Supplementary Information for

Insights into the degradation of 2,4-Dichlorophenol in aqueous solution by α-MnO$_2$ nanowires activated persulfate: catalytic performance and kinetic modeling

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Summary

TEXT S1 Detailed deducing process of the kinetic modelling

TEXT S1 A kinetic study was conducted based on the designed experimental conditions. To establish a kinetic model for the degradation reaction, we presume that 2,4-DCP was mainly degraded by $SO_4\bullet^-$ and $\bullet OH$. The corresponding kinetic equation for DCP and the radicals can be expressed as follows:

$$\frac{d[DCP]}{dt} = -k_{10}[SO_4^-\bullet][DCP] - k_{11}[\bullet OH][DCP] \tag{S1}$$

$$\frac{d[SO_4^-\bullet]}{dt} = k_2[S_2O_8^{2-}][Mn(III)] - k_3[SO_4^-\bullet][OH^-] - k_4[SO_4^-\bullet][H_2O] - k_5[SO_4^-\bullet][S_2O_8^{2-}] \\ - k_7[SO_4^-\bullet][\bullet OH] - k_9[SO_4^-\bullet][SO_4^-\bullet] - k_{10}[SO_4^-\bullet][DCP] \tag{S2}$$

$$\frac{d[\bullet OH]}{dt} = k_3[SO_4^-\bullet][OH^-] + k_4[SO_4^-\bullet][H_2O] - k_6[\bullet OH][S_2O_8^{2-}] - k_7[SO_4^-\bullet][\bullet OH] \\ - k_8[\bullet OH][\bullet OH] - k_{11}[\bullet OH][DCP] \tag{S3}$$

Equations (S2) and (S3) can be simplified as Equations (S4) and (S5):

$$\frac{d[SO_4^-\bullet]}{dt} = k_2[S_2O_8^{2-}][Mn(III)] - k_{10}[SO_4^-\bullet][DCP] - \sum_i k_{sr}[S_i][SO_4^-\bullet] \tag{S4}$$

$$\frac{d[\bullet OH]}{dt} = k_3[SO_4^-\bullet][OH^-] - k_{11}[\bullet OH][DCP] - \sum_j k_{qr}[S_j][\bullet OH] \tag{S5}$$

Where $[S_i]$ represents the scavengers of $SO_4\bullet^-$, such as $OH-$, $SO_4\bullet^-$, and $\bullet OH$, and $[S_j]$ represents the scavengers of $\bullet OH$, including $S_2O_8^{2-}$, $SO_4\bullet^-$, and $\bullet OH$.

Given that the lifetimes of $SO_4\bullet^-$ and $\bullet OH$ are merely microseconds long[1], their concentrations are normally considered to be constantly low. Moreover, the corresponding change rates approach zero at a certain time on the basis of the pseudo-steady state assumption, i.e.,

$$\frac{d[SO_4^-\bullet]}{dt} = 0 \tag{S6}$$

$$\frac{d[\bullet OH]}{dt} = 0 \tag{S7}$$

As per Equations (S4) to (S7), $[SO_4\bullet^-]$ and $[\bullet OH]$ can be derived as follows:

$$[SO_4^- \bullet] = \frac{k_2[S_2O_8^{2-}][Mn(III)]}{k_{10}[DCP] + \sum_i k_{sr}[S_i]} \tag{S8}$$

$$[\bullet OH] = \frac{k_3[SO_4^- \bullet][OH^-]}{k_{11}[DCP] + \sum_j k_{qr}[S_j]} \tag{S9}$$

In the practical implementation of PS oxidation, the dosages of the PS and the catalysts should be sufficient to generate an adequate amount of reactive radicals so as to degrade the pollutants effectively[2]. A significant amount of $SO_4\bullet^-$ and $\bullet OH$ radicals is consumed by multiple scavenger species; as a result, PS levels increase in comparison with the contaminant concentrations. Thus,

$$k_{10}[DCP] + \sum_i k_{sr}[S_i] \approx \sum_i k_{sr}[S_i] \tag{S10}$$

$$k_{11}[DCP] + \sum_j k_{qr}[S_j] \approx \sum_j k_{qr}[S_j] \tag{S11}$$

Therefore, Equations (S8) and (S9) can be expressed as:

$$[SO_4^- \bullet] = \frac{k_2[S_2O_8^{2-}][Mn(III)]}{\sum_i k_{sr}[S_i]} \tag{S12}$$

$$[\bullet OH] = \frac{k_3[SO_4^- \bullet][OH^-]}{\sum_j k_{qr}[S_j]} \tag{S13}$$

$[\bullet OH]$ can be calculated via Equations (S12) and (S13):

$$[\bullet OH] = \frac{k_2 k_3[OH^-][S_2O_8^{2-}][Mn(III)]}{\sum_j k_{qr}[S_j] \sum_i k_{sr}[S_i]} \tag{S14}$$

Substituting Equation (S12) and (S14) into Equation (S1) yields the following:

$$\frac{d[DCP]}{dt} = -k_{10}[DCP]\frac{k_2[S_2O_8^{2-}][Mn(III)]}{\sum_i k_{sr}[S_i]} - k_{11}[DCP]\frac{k_2 k_3[OH^-][S_2O_8^{2-}][Mn(III)]}{\sum_j k_{qr}[S_j] \sum_i k_{sr}[S_i]}$$

$$= -\left(k_{10} + \frac{k_{11} k_3[OH^-]}{\sum_j k_{qr}[S_j]} \right) \frac{k_2[S_2O_8^{2-}][Mn(III)]}{\sum_i k_{sr}[S_i]}[DCP] \tag{S15}$$

The consumption of $\equiv Mn(IV)$ can be expressed by Equation (S16).

$$\frac{d[\equiv Mn(IV)]}{dt} = -k_1[S_2O_8^{2-}][\equiv Mn(IV)] + k_2[S_2O_8^{2-}][\equiv Mn(III)] \tag{S16}$$

As a reaction catalyst, $\equiv Mn(IV)$ concentration should be equal to the initial dosage, and the change rate is zero at a certain time. That is,

$$\frac{d[\equiv Mn(IV)]}{dt} = -k_1[S_2O_8^{2-}][\equiv Mn(IV)] + k_2[S_2O_8^{2-}][\equiv Mn(III)] = 0 \tag{S17}$$

Equation (S17) can be transformed as follows:

$$[\equiv Mn(III)] = \frac{k_1[\equiv Mn(IV)]}{k_2} \tag{S18}$$

The consumption of $S_2O_8^{2-}$ can be expressed as in Equation (S19).

$$\frac{d[S_2O_8^{2-}]}{dt} = -k_1[S_2O_8^{2-}][\equiv Mn(IV)] - k_2[S_2O_8^{2-}][Mn(III)] - k_5[SO_4^{-}\bullet][S_2O_8^{2-}]$$
$$- k_6[S_2O_8^{2-}][\bullet OH] + k_9[SO_4^{-}\bullet][SO_4^{-}\bullet] \tag{S19}$$

As per a comparison of Equations (3) and (7), the reaction rate constant of Equation (5), k_5, is low; thus, $SO_4\bullet^{-}$ is more likely to react with OH^{-} or $\bullet OH$ than with $S_2O_8^{2-}$ and $k_5[SO_4\bullet^{-}][S_2O_8^{2-}]$ can be neglected. As with $SO_4\bullet^{-}$, $k_6[S_2O_8^{2-}][\bullet OH]$ can be disregarded. The concentration of $SO_4\bullet^{-}$ in solution is considerably lower than that of $S_2O_8^{2-}$; therefore, the $k_9[SO_4\bullet^{-}][SO_4\bullet^{-}]$ in Equation (S19) can be neglected. Thus, $[S_2O_8^{2-}]$ can be derived from Equation (S18) and (S19) as follows:

$$[S_2O_8^{2-}] = [S_2O_8^{2-}]_0 e^{-2k_1[\equiv Mn(IV)]t} \tag{S20}$$

Substituting Equations (S18) and (S20) into Equation (S15) yields the following:

$$\frac{d[DCP]}{dt} = -\left(k_{10} + \frac{k_{11}k_3[OH^-]}{\sum_j k_{qr}[S_j]}\right) \times \frac{k_1[\equiv Mn(IV)][S_2O_8^{2-}]_0 e^{-2k_1[\equiv Mn(IV)]t}}{\sum_i k_{sr}[S_i]}[DCP] \tag{S21}$$

To simplify Equation (S21), let $a = -[k_{10}+k_{11}k_3[OH^-] / \sum k_{qr}[S_j]] \; k_1[\equiv Mn(IV)][S_2O_8^{2-}]_0 / \sum k_{sr}[S_i]$ and $b = 2k_1[\equiv Mn(IV)]$. The aforementioned equation can be rearranged in the simplified form shown below.

$$\frac{d[DCP]}{dt} = ae^{-bt}[DCP] \tag{S22}$$

The integrated form of Equation (S22) is:

$$\ln(\frac{[DCP]}{[DCP]_0}) = \frac{a}{b}(1 - e^{-bt}) \tag{S23}$$

Hence, if the relationship between $\ln([DCP]/[DCP]_0)$ versus reaction time t matches Equation (S23), then the DCP degradation process follows the new reaction dynamic model. The experiments conducted did not only demonstrate this degradation but also verified the proposed models.

1.   S. Wang, N. Zhou, S. Wu, Q. Zhang and Z. Yang, *Ultrason. Sonochem.*, 2015, **23**, 128-134.
2.   Y. S. Zhao, C. Sun, J. Q. Sun and R. Zhou, *Sep. Purif. Technol.*, 2015, **142**, 182-188.