

Supporting Information

Efficient Pollutant Degradation by Peroxymonosulfate Activated by a Co/Mn Metal-Organic Framework

Ya Li,^a Chong-Chen Wang,^{a*} Fu-Xue Wang,^a Xing-Yuan Liu,^a Peng Wang,^a Fei Wang,^a Mingyi Sun^a and Baoyi Yu^b

^aBeijing Key Laboratory of Functional Materials for Building Structure and Environment Remediation, Beijing University of Civil Engineering and Architecture, Beijing 100044, China

^bKey Laboratory of Urban Agriculture (North China), Ministry of Agriculture, College of Biological Sciences Engineering, Beijing University of Agriculture, Beijing 102206, China

Test S1. Materials/reagents and characterizations:

Table S1. Reagents used in this work

Regent name	CAS number	Manufacturers
Cobalt(II) carbonate hydroxide	7791-13-1	Beijing Chemical Works
Manganese chloride monohydrate		Beijing Chemical Works
Sodium hydroxide	1310-73-2	Beijing Chemical Reagent Factory
Nitric acid	7697-37-2	Beijing Chemical Works
RhB	81-88-9	J&K Scientific Ltd.
1,2,3,4,5,6-cyclohexane-hexacarboxylic acid monohydrate	2216-84-4	TCI (Shanghai) Development Co., Ltd.
potassium peroxomonosulfate	37222-66-5	J&K Scientific Ltd.
Sodium chloride	7647-14-5	Macklin Inc.
Sodium nitrate	7631-99-4	Macklin Inc.
Sodium dihydrogen phosphate	7558-80-7	Beijing Chemical Works
Acetonitrile	75-05-8	J&K Scientific Ltd.
Methanol	67-56-1	Macklin Inc.
tert-Butanol	75-65-0	Macklin Inc.
1,4-benzoquinone	106-51-4	J&K Scientific Ltd.
Sodium hydrogen phosphate	7558-79-4	Beijing Chemical Works
Rhodamine B	81-88-9	J&K Scientific Ltd.
Ofloxacin	82419-36-1	J&K Scientific Ltd.
Sulfamethoxazole	723-46-6	J&K Scientific Ltd.
Bisphenol A	80-05-7	J&K Scientific Ltd.

*Corresponding author.

E-mail address: wangchongchen@bucea.edu.cn, chongchenwang@126.com (C.-C. Wang)

Test S2. Analytical methods:

The X-ray single-crystal data of BUC-101 was collected utilizing a Rigaku oxford diffraction XtaLAB mini II detector diffractometer with Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) at 293(2) K. The SMART software and SAINT software were used for data collection and extraction, respectively. Besides, empirical absorption correction was performed using the SADABS program and the structure was analyzed utilizing Olex2 with the SIR2004 structure solution program by Direct Methods. Finally, the structure of BUC-101 was refined with the ShelXL refinement package by Least Squares minimization.

Powder X-ray diffraction (PXRD) patterns were recorded on a Dandonghaoyuan DX-2700B diffractometer in the range of $2\theta = 5^\circ - 50^\circ$ with Cu $K\alpha$ radiation. Fourier transform infrared (FTIR) spectra in the range of 4000 to 400 cm^{-1} were recorded by an infrared spectrophotometer with KBr pellets (Thermo, Nicolet 6700, US). The morphology of the materials was measured by a scanning electron microscopy (SEM) (TM3030Plus, Hitachi Limited, Japan). X-ray photoelectron spectroscopy (XPS) was observed using a ThermoFisher Thermo.

The concentration of pollutants (SMX, OFC, BPA) was identified by LC (LC-20A, Shimadzu, Japan). The LC was equipped with a UV-Vis detector and Eclipse Plus C18 column (250mm \times 4.6mm, 5 μ m). BQ were analyzed by using an ultra-high performance liquid chromatography (UHPLC, Thermo Scientific Vanquish Flex) equipped with a multi-wavelength UV detector. The separation was performed on a C18 reversed-phase column (2.1 mm \times 100 mm, 1.7 μ m) at 30 $^\circ\text{C}$. The wavelength of the UV detector was set as 246 nm for BQ detection, the mobile phase for BQ detection was composed of acetonitrile and distilled water (30/70, v/v) with a flow rate of 0.4 mL/min, and the injection volume was 20 μ L.

The generated $\text{SO}_4^{\cdot-}$ radicals were quantified by detecting 4-benzoquinone (BQ) that was generated from the reaction of p-hydroxybenzoic acid (HBA) and $\text{SO}_4^{\cdot-}$.^{1,2} Briefly, 15 mg Co-H₆chhc were added into 50.0 mL deionized water, in which the molar ratios of HBA:PMS were varied between 1:1~11:1. At pre-set time interval, 1.2 mL sample was taken out and filtered by 0.22 μ m PTFE filter. Meanwhile, the excessive methanol (10 μ L) was immediately added to quench ROS. The formed BQ can be detected by an ultra-high performance liquid chromatography (UHPLC, Thermo Scientific Vanquish Flex). Finally, the $\text{SO}_4^{\cdot-}$ concentrations were calculated based on the stoichiometric ratio of $\text{SO}_4^{\cdot-}$ to BQ.

The quantification of residual PMS was carried out by determining I_3^- concentration. In brief, 0.5 mL reacted solution was taken out and mixed with 4.5 mL 1.11 g/L KI aqueous solution, which was stirred for 30 min to ensure the full reaction between I^- and HSO_5^- to produce I_3^- . The I_3^- concentration, proportional to PMS, was determined at $\lambda_{\text{max}} = 352 \text{ nm}$ by UV-vis spectrophotometer³.

Test S3. X-ray crystal structural analysis:

Table S2 Details of X-ray data collection and refinement for BUC-101

Copound	BUC-101		
Empirical formula	C ₄ H ₆ Co _{0.56} Mn _{0.44} O ₆	Z	18
Formula weight	207.26	Dcalcd (g/cm ³)	2.304
Crystal system	trigonal	μ (mm ⁻¹)	2.557
Space group	R-3(148)	Rint	0.0258
a (Å)	14.4552(7)	reflections collected	4275
b (Å)	14.4552(7)	independent reflections	1686
c (Å)	14.8584(9)	F(000)	1874.0
α (°)	90	GOF on F ²	1.086
β (°)	90	R1, wR2 [$I \geq 2\sigma(I)$]	0.0302, 0.0800
γ (°)	120	R1, wR2 [all data]	0.0380, 0.0831
V (Å ³)	2688.8(3)	max/min e- density (e Å ⁻³)	0.78/-0.48

Table S3 Selected bond lengths (Å) and angles (°) for BUC-101

Length (Å)			
Mn—O1	2.137(14)	Co—O1	2.115(10)
Mn—O2	2.114(15)	Co—O2	2.141(11)
Mn—O3	2.061(15)	Co—O3	2.197(10)
Mn—O4	2.192(15)	Co—O4	2.053(10)
Mn—O2W	2.130(15)	Co—O1W	2.158(12)
Mn—O1W	2.197(17)	Co—O2W	2.186(10)

Angle (°)			
O1—Mn—O2	168.7(9)	O1—Co—O2	167.5(6)
O1—Mn—O3	96.4(6)	O1—Co—O3	93.1(4)
O1—Mn—O4	87.6(6)	O1—Co—O4	91.9(4)
O1—Mn—O1W	84.0(6)	O1—Co—O1W	85.5(4)
O1—Mn—O2W	81.1(4)	O1—Co—O2W	80.3(3)
O2—Mn—O3	89.3(6)	O2—Co—O3	85.1(4)
O2—Mn—O4	88.3(6)	O2—Co—O4	91.3(4)
O2—Mn—O1W	106.2(5)	O2—Co—O1W	106.6(4)
O2—Mn—O2W	89.4(7)	O2—Co—O2W	87.2(4)
O3—Mn—O4	171.2(8)	O3—Co—O4	172.6(5)
O3—Mn—O1W	86.4(7)	O3—Co1—O1W	82.0(4)
O3—Mn—O2W	88.1(5)	O3—Co—O2W	84.1(4)
O4—Mn—O1W	86.2(5)	O4—Co—O1W	90.8(4)
O4—Mn—O2W	100.3(7)	O4—Co—O2W	102.9(5)
O1W—Mn—O2W	163.4(8)	O1W—Co—O2W	160.5(5)

Test S4. Results and discussion:

Table S4 the ratio of element in BUC-101

Elt.	Line	Intensity (c/s)	Atomic (wt.%)	Atomic Ratio	Conc (wt.%)
C	Ka	2.80	22.079	0.3536	12.349
O	Ka	16.03	62.437	1.0000	46.518
Mn	Ka	3.50	7.307	0.1170	18.693
Co	Ka	2.48	8.177	0.1310	22.441
			100.000		100.000

Table S5 XPS results of Co and Mn content for the BUC-101 sample

elements		BUC-101 before		BUC-101 after	
		Peaks (eV)	Content (%)	Peaks (eV)	Content (%)
Co	Co ³⁺	781.51, 797.27	55.01%	781.45, 797.32	53.68%
	Co ²⁺	784.88, 801.23	44.09%	784.78, 801.26	46.32%
Mn	Mn ³⁺	643.17, 655.16	40.85%	643.01, 654.94	43.18%
	Mn ²⁺	641.39, 653.37	59.15%	641.25, 653.29	56.82%

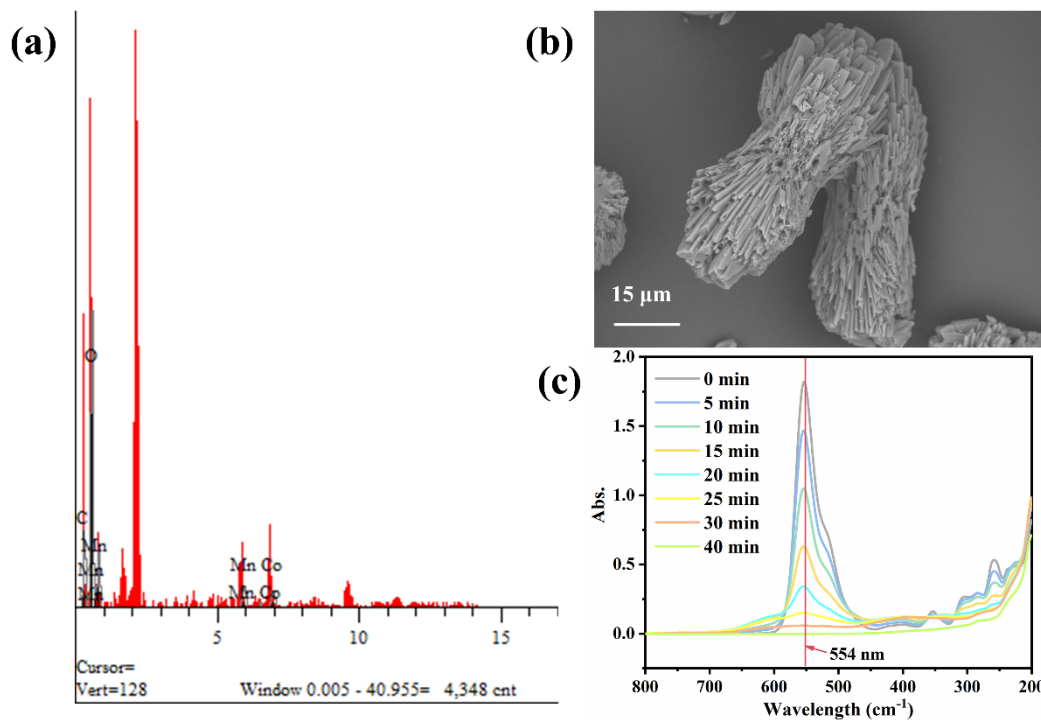


Fig. S1 (a) The EDS spectrum taken from BUC-101; (b) the SEM image of BUC-101 after 5 cycles catalytic reaction; (c) The UV-Vis absorption spectra in in BUC-101/PMS/RhB system.

References

1. J. Criquet and N. K. V. Leitner, *Radiation Physics and Chemistry*, 2015, **106**, 307-314.
2. W.-D. Oh, Z. Dong and T.-T. Lim, *Applied Catalysis B: Environmental*, 2016, **194**, 169-201.
3. J. Yan, J. Li, J. Peng, H. Zhang, Y. Zhang and B. Lai, *Chemical Engineering Journal*, 2019, **359**, 1097-1110.