

Supporting Information for

**Activation of peroxymonosulfate by P-doped cow
manure biochar for enhancing degradation of 17 β -
estradiol**

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Figure S1. The (a) adsorption and (b) catalytic performance of phosphoric acid modified biochar prepared at different pyrolysis temperatures (experiment conditions: $[E2] = 3 \text{ mg/L}$, $[PMS] = 2.0 \text{ mM}$, $[\text{biochar}] = 0.1 \text{ g/L}$).

Figure S2. The (a) adsorption and (b) catalytic performance of modified biochar impregnated with different concentrations of phosphoric acid. (experiment conditions: $[E2] = 3 \text{ mg/L}$, $[PMS] = 2.0 \text{ mM}$, $[\text{biochar}] = 0.1 \text{ g/L}$).

Figure S3. The adsorption and catalytic performance of CBC 500 and PBC500. (experiment conditions: $[E2] = 3 \text{ mg/L}$, $[PMS] = 2.0 \text{ mM}$,

43 [biochar] = 0.1 g/L).

44 **Figure S4.** Zeta potential of PBC500 at different pH values.

45 **Figure S5.** Kinetic fitting curves of E2 degradation at different (a) PBC500
46 dosage, (b) PMS concentration, (c) E2 concentration, (d) pH, (e) Cl⁻
47 concentration and (f) HA concentration.

48 **Figure S6.** (a) C 1s, (b) O 1s and (c) P 2p XPS spectra of CBC500 after
49 the reaction.

Text S1. Kinetic modelling analysis

The pseudo-first order kinetic model (Eq. (S1)) was performed to simulate the reaction kinetics of E2.

$$\ln(C_t/C_0) = -k_{obs}t \quad (S1)$$

Where C_t presents the E2 concentration at time t (min), C_0 is the initial concentration of E2, k_{obs} value is the apparent rate constant of pseudo-first order kinetic model for the E2 degradation process.

Text S2. characterization methods

Total P content in biochar was measured by treating the samples at 500 °C for 2 h, followed by 1 M HCl extraction for 16 h [1]. P concentration was measured with the ascorbic acid molybdenum blue method [2].

The surface morphologies of samples were observed by field emission scanning electron microscopy (SEM, FEI Nova NanoSEM 230, CZ). The specific surface areas and pore structures were determined using the Brunauer-Emmett-Teller (BET) nitrogen adsorption/desorption method on analyzer (ASAP246, USA). The crystalline structures of samples were recorded by X-ray diffraction (XRD, Rigaku Ultima IV, JPN). The surface functional groups of samples were determined by Fourier transform infrared spectrum (FTIR, Nicolet iS50, USA). The elemental compositions of samples were characterized by X-ray photoelectron spectroscopy (XPS, ESCALAB 250XI, USA). The thermogravimetric (TG) analysis was performed with a thermal analyzer (STA449C/6/G, GER). The zeta potential of samples was measured by analyzer

71 (Zetasizer Nano-ZS90, UK) at 298K.

72 **Text S3. analytic methods**

73 The concentration of E2 in the solution was analyzed by high performance liquid
74 chromatography (HPLC). The mobile phase was acetonitrile/ultrapure water (45:55,
75 v/v) with a flow rate of 1.0 mL/min at 30 °C and the injection volume was 20 µL.

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77 **Table S1.** The total P content in CBC500 and PBC500.

Biochar	Total P content (mg/kg)
CBC500	1004 ± 25
PBC500	2798 ± 31

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80 **Table S2.** Properties of pristine and P-doped biochar.

	BET surface area (m ² /g)	Total pore volume (cm ³ /g)	Average pore diameter (nm)
CBC500	12.4252	0.0118	11.1005
PBC500	203.7745	0.2331	5.0613

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83 **Table S3.** Element composition of biochar

Biochar	Atomic (%)				
	C	O	N	Si	P
CBC500	70.17	20.36	3.51	3.48	2.47
PBC500	57.96	29.39	2.43	3.61	6.71

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86 **Table S4.** High deconvolution of C1s XPS spectra of CBC500 and PBC500 before and
 87 after E2 degradation.

	Area (%)			
	C-C	defects	C-O	C=O
CBC500				
before reaction	30.44	37.17	24.36	8.06
PBC500				
before reaction	24.74	39.29	22.32	13.65
PBC500 after reaction	27.48	32.44	28.13	10.17

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90 **Table S5.** High deconvolution of O1s XPS spectra of CBC500 and PBC500 before and
91 after E2 degradation.

	Area (%)		
	C=O	-OH	C-O
CBC500 before reaction	14.52	50.20	35.28
PBC500 before reaction	20.47	59.60	19.33
PBC500 after reaction	17.03	58.71	17.03

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94 **Table S6.** High deconvolution of P 2p XPS spectra of PBC500 before and after E2
95 degradation.

	Area (%)	
	P-C	P-O
PBC500 before reaction	21.05	78.95
PBC500 after reaction	13.01	86.99

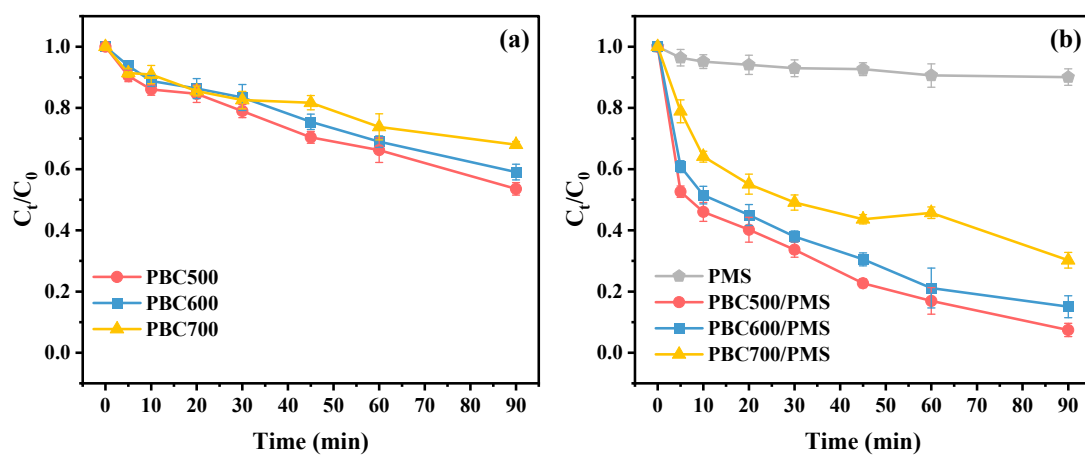


Figure S1. The (a) adsorption and (b) catalytic performance of phosphoric acid modified biochar prepared at different pyrolysis temperatures (experiment conditions: [E2] = 3 mg/L, [PMS] = 2.0 mM, [biochar] = 0.1 g/L).

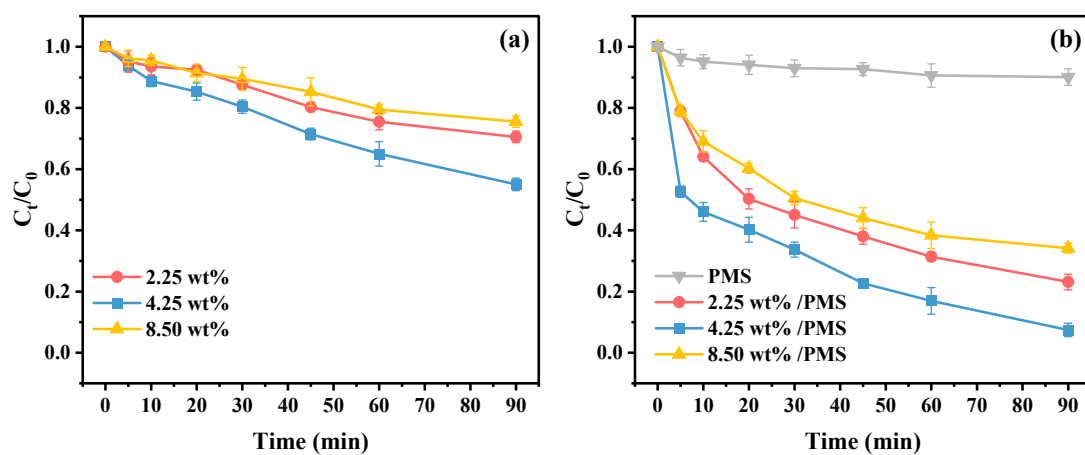


Figure S2. The (a) adsorption and (b) catalytic performance of modified biochar impregnated with different concentrations of phosphoric acid. (experiment conditions: [E2] = 3 mg/L, [PMS] = 2.0 mM, [biochar] = 0.1 g/L).

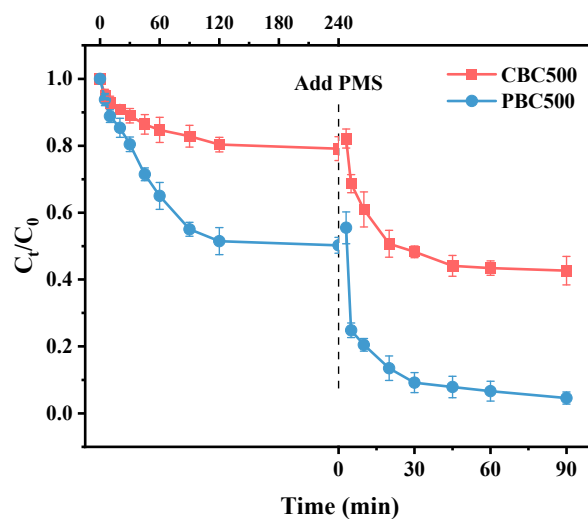
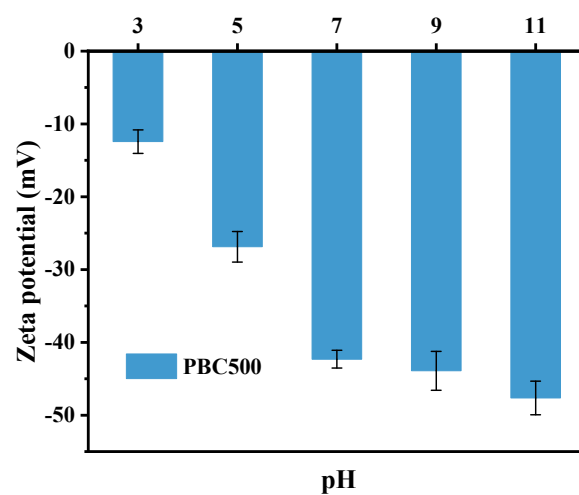


Figure S3. The adsorption and catalytic performance of CBC 500 and PBC500.

(experiment conditions: [E2] = 3 mg/L, [PMS] = 2.0 mM, [biochar] = 0.1 g/L).



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113 **Figure S4.** Zeta potential of PBC500 at different pH values.

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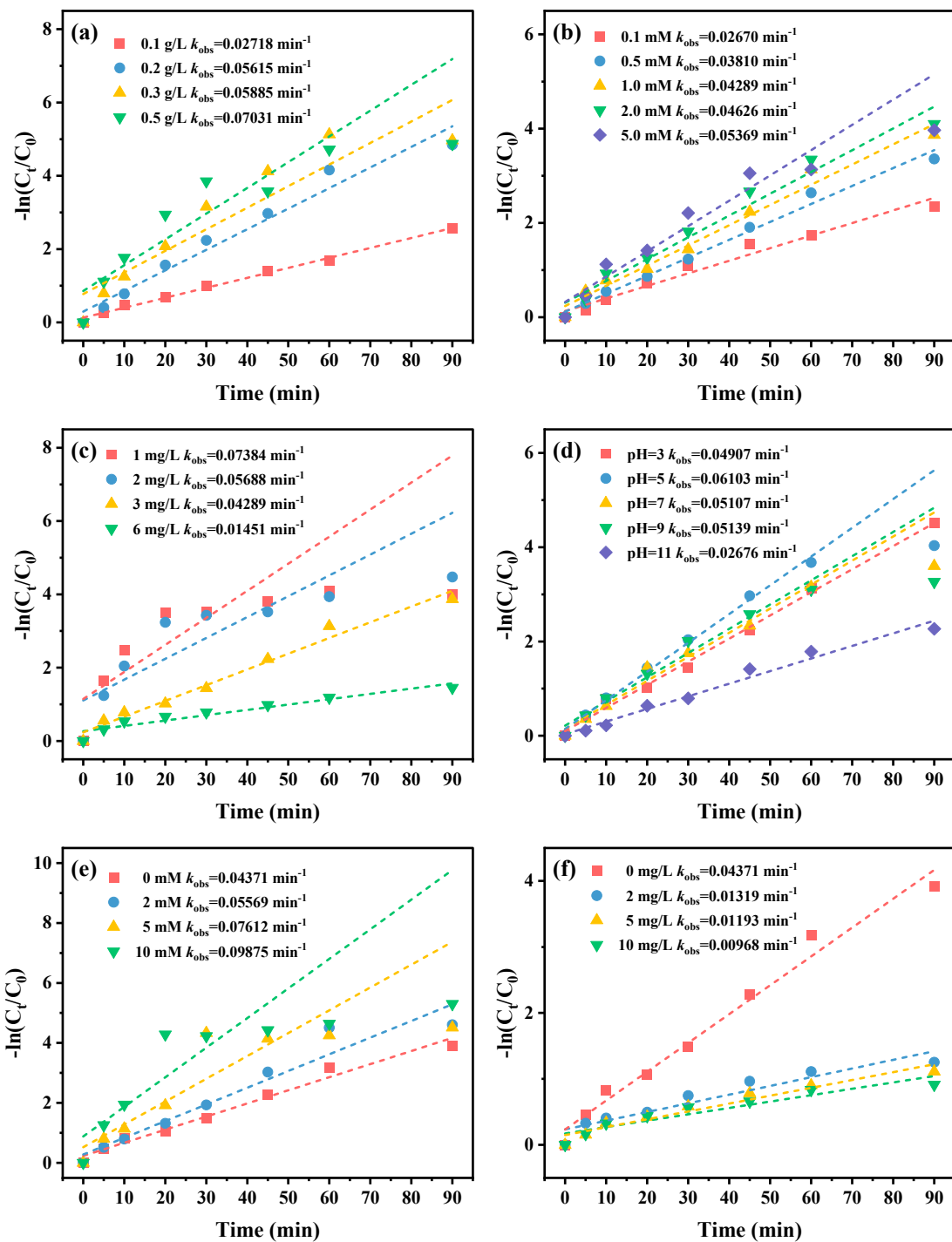


Figure S5. Kinetic fitting curves of E2 degradation at different (a) PBC500 dosage, (b) PMS concentration, (c) E2 concentration, (d) pH, (e) Cl⁻ concentration and (f) HA concentration.

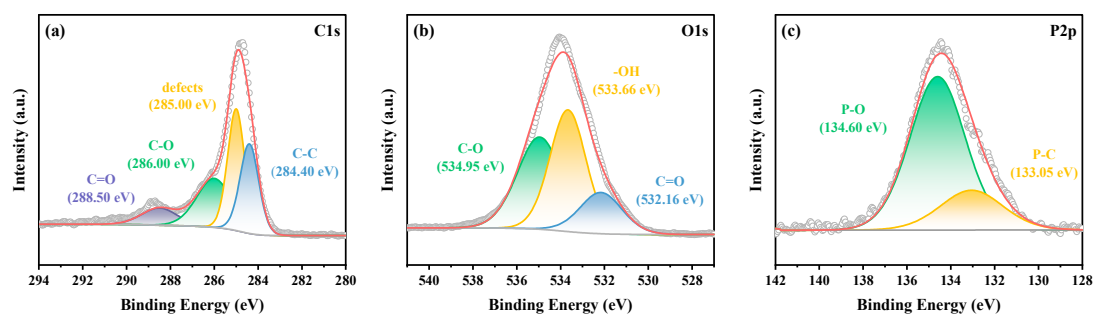


Figure S6. (a) C 1s, (b) O 1s and (c) P 2p XPS spectra of CBC500 after the reaction.

References

1. Xu, G.; Y. Zhang; H.B. Shao; J.N. Sun, Pyrolysis temperature affects phosphorus transformation in biochar: Chemical fractionation and ^{31}P NMR analysis. *Science of the Total Environment*. **2016**, 569, 65-72.
2. Murphy, J.; J.P. Riley, CITATION-CLASSIC - A MODIFIED SINGLE SOLUTION METHOD FOR THE DETERMINATION OF PHOSPHATE IN NATURAL-WATERS. *Current Contents/Agriculture Biology & Environmental Sciences*. **1986**(12), 16-16.