Electronic Supplementary Information

Degradation of Ibuprofen and Acetylsulfamethoxazole by multi-walled Carbon Nanotube Catalytic Ozonation: Surface properties, kinetics and modeling

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Text S1: Method for the determination of rate constants for a macromolecule simultaneously reacting with ozone and serving as the initiator, promoter and inhibitor in the OH· chain reactions in water ozonation

The approach described by Yong and Lin\textsuperscript{1, 2} integrated the following three classical models for water ozonation:

1. The transient steady-state concentration of OH·:

$$[	ext{OH}]=\frac{2k_1[	ext{OH}^-]+\sum k_{i,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}[O_3]$$ (S1)

where $[\cdot\text{OH}]$ represents the transient steady-state concentration of OH·; $k_1$ represents the 2\textsuperscript{nd}-order rate constant between OH$^-$ and ozone; $[M_{I,i}]$ and $k_{I,i}$ represent the concentration of the initiator and its 2\textsuperscript{nd}-order rate constant with O$_3$; $[M_{S,i}]$ and $k_{S,i}$ represent the concentration of the inhibitor and its 2\textsuperscript{nd}-order rate constant with OH·, respectively.

2. The $R_{ct}$ concept:\textsuperscript{4}

$$R_{ct} = \frac{\int [\cdot\text{OH}] dt}{\int [O_3] dt} = -\frac{\ln \frac{[\text{pCBA}]_t}{[\text{pCBA}]_0}}{k_{OH/pCBA} \int [O_3] dt}$$ (S2)

3. Pseudo-1\textsuperscript{st} order ozone decomposition kinetics:\textsuperscript{3}

$$-\frac{d[O_3]}{dt} = k_{obs}$$

$$= 3k_1[\cdot\text{OH}]+k_D[M_{D,i}]+k_I[M_{I,i}]+k_p[M_{P,i}]=\left(\frac{2k_1[\cdot\text{OH}]+\sum k_{i,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}\right)$$ (S3)

Eq (S1) can be substituted to Eq (S2) to yield Eq (S4) assuming that pH value (or $[\cdot\text{OH}]$) and the concentrations of initiator ($[M_{I,i}]$) and inhibitor ($[M_{S,i}]$) do not change during the ozonation.

$$R_{ct} = \frac{\int \left(\frac{2k_1[\cdot\text{OH}]+\sum k_{i,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}\right)[O_3] dt}{\int [O_3] dt} = \frac{2k_1[\cdot\text{OH}]+\sum k_{i,i}[M_{I,i}]}{\sum k_{S,i}[M_{S,i}]}$$ (S4)

Assuming that MWCNT can simultaneously react with ozone and serve as the initiator, promoter and inhibitor in the OH· chain reactions, Eq (S4) can be rewritten as Eq (S5) with the addition of tert-butanol as an external inhibitor (denoted as S with a rate constant of $k_{SS}$ with OH·) in the system\textsuperscript{1}.

$$R_{ct} = \frac{2k_1[\cdot\text{OH}]+k_I[M_{\text{MWCNT}}]}{k_{SS}[S]+k_S[M_{\text{MWCNT}}]}$$ (S5)

where $k_1$ represents the initiation rate constant of MWCNT (unit: L/(mg CNT)$^{-1}$s$^{-1}$), $k_S$ represents the inhibition rate constant of MWCNT (unit: L/(mg CNT)$^{-1}$s$^{-1}$), $k_{SS}$ represents the 2\textsuperscript{nd}-order rate constant between tert-butanol and OH· ($k_{SS}=6.0\times10^8$).
The reciprocal of Eq (S5) gives Eq (S6).

\[ \frac{1}{R_{ct}} = \frac{k_{SS}[S]+k_S[MWCNT]}{2k_1[OH^-]+k_I[MWCNT]} \]  

(S6)

Ideally, a linear relationship exists between \( \frac{1}{R_{ct}} \) and \( k_{SS}[S] \) as shown below. \( k_I \) and \( k_S \) can then be determined from the slope and intercept, respectively.

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\text{Intercept} = \frac{k_S[MWCNT]}{2k_1[OH^-]+k_I[MWCNT]}
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\text{Slope} = \frac{1}{2k_1[OH^-]+k_I[MWCNT]}
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In the same system, substituting Eq (S3) to Eq (S1) gives Eq (S7):

\[ \frac{d[O_3]}{dt} = \frac{1}{[O_3]} = k_{obs} = 3k_1[OH^-]+k_D[MWCNT]+k_I[MWCNT]+k_p[MWCNT]R_{ct} \]  

(S7)

where \( k_D \) represented the direct reaction rate constant of MWCNT, \( k_p \) represented the promotion rate constants of MWCNT (unit: L(mg CNT)^{-1}s^{-1}).

A linear relationship should exist between \( k_{obs} \) and \( R_{ct} \) as shown below. \( k_p \) and \( k_D \) can then be determined from the slope and intercept, respectively.

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\text{Intercept} = 3k_1[OH^-]+k_p[MWCNT]+k_I[MWCNT]
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\text{Slope} = k_p[MWCNT]
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Figure S1. Schematic diagram of ozone experiments
Figure S2. EDS spectra of (a) p-MWCNT, (b) 20-MWCNT, (c) 40-MWCNT and (d) 70-MWCNT.
Figure S3. Adsorption of pCBA onto the 4 MWCNTs. Experimental condition: [pCBA]₀ = 0.5 μM, [B₄O₇²⁻] = 5 mM, MWCNT dosage = 20 mg/L, pH = 7.

References


