Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2018

Supplementary Material

The fate of dichloroacetonitrile in the UV/Cl₂ and UV/H₂O₂ processes: Implications on

potable water reuse

Submitted to:

Environmental Science: Water Research & Technology

Ran Yin^{a, *}, Zhuozhi Zhong^a, Li Ling^{a, *}, Chii Shang^{a, b}

a. Department of Civil and Environmental Engineering, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

 b. Hong Kong Branch of Chinese National Engineering Research Center for Control & Treatment of Heavy Metal Pollution, the Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong

* Corresponding authors: Address correspondence to Ran Yin: Tel: (852) 5489 3675; E-mail: ryin@connect.ust.hk.

The Supplementary Material contains: 1 Text, 9 Figures and 1 Scheme.

Table of Contents

Text S1: Detailed procedures for calculation of steady-state concentrations of ClO ⁻ and HO ₂ ⁻ and their second order rate constants towards $DCAN$
Fig. S1. The experimental setup in this study
Fig. S2. Absorbance changes under UV254 irradiation employing iodide/iodate as chemical
actinometry
Fig. S3 Photolysis of dilute H_2O_2 under UV irradiation at 254 nm. Conditions: $[H_2O_2]_0 = 100 \mu$ M, 22 °C
Fig. S4. The absorption spectrum of DCAN (in black) and the emission spectrum of UV lamps (in red)
Fig. S5. Time-dependent degradation of DCAN by water hydrolysis, UV photolysis, H_2O_2 , Cl_2 , UV/H_2O_2 and UV/Cl_2 processes. Conditions: $[DCAN] = 1 \ \mu M$, $[Chlorine] = [H_2O_2] = 500 \ \mu M$, $pH = 5.0$, UV intensity = 0.54 $\mu W/cm^2$
Figure S6. The pseudo first-order rate constants of DCAN degradation by nucleophilic attack and radical oxidation as a function of (a) Cl_2 dosage in UV/ Cl_2 process and (b) H_2O_2 dosage in UV/ H_2O_2 process. Conditions: [DCAN] = 1 uM, UV intensity = 0.54 μ W/cm ² , pH = 6, [Cl_2] = [H_2O_2] = 50, 100 and 500 μ M
Fig. S7. The photo-decomposition of (a) Cl_2 in the UV/ Cl_2 process and (b) H_2O_2 in the UV/ H_2O_2 process. Conditions: [chlorine] = $[H_2O_2] = 500 \ \mu\text{M}$, pHs = 5 and 6, UV intensity = 0.54 $\mu\text{W/cm}^2$
Fig S8. Comparison of cost effectiveness for 1-order of DCAN degradation by using UV/Cl ₂ and UV/H ₂ O ₂ processes in 1 m ³ of water. Conditions: [DCAN] = 1 uM, UV intensity = 0.54 μ W/cm ² , pH = 6, [Chlorine] = [H ₂ O ₂] = 500 μ M
Fig. S9. The degradation products of DCAN by chlorination (b) and in the UV/Cl ₂ process
(c). Conditions: [chlorine] = 500 μ M, pHs = 6, UV intensity = 0.54 μ W/cm ² 12
Scheme S1. Proposed pathways of DCAN degradation in the UV/Cl ₂ and UV/H ₂ O ₂ processes.

Text S1: Detailed procedures for calculation of steady-state concentrations of ClO⁻ and $HO_2^$ and their second-order rate constants towards DCAN.

The steady-state concentrations of ClO⁻ and HO₂⁻ can be directly obtained from Eqs. S1 – S4. The second order rate constant of ClO⁻ and HO₂⁻ towards DCAN was calculated in Eq. S5, where k'_{oCl-} is the pseudo first order rate constant of DCAN degradation by ClO⁻ (in the absence of UV) and [ClO⁻] is the steady state concentration of ClO⁻ that was obtained from Eqs. S1 – S4.

$$HOCl \leftrightarrow ClO^- + H^+$$
 $pKa = 7.5$ Eq. S1

$$[ClO^{-}] = \frac{[free \ chlorine]}{1+10^{pK_a - pH}}$$
Eq. S2

 $OH^{-} + H_2O_2 \leftrightarrow H_2O + HO_2^{-}$ pKa = 11.8 Eq. S3

$$[HO_2^{-}] = \frac{[H_2O_2]}{10^{pK_a^{-}pH}}$$
Eq. S4

$$k'_{ClO-} = k_{ClO-DCAN}[ClO^{-}]$$
Eq. S5



Fig. S1. The experimental setup in this study.



Fig. S2. Absorbance changes under UV254 irradiation employing iodide/iodate as chemical actinometry.



Fig. S3 Photolysis of dilute H_2O_2 under UV irradiation at 254 nm. Conditions: $[H_2O_2]_0 = 100 \mu$ M, 22 °C.



Fig. S4. The absorption spectrum of DCAN (in black) and the emission spectrum of UV lamps (in red).



Fig. S5. Time-dependent degradation of DCAN by water hydrolysis, UV photolysis, H_2O_2 , Cl_2 , UV/H_2O_2 and UV/Cl_2 processes. Conditions: [DCAN] = 1 μ M, [Chlorine] = [H_2O_2] = 500 μ M, pH = 5.0, UV intensity = 0.54 μ W/cm².



Figure S6. The pseudo first-order rate constants of DCAN degradation by nucleophilic attack and radical oxidation as a function of (a) Cl_2 dosage in UV/ Cl_2 process and (b) H_2O_2 dosage in UV/ H_2O_2 process. Conditions: [DCAN] = 1 uM, UV intensity = 0.54 μ W/cm², pH = 6, [Cl₂] = [H_2O_2] = 50, 100 and 500 μ M.



Fig. S7. The photo-decomposition of (a) Cl_2 in the UV/ Cl_2 process and (b) H_2O_2 in the UV/ H_2O_2 process. Conditions: [chlorine] = $[H_2O_2] = 500 \ \mu\text{M}$, pHs = 5 and 6, UV intensity = 0.54 μ W/cm².



Fig S8. Comparison of cost effectiveness for 1-order of DCAN degradation by using UV/Cl₂ and UV/H₂O₂ processes in 1 m³ of water. Conditions: [DCAN] = 1 μ M, UV intensity = 0.54 μ W/cm², pH = 6, [Chlorine] = [H₂O₂] = 500 μ M.



Fig. S9. The degradation products of DCAN by chlorination (b) and in the UV/Cl₂ process (c). Conditions: [chlorine] = 500 μ M, pHs = 6, UV intensity = 0.54 μ W/cm².



Scheme S1. Proposed pathways of DCAN degradation in the UV/Cl_2 and UV/H_2O_2 processes.