*Supporting Information* for

# Upscale catalyst Wood-N-CoPc for PMS activation in antibiotics degradation

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## Experimental Procedures

### 1. Materials

All materials, ethanol (EtOH), hydrogen peroxide ($H_2O_2$), wood, sodium hydroxide (NaOH), sodium sulfite ($Na_2SO_3$), tert-butanol (TBA), cobalt phthalocyanine (CoPc), peroxymonosulfate (PMS), sulfamethoxazole (SMX), 5,5-dimethyl-1-pyrrolidamine-N-oxide (DMPO), 2,2,6,6-tetramethylpiperidine (TEMP), sulfuric acid ($H_2SO_4$), and methyl phenyl sulfone (PMSO) are obtained from Aladdin Co., Ltd. All the chemicals are used without further purification.

### 2. Preparation of wood-N-CoPc

**Preparation of lignin-removal treated wood.** According to the method previously reported by Hu et al[1, 2], the treated wood was successfully prepared. Natural wood blocks were immersed in a boiling aqueous solution of 2.5 M NaOH and 0.4 M $Na_2SO_3$ for 3 h to remove a portion of the lignin. The blocks were then thoroughly washed with deionized water and transferred into an $H_2O_2$ solution to eliminate the remaining lignin. The progress of lignin removal was monitored by changes in wood color (lignin is colored, cellulose is colorless). After washing with deionized water and freeze-drying, the pretreated wood was obtained. Finally, this wood was calcined at 800 °C for 3 h to produce the carbonized wood support.

**Preparation of wood-N-CoPc.** The treated wood was immersed in a solution of CoPc and stirred for 6 h to allow CoPc loading. Then, these wood blocks (after CoPc loading) were processed with an acid wash (1 M HCl) to remove excess CoPc (because the excess CoPc tended to aggregate and form clusters, which can cover the surface active sites and thereby affect subsequent degradation). After drying in an oven at 200 °C, the wood blocks were further calcined in a tube furnace at 500 °C for 2 h under an $NH_3$ atmosphere, yielding the final wood-N-CoPc blocks.

**Preparation of wood/CoPc.** All the processes were the same as above, except the calcination under an $N_2$ atmosphere rather than $NH_3$.

## 3. Characterization of catalysts

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku MiniFlex 600 X-ray diffractometer. Scanning electron microscopy (SEM) images were collected on a FEI Quanta 450 FEG Environmental Scanning Electron Microscope. Transmission electron microscopy (TEM) images were collected on FEI Tecnai G2 Spirit TEM. High-angle annular dark-field scanning TEM (HAADF-STEM) images with EDS analysis were obtained on a FEI Titan Themis 80-200 operating at 200 kV. Raman spectra were measured using a Raman spectrometer (Horiba Scientific, Germany) equipped with a 532 nm laser. X-ray photoelectron spectroscopy (XPS) spectra were collected from a Thermo Scientific K-Alpha. Extended X-ray absorption fine structure (EXAFS) was acquired at the Australian Synchrotron in Melbourne.

## 4. Experimental processes

All experiments were performed in glass beakers with magnetic stirring to keep the uniformity of solution during the reaction.

### 4.1 PMS activation for SMX degradation

Wood-N-CoPc was put in SMX solution and then magnetically stirred during the whole reaction. Then, 4.45 mM PMS was added to initiate the reaction. Water samples were taken out at regular intervals, centrifuged and measured by high performance liquid chromatography (HPLC).

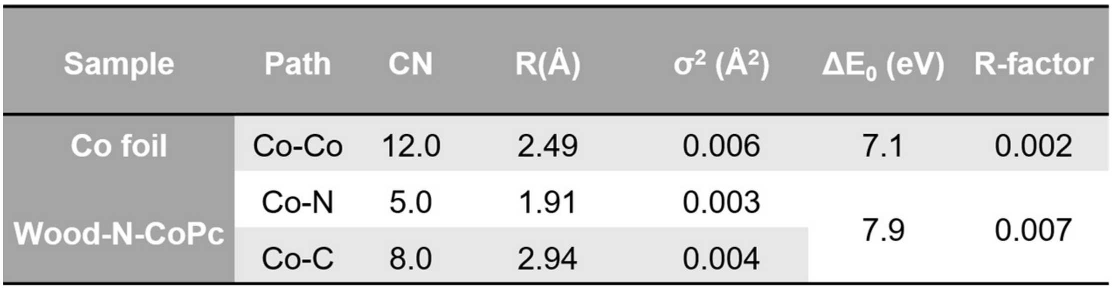
### 4.2 Radical quenching tests

Radical quenching tests were conducted to identify the dominant radicals in a wood-N-CoPc/PMS system with ethanol, TBA, FFA, PMSO, and $CHCl_3$, which were added before the addition of PMS. Other procedures were the same as the experiments above. The radical species were further detected by electron paramagnetic resonance (EPR) technology, where DMPO was used as a spin-trapping reagent.

### 4.3 Detection of •OH

The content of •OH generated during a Fenton-like reaction was detected with a Fluorescence analysis method and the photo-fluorescence (PL) signal of hydroxybenzoic acid results from the capture of •OH by benzoic acid, which indicates the concentration of •OH. The test details are as follows: 100 mL $H_2O$ containing Wood-N-CoPc co-catalyst and 40 mg benzoic acid; After adding 4.45 mM PMS for 30 min, the solution was measured by PL emission spectroscopy to measure the contents of •OH (excitation wavelength: 330 nm).

**Table S1**. Co K-edge EXAFS spectra fitting parameters.



| Sample | Path | CN | R(Å) | $\sigma^2$ (Å$^2$) | $\Delta E_0$ (eV) | R-factor |
|---|---|---|---|---|---|---|
| Co foil | Co-Co | 12.0 | 2.49 | 0.006 | 7.1 | 0.002 |
| Wood-N-CoPc | Co-N | 5.0 | 1.91 | 0.003 | 7.9 | 0.007 |
|  | Co-C | 8.0 | 2.94 | 0.004 |  |  |

$S_0^2$ was fixed as 0.711. *CN, coordination number; R, distance between absorber and backscatter atoms; $\sigma^2$, Debye-Waller factor to account for both thermal and structural disorders; $\Delta E_0$, inner potential correction; R factor indicates the goodness of the fit.

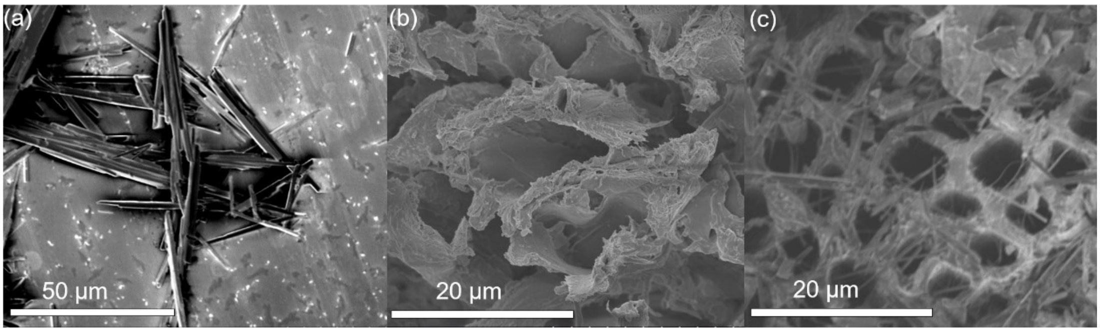


**Figure S1.** SEM image of (a) CoPc, (b) treated wood, and (c) wood-N-CoPc.

Lignin-removed wood was first carbonized by calcination at 800 °C to produce the wood support. The porous wood framework was then immersed in a CoPc solution under stirring for 6 h to load CoPc, followed by drying at 200 °C. The blocks were finally calcined under an $NH_3$ atmosphere at 500 °C to form the wood-N-CoPc.

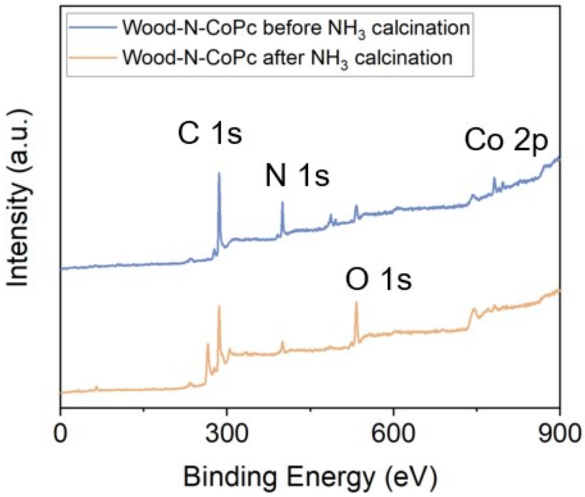


**Figure S2.** XPS spectra of wood-N-CoPc: survey scan.

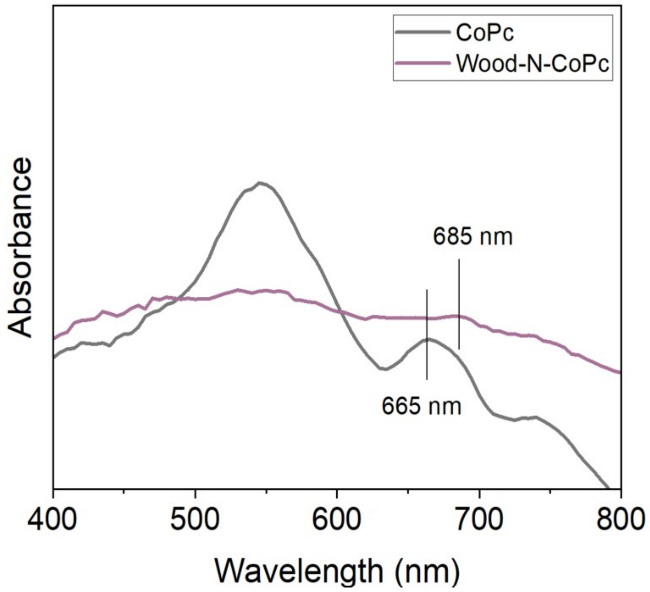


**Figure S3.** Q band region in the UV-vis spectra of wood and wood-N-CoPc.

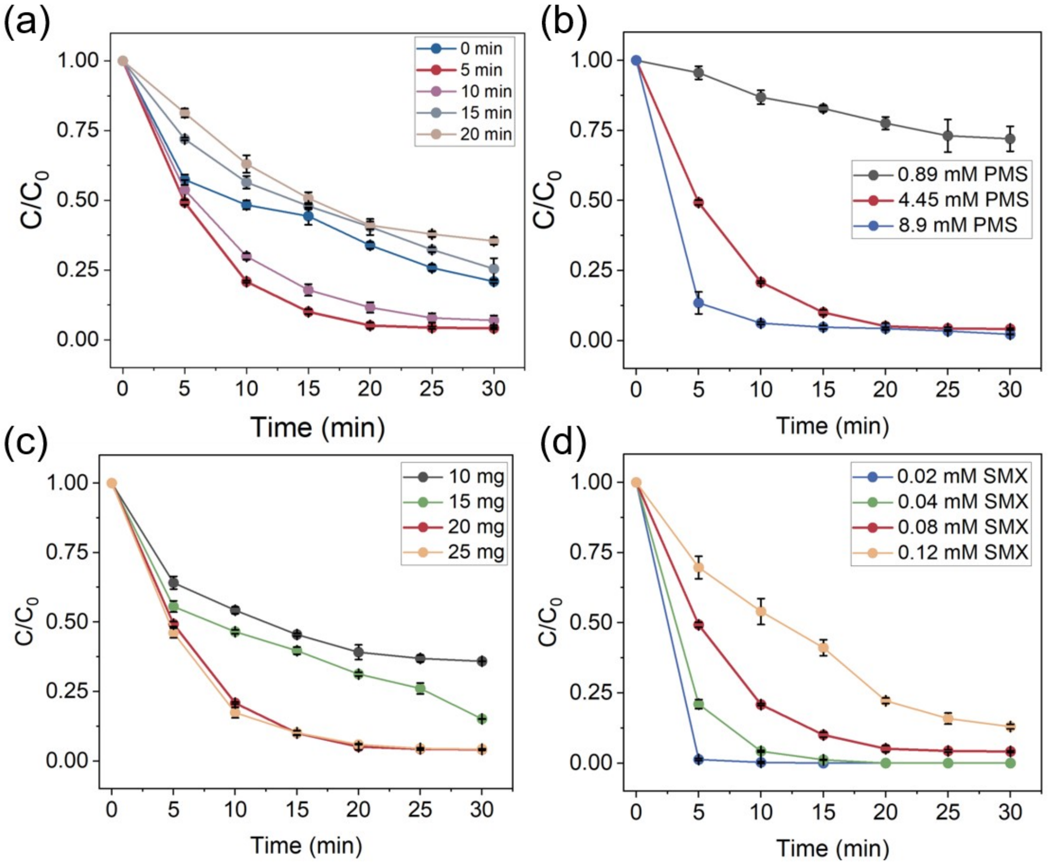


**Figure S4.** The SMX degradation performance of wood-N-CoPc with (a) different acid-wash time; different dosage of (b) PMS, (c) catalyst, and (d) SMX.

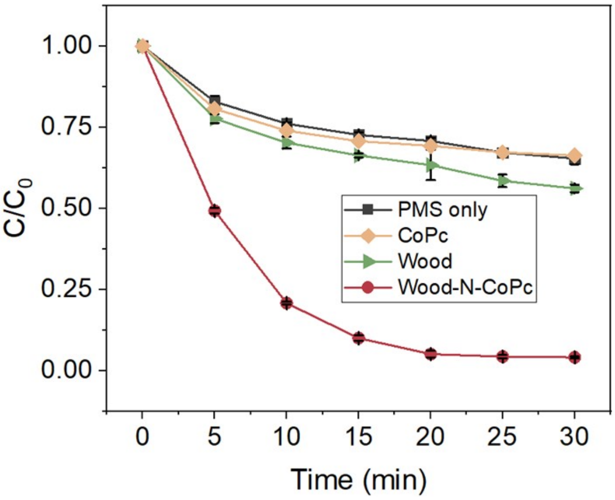


**Figure S5.** SMX degradation performance with different catalysts, including Copc and wood@Copc (Reaction conditions: 4.45 mM PMS, 0.08 mM SMX).

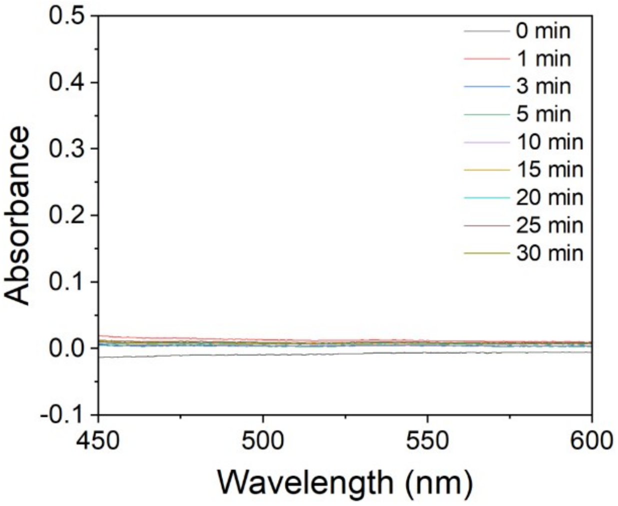


**Figure S6.** Oxidation of NBT in wood-N-CoPc degradation system over time.

The reduction of NBT by superoxide typically produces a pronounced band centered at ~550 nm[3], making it a standard method for evaluating SOD-related reactions. In this study (**Figure S6**), no such optical response was observed, indicating that the wood-N-CoPc/PMS system does not promote $O_2^{\bullet -}$ formation or associated SOD-type activity.

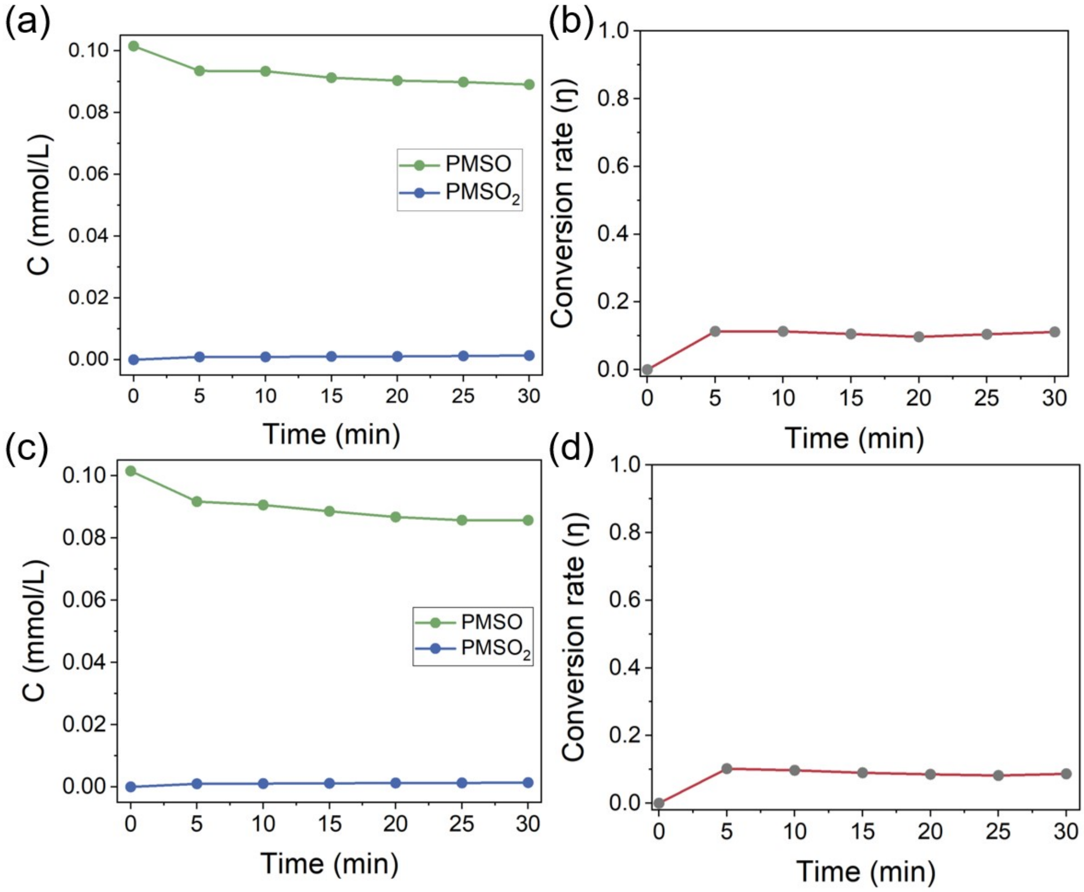


**Figure S7.** PMSO consumption and PMSO$_2$ generation, and corresponding conversion rate in degradation system (a-b) without, and (c-d) with wood-N-CoPc.

**Role of high-valent cobalt species.** Previous studies indicate that metal-oxo species such as Fe$^{IV}$=O and Co$^{IV}$=O often serve as potent oxidizing intermediates in AOP reactions**[4]**. To assess the involvement of Co$^{IV}$=O in the wood-N-CoPc/PMS system, we used p-toluenesulfoxide (PMSO) as a mechanistic probe. PMSO reacts selectively with Co$^{IV}$=O via an oxygen-transfer pathway to yield PMSO$_2$, enabling indirect identification of the high-valent cobalt species. As shown in **Figures S5-S6**, negligible PMSO selectivity (<15%) toward PMSO$_2$ was observed, suggesting that Co$^{IV}$=O was not formed or did not serve as the primary species during the degradation reaction.

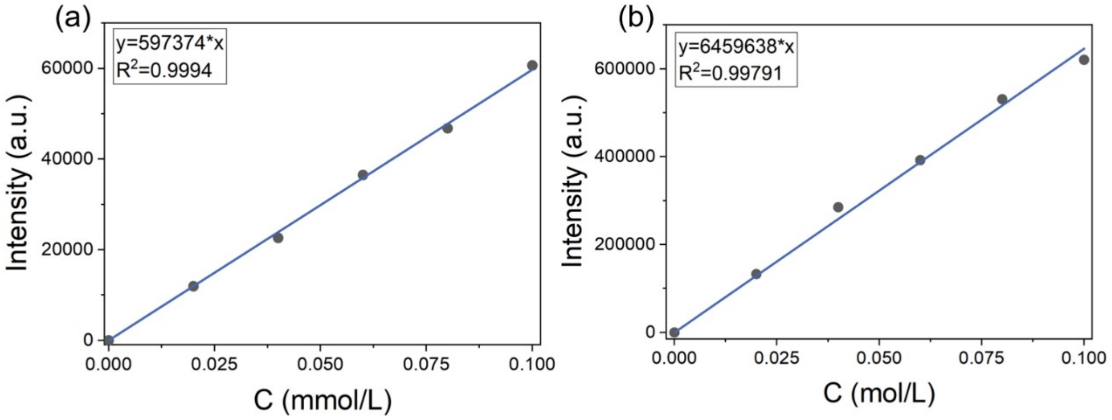


**Figure S8.** The standard curves of (a) PMSO and (b) $PMSO_2$.

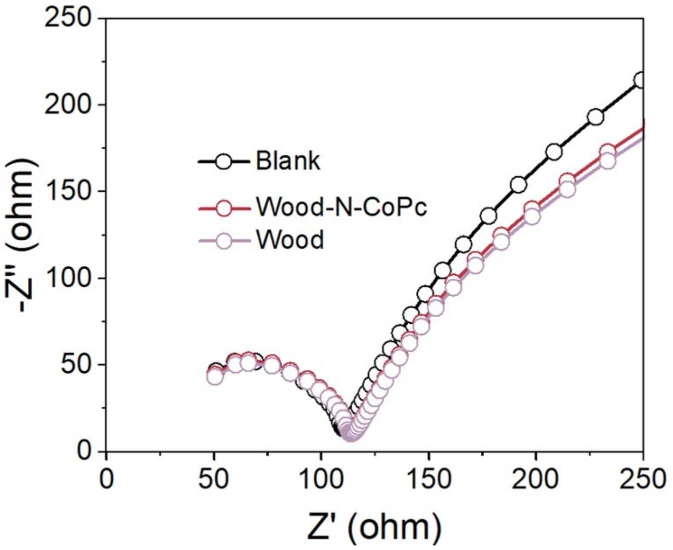


**Figure S9.** EIS spectra of wood and wood-N-CoPc.

**Electron-transfer process (ETP).** Electrochemical impedance spectroscopy (EIS) using wood and wood-N-CoPc-coated carbon cloth electrodes showed negligible reduction in charge-transfer resistance (**Figure S9**), indicating minimal electron conduction enhancement**[5]**. It meant the increase of potential was not owing to the electroconductibility.

In nonradical AOP mechanisms, PMS is often converted into a high-energy PMS* complex. If the redox potential of PMS* exceeds that of the contaminant, the system favors an electron-transfer oxidation process, enabling PMS* to oxidize the organic molecules stepwise[6, 7].

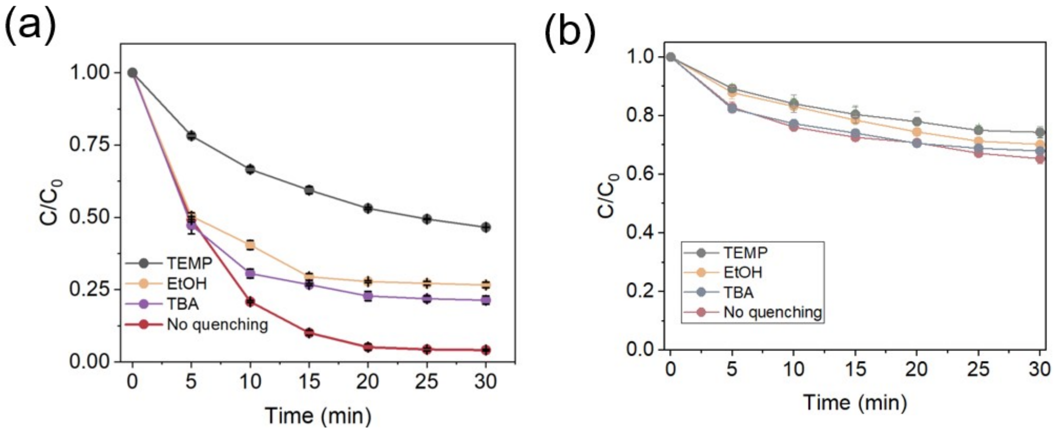


**Figure S10.** Sacrificial experiments of adding different sacrificial agents into pure PMS degradation system.

In the wood-N-CoPc/PMS degradation system, TEMP had the most pronounced inhibitory effect, reducing SMX removal to 53.44%. The SMX removal results for adding Ethanol (EtOH) and tert-butanol (TBA) were very close, both reducing SMX by ~15%, indicating that $\cdot OH$ was the main radical in this degradation system, while $SO_4^{\cdot -}$ made a relatively small contribution.

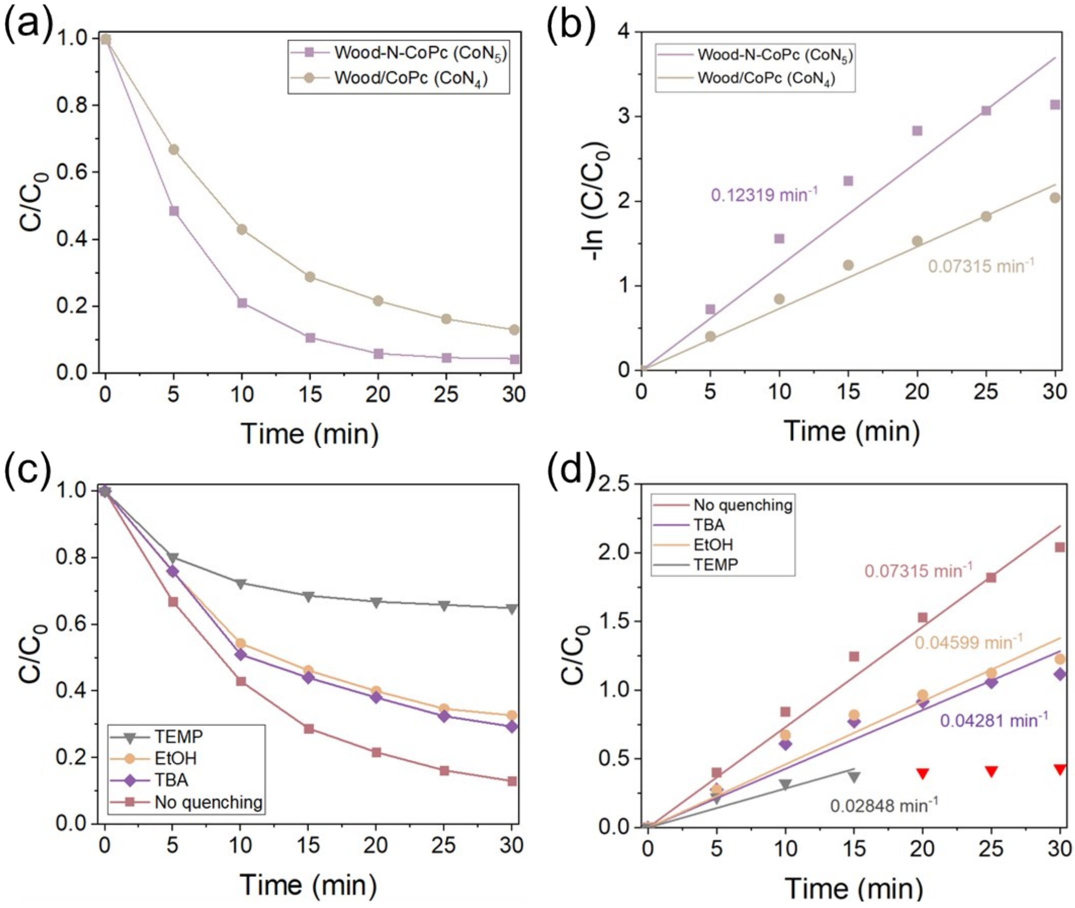


**Figure S11**. (a) The SMX degradation performance of wood-N-CoPc ($CoN_5$) and wood/CoPc ($CoN_4$); (b) The corresponding pseudo-first-order kinetics; (c) Sacrificial experiments of adding different sacrificial agents into wood/CoPc ($CoN_4$) degradation system; (d) The corresponding pseudo-first-order kinetics.

The percentage contribution of ·OH was computed via $[(k_{\text{No quenching}}-k_{\text{EtOH}})/\ k_{\text{No quenching}}]$*100%**[8]**. In comparison, the TEMP-induced rate decline— $[(k_{\text{No quenching}}-k_{\text{TEMP}})/\ k_{\text{No quenching}}]$*100% —represented the joint influence of radical pathways and $^1O_2$. The remaining amount after deduction was considered the ETP contribution. As shown in **Figure S11d**, the degradation rate decreased slightly, and k decreased from 0.123 $min^{-1}$ (wood-N-CoPc, Co-$N_5$) to 0.073 $min^{-1}$ at the same time.

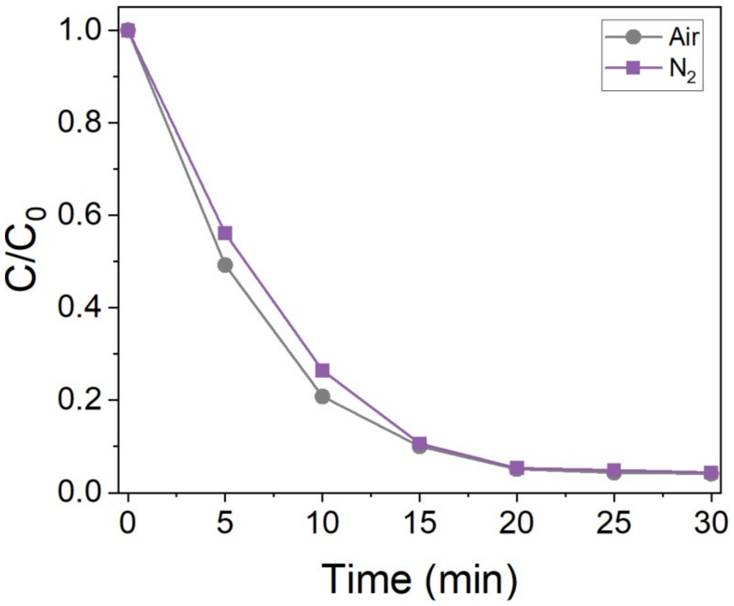


**Figure S12**. The degradation rate of wood-N-CoPc/PMS in $N_2$.

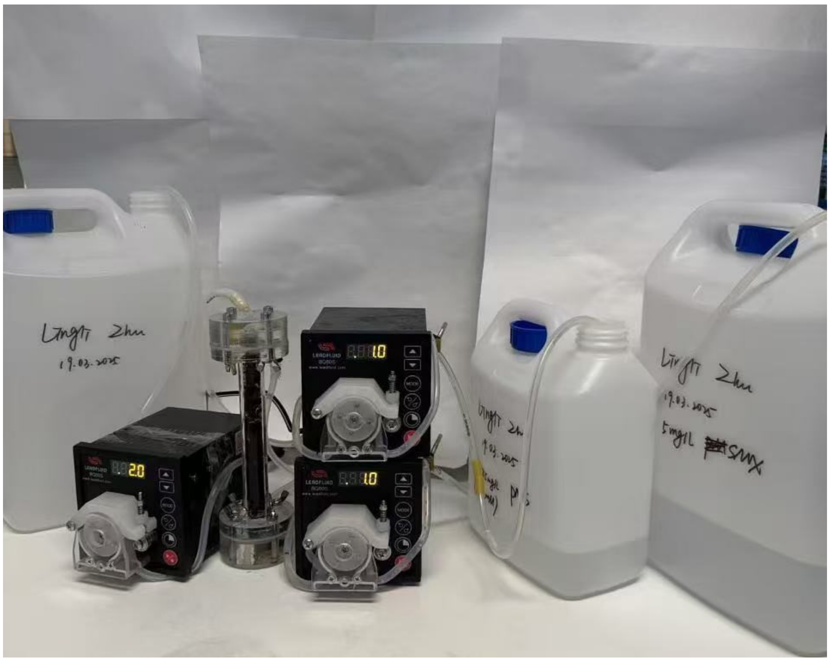


**Figure S13.** The photo of continuous degradation reactor.

In **Figure S13**, wood-N-CoPc (>20 pieces) was packed successively into a polymethyl methacrylate (PMAA) column (1 cm i.d., 10 cm height). SMX (5 mg/L) and PMS (0.6 mM) were continuously fed at 1 mL/min each using two peristaltic pumps, with effluent collected at 2 mL/min. The leached cobalt concentration was further tested after the long-term degradation (128 h), which was 0.03 ppm.

## Reference

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