Supplementary Material

The fate of dichloroacetonitrile in the UV/Cl\(_2\) and UV/H\(_2\)O\(_2\) processes: Implications on potable water reuse

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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 HO$_2^-$ can be directly obtained from Eqs. S1 – S4. The second order rate constant of ClO$^-$ and HO$_2^-$ towards DCAN was calculated in Eq. S5, where $k'_{Cl^-}$ 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.

\[ \text{HOCl} \leftrightarrow \text{ClO}^- + H^+ \quad pKa = 7.5 \quad \text{Eq. S1} \]

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

\[ \text{OH}^- + H_2O_2 \leftrightarrow H_2O + HO_2^- \quad pKa = 11.8 \quad \text{Eq. S3} \]

\[ [\text{HO}_2^-] = \frac{[H_2O_2]}{10^{pK_a-pH}} \quad \text{Eq. S4} \]

\[ k'_{Cl^-} = k_{Cl^-DCAN}[ClO^-] \quad \text{Eq. S5} \]
Fig. S1. The experimental setup in this study.
Fig. S2. Absorbance changes under UV254 irradiation employing iodide/iodate as chemical actinometry.

\[ y = 0.0037x + 0.1142 \]
\[ R^2 = 0.9936 \]
Fig. S3 Photolysis of dilute H$_2$O$_2$ under UV irradiation at 254 nm. Conditions: [H$_2$O$_2$]$_0$ = 100 μM, 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\textsubscript{2}O\textsubscript{2}, Cl\textsubscript{2}, UV/H\textsubscript{2}O\textsubscript{2} and UV/Cl\textsubscript{2} processes. Conditions: [DCAN] = 1 μM, [Chlorine] = [H\textsubscript{2}O\textsubscript{2}] = 500 μM, pH = 5.0, UV intensity = 0.54 μW/cm\textsuperscript{2}.
Figure S6. The pseudo first-order rate constants of DCAN degradation by nucleophilic attack and radical oxidation as a function of (a) Cl\textsubscript{2} dosage in UV/Cl\textsubscript{2} process and (b) H\textsubscript{2}O\textsubscript{2} dosage in UV/H\textsubscript{2}O\textsubscript{2} process. Conditions: [DCAN] = 1 uM, UV intensity = 0.54 μW/cm\textsuperscript{2}, pH = 6, [Cl\textsubscript{2}] = [H\textsubscript{2}O\textsubscript{2}] = 50, 100 and 500 μM.
Fig. S7. The photo-decomposition of (a) Cl₂ in the UV/Cl₂ process and (b) H₂O₂ in the UV/H₂O₂ process. Conditions: [chlorine] = [H₂O₂] = 500 μM, pHs = 5 and 6, UV intensity = 0.54 μW/cm².
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 μM, UV intensity = 0.54 μW/cm$^2$, pH = 6, [Chlorine] = [H$_2$O$_2$] = 500 μM.
Fig. S9. The degradation products of DCAN by chlorination (b) and in the UV/Cl₂ process (c). Conditions: [chlorine] = 500 μM, pHs = 6, UV intensity = 0.54 μW/cm².
Scheme S1. Proposed pathways of DCAN degradation in the UV/Cl₂ and UV/H₂O₂ processes.