

Supplementary Materials: N-Rich Algal Sludge Biochar for Peroxymonosulfate Activation toward Sulfadiazine Removal

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This information contains: 6 Texts, 3 Tables and 7 Figures.

Texts

Text S1. Chemicals and reagents.

SDZ (Table S1), PMS, 5,5-Dimethyl-1-pyrroline-N-oxide (DMPO, 97%), and 2,2,6,6-tetramethyl-4-piperidinol (TEMP, >98%) were obtained from Aladdin, China. Tert-butanol (TBA), methanol (MeOH) and other chemical reagents were at least analytical grade and used without further purification. Deionized (DI) water was produced via a water purification system (EPED-10TF).

Text S2. Characterizations of the biochars.

Transmission electron microscope (Fei Talos F200S (200 kV)) and scanning electron microscope (Fei Quanta 400 Feg) were adopted to determine the morphologies of the AS-BCx, respectively. The XPS measurements were carried out on an ESCALAB 250Xi spectrometer (Thermo Scientific, Waltham, Massachusetts, USA) equipped with a pass energy of 30 eV with a power of 100 W (10 kV and 10 mA) and a mono-chromatized AlK α X-ray ($h\nu = 1486.65$ eV) source. All samples were analyzed under a pressure of less than 1.0×10^{-9} Pa. Spectra were acquired through the Avantage software (Version 5.979) with a step of 0.05 eV. The N₂ adsorption-desorption isotherms of the catalyst were tested at 77.3 K by ASAP 3020. The outgas temperature was 300 °C. Raman spectra were recorded with LabRAM HR Evolution (HORIBA). The FTIR spectra were recorded with Thermo Scientific Nicolet iS5.

Text S3. Details of electrochemical experiment.

Firstly, the carbon paper electrode loaded with ASBCx powder was prepared. Nafion solution (5.0 wt.%, 100 μ L) and ASBCx powder (10 mg) were mixed with ethanol (1 mL), then ultrasonic dispersion for 2 h to obtain the mixture. Then, 20 μ L suspension solution was dropped onto the surface of the carbon paper electrode and then dried at 60 °C for 2 h. The electrochemical experiments were conducted on an electrochemical workstation (CHI 760E) and were carried out in a three-electrode system, in which Ag/AgCl electrode and Pt wire functioned as the reference electrode and counter electrode, respectively. Electrochemical impedance spectroscopy (EIS) was performed in 50 mM Na₂SO₄ solution (40 mL) at open potential with a frequency range of 1.5×10^6 to 1 Hz. Linear sweep voltam-

metry (LSV) was measured at the potential from -0.5 – 1.5 V (vs. Ag/AgCl) and the scanning rate was 100 mV/s. Chronoamperometries were carried out at the bias of 0.0 V (vs. Ag/AgCl), and 50 mM Na_2SO_4 solution (40 mL) was used as electrolyte solution.

Text S4. Adsorption kinetics.

The adsorption kinetics were analyzed via pseudo-first-order and pseudo-second-order kinetic models, respectively:

Pseudo first-order kinetic model

$$q_t = q_e(1 - e^{-k_1 t}) \quad (1)$$

Pseudo second-order kinetic model:

$$q_t = \frac{k_2 q_e^2 t}{1 + k_2 q_e t} \quad (2)$$

where, q_e and q_t are the adsorption amounts (mg g^{-1}) of SDZ by ASBCx at equilibrium and time t , respectively. k_1 (min^{-1}) and k_2 ($\text{g mg}^{-1} \text{min}^{-1}$) represent the corresponding adsorption rate constants, respectively.

Text S5. Details of degradation experiments.

All the degradation experiments were carried out in a 100 mL glass beaker containing 50 mL SDZ solution (5 mg L^{-1}). In a typical test, 10 mg ASBCx was dispersed in SDZ solution and stirred for 30 min to reach adsorption equilibrium. Then, 0.5 mM oxidants were added into the suspension to initiate catalytic reaction. At certain time intervals, 0.5 mL solution was withdrawn, filtered with 0.2 mm filter to remove the solid catalyst, and quenched with 0.5 mL methanol for analysis. The pseudo-first order kinetic model was adopted to evaluate the degradation kinetics of SDZ:

$$\ln \frac{c_0}{c_t} = -k_{app} t \quad (3)$$

where, c_0 and c_t are the initial and the instant (at the time of t) concentrations of SDZ. The k_{app} represent the pseudo-first-order kinetic rate constant (min^{-1}).

Supporting Information Text S6 Analytical methods.

The concentration of SDZ was measured by high performance liquid chromatography (HPLC, FL 5090) equipped with a C18 reversed-phase column and a UV detector at 268 nm. The mobile phase was a mixture of acetonitrile / deionized water with 0.4% acetic acid ($25:75$, v/v) at a flow rate of 1 mL min^{-1} .

Tables

Table S1. The physicochemical properties of SDZ.

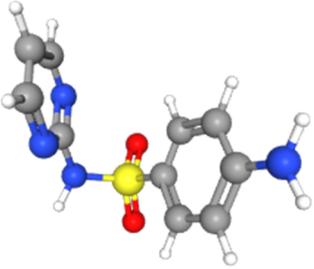
Contaminants	Sulfadiazine (SDZ)
Chemical structure model	
Molecular formula	C ₁₀ H ₁₀ N ₄ O ₂ S
Molecular weight (g/mol)	250.28
Density (g/cm ³)	1.3780
pK _a	6.36

Table S2. Catalytic performance of reported Fenton-like catalysts for PMS activation.

Catalyst	Loading (g L ⁻¹)	SDZ concentration (mg L ⁻¹)	Removal efficiency	SDZ reduction per g (mg g ⁻¹)	Equilibrium time(min)	PMS loading (mM)	PMS /SDZ (mM/mM)	Ref.
ASBC800	0.2	5	100%	25	70	0.5	25.028	This work
MnFe ₂ O ₄ /δ-MnO ₂ hybrid	0.2	10	100%	50	60	2	50.506	[8]
δ-MnO ₂	0.2	10	85 %	42.5	60	2	50.506	[8]
MnFe ₂ O ₄	0.2	10	76%	38	60	2	50.506	[8]
MBC	1	40	91.97%	1.1	60	1.5	9.385	[1]
Fe-Cu hollow sphere	0.2	5	93.5%	46.75	240	2	100.112	[5]
CuOx hollow spheres	0.2	5	80.8%	40.4	240	2	100.112	[5]
BC	0.1	25	5%	12.5	10	1	10.011	[3]
0.8CoAl-LDH/CN	0.2	2.5	49.9%	6.24	16	0.5	50.506	[7]
Cu ₂ O	0.1	2	57%	11.4	40	0.033	4.125	[2]
Fe ₃ O ₄	0.8	10	37.9%	4.736	90	0.3	7.508	[6]
MoS ₂	0.5	5	56.4%	5.64	30	0.5	25.028	[4]

Table S3. Second-order rate constants for reactions of the MeOH and TBA with different radicals.

Compounds	Reaction rate constant (M ⁻¹ s ⁻¹)		
	·OH	SO ₄ ^{·-}	¹ O ₂
MeOH	(1.2–2.8) × 10 ⁹	(1.6–7.7) × 10 ⁷	-
TBA	(3.8–7.6) × 10 ⁸	(4–9.1) × 10 ⁵	-

Figures

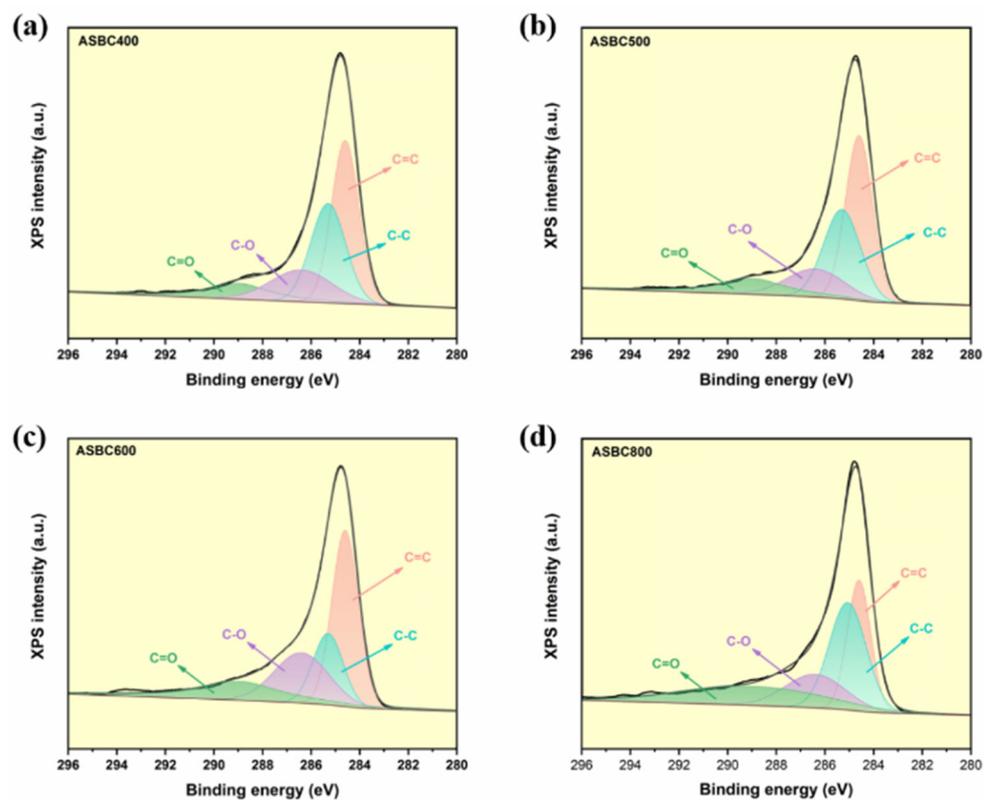


Figure S1. Deconvoluted C 1s XPS spectra of the ASBCx samples.

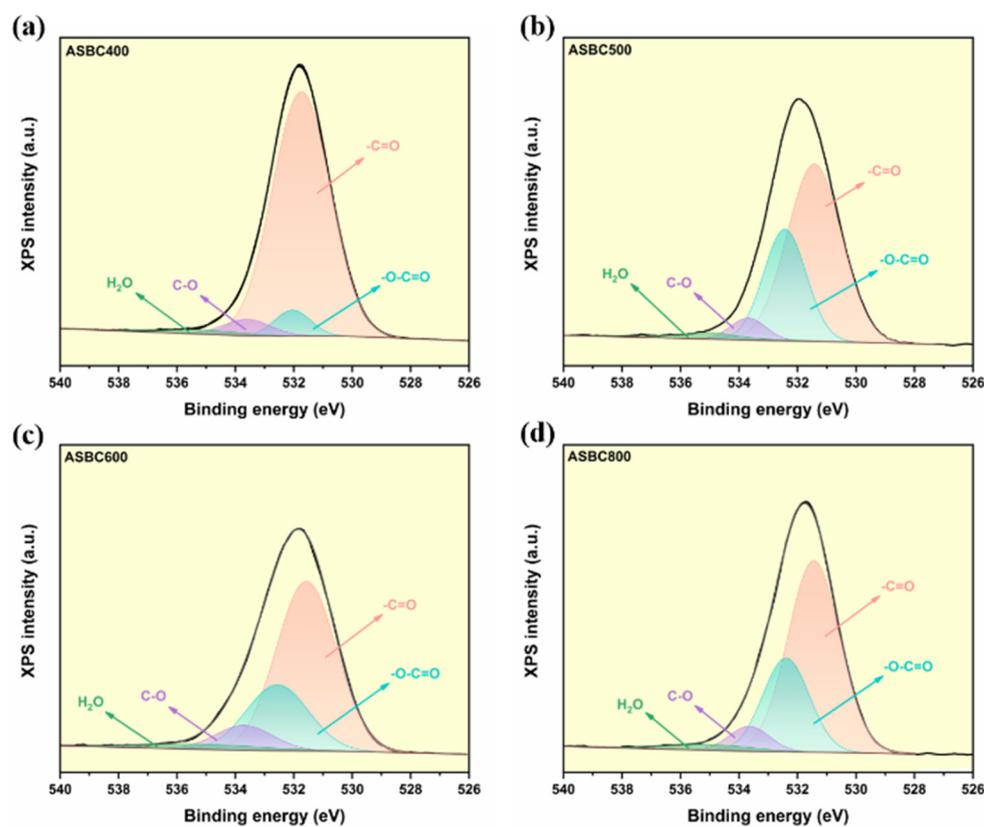


Figure S2. Deconvoluted O 1s XPS spectra of the ASBCx samples.

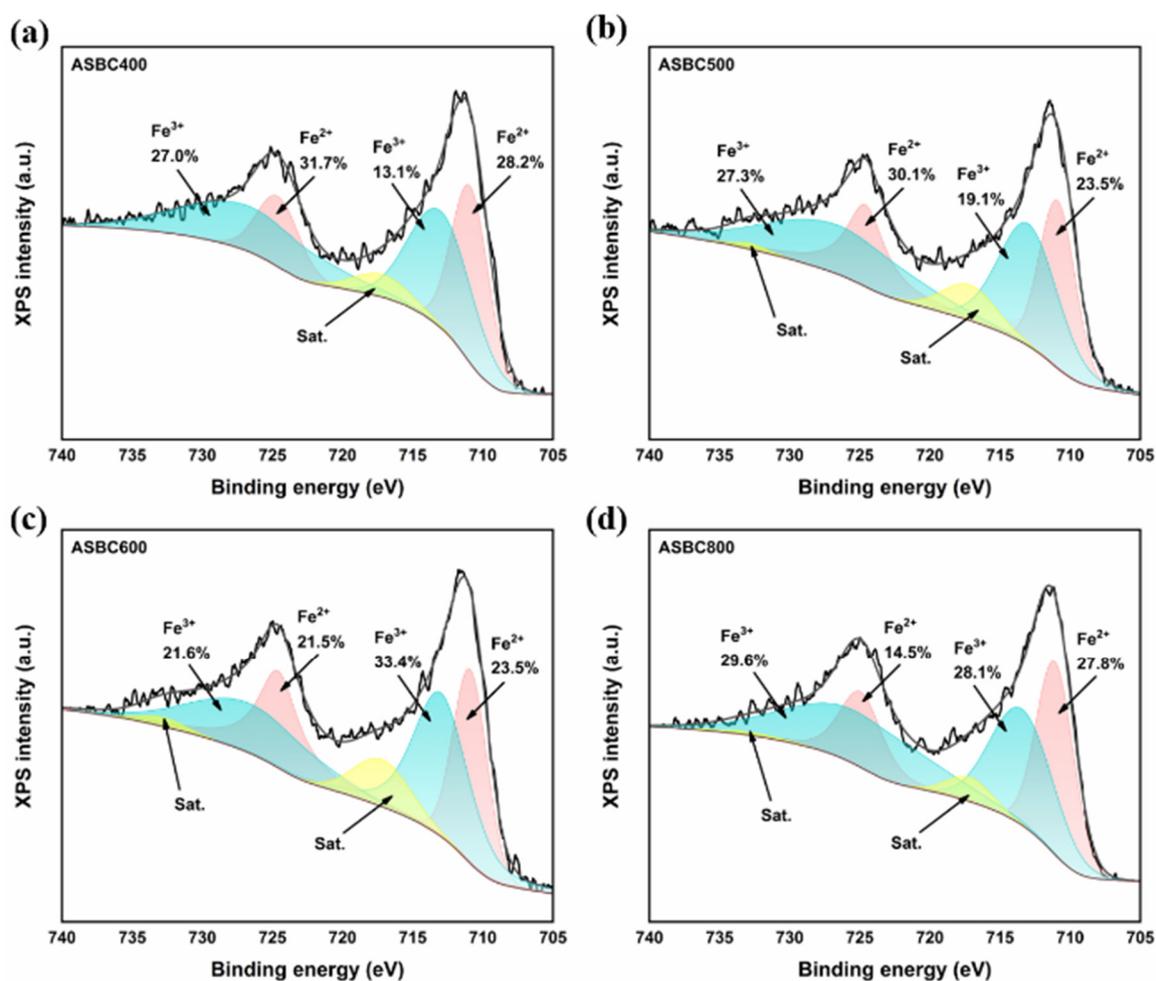


Figure S3. Deconvoluted Fe 2p XPS spectra of the ASBCx samples.

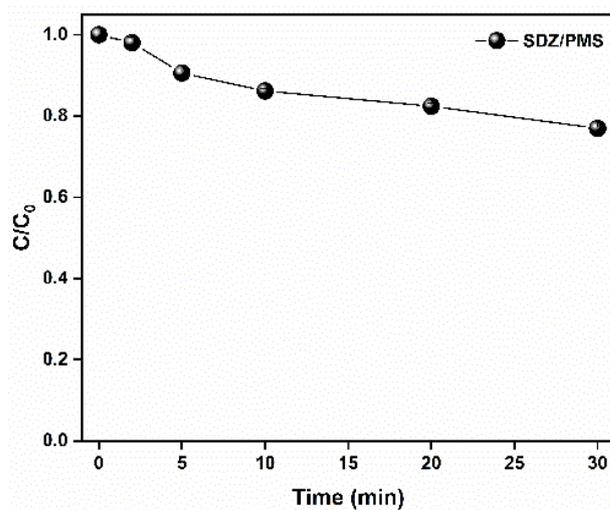


Figure S4. Removal of SDZ by PMS alone.

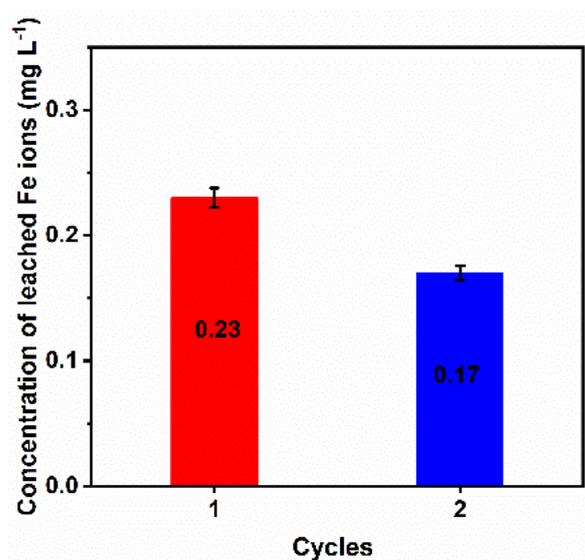


Figure S5. The leached Fe²⁺ during PMS activation.

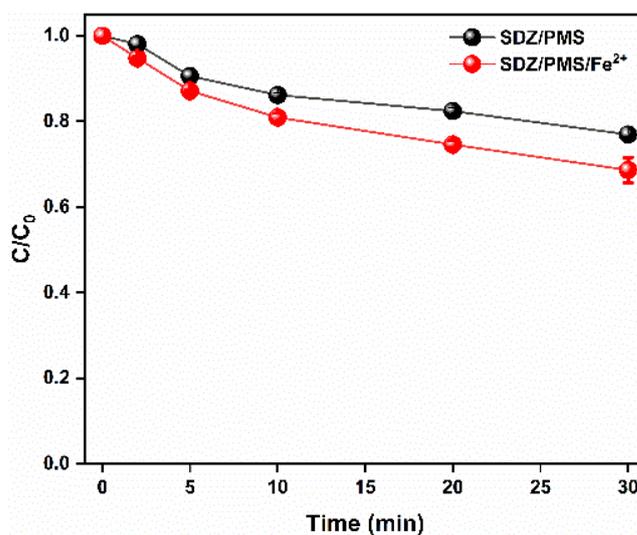


Figure S6. Removal of SDZ by PMS alone and Fe²⁺/PMS.

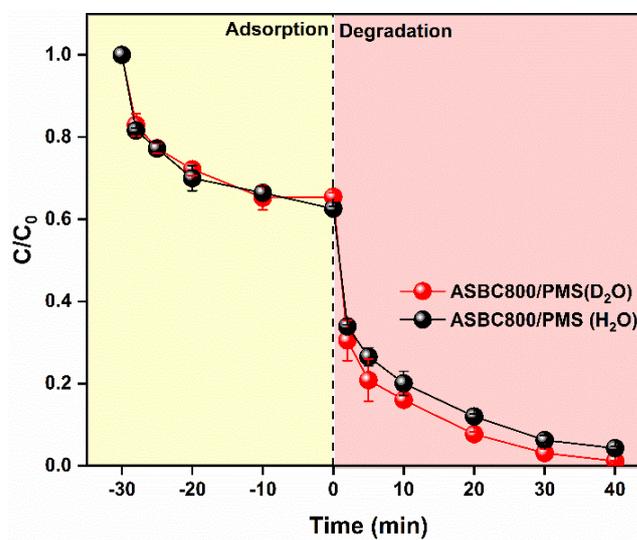


Figure S7. Removal of SDZ by solvent exchange experiment.

Reference

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