

1 **Supporting Information:**

2 **Elucidating Multiple Reaction Pathways for the Degradation of Antibiotics in Water by**  
3 **Self-Active Single-Atom Zinc Catalyst on Biochar**

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## 47 **Section A. Materials**

### 48 **Chemicals and Materials**

49 Post oak pellet was obtained from B&B Charcoal (Weimar, USA). Trimethoprim (TMP,  
50  $\geq 98.0\%$ ) and sulfamethoxazole (SMX,  $\geq 98.0\%$ ) were purchased from TCI America (Portland,  
51 USA). 5,5-dimethyl-1-pyrroline N-oxide (DMPO,  $\geq 98.0\%$ ), hydrogen peroxide ( $H_2O_2$ , 30%)  
52 and hydrochloric acid (HCl, 33-38%) were obtained from Fisher Chemical (Waltham, USA).  
53 2,2,6,6-tetramethyl-4-piperidinol (TEMPO, 99%) and ammonium metavanadate ( $NH_4VO_3$ ,  
54 99.5%) were purchased from ACROS Organics (Waltham, USA). L-histidine (L-his,  $\geq 98.0\%$ ),  
55 nitro blue tetrazolium (NBT,  $\geq 98.0\%$ ) and dicyandiamide (98.0%) were purchased from Alfa  
56 Aesar (Haverhill, USA). The following chemicals were purchased from different suppliers:  
57 methanol (MeOH, reagent grade) from VWR Chemicals (Radnor, USA), acetonitrile ( $CH_3CN$ ,  
58  $\geq 99.7\%$ ) from BTC (Hudson, USA), superoxide dismutase (SOD, 6010 U/mg) from Millipore  
59 Sigma (Burlington, USA), and zinc nitrate ( $Zn(NO_3)_2$ ,  $\geq 98.5\%$ ) from Spectrum Chemical  
60 (New Brunswick, USA). All chemicals were used as received. Industrial-grade nitrogen used  
61 in the experiment was purchased from Airgas (Radnor, USA). All solutions were prepared  
62 using ultrapure water produced by a NANOpure II filter from Thermo Fisher Scientific  
63 (Waltham, USA)

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## 69 **Degradation products of TMP**

70 Samples collected at 0, 0.5, and 2.0 hours were used to identify TMP degradation products.  
71 Solid-phase extraction (SPE) was used to concentrate TMP and its metabolites in the samples.  
72 Waters Oasis HLB cartridges (WAT106202, 6 cc/200 mg) were pre-conditioned with 5.0 mL  
73 methanol and 5.0 mL ultrapure water in the SPE analysis before they were loaded with 1.0 mL  
74 samples. The cartridges were vacuum-dried for 10 minutes after loading, and the samples were  
75 eluted with 1.0 mL of methanol and stored in 2 mL microtubes. Untargeted analysis was  
76 performed with a liquid chromatography high-resolution accurate mass spectrometry (LC-  
77 HRAM) fitted with a Q Exactive Plus Orbitrap mass spectrometer (Thermo Fisher Scientific,  
78 Waltham, USA) and connected to a binary pump UltiMate 3000 HPLC (Sunnyvale, USA).

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## 80 **Superoxide radical detection**

81 The presence of superoxide radical ( $O_2^{\cdot-}$ ) was determined by the reaction between  $O_2^{\cdot-}$   
82 and nitroblue tetrazolium chloride (NBT) (Goto et al. 2004). Briefly, 0.5 mg SAZn@BC was  
83 added into 10  $\mu$ M NBT solution (10 mL) and stirred at 400 rpm for one hour. 2 mL samples  
84 were taken at 0, 30, and 60 mins and filtered through a 0.45  $\mu$ m syringe filter. NBT in the  
85 filtrate was analyzed by a UV-vis-NIR spectrophotometer (Hitachi U-4100) at 260 nm.

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## 87 **Hydrogen peroxide detection**

88 The generation of hydrogen peroxide ( $H_2O_2$ ) was confirmed by the reaction between  $H_2O_2$

89 and metavanadate to produce peroxovanadate (Nogueira et al. 2005). 0.5 mg SAZn@BC was  
90 added into 0.2 mM ammonia metavanadate solution (10 mL) and stirred at 400 rpm for 20  
91 minutes with pH adjusted to 3.0, 5.0, and 6.0, respectively. The mixture of 0.2 mM H<sub>2</sub>O<sub>2</sub> and  
92 0.2 mM ammonia metavanadate was stirred at 400 rpm for 20 minutes as a control. The  
93 produced peroxovanadate was detected with a UV-vis-NIR spectrophotometer (Hitachi U-  
94 4100) at 450 nm.

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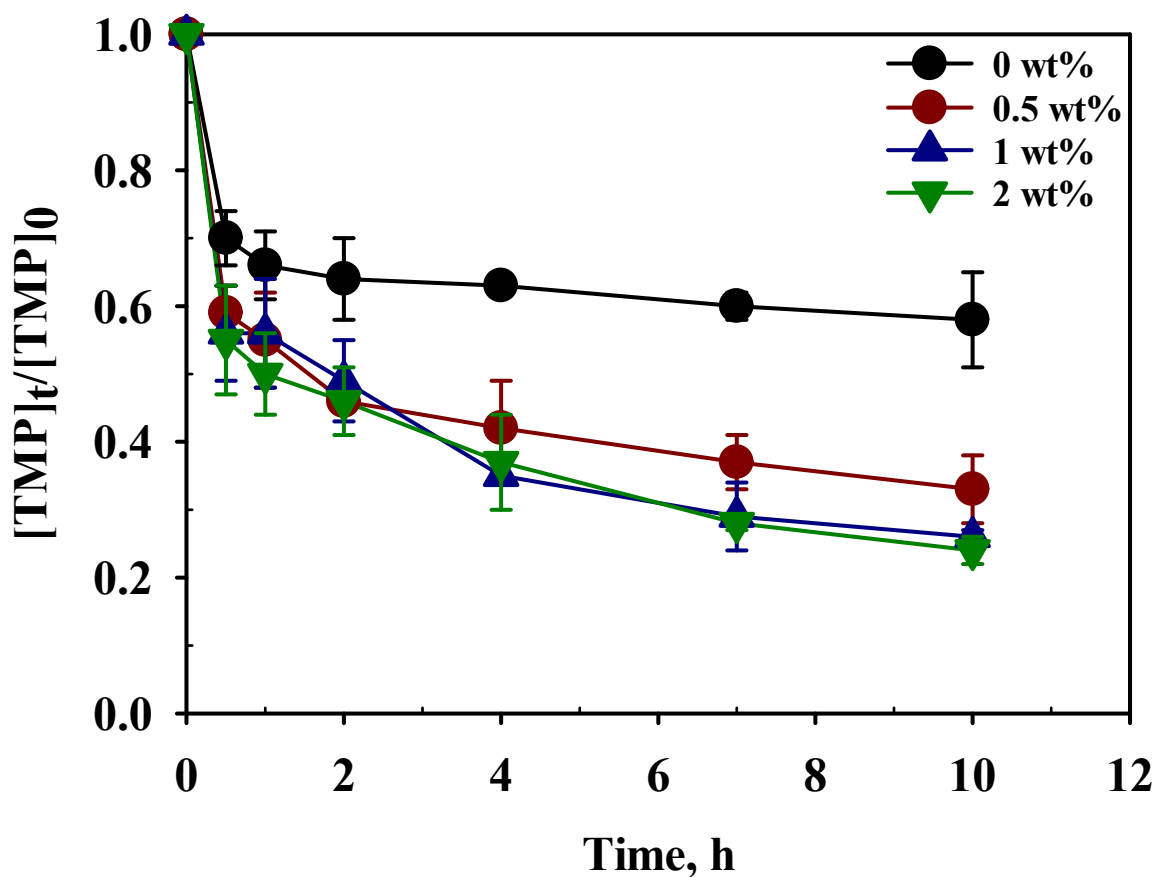
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111 Section B. Supporting Figures



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113 **Figure S1.** TMP removal by SAZn@BC with different Zn wt%. Reaction conditions:  $[TMP]_0 =$

114  $10.0 \mu\text{M}$ ,  $[\text{Biochar}] = 0.2 \text{ g/L}$ ,  $[\text{pH}] = 4.3$ ,  $T = 25.0^\circ\text{C}$ .

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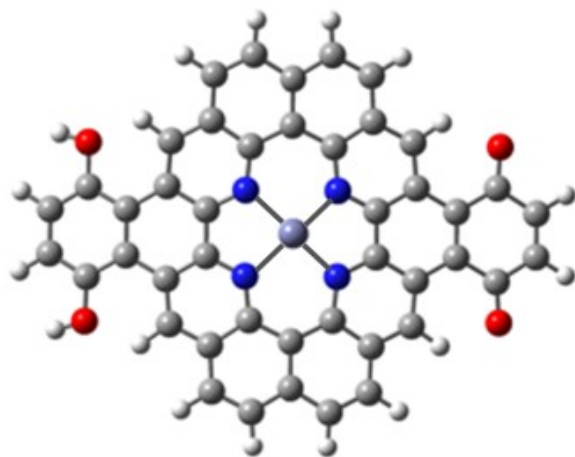
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123 **Figure S2.** Single catalyst model of SAZn@BC for DFT calculation.

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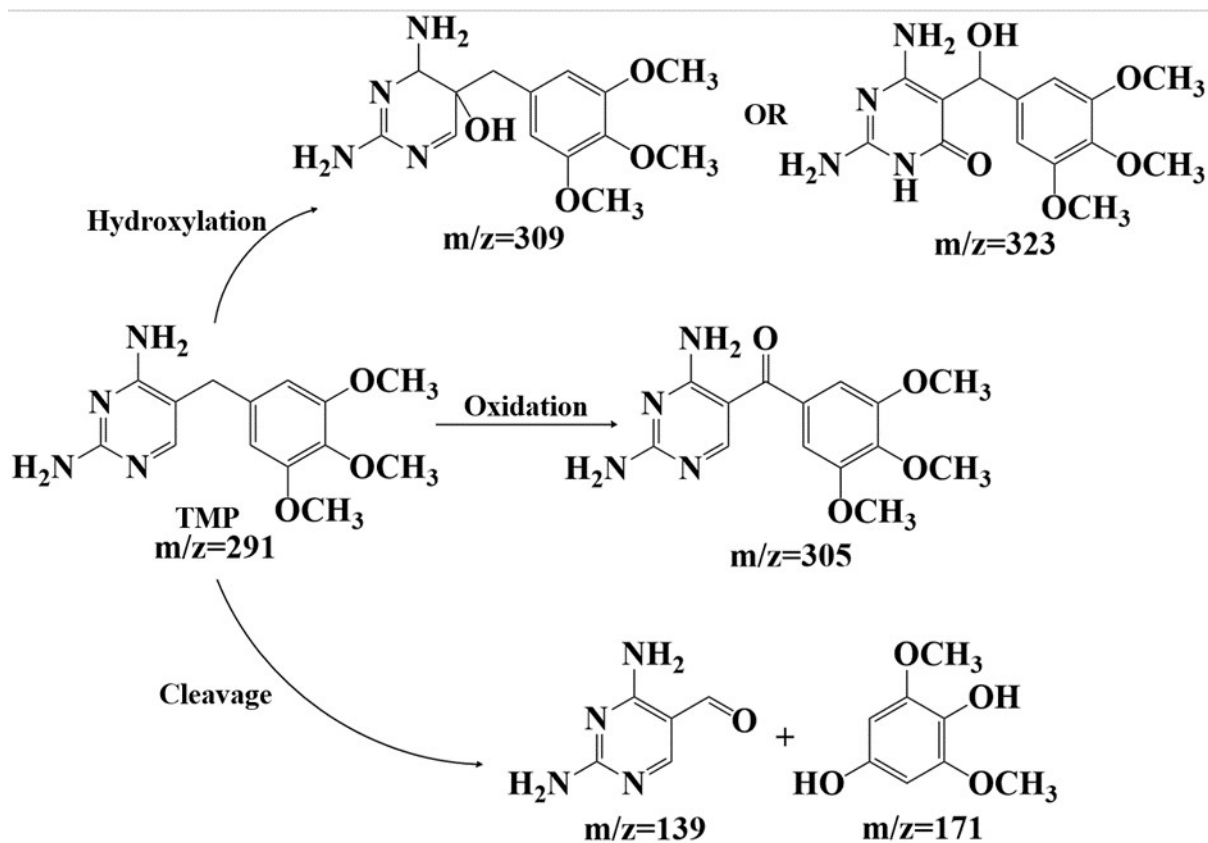
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138 **Figure S3.** Plausible degradation products and degradation pathways of TMP by SAZn@BC.

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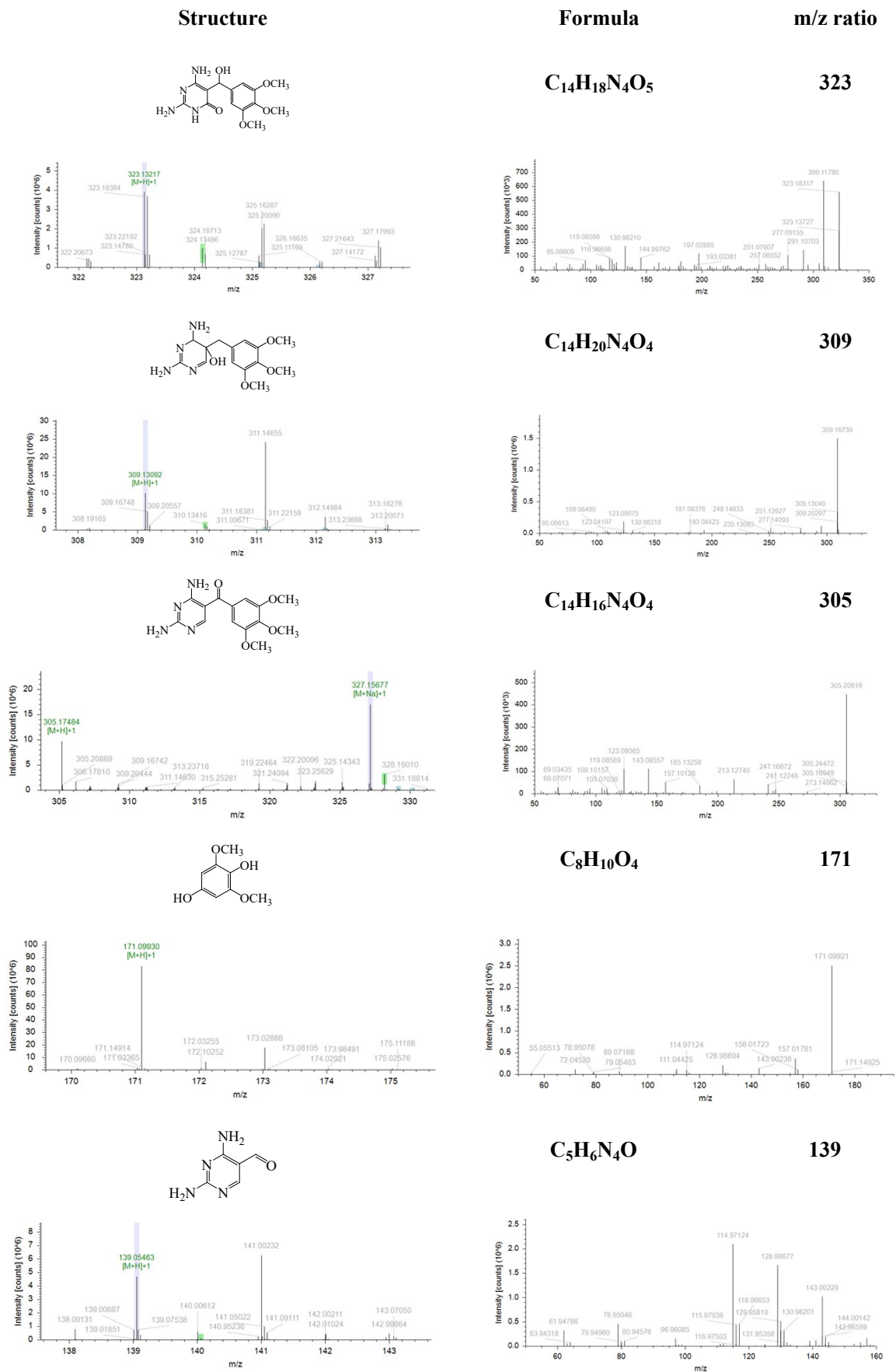
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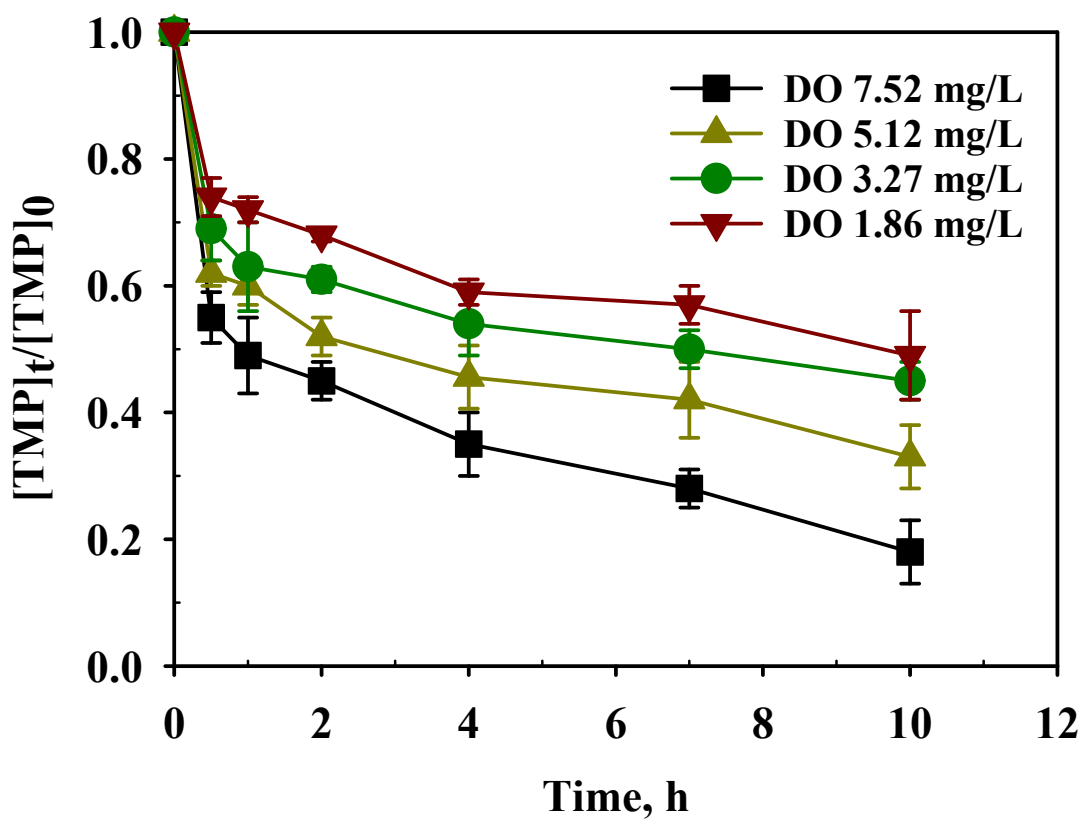
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148 **Figure S4.** MS1 and MS2 spectra of possible TMP degradation metabolites.



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150 **Figure S5.** The effect of Do level on the performance of TMP removal by SAZn@BC Reaction

151 conditions:  $[TMP]_0 = 10 \mu\text{M}$ ,  $[\text{Biochar}] = 0.2 \text{ g/L}$ ,  $[\text{pH}] = 4.5$ ,  $T = 25^\circ\text{C}$ .

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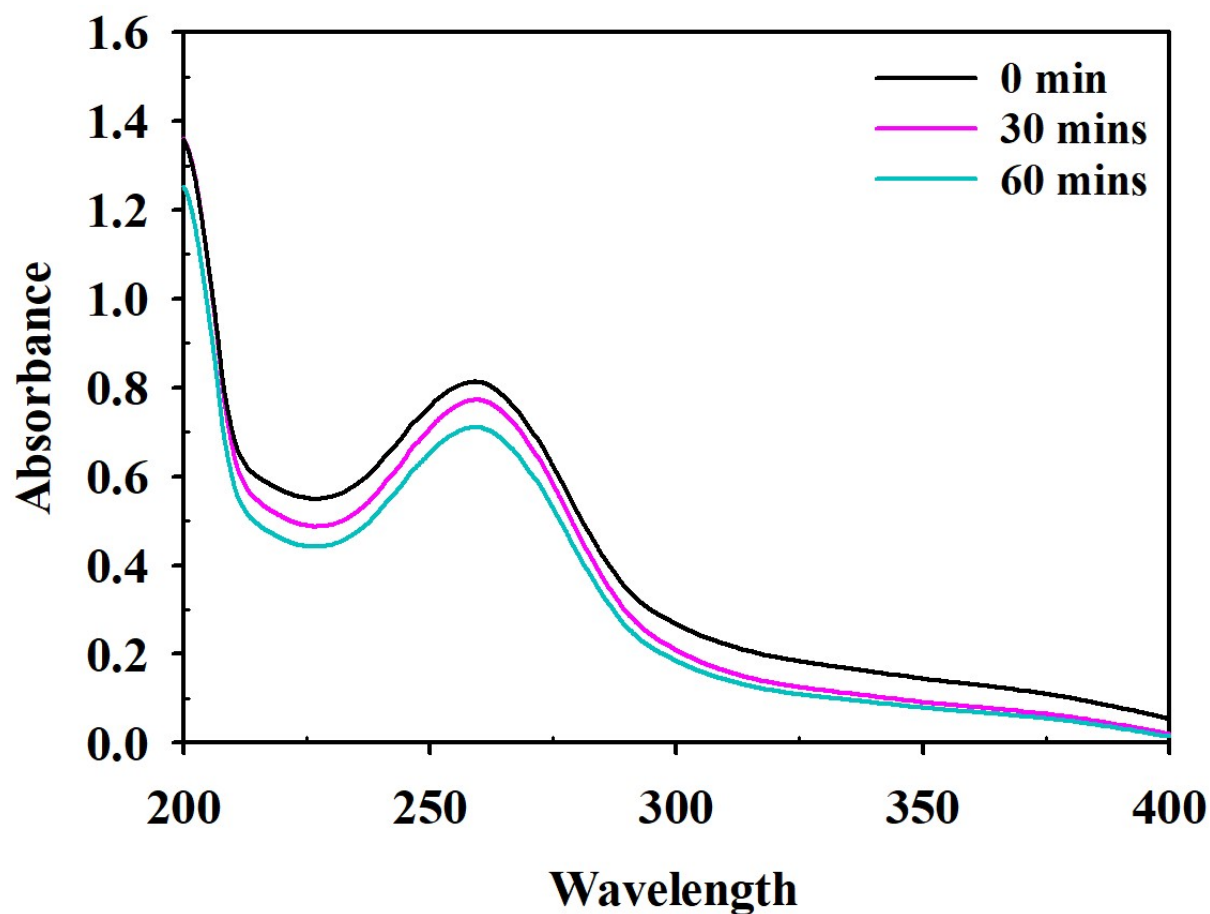
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161 **Figure S6.** Detection of superoxide radical in SAZn@BC system. Reaction condition:

162 [Biochar] = 0.5 g/L, [NBT]<sub>0</sub> = 10 μM.

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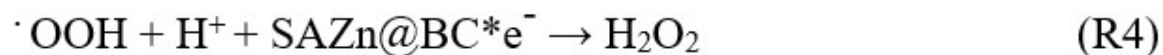
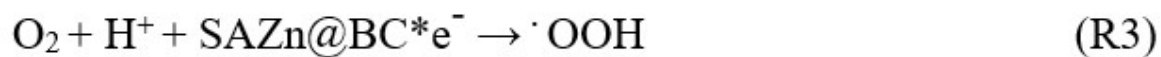
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173 **Figure S7.** Proposed reactions for the reactive species generation by the SAZn@BC.

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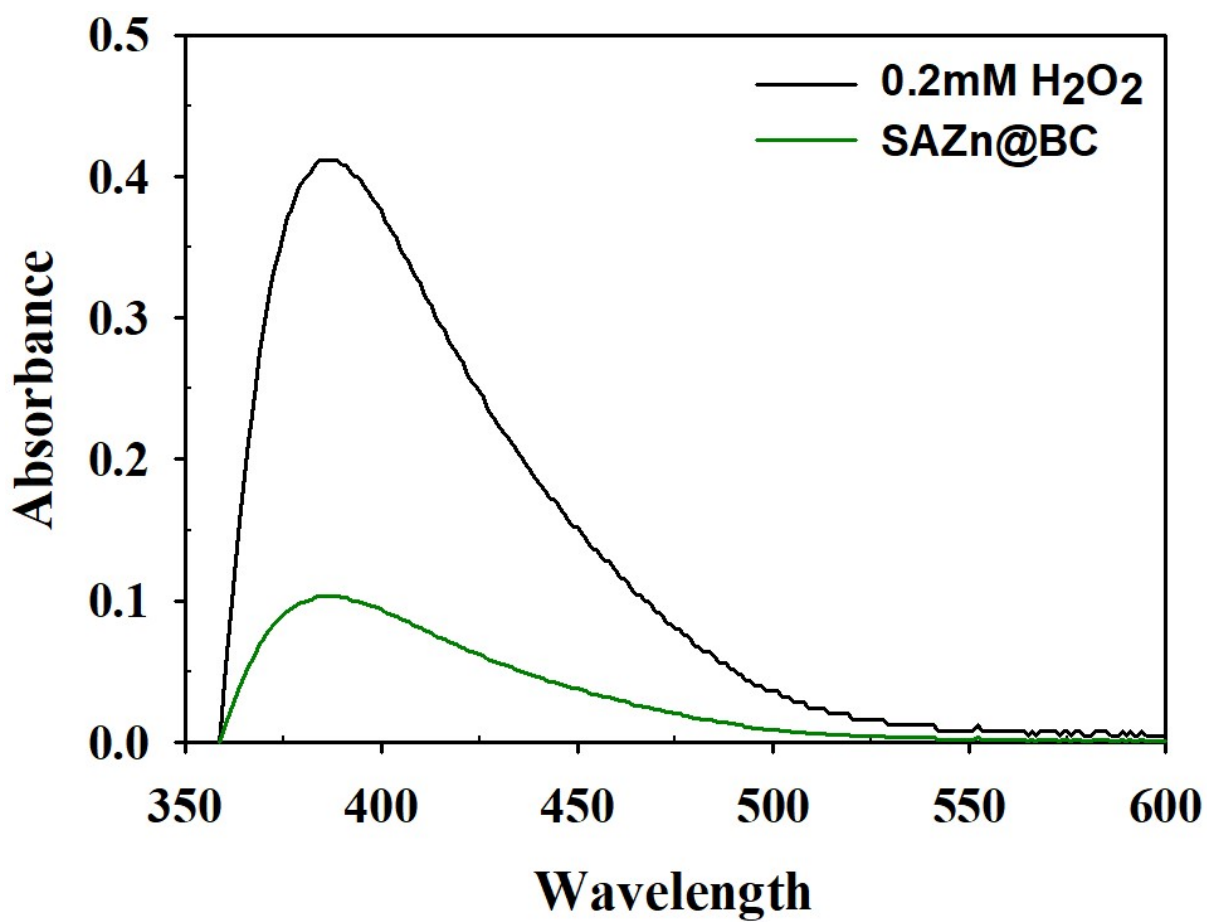
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190 **Figure S8.** Detection of H<sub>2</sub>O<sub>2</sub> in SAZn@BC system. Reaction condition: [Biochar] = 0.5 g/L,

191 [NH<sub>4</sub>VO<sub>3</sub>]<sub>0</sub> = 0.2 mM. H<sub>2</sub>O<sub>2</sub> reference has a concentration of 0.2 mM.

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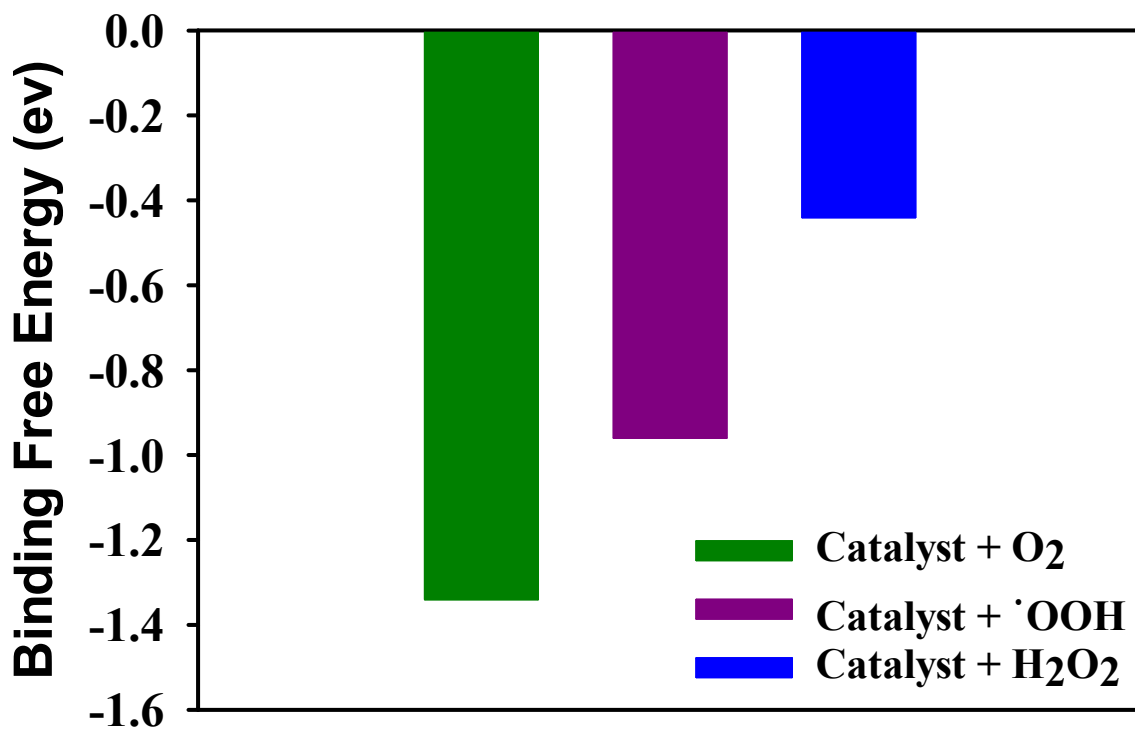
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202 **Figure S9.** Binding free energy between SAC, O<sub>2</sub>, OOH and H<sub>2</sub>O<sub>2</sub> (H<sub>2</sub>Q for hydroquinone  
203 state and Q for quinone state).

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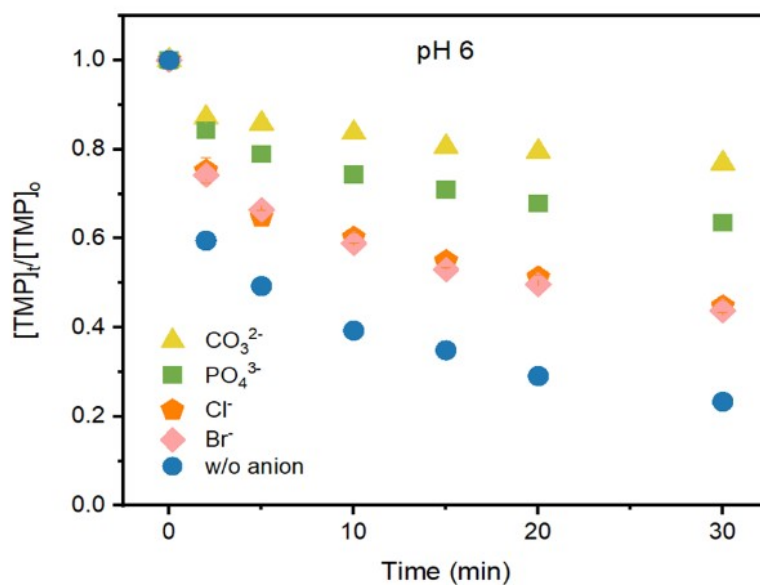
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215 **Figure S10.** (a) Trimethoprim (TMP) removal by SAZn@BC in the presence of different

216 inorganic anions in the solution. Reaction conditions: Running time = 10 hours, [TMP<sub>0</sub>] = 10

217 μM, [Biochar] = 0.2 g/L, [CO<sub>3</sub><sup>2-</sup>] = 50 mM, [PO<sub>4</sub><sup>3-</sup>] = 50 mM, [Cl<sup>-</sup>] = 50 mM, [Br<sup>-</sup>] = 50 mM.

218 pH = 6.0, T = 25.0°C.

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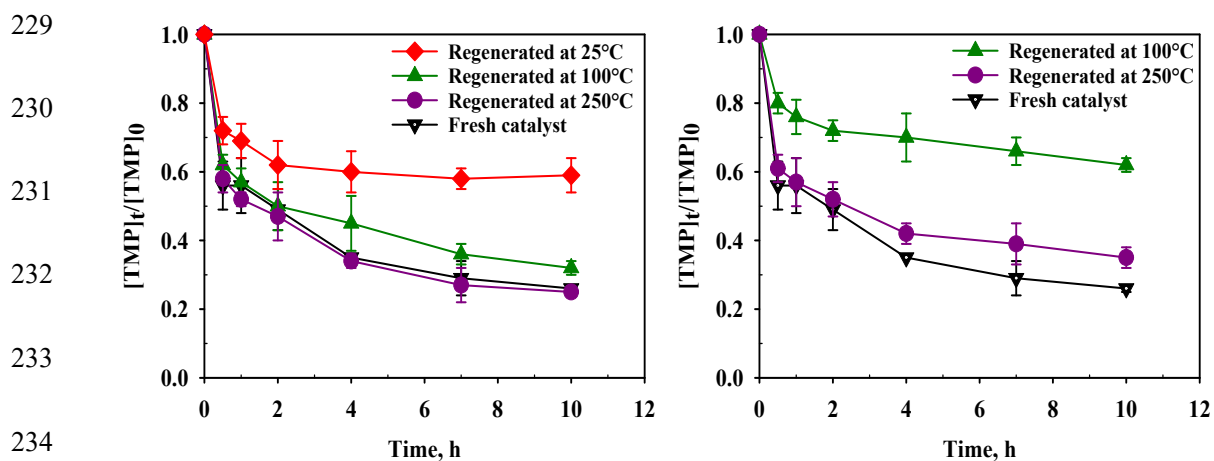
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235 **Figure S11.** (a) Trimethoprim (TMP) degradation by SAZn@BC regenerated at different  
 236 reheating temperatures after first cycle of reaction. (b) TMP degradation by SAZn@BC  
 237 regenerated at different reheating temperatures after second cycle of reaction.

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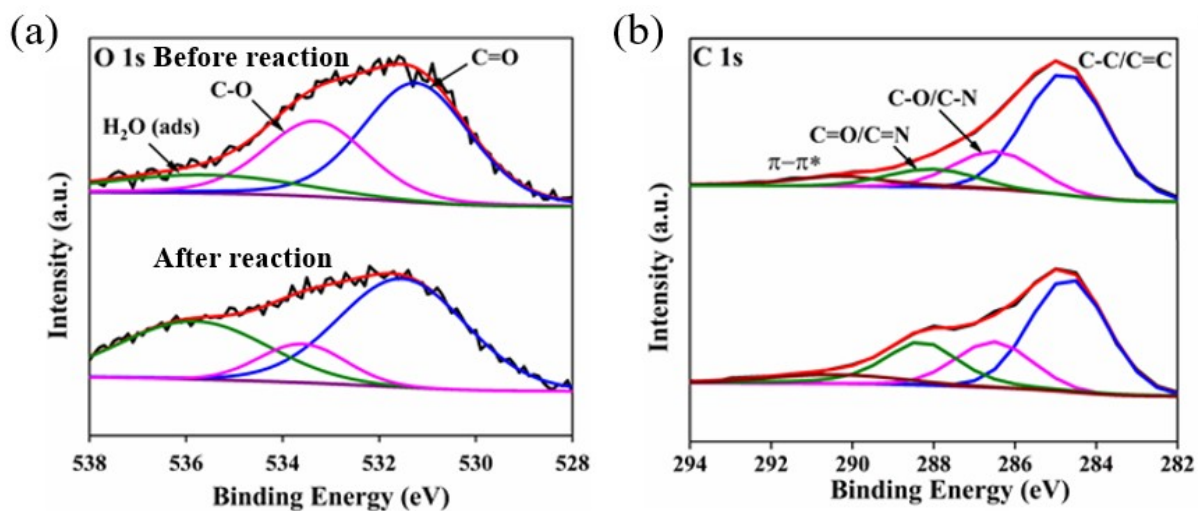
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252 **Figure S12.** XPS spectra of SAZn@BC before and after the reaction. (a) The O 1s spectrum,  
 253 and (b) The C 1s spectrum. The spectra of SAZn@BC before the reaction are at the top and  
 254 after the reaction are at the bottom in each panel.

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267 **Section C. Supporting Tables**

268 **Table S1.** Free energy of intermediates at potential relative to free catalyst and oxygen for

269 SAZn@BC containing Zn sites.

Reaction	R1	R3	R4
Free energy (eV) at U = 0 V	-1.70	-1.91	-1.40
Free energy (eV) at U = 0.22 V	-1.70	-1.69	-0.96

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272 **Table S2.** Free energy of intermediates at potential relative to free catalyst and oxygen for

273 SAZn@BC without Zn sites.

Reaction	R1	R3
Free energy (eV) at U = 0 V	0.48	-0.85
Free energy (eV) at U = 0.22 V	0.48	-0.62

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276 **Table S3.** Partial charge from Natural Population Analysis values for catalyst

Combination	SAC/O <sub>2</sub>	SAC/·OOH	SAC/TMP
Partial charge	0.76	0.76	-0.10

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<b>Catalyst</b>	<b>Dosage (g L<sup>-1</sup>)</b>	<b>System</b>	<b>Initial TMP concentrat ion (μM)</b>	<b>Secon rate constant (L/g.min)</b>	<b>Reference</b>
SAZn@BC	0.2	Catalyst only	10	8.07x10 <sup>-2</sup>	This work
N-doped Biochar	1	Persulfate activation	45	8.7x10 <sup>-3</sup>	(Annamalai and Shin 2022)
Malt rootlet biochar	0.045	persulfate activation	3.7	6.88x10 <sup>-2</sup>	(Grilla et al. 2020)
Co <sub>3</sub> O <sub>4</sub> /BiOI	0.8	Photocatalysis	0.07	1.57x10 <sup>-2</sup>	(Malefane et al. 2020)
Co-doped organic aerogels	0.01	Photocatalysis	10	1.31	(Bolobajev et al. 2019)
Ni-doped organic aerogels	0.01	Photocatalysis	10	1.48	(Bolobajev et al. 2019)
Zn-doped organic aerogels	0.01	Photocatalysis	10	1.24	(Bolobajev et al. 2019)
Fe-doped organic aerogels	0.01	Photocatalysis	10	1.21	(Bolobajev et al. 2019)
TiO <sub>2</sub> -P25	1	Photocatalysis	1	2.4 x10 <sup>-3</sup>	(Oros-Ruiz et al. 2013)
Au/TiO <sub>2</sub> -P25	1	Photocatalysis	1	5.2x10 <sup>-3</sup>	(Oros-Ruiz et al. 2013)
Ag/TiO <sub>2</sub> -P25	1	Photocatalysis	1	5.2x10 <sup>-3</sup>	(Oros-Ruiz et al. 2013)

Cu/TiO <sub>2</sub> -P25	1	Photocatalysis	1	4.5x10 <sup>-3</sup>	(Oros-Ruiz et al. 2013)
Ni/TiO <sub>2</sub> -P25	1	Photocatalysis	1	3.0x10 <sup>-3</sup>	(Oros-Ruiz et al. 2013)

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