Supporting Information

Sulfate radical induced transformation of Trimethoprim with $CuFe_2O_4$/MWCNTs as a heterogeneous catalyst of peroxymonosulfate： mechanisms, and reaction pathways

Jing Kong[a], Ruobai Li[a], Fengliang Wang[a], Ping Chen[b], Haijin Liu[c], Guoguang Liu[a*], Wenying Lv[a]

[a]School of Environmental Science and Engineering, Guangdong University of Technology, Guang zhou 510006, China
[b]School of Environment, Tsinghua University, Beijing 100084, China
[c]School of Environment, Henan Normal University, Henan Key Laboratory for Environmental Pollution Control, Xinxiang 453007, China

Pages: 9.

Text: 1.

Figures: 5.

Tables: 1.

* Corresponding author. Tel.: +86 13533635690; Fax: 86-20-3932 2548.
*E-mail addresses:*liugg615@163.com (G. Liu).

Text S1

Chemicals

Trimethoprim, Peroxymonosulfate, $Fe(NO_3)_2·9H_2O$, $Cu(NO_3)_2 • 3H_2O$, multi-walled carbon nanotubes, citric acid, $Na_2S_2O_3 • 5H_2O$, Ethanol and tert-butanol were all purchased from Aladdin Industrial Corporation (America). All of the reagents above were of analytical grade and required no further purification. The acetonitrile purchased from Anaqua Chemicals Supply Co. Ltd (America) was of HPLC grade. High purity (99.99%) compressed N_2 or O_2 was purchased from Jingong (China), and all solutions were prepared with ultrapure Milli-Q water of 18.25 MΩ cm-1.

Preparation of $CuFe_2O_4$/MWCNTs

The $CuFe_2O_4$/MWCNTs nanoparticles were prepared using a sol-gel combustion method, where 1.208 g $Cu(NO_3)_2·3H_2O$ (0.005 mol), 4.040 g $Fe(NO_3)_2·9H_2O$ (0.01 mol) , and 0.4 g MWCNTs were added into Milli-Q water and thoroughly ultrasonically mixed (5 min). The mass ratio of $CuFe_2O_4$ to MWCNTs was optimizesd as 3:1. After stirring at 60℃ for 2h, a 3.152 g citric acid (0.015 mol) was added. The mixed solution was continuously stirred at 60℃ for 2h, and subsequently, the heterogeneous solution was dried at 130℃ for 12h. The obtained nitrate-citrate-MWCNTs complex gel was calcined at a given temperature (typically at 400 ℃) for 2h to decompose the citric acid, where after the $CuFe_2O_4$/MWCNTs catalysts were finally formed.

Characterization methods

The Transmission micrographs of the $CuFe_2O_4$/MWCNTs MNPs were generated by a JEOL JEM-2100F transmission electron microscope (TEM). X-ray power diffraction (XRD) was performed on a Rigaku Ultima III diffractometer using Cu Kαradiation (λ= 1.5406 Å), with a scanned area of 2θ=10-70◦.The oxidation states of metals in the composites were analyzed using x-ray photoelectron spectroscopy (XPS, PHI Quantera 2X) with nonmonochromated Mg-Kαradiation as the excitation source. Fourier transform infrared spectra (FT-IR) were conducted on a Thermofisher Nicolet 6700 spectrometer in the range of 500-4000 cm^{-1}. The magnetic properties (M-H curve) were measured with a vibrating sample magnetometer (MPMS (SQUID)XL,USA) at 300K. The nitrogen gas uptake isotherms were measured by a Micromeritics ASAP 2020, whereas the specific surface areas (SSAs) were calculated based on a Brunauer-Emmett-Teller (BET) model. The pH_{PZC} of $CuFe_2O_4$/MWCNTs was determined by mass titration. The Cu and Fe ion leaching was monitored by atomic absorption spectroscopy (AAS, Analyst 300).

Furthermore, to monitor the EPR signals of free radicals, experiments were using a Bruker A200-9.5/12 spectrometer (Germany) and employed DMPO as spin trapping agent. Before application, DMPO was distilled and stored at −15℃.

Analysis of transformation products

The degradation experiment samples were transferred to a sample vial for characterization by HPLC/MS/MS (Agilent Technologies, USA), which was conducted to measure the relative quantities of by-products in this study. A reverse phase column SB-C18 (5μm, 4.6×150 mm, Agilent, USA) was used as stationary phase. A mixture of 65% HPLC-grade acetonitrile and 35% Milli-Q water (containing 5 mM ammonium acetate) was employed as the eluent, at a flow rate of

0.6 mL min^{-1}. A 10 μL of sample was injected by using an auto sampling device, with a 239 nm detection wavelength. Mass spectrometry analysis was conducted in negative mode using an electrospray ionization (ESI) source. Mass spectra were obtained in ESI (+) mode and data collected in Q1 full scan mode, with a scan range of 100-600.The other optimized parameters were: dry temperature of 350 ºC, fragmentor of 125 V, capillary voltage of 3.5 kV, desolvation gas (nitrogen, P99.99%) flow rate of 101 min^{-1}, nebulizer pressure of 40 psi, and argon (P99.99%) was used as the collision gas.

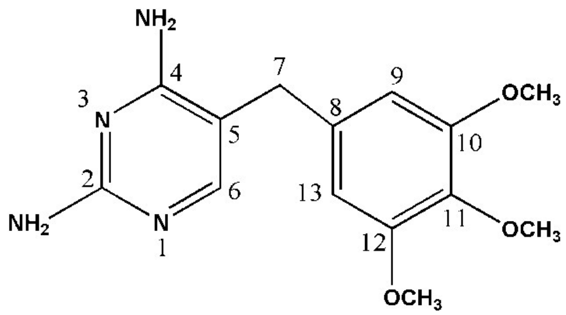


Fig. S1 Structure of Trimethoprim

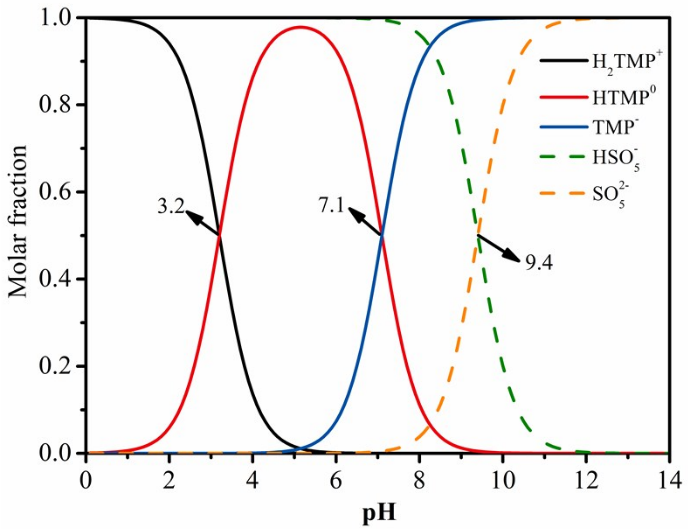


Fig. S2 Distribution of different species of TMP and PMS under different pH

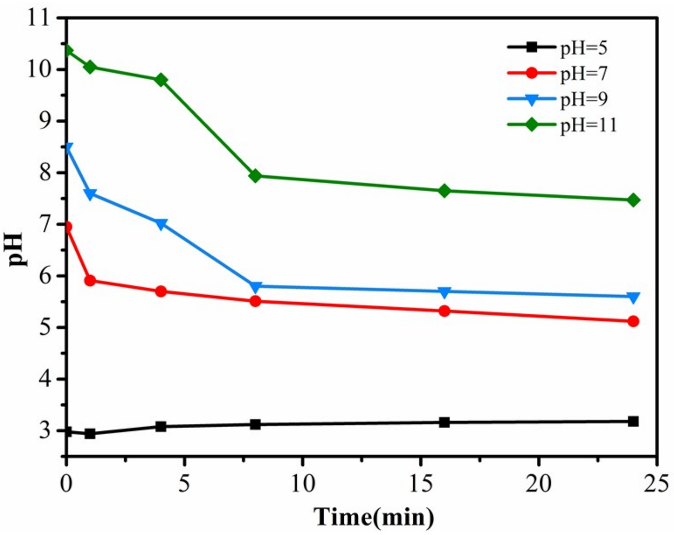


Fig. S3 pH variation during the reaction. Reaction conditions: initial TMP and PMS concentrations were 0.02 mM and 0.6mM; catalyst dose 0.2 g L^{-1}; temperature was 27℃

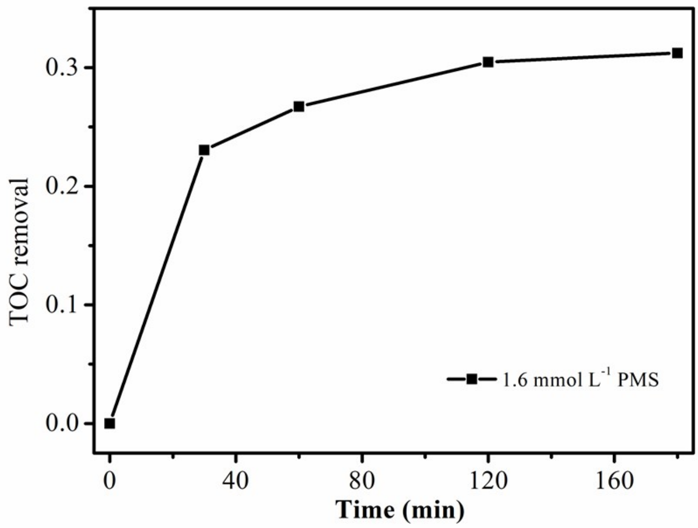


Fig. S4 Removal of TOC during the degradation of TMP. Reaction conditions: initial TMP and PMS concentrations were 0.02 mM and 0.6mM; catalyst dose 0.2 g L^{-1}; pH=7.0, temperature was 27℃

Table S1 By-products from TMP degradation

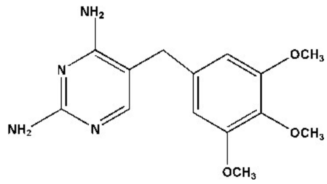
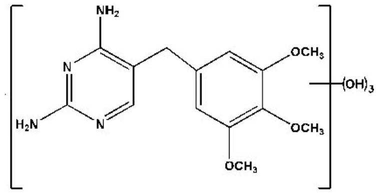
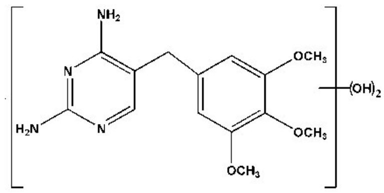
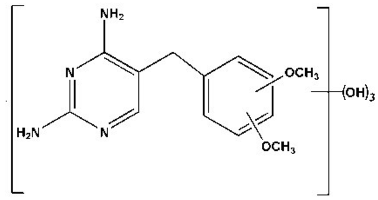
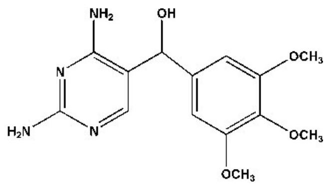
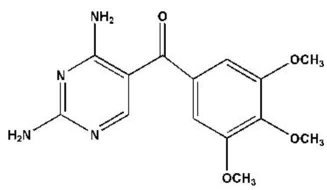
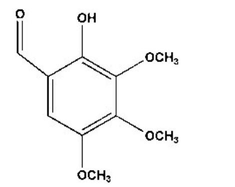
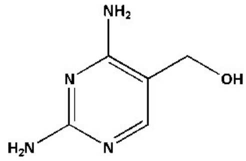
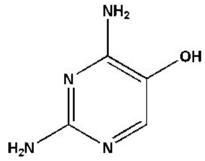
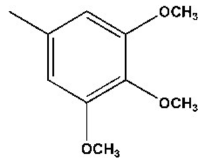
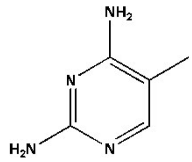
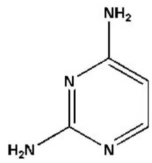
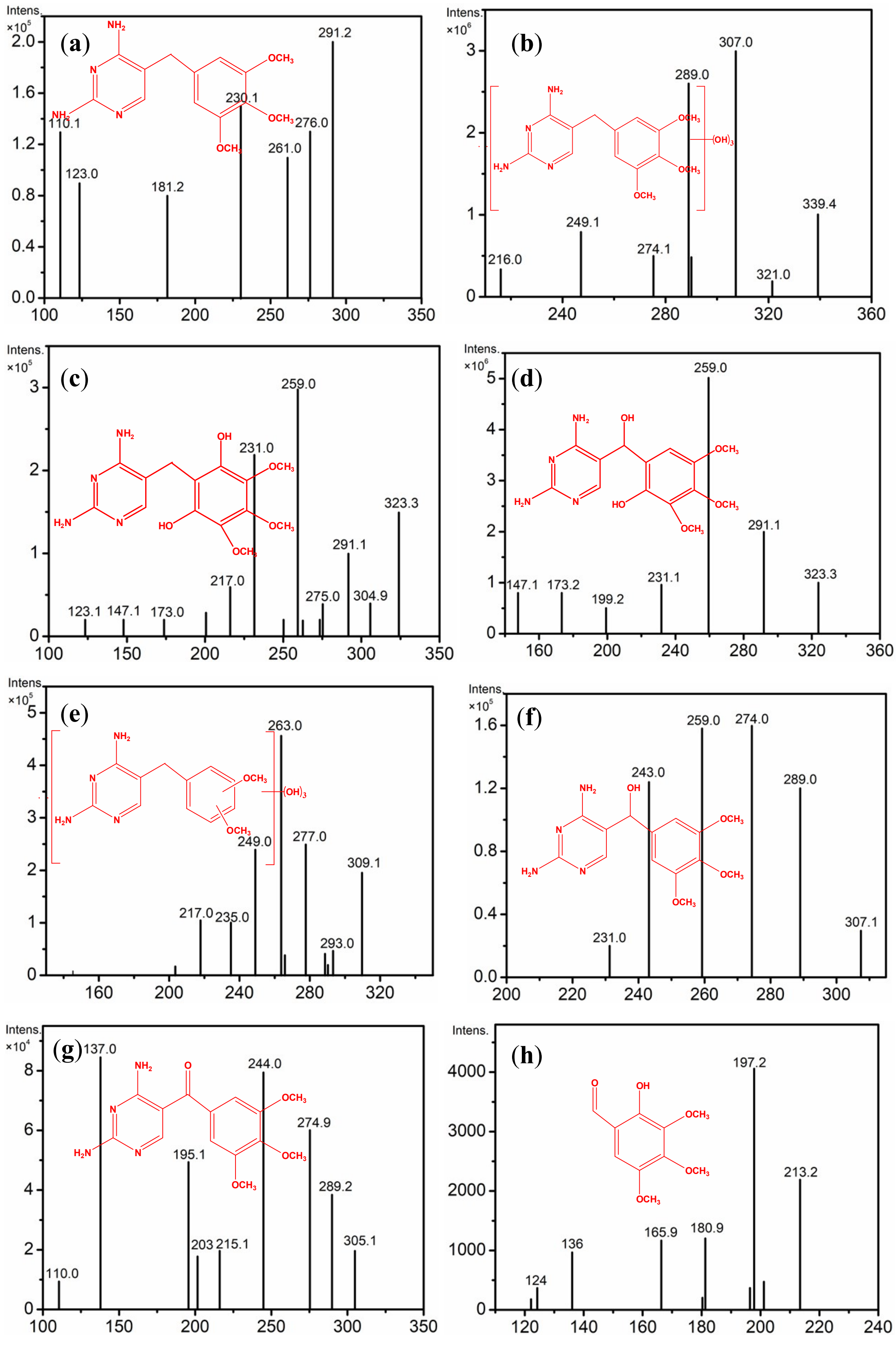
product	R.T. (min)	Molecular Formula	$[M+H]^+$ (m/z)	MS/MS(m/z)	ProposedStructure
TMP	13.4	$C_{14}H_{18}N_4O_3$	291	276,261,230, 181,123,110	
P1	5.1	$C_{14}H_{18}N_4O_6$	339	307,289,274, 249,216	
P2	7.4 5.8	$C_{14}H_{18}N_4O_5$	323	[1]305,291,275,259, 231,216173,147, 123 [2]291,259,231,199, 173,147	
P3	4.4	$C_{13}H_{16}N_4O_5$	309	293,277,263, 249,217	
P4	5.0	$C_{14}H_{18}N_4O_4$	307	289,274,259, 243,231	
P5	7.2	$C_{14}H_{16}N_4O_4$	305	289,275,244, 195,137	
P6	2.2	$C_{10}H_{12}O_5$	213	197,181,166,136	

Table 1 continue

P7	2.1	$C_5H_8N_4O$	141	123	
P8	2	$C_4H_8N_4O$	128	123,110	
P9		$C_{10}H_{12}O_3$	181		
P10		$C_4H_8N_4$	123		
P11		$C_3H_6N_4$	110		


(a)
Intens. ×10^5
NH2
OCH3
OCH3
OCH3
110.1
123.0
181.2
230.1
261.0
276.0
291.2
(b)
Intens. ×10^6
(OH)3
216.0
249.1
274.1
289.0
307.0
321.0
339.4
(c)
Intens. ×10^5
OH
HO
123.1
147.1
173.0
217.0
231.0
259.0
275.0
291.1
304.9
323.3
(d)
Intens. ×10^6
147.1
173.2
199.2
231.1
259.0
291.1
323.3
(e)
Intens. ×10^5
217.0
235.0
249.0
263.0
277.0
293.0
309.1
(f)
Intens. ×10^5
231.0
243.0
259.0
274.0
289.0
307.1
(g)
Intens. ×10^4
110.0
137.0
195.1
203
215.1
244.0
274.9
289.2
305.1
(h)
Intens.
124
136
165.9
180.9
197.2
213.2

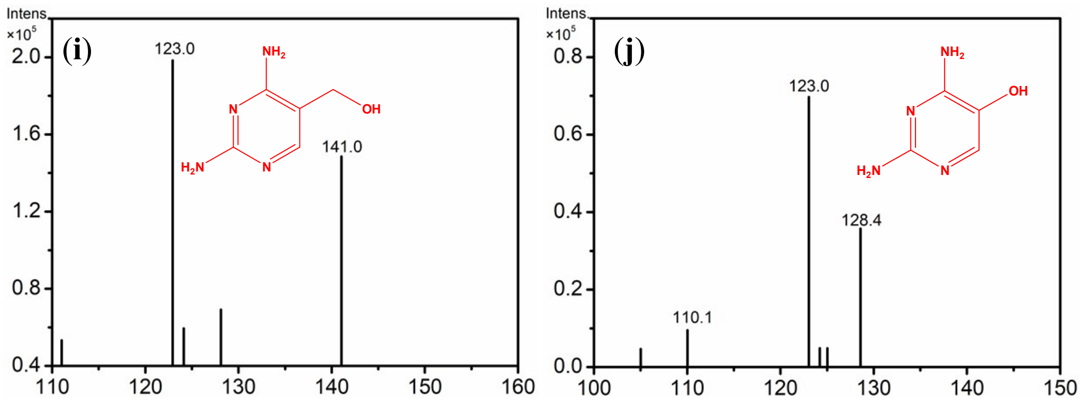


Fig. S5 MS^2 spectrum and proposed structure of TMP and each by-products
(a)TMP (b)P1 (c)P2-1 (d)P2-2 (e)P3 (f)P4 (g)P5 (h)P6 (i)P7 (j)P8