Supplementary materials for

Abatement of Nitrophenol in Aqueous Solution by HOCl and UV/HOCl Processes: Kinetics, Mechanisms, and Formation of Chlorinated Nitrogenous Byproducts

Xiaoci Li [1], Yan Cai [1], Junhe Lu [1], Jean-Marc Chovelon [2], Jing Chen [1], Canlan Jiang [1] and Yuefei Ji [1,*]

[1] College of Resources and Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China
[2] Univ Lyon, Université Claude Bernard Lyon 1, CNRS, IRCELYON, F-69626 Villeurbanne, France
* Correspondence: yuefeiji@njau.edu.cn

Texts

Text S1. Chemicals, suppliers, and purities.

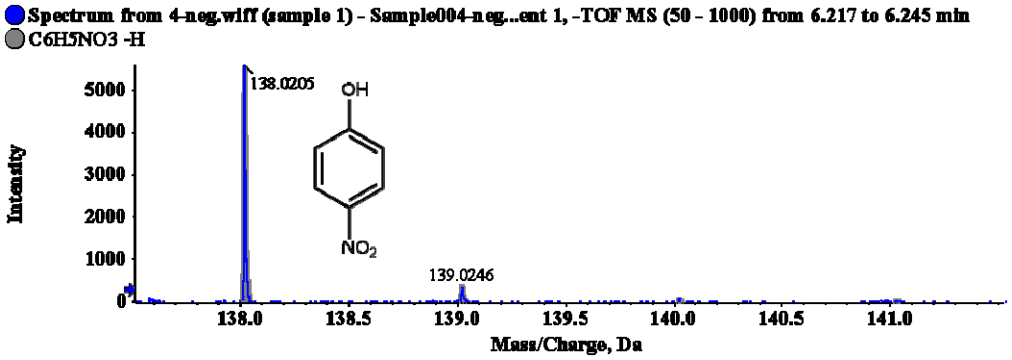
All reagents were of the purest quality available. 4-Nitrophenol, sodium hypochlorite (NaOCl), 2-chloro-4-nitrophenol, 2,6-dichloro-4-nitrophenol, *tert*-butanol (TBA) and *N,N*-dimethyl-1,4-phenylenediamine monohydrochloride (DPD) were all obtained from Aladdin (Shanghai, China). Methanol, formic acid and methyl *tert*-butyl ether (MtBE) were all high-performance liquid chromatography (HPLC) grade, supplied by Fisher (Waltham, MA). All the stock solutions were prepared by adding the chemicals into Milli-Q water (18 MΩ cm) produced using a Stakpure OmniaTap water purification system (Peculiar Instrument Technology Limited, UK). Prior to use, the concentration of NaOCl stock solution was calibrated with DPD method [1]. Oasis hydrophilic-lipophilic balance (HLB) cartridges (3 cc/60 mg, WAT094226) were obtained from Waters Corporation (Milford, MA, USA).

Text S2. Detailed procedures for concentration of products using SPE.

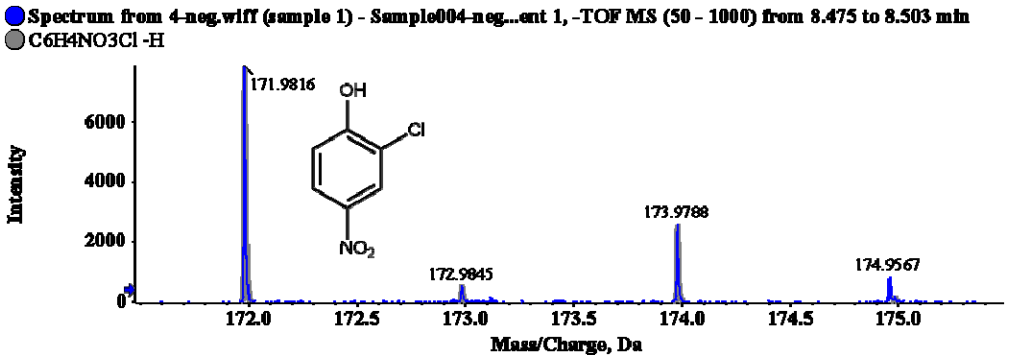
Two aqueous solutions (50 mL, pH 7.0) containing 10 μM 4-nitrophenol and 60 μM HOCl were irradiated for 30 min and then concentrated by solid phase extraction (SPE) using a Supelco Visiprep vacuum manifold (Sigma-Aldrich) coupled with HLB cartridges. The cartridges were activated by 3 mL MeOH and 3 mL Milli-Q H_2O sequentially after adjusting pH to ~2 using concentrated sulfuric acid. Thereafter, 100 mL irradiated solutions passed through the HLB cartridges at an infiltration rate of 5 mL min^{-1}. 2 mL Milli-Q H_2O and 2 mL 3% MeOH were added sequentially to elute impurities and the cartridges were blown to dryness under vacuum. Finally, 1 mL MeOH was used to elute the products.

Figures

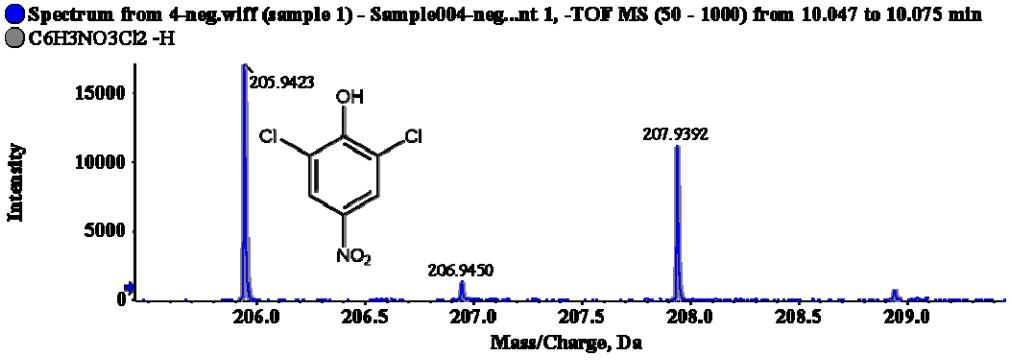
4-Nitrophenol



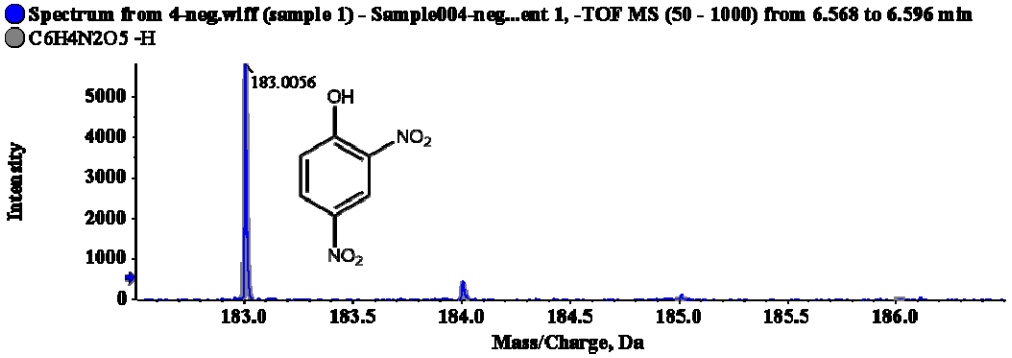
P1



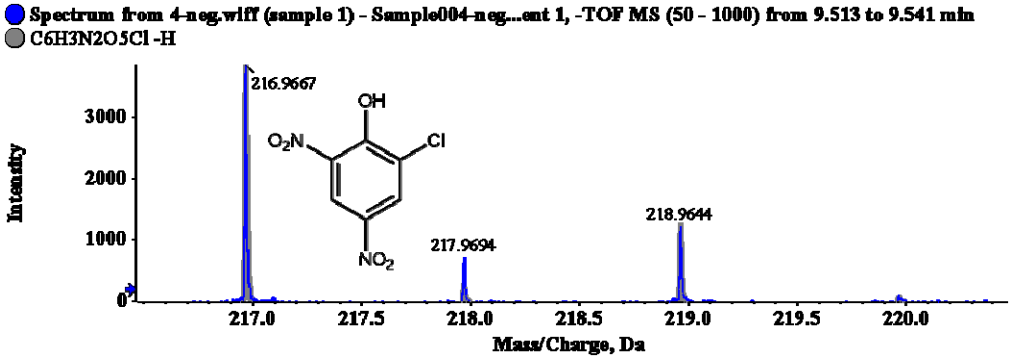
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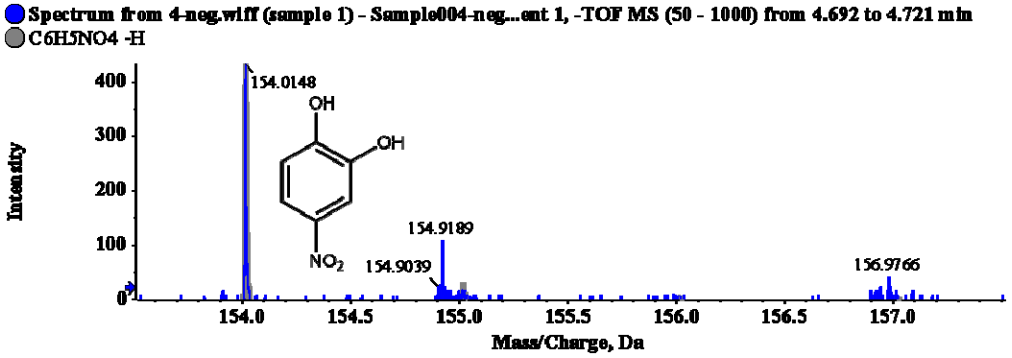


Fig. S1. Detailed mass spectra of intermediate products generated during the UV/HOCl treatment of 4-nitrophenol.

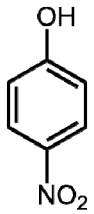
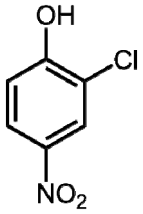
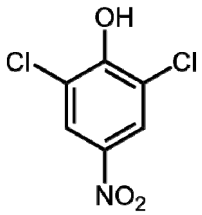
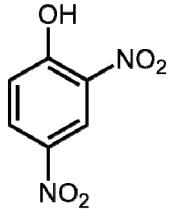
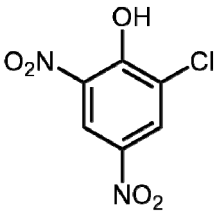
Tables

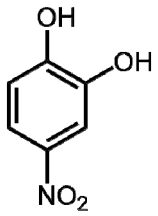
Table S1. Characteristics of wastewater used in this work.

TOC (mg/L as C)	Nitrate (mg/L)	Nitrite (mg/L)	Abs_{254}	Cl^- (mg/L)	Br^- (mg/L)	Na^+ (mg/L)	Mg^+ (mg/L)	pH
27	5.348	ND	0.3977	233.590	64	16.033	10.315	8.33

ND: not detected with limit of detection (LOD) 0.016 mg/L.

Table S2. Mass spectra data and proposed molecular structures for the intermediate products generated during the UV/HOCl treatment of 4-nitrophenol.

TPs	Formula	Molecular structure	Theoretical mass[M-H]$^-$	Experimental mass[M-H]$^-$	Error (ppm)	Isotope distribution pattern
4-Nitrophenol	$C_6H_5NO_3$		138.0197	138.0205	5.7	–
P1	$C_6H_4NO_3Cl$		171.9880/173.9880	171.9816/173.9788	5.2	3:1
P2	$C_6H_3NO_3Cl_2$		205.9490/207.9490/209.9490	205.9423/207.9392/–	2.8	9:6:1
P3	$C_6H_4N_2O_5$		183.0120	183.0056	4.7	–
P4	$C_6H_3N_2O_5Cl$		216.9731/218.9731	216.9667/218.9644	4.2	3:1

P5	$C_6H_5NO_4$		154.0219	154.0148	1.3	–

References of Supplementary Materials

1. APHA/AWWA/WEF. *Standard Methods for the Examination of Water and Wastewater*, 21st ed.; American Public Health Association/American Water Works Association/Water Environment Federation: Washington. DC, USA, 2005.