Unveiling the degradation of lamotrigine in sulfate radical-mediated oxidation: Kinetics, influencing factors and transformation mechanisms

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Text S1 Solid phase extraction

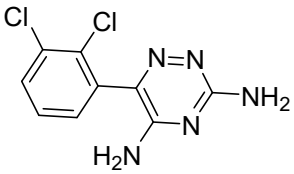
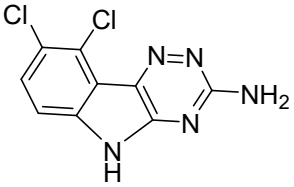
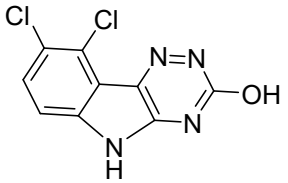
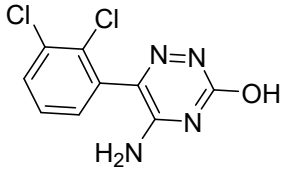
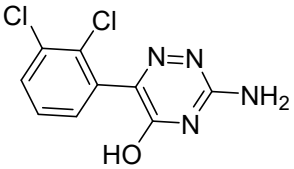
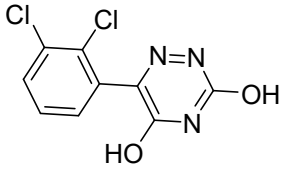
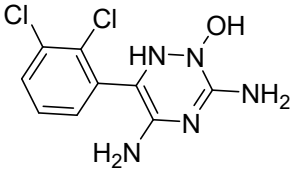
The samples were adjusted to pH < 2 by concentrated sulfuric acid before solid phase extraction (SPE) by Oasis HLB SPE cartridges (3 cc, 0.1 g, Waters, Milford, MA). The cartridge was conditioned with 5 mL methanol and 5 mL pH 3 water sequentially, followed by sample loading. After finishing loading, each cartridge was rinsed with 2 mL water and 2 mL 3% methanol-water and blown to dryness under vacuum. The cartridge was then eluted with 1 mL methanol.

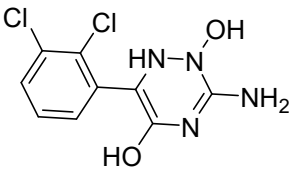
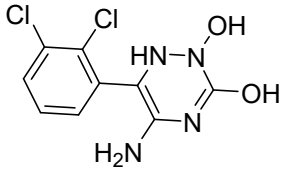
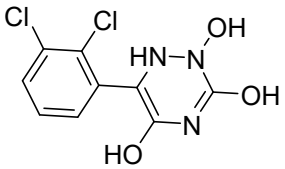
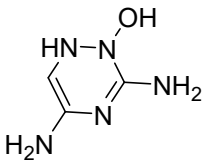
Text S2 Acute toxicity assay

For toxicity experiments, a 200 mL reaction aliquot containing 10 μM LMG, 1 mM PDS, and 10 mM phosphate buffer (pH 7) was prepared in an rlenmeyer flask. The flask was placed in a 60^{o}C water bath for heat/PDS treatment. At pre-selected time intervals, reaction aliquots (5 mM) were collected and immediately transferred to the 10 mL centrifuge tube in ice bath to stop the reaction. Then, add 0.15 g NaCl powder in this sample to ensure NaCl concentration at 3%.

The acute toxicity was evaluated by the luminescent bacteria test based on the standard method published by Ministry of Ecology and Environmental of China. The luminescent bacteria were activated in 1 mL of 2% NaCl solution for 2 min, and then diluted with appreciate amount of 3% NaCl solution. After activation, 190 μL reaction sample was mixed with 10 μL luminescent bacteria solution in a black 96-well plate for 12 min reaction. Luminescence intensity was recorded by Ensight Multimode Microplate Reader coupled with Kaleido workflow software (PerkinElmer, MA, USA). Control with only 3% NaCl was run concurrently. The toxicity test for each sample was run in eight replicates.

Table S1 Mass spectrum data and proposed molecular structures for the transformation products generated from LMG in heat/PDS system.

Transformation products	Retention time	Measured exact mass	Formula of derived molecule	Proposed structure
LMG	3.83 min	256.0149 $[M+H]^+$	$C_9H_7Cl_2N_5$	
P1	4.65 min	254.0434 $[M+H]^+$	$C_9H_5Cl_2N_5$	
P2	4.68 min	255.0026 $[M+H]^+$	$C_9H_4Cl_2N_4O$	
P3a	4.47 min	254.9846 $[M-H]^-$	$C_9H_6Cl_2N_4O$	
P3b	4.47 min	254.9846 $[M-H]^-$	$C_9H_6Cl_2N_4O$	
P4	4.79 min	255.9878 $[M-H]^-$	$C_9H_5Cl_2N_3O_2$	
P5	5.49 min	272.0081 $[M-H]^-$	$C_9H_9Cl_2N_5O$	

Transformation products	Retention time	Measured exact mass	Formula of derived molecule	Proposed structure
P6a	4.41 min	272.9767 $[M-H]^-$	$C_9H_8Cl_2N_4O_2$	
P6b	4.41 min	272.9767 $[M-H]^-$	$C_9H_8Cl_2N_4O_2$	
P7	5.57 min	273.9802 $[M-H]^-$	$C_9H_7Cl_2N_3O_3$	
P8	9.09 min	128.0343 $[M-H]^-$	$C_3H_7N_5O$	

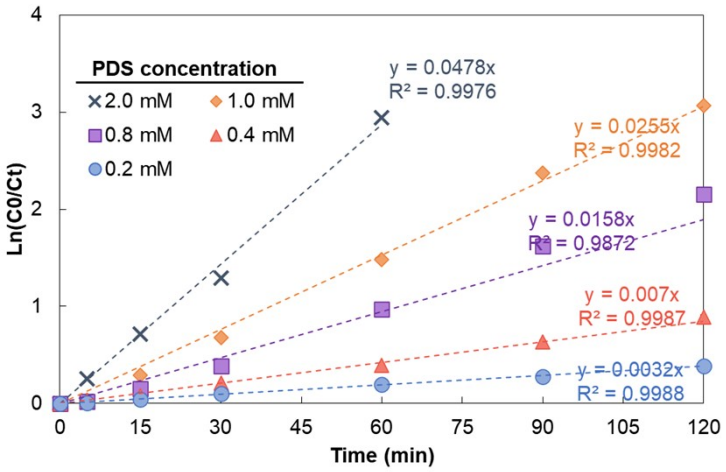


Fig.S1 Effect of PDS on the degradation of LMG by heat/PDS oxidation. Experimental conditions: LMG 10 μM, PDS 0.0-2.0 mM, pH 7.0, temperature 60°C.

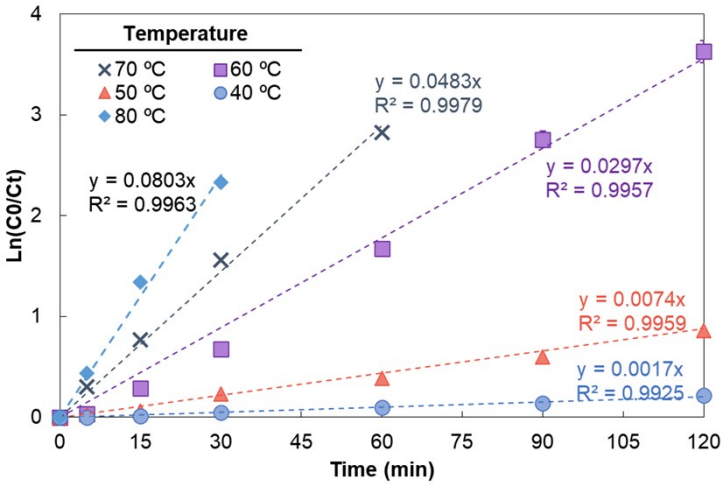


Fig. S2 Effect of temperature on the degradation of LMG by heat/PDS oxidation. Experimental conditions: LMG 10 μM, PDS 1.0 mM, pH 7.0, temperature 40-80°C.

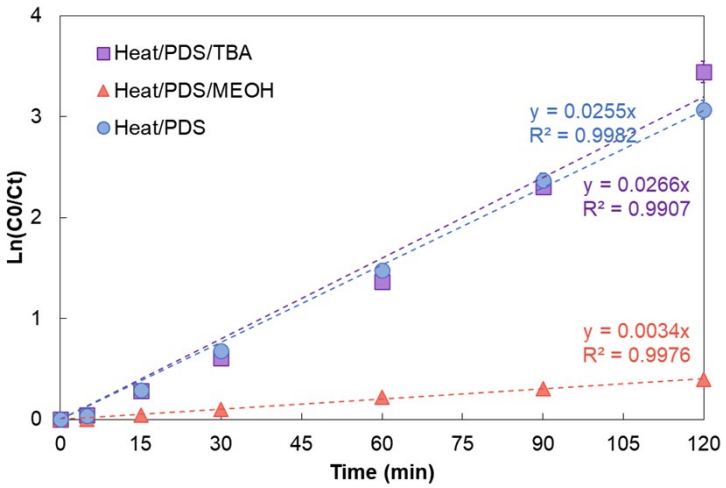


Fig.S3 Effect of MEOH or TBA on the degradation of LMG by heat/PDS oxidation. Experimental conditions: LMG 10 μM, PDS 1.0 mM, MEOH or TBA 10 mM, pH 7.0, temperature 60°C.

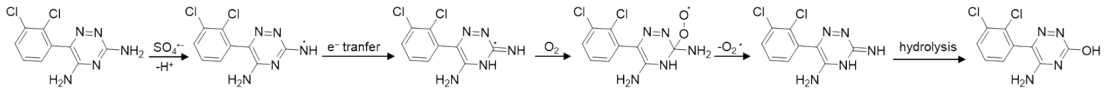


Fig.S4 Reaction mechanism between LMG and $SO_4^{\bullet-}$ on N16.

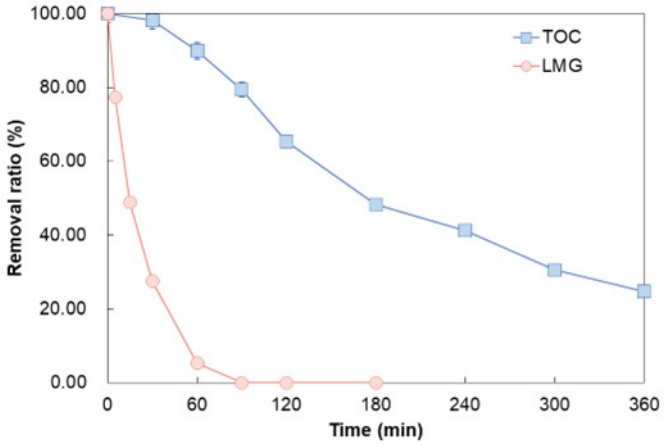


Fig. S5 Removal of LMG and TOC in heat/PDS treatment. Experimental conditions: LMG 10 μM, PDS 2.0 mM, pH 7.0, temperature 60 °C.

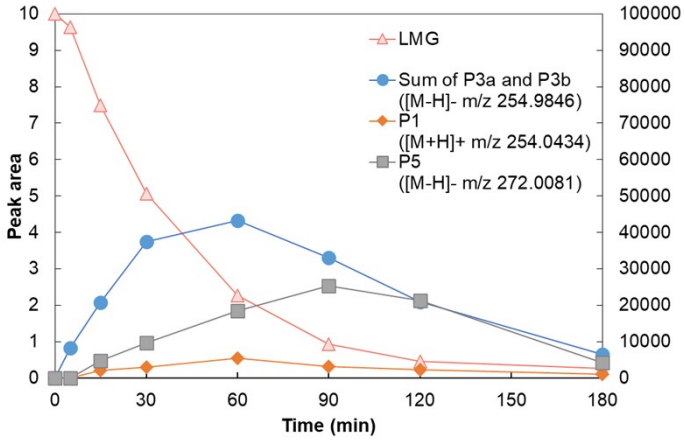


Fig. S6 Formation of primary products during the degradation of LMG by heat/PDS oxidation.

Experimental conditions: LMG 10 μM, PDS 1.0 mM, pH 7.0, temperature 60°C.