Electronic Supplementary Information

In situ synthesis of CoFe-LDH on biochar for peroxymonosulfate activation toward sulfamethoxazole degradation: Cooperation of radical and non-radical pathways

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Text S1 Materials and reagents

Rape straw was obtained from agricultural waste on a nearby farm (Hubei, China). Sulfamethoxazole (SMX), PMS ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), humic acid (HA), *p*-benzoquinone (*p*-BQ), 5,5-dimethyl-1-pyrrolineN-oxide (DMPO) and 2,2,6,6-tetramethylpiperidine (TEMP) were purchased from Shanghai Aladdin Reagent Co., Ltd. Zinc chloride ($ZnCl_2$), hydrochloric acid (HCl), cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$), ferric nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$), sodium hydroxide (NaOH), sodium carbonate (Na_2CO_3), sodium chloride (NaCl), sodium dihydrogen phosphate (NaH_2PO_4), sodium hydrogen carbonate ($NaHCO_3$), sodium sulfate (Na_2SO_4), L-histidine (L-His, BR), furfuryl alcohol (FFA), ethanol (EtOH), methanol (MeOH), L-ascorbic acid (L-AA) and tert-butyl alcohol (TBA) were bought from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All of the chemical reagents utilized in this research were analytical grade and had not been purified further.

Text S2 Analytical methods

A Purkinje General TU-1810 spectrophotometer was used to determine the SMX concentration at 266 nm. The EPR tests were carried out to explore the presences of reactive oxygen species (ROS) by an EPR 200M spectrometer. The concentrations of cobalt and iron leaching in the system were detected by AA320N atomic absorption spectroscopy. A liquid chromatography-mass spectrometry system (LC-MS, Ultimate 3000 UHPLC-Q Exactive, Thermo Scientific, US) was used to ascertain he degradation intermediates of SMX. Total organic carbon (TOC) was evaluated by a TOC-2000 analyzer (Shanghai, Metash) to detect the mineralization degree during degradation reaction.

Text S3 Electrochemical measurement

The electrochemical impedance spectroscopy (EIS) and current-time curves of as-prepared samples were performed on an electrochemical workstation (CHI 760E, Shanghai Chenhua, China) in a typical three-electrode system with the glassy carbon electrode (GCE), the Ag/AgCl electrode, and Pt foil as the working, reference and counter electrode, severally. Besides, 0.1 M Na_2SO_4 solution was used as the electrolyte. Specifically, the working electrode preparation process was as follows: the naked GCE was initially polished with alumina suspension (0.05 μm) to attain a brilliant surface prior to modification. The polished GCE was successively rinsed in deionized water and ethanol. Subsequently, 3 mg of catalyst was uniformly scattered in 300 μL of Nafion and 200 μL of ethanol solution. 10 μL of sample suspension was dripped onto the polished GCE surface and then dried under infrared light.

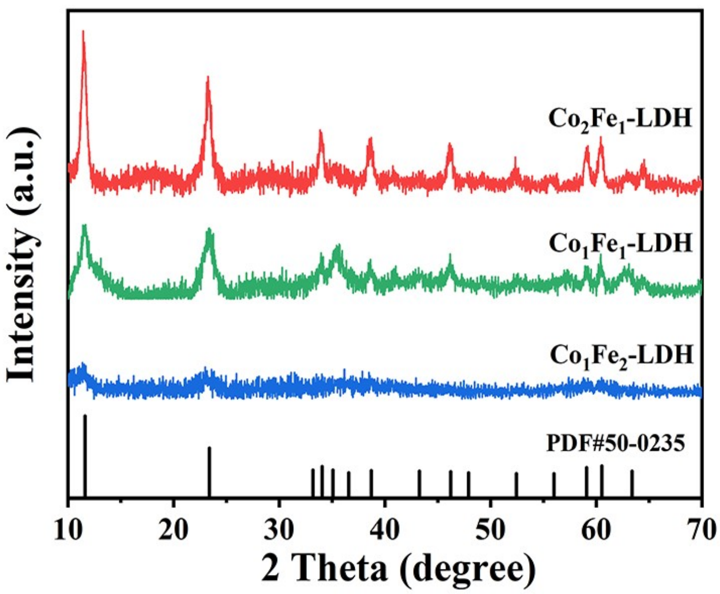


Figure S1. The XRD patterns of CoFe-LDHs with different Co:Fe mole ratios.

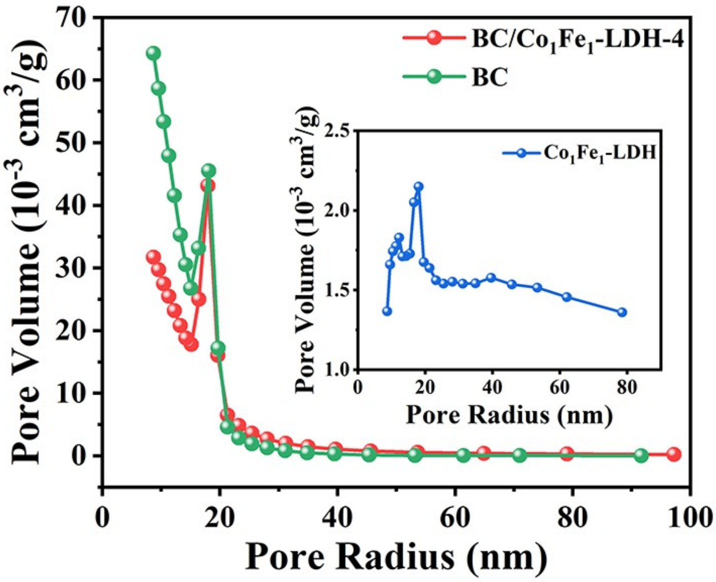


Figure S2. The pore size distribution of as-prepared samples.

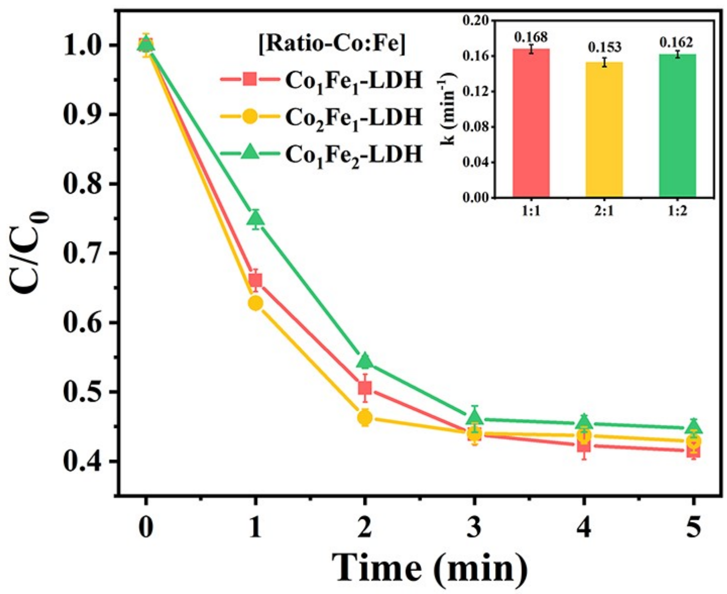


Figure S3. The effect of Co:Fe mole ratio in pristine CoFe-LDH on SMX degradation (inset: the corresponding pseudo-first-order rate constant)

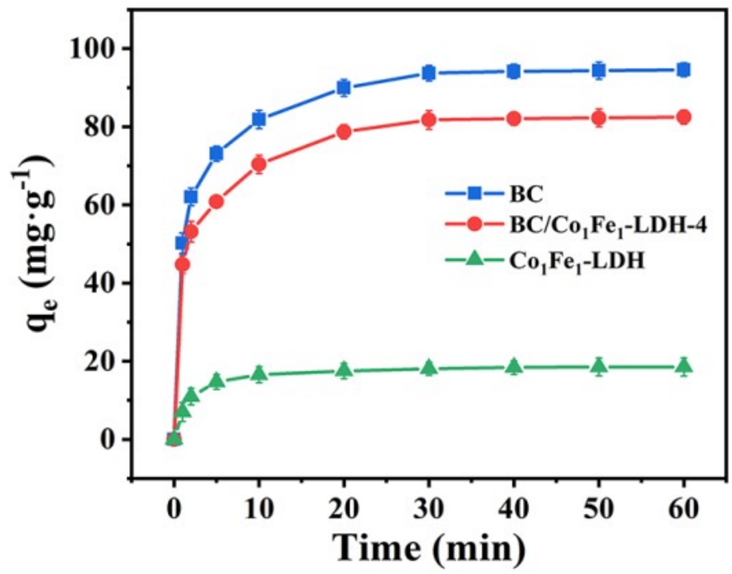


Figure S4. The adsorption performance of the catalysts on SMX. Experimental conditions: [SMX] = 30 mg·L^{-1}, [Catalyst] = 0.25 g·L^{-1}

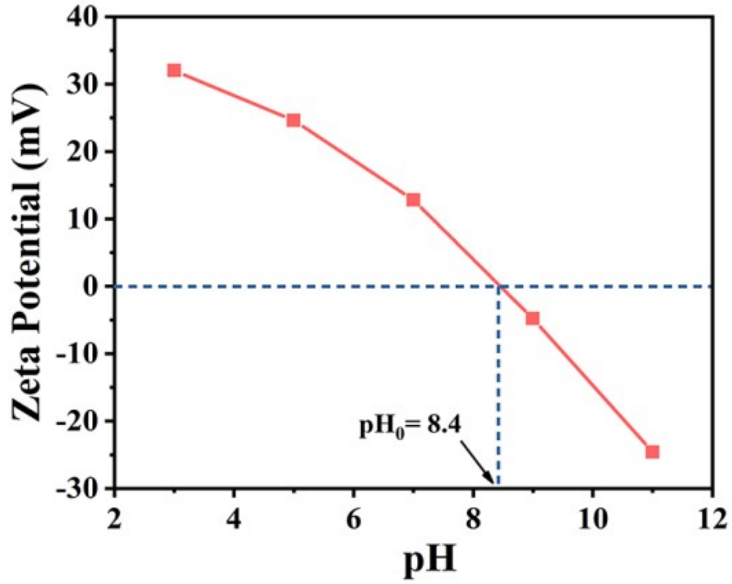


Figure S5. The zeta potential of the BC/Co_1Fe_1-LDH-4 catalyst

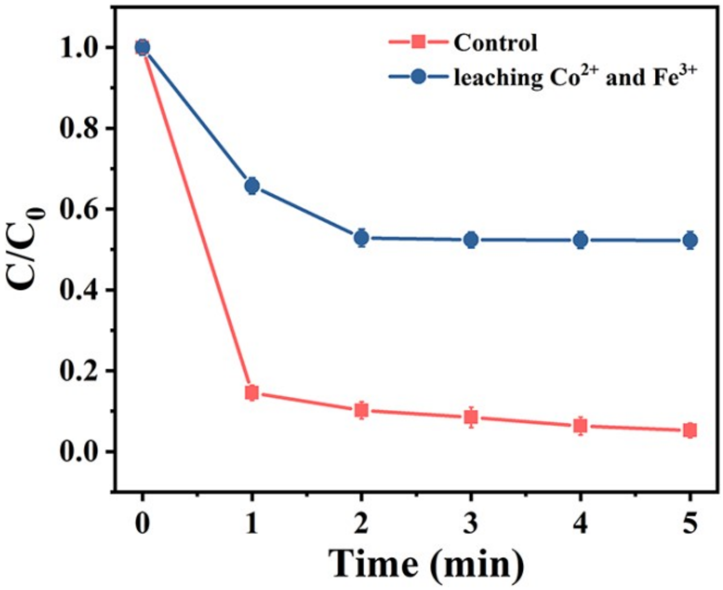
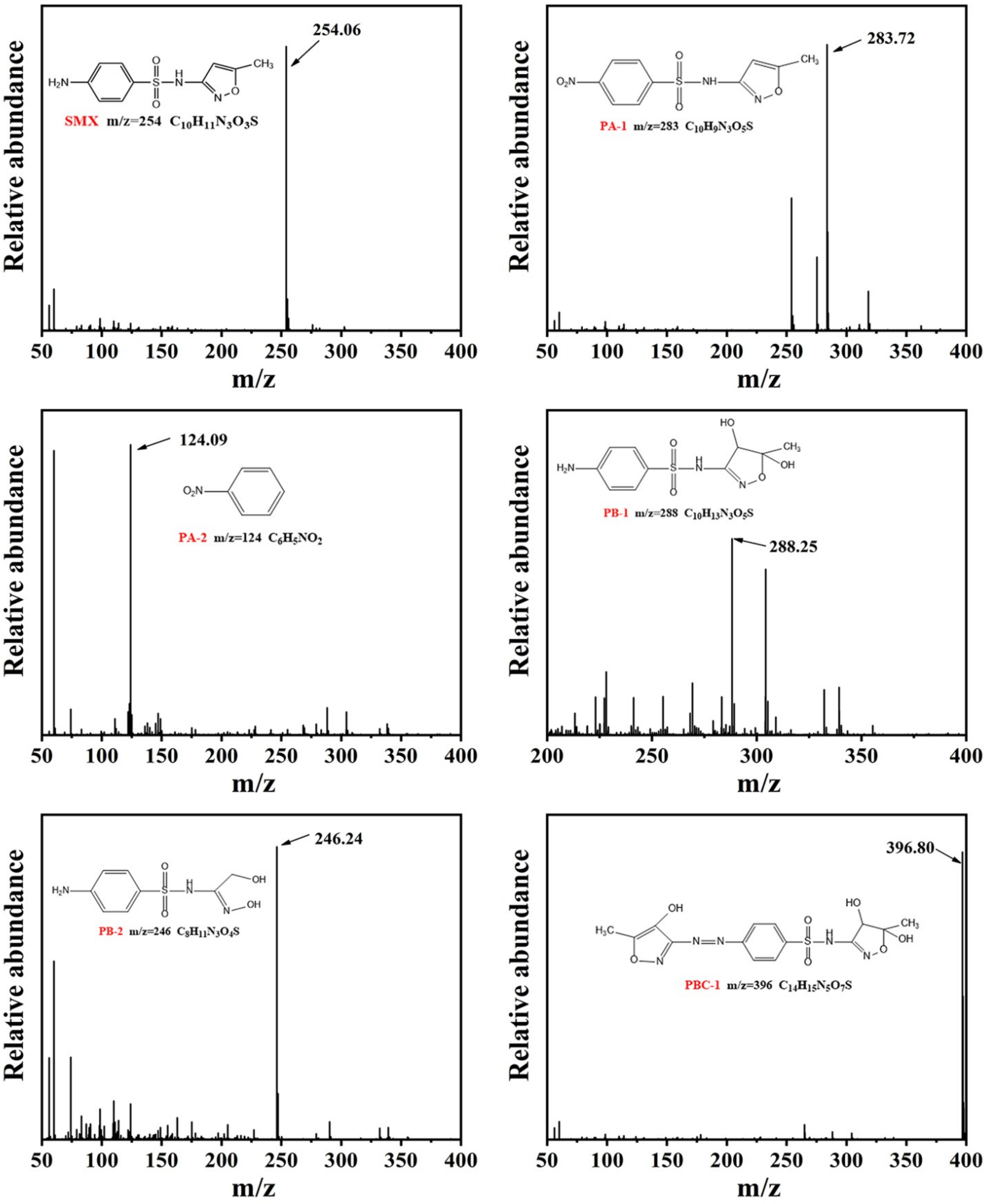


Figure S6. The effect of leaching metal ions from the first cycle on the degradation of SMX ([Co^{2+}] = 8.01 mg·L^{-1}, [Fe^{3+}] = 0.37 mg·L^{-1})



254.06
SMX m/z=254 $C_{10}H_{11}N_3O_3S$
283.72
PA-1 m/z=283 $C_{10}H_9N_3O_5S$
124.09
PA-2 m/z=124 $C_6H_5NO_2$
288.25
PB-1 m/z=288 $C_{10}H_{13}N_3O_5S$
246.24
PB-2 m/z=246 $C_8H_{11}N_3O_4S$
396.80
PBC-1 m/z=396 $C_{14}H_{15}N_5O_7S$
Relative abundance
m/z

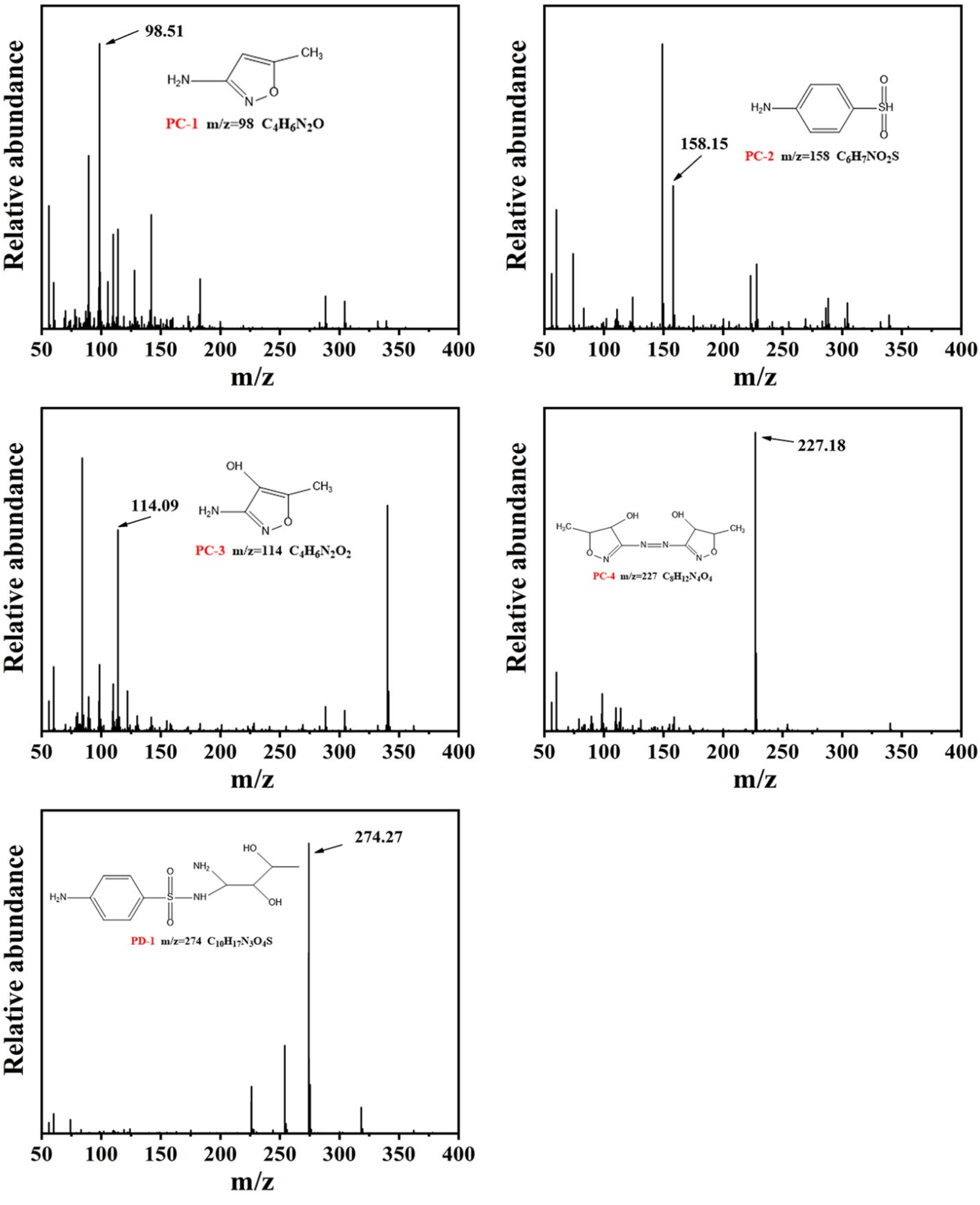


Figure S7. Mass spectra of SMX degradation intermediates.

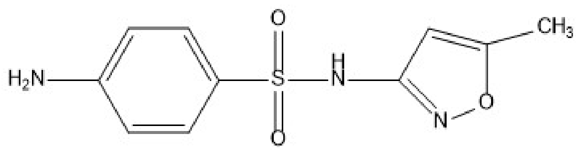
Table S1. BET surface area and pore structure parameters of catalysts.

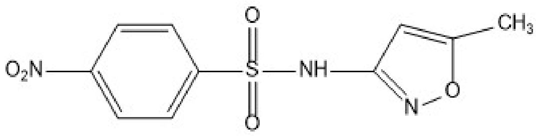
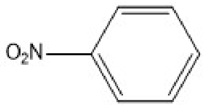
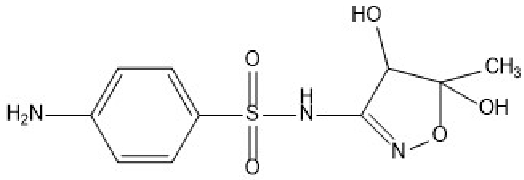
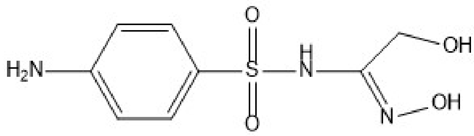
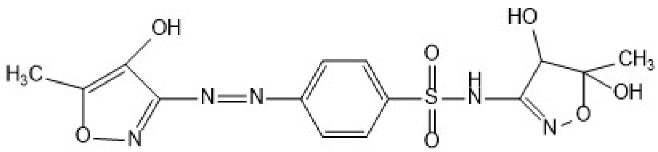
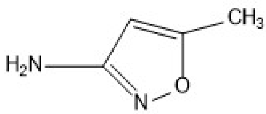
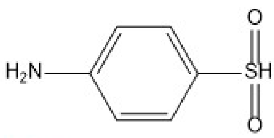
Samples	BET surface are ($m^2\ g^{-1}$)	Average pore radius (nm)	Cumulative volume of pores ($cm^3\ g^{-1}$)
BC	1314.77	13.08	0.52
Co_1Fe_1-LDH	105.73	72.86	0.40
BC/Co_1Fe_1-LDH-4	748.41	16.12	0.43

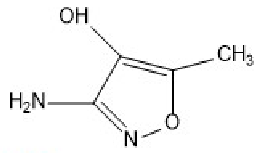
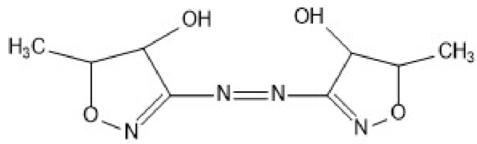
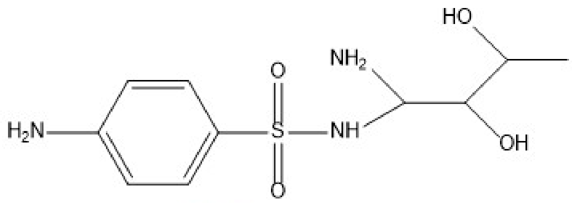
Table S2. The Co and Fe ions leaching concentration of BC/Co_1Fe_1-LDH-4 catalyst and Co_1Fe_1-LDH in in the four recycling tests

	Co leaching concentration ($mg\cdot L^{-1}$)		Fe leaching concentration ($mg\cdot L^{-1}$)	
	BC/Co_1Fe_1-LDH-4	Co_1Fe_1-LDH	BC/Co_1Fe_1-LDH-4	Co_1Fe_1-LDH
Run 1	8.01	12.02	0.37	0.65
Run 2	3.03	11.87	0.27	0.62
Run 3	2.40	10.48	0.24	0.55
Run 4	2.31	10.24	0.19	0.29

Table S3. Intermediates detected by LC-MS during SMX degradation by BC/Co_1Fe_1-LDH-4/PMS system.

Products	m/z	Formula	Proposed structure
SMX	254	$C_{10}H_{11}N_3O_3S$	 SMX m/z=254 $C_{10}H_{11}N_3O_3S$

PA-1	283	$C_{10}H_9N_3O_5S$	 **PA-1 m/z=283 $C_{10}H_9N_3O_5S$**
PA-2	124	$C_6H_5NO_2$	 **PA-2 m/z=124 $C_6H_5NO_2$**
PB-1	288	$C_{10}H_{13}N_3O_5S$	 **PB-1 m/z=288 $C_{10}H_{13}N_3O_5S$**
PB-2	246	$C_8H_{11}N_3O_4S$	 **PB-2 m/z=246 $C_8H_{11}N_3O_4S$**
PBC-1	396	$C_{14}H_{15}N_5O_7S$	 **PBC-1 m/z=396 $C_{14}H_{15}N_5O_7S$**
PC-1	98	$C_4H_6N_2O$	 **PC-1 m/z=98 $C_4H_6N_2O$**
PC-2	158	$C_6H_7N_2O_2S$	 **PC-2 m/z=158 $C_6H_7NO_2S$**

PC-3	114	$C_4H_6N_2O_2$	 **PC-3 m/z=114 $C_4H_6N_2O_2$**
PC-4	227	$C_8H_{12}N_4O_4$	 **PC-4 m/z=227 $C_8H_{12}N_4O_4$**
PD-1	274	$C_{10}H_{17}N_3O_4S$	 **PD-1 m/z=274 $C_{10}H_{17}N_3O_4S$**