# Interior engineering of seaweed-derived N-doped versatile carbonaceous beads with $Co_x O_v$ for universal organic pollutant degradation

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Fig. S11. Effect of illumination on MB degradation. Reaction conditions: [MB] = 120 mg/L, [PMS] = 3 mM, catalyst = 0.4 g/L, T = 298 K, initial solution pH 7.62.

Fig. S12. The HPLC for different reaction times of MB degradation: a) origin, (b-d)

during the reaction and (e) after the reaction. Injection conditions: methanol: $H_2O =$ 

60:40, injection rate = 0.8 mL/min, injection rate = 10 uL. Reaction conditions: [MB]

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# Text S1.

## 2.1. Materials and Chemicals

Potassium monopersulfate triple salt (K<sub>4</sub>H<sub>3</sub>S<sub>4</sub>O<sub>18</sub>, 42–46% KHSO<sub>5</sub>) was purchased from shanghai Macklin Biochemical Co., Ltd (Shanghai, China). Polyethyleneimine (PEI, 99%), cobalt nitrate hexahydrate  $(Co(NO_3)_2 \cdot 6H_2O)$ , methyl blue (C37H27N3Na2O9S3, MeB), alizarin red (C14H7NaO7S·H2O, AR ), orange G  $(C_{16}H_{10}N_2NaO_7S_2, \geq 96\%, OG)$ , tetracycline  $(C_{22}H_{24}N_2O_8 \cdot xH_2O, TC)$ , p-nitrophenol (C<sub>6</sub>H<sub>5</sub>NO<sub>3</sub>, PNP) were purchased from Aladdin Industrial Corporation. Ponceau S (C22H12N4Na4O13S4, PS), acid orange 7 (C16H11N2NaO4S, AO7), Acid Red 94 (C<sub>20</sub>H<sub>2</sub>Cl<sub>4</sub>I<sub>4</sub>Na<sub>2</sub>O<sub>5</sub>, AR94) were obtained from No.67 Changlin Rd Linshu Shandong. Methylene blue trihydrate ( $C_{16}H_{18}CIN_3S_{3}H_2O$ , MB), Tert-butanol (TBA) were obtained from Sinopharm Chemical Reagent Co., Ltd. Sodium alginate, Glutaraldehyde solution (50%, GA), Sodium nitrate (NaNO<sub>3</sub>), Sodium phosphate tribasic dodecahydrate (Na<sub>3</sub>PO<sub>4</sub>·12H<sub>2</sub>O), Sodium thiosulfate (Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>), Sodium hydrogen carbonate (NaHCO<sub>3</sub>) were supplied from Tianjin GuangFu Technology development Co., Ltd. Sodium sulfate anhydrous (Na<sub>2</sub>SO<sub>4</sub>), Sodium Chloride (NaCl) were supplied from Tianjin Kermel Chemical Reagent Co., Ltd. Ethanol (EtOH) was supplied from Tianjin Fuye Fine Chemical Reagent Co., Ltd. Deionized water was produced by selfowned equipment. All the materials and chemicals were used as obtained without further purification.

## Text S2.

First, a certain amount of cobalt nitrate hexahydrate was uniformly dispersed in 100 mL of deionized water to form  $Co^{2+}$  solution with a certain concentration, which was detected by ICP (Fig. S4a). Subsequently, ICP was used to detect the concentration of  $Co^{2+}$  in the mixed solution after the chelation of SA/PEI macromolecule with  $Co^{2+}$  for 6 hours (Fig. S4b). Thus, the co-crosslinking degree of  $Co^{2+}$  and SA/PEI macromolecule was preliminarily evaluated, and the energy load of 2g SA/1.5g PEI macromolecules was calculated to be about 0.324g  $Co^{2+}$ .

# Text S3.

### 2.3. Characterization

The functional groups of as-prepared materials were measured by Fourier transform infrared (FT-IR) spectra (Nicolet, USA) using the KBr pellet technique. The morphology and structure of the composites were characterized by scanning electron microscopy (SEM, JSM-6460LV, JEOL, Japan) with energy dispersive X-ray spectroscopy (EDS). TEM, high-resolution TEM (HRTEM) and selected-area electron diffraction (SAED) images were observed using a FEI Tecnai 20 TEM. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCALAB250 spectrometer (Thermo VG, USA) equipped with an Al-Ka X-ray source (1486.6 eV) for chemical composition and fitted to use the XPSPEAK41 software. The crystal structures were investigated by X-ray diffraction (XRD) operating with Cu Ka radiation (40 kV, 100 mA) ranging from 10° to 70°. The specific surface area was analyzed by the Brunauer-Emmett-Teller (BET) method and pore size distribution plots were taken from the desorption branch of the isotherms based on the BJH model. The Raman spectra were performed on an ISA dispersive Raman spectrometer (RM2000, Renishaw, UK). Vibrating sample magnetometer (VSM) were tested on Lakeshore 7407 with 5×10<sup>-7</sup> emu sensitivity. Total organic carbon (TOC) was identified on a Shimadzu TOC-vcph analyzer. High Performance Liquid Chromatography (HPLC) was detected on Agilent 1100. The leaching of cobalt ions in Co-NC-0.25-700 °C and the quantification of cobalt ions in the Co-SA/PEI were detected by inductively coupled plasma (ICP). All pH values were measured by Delta320 digital pH meter (Mettler-Toledo, Switzerland). The concentration of all organics was assessed by a UVvis spectrophotometer (Agilent Cary 60 spectrophotometer, Germany).

# Text S4.

### 2.4. Catalytic activity measurements

The degradation of MB by PMS was selected as the model reaction to investigate the catalytic performance of composites. Typically, 50 mL aqueous solution containing MB (120 mg/L) and PMS (3 mM) was prepared in a 100 mL beaker with constant stirring (400 rpm) at room temperature. Then, the as-prepared catalysts (20 mg) were added to the above solution, and a certain amount of reaction mixture was transferred to a quartz cuvette for analyzing at selected time intervals. It is worth noting that the critical time

of the reaction was strictly controlled with a stopwatch, and the maximum absorption wavelength of methylene blue at 664 nm is taken as the absorption band of the model reaction. The catalysts were collected by magnetic filtration (Fig. S2) and washed with deionized water after each cycle, and dried in an oven at 60 °C during the cycling tests.

The pseudo-first-order kinetic model was applied to investigate the degradation of MB, which can be expressed as follows (Eq.(1)).

$$Ln\frac{C_t}{C_0} = -k_1 t \tag{1}$$

Where  $C_t$  and  $C_0$  are the instantaneous and initial concentrations of MB, respectively,  $k_1$  is the rate constant, and t is the reaction time.

The universal applicability of the as-prepared Co-NC-0.25-700 °C was carefully demonstrated through the degradation of different organic contaminants: Tetracycline, p-Nitrophenol, Ponceau S, and so on. To further examine the catalytic mechanism, quenching agent such as tert-butyl alcohol (TBA) and ethanol (EtOH) was added in the system, and the degradation efficiency was evaluated as above. Each experiment was conducted for three times, and variations are shown as error bars in the figures.



Scheme S1. The flow chart of column catalysis experiments.



Fig. S1. The physical illustration of the preparation process of Co-SA/PEI.



Fig. S2. The catalyst was collected by magnetic filtration.



Fig. S3. The fixed-bed reactor with full samples.

(a)	Replic Repl# 1 2 3	ate Data: Sa Analyte Co 228.616 Co 228.616 Co 228.616	mple041 Net Intensity 703739.2 688121.9 690979.0	Corrected Intensity 693594.1 677976.8 680833.9	Calib. Conc. Units 1.788 mg/L 1.753 mg/L 1.759 mg/L		Conc. 1.788 1.753 1.759	Sample Units mg/L mg/L mg/L	Analysis Time 15:12:52 15:12:55 15:12:57
	Mean D Analyt Co 228	e 8.616	41 Mean Corrected Intensity 684135.0	Calib. Conc. Units 1.767 mg/L	Std.Dev. 0.0189	Conc. 1. 767	Sample Units mg/L	Std. De 0. 018	ev. RSD 9 1.07%
(b)	Replic Repl# 1 2 3	ate Data: Sa Analyte Co 228.616 Co 228.616 Co 228.616	mple042 Net Intensity 564426.7 550770.6 540909.1	Corrected Intensity 554281.6 540625.5 530764.0	Calib. Conc. Units 1.472 mg/L 1.441 mg/L 1.418 mg/L		Conc. 1. 472 1. 441 1. 418	Sample Units mg/L mg/L mg/L	Analysis Time 15:14:05 15:14:09 15:14:11
	Mean D Analyt Co 228	e 8.616	42 Mean Corrected Intensity 541890.4	Calib. Conc. Units 1.443 mg/L	Std.Dev. 0.0268	Conc. 1. 443	Sample Units mg/L	Std. De 0. 026	v. RSD 8 1.86%

Fig. S4. The quantification of the co-crosslinking degree of  $Co^{2+}$  and SA/PEI macromolecules.



Fig. S5. FT-IR spectra of Co-SA and Co-SA/PEI.



**Fig. S6.** SEM images of (a-d) Co-NC-0.25-*y* (*y*=500, 600, 700, and 800 °C. TEM images of (e, f) Co-NC-*x*-700 °C (*x* =0.1 and 0.4).



**Fig. S7.** BJH pore size distribution (inset shows magnified view of BJH pore size distribution) of the as-prepared catalysts.



Fig. S8. Raman spectra of as-prepared catalysts.



Fig. S9. Vibrating sample magnetometer of Co-NC-0.25-700 °C.



**Fig. S10.** The pseudo-first-order kinetic model for the degradation of MB by the "Co-NC-0.25-700 °C + PMS" system. Reaction conditions: [MB] = 120 mg/L, [PMS] = 3 mM, catalyst = 0.4 g/L, T = 298 K, initial solution pH 7.62.



Fig. S11. Effect of illumination on MB degradation. Reaction conditions: [MB] = 120 mg/L, [PMS] = 3 mM, catalyst = 0.4 g/L, T = 298 K, initial solution pH 7.62.



Fig. S12. The HPLC for different reaction times of MB degradation: a) origin, (b-d) during the reaction and (e) after the reaction. Injection conditions: methanol:H2O = 60:40, injection rate = 0.8 mL/min, injection rate = 10 uL. Reaction conditions: [MB] = 120 mg/L, [PMS] = 3 mM, catalyst = 0.4 g/L, T = 298 K, initial solution pH 7.62.

Sequence No.: 7 Sample 1D: SampleO Analyst: Initial Sample Wt: Dilution: Wash Time:	06	Autosampler Location: Date Collected: 2018/6/6 14:21:45 Data Type: Original Initial Sample Vol: Sample Prep Vol:					
Replicate Data: Sa	mple006 Net	Corrected	Calib Cone Units	Cong	Sample	Analysis	
1 Co 228, 616 2 Co 228, 616 3 Co 228, 616	137723. 4 137757. 9 137135. 7	137813. 0 137847. 5 137225. 2	-1. 043 mg/L -1. 043 mg/L -1. 043 mg/L	-1. 043 -1. 043 -1. 043	mg/L mg/L mg/L	14:22:27 14:22:34 14:22:41	
Mean Data: Sample0 Analyte Co 228.616	06 Mean Corrected Intensity 137628.6	Calib. Conc. Units -1.043 mg/L	Std. Dev. 0.0004	Sample Conc. Units -1.043 mg/L	Std. D 0.000	ev. RSD 04 0.04%	

Fig. S13. Leaching of cobalt ions on MB degradation. Reaction conditions: [MB] = 120 mg/L, [PMS] = 3 mM, catalyst = 0.4 g/L, T = 298 K, initial solution pH 7.62.

Samples	$S_{BET}\left(m^2g^{\text{-}1}\right)$	V <sub>totle</sub> (cm <sup>3</sup> g <sup>-1</sup> )	Average pore size (nm)
Ca-C-700 °C	89.499	0.265	12.566
Ca-NC-0.25-700 °C	7.725	0.039	8.855
Co-C-700 °C	201.48	0.609	15.778
Co-NC-0.25-500 °C	50.629	0.179	11.775
Co-NC-0.25-600 °C	105.695	0.21	9.924
Co-NC-0.25-700 °C	191.24	0.304	7.278
Co-NC-0.25-800 °C	125.128	0.302	10.425

Tab. S1. Textural characteristics of prepared materials.

		Concentration	Catalyst	PMS dosage	DMC	Removal	Time	
Catalyst	Pollutant	of pollutant	dosage		efficiency	(min)	Ref.	
		(mg/L)	(g/L)		(%)			
FeCo <sub>2</sub> @APCFs	MB	20	0.1	0.5 g/L	100	7	45	
Fe <sub>x</sub> O <sub>y</sub> /N-GN/CNTs	MB	100	0.4	2 mM	100	20	15	
Co-DTPMP	MB	80	0.5	2 mM	100	25	46	
Co-200	MB	75	0.25	1.5 mM	100	9	47	
Fe-Co-200	MB	75	0.25	1.5 mM	100	5	48	
FMO-46	TC	50	0.4	0.4 g/L	76	80	1	
ZIF-12@GEL	TC	30	0.6	0.6 g/L	94	60	2	
ZIF-12@GEL	PNP	20	0.6	0.6 g/L	90	50	2	
C. N.C. 0.25 700.0C	PNP	20	0.2	NaBH <sub>4</sub>	00	44	Current	
CO-INC-0.25-700 °C		20	0.3	0.6 mM	98			
Co-NC-0.25-700 °C	PNP	20	0.3	0.6 mM	60	24	Current	
Co-NC-0.25-700 °C	TC	20	0.3	0.6 mM	83	8	Current	
Co-NC-0.25-700 °C	AO7	60	0.3	0.6 mM	100	6	Current	
Co-NC-0.25-700 °C	OG	80	0.3	0.6 mM	100	5	Current	
Co-NC-0.25-700 °C	PS	160	0.3	0.6 mM	100	6	Current	
Co-NC-0.25-700 °C	AR94	240	0.3	0.6 mM	100	5	Current	
Co-NC-0.25-700 °C	AR	40	0.3	0.6 mM	100	5	Current	
Co-NC-0.25-700 °C	MeB	160	0.3	0.6 mM	100	7	Current	
Co-NC-0.25-700 °C	MB	120	0.4	3 mM	100	6	Current	

Tab. S2. Comparison of different catalysts for PMS activation.