

The identity and presence of crystalline substances in the biochars were investigated by powder X-ray diffraction (PXRD) with a PANalytical X’Pert Pro MPD instrument using Co-Kα radiation (Kα1 = 1.789 Å, 40 kV, 40 mA). Randomly oriented packed powders were measured at 2θ from 5° to 90°, with a step size of 0.02° and 10 s step$^{-1}$. Scanning electron microscopy (SEM) was performed using a FEI Quanta 200 at 10.0 kV to study the morphology of CBs. Energy-dispersive spectroscopy (EDS) analysis was carried out using a Quanta FEG-250 ESEM system with an Oxford X-Max EDS detector. The sample was adhered to the sample holder with conductive glue, while nitrogen gas was used to prevent dust contamination, the SEM samples were also coated with a thin layer of gold to increasing the image quality by using a Q150T Quorum Coater. Surface functional groups on the biochar particles were characterized by Fourier transform infrared spectroscopy (FT-IR) using a Perkin Elmer Frontier MIR/FIR + SP10 STD instrument and with universal ATR sampling accessory in the wavenumber range of 400–4000 cm$^{-1}$. X-ray photoelectron spectroscopy (XPS) using a Thermo Scientific™ Nexsa G2 instrument with monochromatic Al-K radiation (300 W) was used to determine the surface elemental composition of the CBs, peak deconvolution was performed using CasaXPS 2.3.2.52 software. Zeta potential was measured at pH 2–12 in water using a Zetasizer Nano ZS (Malvern Instruments). The Brunauer-Emmett-Teller (BET)-N$_2$ surface area of CBs (~0.5 g) was quantified by Micromeritics Gemini VII following degassing (N$_2$ flux) at 200 °C for 6 h, using carbon black (004/16833/00MSDS) as reference material. Carbon (C) and nitrogen (N) content was determined using an organic elemental analyzer (Elementar Vario Macro Cube). The content of other elements was analyzed by Inductively Coupled Plasma-Emission Spectrometry (ICP-OES) (5100, Agilent Technologies) on CBs first ashed at 500 °C followed by digestion in acid (details in Text S2 in the SI).

3.4. NOR adsorption to biochar

Both adsorption kinetic and isotherm experiments were conducted. The experiments were performed at 20 °C with constant shaking (125 rpm) in a 250 mL Erlenmeyer flasks with 10 mg adsorbent and 100 mL NOR solution. For adsorption kinetic experiments, the initial concentration of NOR was set as 5 mg L$^{-1}$, and the pH was fixed at about 6.8 using Na$_2$HPO$_4$ - NaH$_2$PO$_4$ pH buffer (0.2 M). At certain time intervals, 1 mL of the suspension was filtered through a 0.22 μm filter (Nylon, 25 mm, CHROMAFIL) and NOR in the filtrates was determined by HPLC. The pH was also measured simultaneously with the interval sampling. For adsorption isotherm experiments, after adsorption equilibrium was reached (2 h) at multiple initial NOR concentrations (5, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100 mg L$^{-1}$), 1 mL of sample was taken and the NOR...
concentration was determined to calculate and establish the adsorption isotherm. The Freundlich isotherm model was used to fit the adsorption data and to estimate the adsorption affinity.

3.5. NOR degradation

The ability of biochars to degrade NOR with PDS was evaluated in experiments with 250 mL Erlenmeyer flasks containing 100 mL of 5 mg L\(^{-1}\) NOR solution under continuous shaking (125 rpm) at 20°C. Briefly, an adsorption process was first performed (see above) where NOR was equilibrated with the biochar before adding PDS. Immediately after completion of the above adsorption reaction, a PDS stock solution was added to the reaction vessel to ensure an initial PDS concentration of 10 mM. At specific time intervals, 0.8 mL of the suspension was collected and filtered through a 0.22 μm filter (Nylon, 25 mm, CHROMAFIL) into a 2 mL HPLC glass vial. The vial was pre-filled with 0.2 mL of 0.1 M Na\(_2\)SO\(_4\) solution to quench the reaction. Finally, the NOR concentration was determined by HPLC. The oxidation of NOR by another common persulfate, PMS, was also tested. In the CB950/persulfate system, PDS was far more effective than PMS (Fig. S2B). In addition, PMS costs twice as much as PDS (Lee et al., 2021). Therefore, PDS was used for the remaining experiments in this study. Separate experiments were conducted to investigate the effects of the initial NOR and PDS concentrations, the CB dosage, and the pH on the rate of NOR degradation. The preparation procedures were similar to those described above. In each experiment, NOR initial concentrations of either 10 or 20 mg L\(^{-1}\) were used, keeping other conditions constant. Similarly, different PDS concentrations of 10 mM or 20 mM, CB dosages of 0.1 or 0.2 g L\(^{-1}\), and different pH of 3, 7, and 10 were studied.

The performance of NOR degradation in natural water was tested with simulated water, real groundwater (Grindsted, Denmark, Table S3 for specific parameters), and highly contaminated groundwater (Kalundborg, Denmark, Table S4 for specific parameters). The simulated water contained 1 mM Na\(^+\), K\(^+\), Mg\(^2+\), Ca\(^2+\), Cl\(^-\), H\(_2\)PO\(_4\)\(^-\), HPO\(_4\)\(^2-\), HCO\(_3\)\(^-\), SO\(_4\)\(^2-\), NO\(_3\) and 1 mg L\(^{-1}\) HA. For these tests the following conditions applied: [NOR]\(_0\) 5 mg L\(^{-1}\), [PDS] 10 mM, CB950 dosage 100 mg L\(^{-1}\); temperature 20°C and no pH adjustment.

3.6. Analytical methods

NOR was determined by High Performance Liquid Chromatography (HPLC) (Agilent 1200 series gradient HPLC) in conjunction with a 1 C18 chromatographic column (LiChrospher\(^\text{®}\) RP-18 HPLC column, 21% carbon loading, 5 μm particle size, L × I.D. 25 cm × 4.6 mm, endcapped) and UV detector. The mobile phase consisted of acetonitrile (HPLC grade) and ultrapure water (22:78, pH 3 ± 0.1, 0.025 M phosphoric acid adjusted with triethylamine) at a flow rate of 0.8 mL min\(^{-1}\). The injection volume was 20 μL and the wavelength was set to 278 nm. All degradation experiments were performed in triplicates.

Oxidation intermediates were identified by Liquid Chromatography-tandem Mass Spectrometry (UPLC-MS/MS) (Waters UPLC Acquity Class I Xevo TQD) using a solid phase extraction cartridge (SPE, Oasis HLB 60 mg) as a pretreatment before testing because a large amount of salts in the sample could damage the instrument and affect the test results. The test method was adapted from the method of Mokh et al. (2017) (Mokh et al., 2017). The mobile phase consisted of eluent A) water with 0.1% (v/v) formic acid, and eluent B) acetonitrile with 0.1% (v/v) formic acid. The eluent program was 0-0.10 min B 20%, gradient to 90% B at 5.00 min and hold, increase to 95% B at 5.10 min and hold until 6.00 min, reduce to 20% B at 6.10, and hold at 20% B until 9.00 min with total run time of 9 min. Fluoride was determined by Ion Chromatography (930 Compact IC Flex) with a 100 mm × 4.0 mmID column (Metrosep A Supp 5 100/4.0) and the eluent consisted of 3.2 mM Na\(_2\)CO\(_3\), 1.0 mM NaHCO\(_3\) and 2.0 v/v % aceton. Details of the methods can be found in Texts S3 and S4, and Table S8.

Determination of total dissolved organic carbon (TOC) for samples before and after degradation reactions in CB500/PDS and CB950/PDS systems was performed using a Total Organic Carbon Analyzer (Shimadzu TOC-V CNP). The number of sample replicates was 4, and the Limit of Quantitation (LoQ) was 1 mg L\(^{-1}\). TOC in background samples only with CBs was subtracted to calculate the mineralization rate. PDS in solution was determined by a iodometric method and spectrometric analysis at 400 nm (Liang et al., 2008). The calibration curve was linear up to 40 mM PDS (R\(^2\) > 99%).

3.7. Monitoring of radicals by Electron Paramagnetic Resonance (EPR) and quenching experiment

The radicals generated in the reaction were detected using an Electron Paramagnetic Resonance (EPR) spectrometer (MiniScope MS500, Magnettech, Berlin, Germany) (Munk et al., 2017). Different quenching agents were used to determine the formation of radical species in the biochar/PDS reactions. Methanol (MeOH) can quench both OH and SO\(_4\)\(^2-\) at high reaction rates, chloroform (CF) is preferred for quenching super oxide radical anion O\(_2\)\(^-\) while O\(_2\)\(^-\) can be quenched by β-carotene. g-values in EPR spectra were determined by using pitch as the standard with a known g-value (2.0028) (Trubetskaia et al., 2016). Reactive radicals were captured by DMPO and TEMP. Detailed information on the free radical detection is provided in Texts S5.

3.8. Electrochemical measurements

In order to identify direct electron transfer during NOR degradation, linear sweep voltammetry (LSV) analysis was performed with a potentiostat (Metrohm) in a three-electrode setup. Two mg of CB was suspended in 1 mL of deionized water. The mixture was blended by ultrasonication (Branson sonic bath, M1800H-E, 70 W, 40 KHz) for 10 min and then placed on a glassy carbon electrode (GCE). After drying for 20 min, the CB coated GCE was used as a working electrode, while a 1 cm × 1 cm platinum plate and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. LSV scans were measured over a potential range of 0–1.6 V (vs Ag/AgCl) in 40 mL of 0.2 M phosphate buffer (pH ≈ 7) in 150 mL cylinder, with the following LSV parameters set: Sampling interval of 1 mV, scan rate of 0.05 V s\(^{-1}\), and delay time of 2 s. The PDS concentration was 10 mM and initial NOR concentration 5 mg L\(^{-1}\). The current was recorded over time. Amperometric i–t monitoring was performed under the same solution conditions as the LSV, but the working electrode was maintained at +0.6 V (vs Ag/AgCl). To further test electron transfer, we prepared a two-chamber reactor separated by a proton exchange membrane (PEM), equipped with interconnected carbon fiber electrodes and loaded with CBs as catalyst for the degradation of NOR in PDS (Wan et al., 2019; Yun et al., 2018). Detailed information is provided in Texts S6.

3.9. Data analysis

Data for NOR removal was fitted with a pseudo-first-order kinetic model (Eq. (2.1)) using non-linear fitting in OriginPro 9.6 (Ma et al., 2022):

\[
\frac{C_{\text{NOR}(t)}}{C_{\text{NOR}(0)}} = e^{-k_{\text{obs}}t}
\]  

(2.1)

where \(C_{\text{NOR}(t)}\) and \(C_{\text{NOR}(0)}\) (mg L\(^{-1}\)) are the NOR concentrations at time t and time zero, and \(k_{\text{obs}}\) (min\(^{-1}\)) is the first-order constant for NOR removal. A surface area normalized rate constant (\(k_{\text{SAA}}\), min\(^{-1}\) m\(^{-2}\) L) for NOR degradation is given by:

\[
k_{\text{SAA}} = k_{\text{obs}} \frac{\text{SSA}}{S \times \rho_m}
\]  

(2.4)

where SSA is the specific surface area of the material (m\(^2\) g\(^{-1}\)), and \(\rho_m\) is
the mass concentration of the biochar (g L\(^{-1}\)).

Similarly, data for NOR adsorption were fitted with Freundlich (Eq. (2.2)) adsorption isotherm models, using OriginPro 9.6:

\[
q_e = K_f C^n_e \tag{2.2}
\]

where \(C_e\) (mg L\(^{-1}\)) is the NOR equilibrium concentration, \(q_e\) (mg g\(^{-1}\)) the adsorbed amount of NOR, \(K_f\) [mg\(^1\)g\(^{-1}\) L\(^n\)] the Freundlich adsorption affinity coefficient, and \(n\) is the Freundlich nonlinear index.

To further investigate the contribution of \(\text{O}_2\) in CB950/PDS system, the available proportion of \(\text{O}_2\) for NOR oxidation after the physical quenching of water can be calculated using Eq. 2.3.

\[
f(\text{O}_2) = \frac{k_2,102,\text{NOR}}{K_2 \times [\text{NOR}]^{1/2} + k_1 \times \text{water}^{1/2}} \tag{2.3}
\]

where \(k_2,102,\text{NOR}\) (10\(^6\) M\(^{-1}\) s\(^{-1}\)) is the second-order rate constant of NOR oxidation by \(\text{O}_2\) (Martinez et al., 1998). \(k_1,102,\text{water}\) (2.5 \(\times\) 10\(^5\) s\(^{-1}\)) is the first-order rate constant of the physical quenching effect of water (Pei et al., 2021) and \(\text{CNOR}\) is the initial concentration of NOR (0.016 mM).

4. Results and discussion

4.1. Characterization of CBs

SEM images of the cyanobacterial biochars prepared at different PTs exhibited completely different morphologies (Fig. 1A). The surface of the raw cyanobacterial powder showed a regular arrangement of spherical cells. CB200 did not change much compared with the raw cyanobacterial powder showed a regular arrangement of micro pores and fragments appeared. For CB500, the cell structure of cyanobacteria was disrupted, the spherical structure was broken and fragments appeared. For CB950, the cell structure of cyanobacteria contained only 0.003% Mn, while CB contained 0.07%, resulting in lower nitrogen content (Perez-Garcia and Bashan, 2015). Overall, a dramatic change in the carbon to nitrogen (CN) ratio can be observed between the two cultures. CL, grown on glucose, resulted in a C:N of approximately 14:1, compared to CB at 7:1. It is noteworthy that cyanobacteria and the resulting biochar had not only high nitrogen but also high in manganese. Thus, CL contained only 0.003% Mn, while CB contained 0.07%, i.e. 23 times as much Mn. This is due to the unique role of Mn-containing enzymes in water splitting under photosystem II, where Mn is essential for photosynthetic growth of plants and algae, including cyanobacteria (Schmidt and Husted, 2019). Claes et al. (2015) found that Mn changes from nonvolatile to semivolatile during pyrolysis of biomass at 650 °C (Raclavská et al., 2015), which is why CB500 contained more Mn than CB950 (Table S5). Because of the large difference between CB and CL elemental compositions, we first compared the effects of the two on the catalytic PDS removal of NOR. CBs outperformed CLs for all pyrolysis temperatures. The degradation rate constants for CBs were on average 1.8 times higher than those of CLs (Fig. S2A). Therefore, we used only CB biochar in all further work.

The broad FTIR absorbance peaks from 3200 cm\(^{-1}\) to 3500 cm\(^{-1}\) are assigned to the hydroxyl functional groups (\(-\text{OH}\)) of phenols, alcohols, and carboxylic acids (Fig. 2A) (Wu et al., 2019). The \(-\text{OH}\) groups gradually disappear with increasing PT. Since C=O and O-P-O tend to generate gaseous or liquid products at high temperatures, no carbonyl units (1626 cm\(^{-1}\)) or O-P-O bands (1240 cm\(^{-1}\)) are present above PT of 500 °C (Bi et al., 2020b). The FTIR spectra of all biochars show C-H, C=C, O-H, C-O and C-C vibrations at approximately 2930, 1449, 1400,
1046 and 827 cm\(^{-1}\), respectively, and all these bands decrease with increasing PT (Mohan et al., 1991). Two additional bands were observed at 620 and 518 cm\(^{-1}\) in the FTIR spectrum of CB500, which can be assigned to the asymmetric and symmetric stretch of Mn-O (Zuizi et al., 2022). The two bands were not present in CB950 due to its low Mn content (Table S5). In the XRD diffractograms of CB, CB200 and CB500, the diffraction peaks at 34.3\(^{\circ}\) and 46.2\(^{\circ}\) can be attributed to calcite (CaCO\(_3\) JCPDS# 01–085–1108) (Niu et al., 2019) (Fig. 2B). With the increase of PT, CaCO\(_3\) peaks disappear and graphite peaks appear in CB950, identified by the diffraction peaks at 27.8\(^{\circ}\), 37.4\(^{\circ}\), 47.3\(^{\circ}\), 49.8\(^{\circ}\), 52.3\(^{\circ}\) and 56.2\(^{\circ}\) (JCPDS# 01–074–2328 and #01–074–2328) (Kakaei et al., 2019).

The surface chemical state and elemental composition of CB500 and CB950 were further investigated by XPS spectroscopy (Fig. 2 C-F). The XPS survey spectra showed that the surface N content of CB500 and CB950 was 11% and 2%, respectively (Fig. S3). The N1s XPS spectra were decomposed into four peaks: pyridinic N, pyrrolic N, pyridinic-N-oxide and graphitic N peaks (Miao et al., 2021). In addition to the high content of pyridinic-N-oxide, CB500 also contains a considerable amount of pyrrolic N (Ma et al., 2022). In contrast, CB950 contains 28% graphitic N, which is beneficial for binding PDS and promoting non-radical oxidation (Duan et al., 2018b). The C1s XPS data show that CB500 and CB950 contain considerable oxygen-containing functional groups (Chen et al., 2020), such as C-O, C=O, COO-. These oxygen-containing functional groups on the surface can effectively activate S\(_2\)O\(_8^2-\) to generate SO\(_4^{2-}\). In addition, \(^{1}\)OH can be generated due to SO\(_4^{2-}\) hydrolysis (Wang et al., 2019a).

Overall, the elemental composition analysis, XRD, FTIR and XPS clearly showed the conversion of amorphous C (aromatic and aliphatic forms) to graphitic materials with different surface functional group speciation with increasing PT (Lian and Xing, 2017). Cyanobacterial biochar has a unique elemental composition, such as high content of N and Mn.
4.3. NOR adsorption to biochars

NOR adsorption isotherms at pH 6.8 were well described by the Freundlich model for all CBs. Adsorption isotherms and fitting parameters can be found in Fig. S4 and Table S6. CB is a relatively strong sorbent for NOR with distribution coefficients far above 100 L kg⁻¹ at solution concentrations below 100 mg NOR L⁻¹. Pristine CB and CBs pyrolysed at 200 and 500 °C had similar adsorption affinities (Kₐ), whereas the CBs prepared at high PT had approximately only half the adsorption affinity compared with CB200 and CB500 (Fig. 3 A). This observation is unexpected since the SSA increased with PT. This may indicate that surface functional groups on the CB are important for adsorption of NOR as the biochar loses some surface functional groups and turn more hydrophobic with increasing PT. The zeta potential data show negative particle charge of CB950 in the pH range from 2 to 12 (Fig. S5). NOR is an amphoteric compound with a pKa of 6.32 for the carboxylic acid group and 9.47 for the secondary amine in the piperazine ring (Fig. S1A) (Chen et al., 2018a). Hence, NOR is mainly in the zwitterionic form at pH 6.8 (Fig. S1B). This suggests that sorption of NOR to CBs occurs via specific bonding. Uivarosi found that quinolone molecules possess two main sites for the formation of metal chelates, i.e. the carboxylic acid group and the ring carbonyl oxygen atom (Uivarosi, 2013).

NOR adsorption kinetics was studied as a pre-equilibration step in the reactivity experiments and equilibrium obtained within 60 mins (Fig. 3B-D). In these experiments NOR adsorption was very low due to the small amount of CBs in the systems. The sorbed amounts of NOR are consistent with the Freundlich parameters.

4.4. NOR degradation

After reaching adsorption equilibrium, NOR degradation was initiated by adding 10 mM PDS. The results of the control experiment without CBs showed that PDS reacted insignificantly with NOR. Addition of the different CBs strongly stimulated NOR degradation but to different extents (Fig. 3B). The degradation rate of CBs increased with increasing PT, and CB950 achieved complete NOR removal within 120 min. The degradation data were well fitted by a pseudo-first-order kinetic model (Fig. S6), with the highest rate constant (0.043 min⁻¹) in presence of CB950 (see Fig. 3E for all rate constants). In the following, we have focused on comparing the reactivities of CB950 and CB500 to represent high and low PT biochars. CB500 rather than CB200 has been used for comparison as pyrolysis at 500 °C is common, CB500 has higher reactivity than CB200.

CB950 performed well for NOR degradation in four consecutive rounds (Fig. 3C). CB950 showed the fastest NOR degradation during the first run and then slowed down in subsequent runs. High reactivity was
maintained during all 4 cycles with complete NOR removal within 120 min for all cycles. The first-order rate constant of CB950 decreased by 49% from 0.043 min⁻¹ to 0.022 min⁻¹ from the first to the fourth cycle. Similarly, the rate constant of CB500 decreased by 75% from the first to the fourth cycle (Fig. 3F).

Overall, only a very small fraction of NOR (5–10%) was adsorbed to the CBs in the test systems. Despite the low sorption, the degradation rate was high and increased with increasing PT.

4.5. Influencing factors of NOR degradation

It is known that the reactivity of PDS and its activation is related to pH. PDS may be effectively activated at acidic conditions (Ding et al., 2017). However, NOR degradation by PDS in the presence of CB500 and CB950 showed no significant differences in degradation rates at pH 3.0 and 7.0 (Fig. 4A). Conversely, NOR degradation strongly increased in alkaline solutions at pH 10. The mechanism of alkaline activation of PDS is summarized in Eqs. 3.1 and 3.2 taken from Furman et al. (2010).

Under alkaline conditions, PDS is activated to produce \( \cdot OH \) and \( SO_4^- \) radicals. When \( \cdot OH \) is present in large amounts, the \( SO_4^- \) radicals are converted to \( \cdot OH \) radicals. Our EPR results confirm that CB500/PDS generates \( \cdot OH \) radicals under alkaline conditions rather than acidic conditions (Fig. S7C). In addition, by comparing the EPR signal intensities of the radicals at different pH, a major increase in organic intermediates during NOR degradation (Ho et al., 2019).

4.6. Degradation by radicals or electron transfer

The use of chemical scavengers such as methanol and chloroform can indicate which type of reactive oxygen species (ROS) that form as intermediates during NOR degradation (Ho et al., 2019). Methanol quenches both \( \cdot OH \) and \( SO_4^- \) radicals with high second order rate constants, \( k_{\cdot OH} = 2.5 \times 10^7 \text{ M}^{-1}\text{s}^{-1} \) and \( k_{\cdot OH} = 9.7 \times 10^6 \text{ M}^{-1}\text{s}^{-1} \), while chloroform preferably reacts with \( O_2 \) with rate constant of \( 3.0 \times 10^{10} \text{ M}^{-1}\text{s}^{-1} \) (Chen et al., 2018b) and \( \beta \)-carotene is a typical scavenger of \( O_2 \) \( (k_{\cdot O_2} = 2.3 \times 10^{10} \text{ M}^{-1}\text{s}^{-1}) \) (Li et al., 2020). The initial concentration of NOR was increased to 20 mg L⁻¹ to compare the quenching results more clearly (Fig. 5A). There was no obvious decrease in NOR degradation rate in the CBs/PDS reaction system when CF and \( \beta \)-carotene were added as quenching agents, indicating that \( O_2 \) and \( \cdot O_2 \) were not active during the oxidation of NOR (Fig. 5A). Methanol partially quenched NOR degradation by CB and CB500, while the degradation
rate of CB950 was slightly slowed down compared to the reaction without MeOH. This suggests that *OH and SO{sub 4}{sup -} radicals are important reactants formed by low PT CBs while for the CB950 these radicals appear to play a much smaller role.

The nature of the radicals was further studied using DMPO as a spin trap to capture radicals that may be generated in the CB/PDS systems. Both DMPO-OH spin adducts with hyperfine splitting constants $\alpha = 1.49$ mT (Walger et al., 2021) and DMPO-SO{sub 4}{sup -} spin adducts with hyperfine splitting constants $\alpha = 1.37$ mT, $\delta = 0.73$ mT, $\gamma = 0.39$ mT (Meng et al., 2022) was observed in the CB950 system (Fig. 5C), which is tentatively ascribed to the nitroxide radical 5,5-dimethyl-2-pyrrolidone-N-oxyl (DMPOX) formed by oxidation of DMPO (Qin et al., 2016). SO{sub 4}{sup -} radicals were formed in high PT biochar CB950, indicating that they are not significantly involved in the degradation of NOR.

Besides the short lived highly reactive *OH and SO{sub 4}{sup -} radicals, the EPR spectra of CBs also showed the presence of two long lived characteristic radical signals which could be detected directly without the use of spin traps (Fig. 6). One of the signals is an isotropic sharp single line appearing at about 330 mT with a peak-to-peak width of 1.28 mT assigned to the oxidation of TEMP by H{sub 2}O{sub 2} (Gehling and Dellinger, 2013). CBs share similarities with PM2.5 combustion particles, and we infer that organic radicals from CBs may also provide redox sites to induce the formation of ROSs. Gehling and Dellinger (2013) found that PFRs present in PM2.5 organic particles from the combustion of biomass such as wood can induce the formation of *OH from H{sub 2}O{sub 2} without the addition of H{sub 2}O{sub 2} (Gehling and Dellinger, 2013). CBs share similarities with PM2.5 combustion particles, and we infer that organic radicals from CBs may also provide redox sites to induce the formation of *OH. The studies by Fang et al. (2015) and Wang et al. (2019) also confirmed that PFRs are the primary electron donors, which transfer electrons to PDS to induce the formation of SO{sub 4}{sup -} radicals (Fang et al., 2015; Wang et al., 2019b).

The EPR data are consistent with the quenching experiments and confirm that both *OH and SO{sub 4}{sup -} radicals are important reactants in the oxidation of NOR in the presence of the low PT CBs. Neither *OH nor SO{sub 4}{sup -} radicals were formed in high PT biochar CB950, indicating that they are not significantly involved in the degradation of NOR.
oxidation of NOR. Mn$^{II}$ is known to be able to activate PDS to generate \textsuperscript{•}OH and SO$^{4}$\textsuperscript{•} radicals to further oxidize and degrade the target contaminant (Wang et al., 2021). At the same time, the intensity of the organic radical EPR signal decreased. This is probably due to the fact that PFRs formed during biochar formation at low temperatures (200–500 °C), are consumed during NOR degradation.

When examining the signal of organic radicals for dry biochar samples, it was observed that the intensity of the detected radical signal increased with PT from 200° to 500 °C and then decreased markedly with PT to 950 °C (Fig. 6A and Table S7). Samples made at a PT at 500 °C showed the highest signal intensity. Similarly, the intensity of the manganese signal in the aqueous PDS solution followed the same trend. Comparing the $k_{\text{obs}}$ for NOR degradation and the radical signal intensity, it can be seen that the higher the PT, the higher the $k_{\text{obs}}$ while the EPR signal intensity peaked at 500 °C and then decreased markedly at high PT (Fig. 6D). This indicates that NOR oxidation follows different reaction mechanisms for CBs produced at different PTs, where radicals dominate NOR degradation for low PT CBs, whereas non-radical pathways may be more important for high PT CBs. We also tested the radical generation from CLs (Fig. S10). However, CLs did not show signals corresponding to Mn$^{II}$, and the overall signal intensity for organic radicals was also much lower than that of CBs. This could explain why CBs are superior to CLs for NOR degradation.

In the non-radical pathway, PDS may oxidize NOR by a direct electron transfer as in a conventional redox reaction (Duan et al., 2018a). Here, we tested the electron shuttling mechanism by linear-sweep voltammetry. When the electrodes were not coated with CBs, the current was very low and the current in the combined NOR and PDS solution did not differ from the background values (Fig. S10). However, CLs did not show signals corresponding to Mn$^{II}$, and the overall signal intensity for organic radicals was also much lower than that of CBs. This could explain why CBs are superior to CLs for NOR degradation.

The direct electron transfer was further tested using a two-chamber reactor (Fig. S11C–E). The results showed that in the presence of CB950, the NOR in separate chamber decreased to below 50% within 360 min and approximately 0.3 mM PDS was decomposed simultaneously, with no detectable PDS or NOR on the opposite side of the membrane (Fig. S11D). No significant NOR degradation or PDS

Fig. 6. EPR spectra for (A) dried CB, CB200, CB500 and CB950 samples, and (B) and (C) CB500 and CB950 samples with PDS and PDS + NOR in aqueous solution. (D) EPR signal intensity comparison of organic radical of dry CBs and Mn$^{II}$ in CBs/PDS solutions and $k_{\text{obs}}$ for NOR degradation of different CBs. Error bars represent standard deviation of triplicates.
are proposed in Fig. S14, including defluorination (P1), piperazine ring cleavage (P2) and dehydroxylation (P3). The defluorination reaction is further degraded to low molecular weight metabolites and products are identified in Table S8. Molecular structures and mass spectra are summarized in Fig. S13. As the sampling time increased, the signal from NOR gradually disappeared and signals from the small molecule fragments were enhanced. Table S8 summarizes the intermediate products based on the different [M+H]+ m/z ratios in ESI-MS/MS spectra. According to the intermediate identification and previous studies, possible degradation pathways of NOR are proposed in Fig. S14, including defluorination (P1), piperazine ring cleavage (P2) and dehydroxylation (P3). The defluorination reaction product N9 (m/z = 292), is observed only in the CB950/PDS system. All products are further degraded to low molecular weight metabolites and F. Remarkably high defluorination and mineralization was observed in the NOR degradation reaction. For instance, for an initial concentration of NOR of 20 mg L⁻¹, complete defluorination should result in 1.025 mg L⁻¹ fluorine. A fluoride concentration of 1.00 mg L⁻¹ was seen corresponding to a defluorination rate of 82%.

With an initial TOC concentration of 5.6 mg L⁻¹, the remaining TOC concentration in the CB950/PDS system at the end of the reaction was lower than the LoQ of 1 mg L⁻¹, corresponding to a mineralization extent of at least 82% over 2 h. In contrast, the remaining TOC concentration in the CB500/PDS system was 2.8 mg L⁻¹, resulting in a mineralization extent of only 50%. The ECOSAR software predicted the toxicity of NOR and its corresponding degradation intermediates as shown in Table S9. Acute toxicity values for some intermediates such as N7 and N10 are lower than NOR, but they are still higher than 100 mg L⁻¹. According to the acute toxicity classification based on the European Union criteria as LC₅₀ or EC₅₀ > 100 mg L⁻¹ (Harmless), NOR and the degradation products generally proved to be harmless (Lv et al., 2022).

Taking all these observations into consideration, we suggest the following mechanisms of high or low PT CBs facilitating PDS to degrade NOR. For low PT CBs, such as CB500, NOR is entirely degraded due to radicals, including organic radicals, •OH and SO₄²⁻ radicals. For high PT CBs, CB950, NOR degradation takes place by a combination of predominantly electron transfer, assisted by oxidation by radicals. The attack on NOR by PDS makes NOR susceptible for further reaction via electron exchange processes between PDS and NOR mediated by CB950. CB950 is a strong catalyst for PDS oxidation of NOR, as shown in the comparisons in Table 1. Thus, CB950 achieved the highest surface area performance and reusability of the CB catalyst.

4.8. NOR degradation in natural waters

In practice, naturally occurring inorganic ionic solutes such as K⁺, Mg²⁺, Ca²⁺, Cl⁻, H₂PO₄⁻, HCO₃⁻, SO₄²⁻, and NO₃ may have a significant impact on NOR degradation (Chen et al., 2018a). The influence of HA was also considered (Hu and Long, 2016). Therefore, the NOR degradation rate of CB950/PDS was tested in simulated, actual and highly polluted water matrices to evaluate its applicability under more natural conditions.
conditions. Tests were carried out using simulated water containing 1 mM of the above listed common anions and cations and 1 mg L\(^{-1}\) of HA, actual groundwater and groundwater with high concentrations of organic contaminants (including 520 µg L\(^{-1}\) benzene) respectively, to investigate the effects of the water matrix on NOR degradation (Fig. 8A).

It was observed that NOR degradation rates in the simulated groundwater and natural groundwaters were similar to that of pure deionized water, with NOR being completely removed within 120 min (Fig. 8B). However, the degradation rate of NOR in the highly contaminated water matrix was reduced, possibly due to the presence of competing organic contaminants (e.g. barbituric acid, sulfamethazine, benzene, etc.). Nevertheless, NOR removal rates in contaminated waters can reach nearly 100% in 720 min, demonstrating a high potential for application of CB950 for contaminant degradation in natural water bodies.

5. Conclusions

This study demonstrates that N-enriched cyanobacterial biochar exhibits excellent catalytic performance in the degradation of organic pollutants by PDS, outperforming many conventional metal- or carbon-based materials. Despite the low SSA of CBs and its negative particle surface charge resulted in low adsorption of NOR, CBs showed good efficiency in degrading NOR and with highest reactivity for high PT CBs. Compared with other commonly used catalysts for PDS activation, CB950 shows the highest \(k_{\text{ads}}\) as well as high NOR defluorination rates. CBs were active over a wide pH range (3–10), but with double rates under alkaline conditions. Furthermore, CBs showed good performance in removing NOR from natural waters (groundwater and highly contaminated water bodies). Compared to CB500, CB950 is more stable when recycled. High extents of defluorination (82%) and mineralization (>82%) was observed for reaction periods of 2 h in CB950/PDS. The underlying mechanisms were illustrated by EPR and electrochemical analyzes and radical quenching tests. For the CB500/PDS system the degradation of NOR may be a radical process, whereas in the CB950/ PDS system, electron transfer mediated by CB950 adds to the oxidation process. This study demonstrates for the first time the involvement of Mn\(^{II}\) in the activation of PDS by algal biochar and compares the effects of photosynthesis on biomass to provide a theoretical basis for the screening of biochar feedstocks. A promising approach to advanced oxidation reactions with reaction pathways (radicals or electron transfer) for the degradation of organic pollutants in even complex aqueous bases is proposed.

![Fig. 8. (A) NOR degradation in different water matrices and (B) respective rate constants ([NOR] = 5 mg L\(^{-1}\); [PDS] = 10 mM; Biochar dosage = 100 mg L\(^{-1}\); temperature = 20 °C). Error bars represent standard deviation of triplicates.](https://example.com/image.png)
Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Supplementary material

Additional details on materials and methods, results, and their discussion are provided. Tables show adsorption isotherm model parameters, elemental composition, the surface area of biochar and radical signals. The figures show the degradation of NOR by different algal bioschar and the effect of different persulfate formulations, PDS and FTS, sorption behavior and adsorption isotherm fitting, zeta potential, radical signal spectra detected by EPR for biochar samples and during oxidative degradation of NOR in the presence of DMPO. Total ion current (TIC) chromatograms for NOR reaction at different pH and product ion spectra for NOR and its degradation intermediates are all presented.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jhazmat.2022.129655.

References


