

A Kinetic Model for the Degradation of Natural Organic Matter During the Ultraviolet Hydrogen Peroxide Advanced Oxidation Process

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ABSTRACT

A completely dynamic, kinetic model was developed to predict the degradation of chromophoric natural organic matter (CNOM) and H_2O_2 during the UV/ H_2O_2 . Model parameters were estimated numerically by optimizing fitting to experimental results obtained with a "synthetic water" using Suwannee River NOM. The reaction rate constant for the reaction between hydroxyl radicals ($\bullet OH$) and NOM was estimated at $1.14E4 \text{ L mg}^{-1} \text{ s}^{-1}$, in close agreement with past literature reports. The reaction rate constant for the reaction between $\bullet OH$ and CNOM was estimated at $3.08E8 \text{ L mol}^{-1} \text{ s}^{-1}$. Considering the change in CNOM helped improved prediction of H_2O_2 degradation but the model still under predicted experimental measurements. This discrepancy is hypothesized to be due to the model's neglect of the reaction between H_2O_2 and carbon-centered radicals, formed when $\bullet OH$ react with NOM.

Key Words: Ultraviolet; Hydrogen peroxide; Natural organic matter; Advanced oxidation; Drinking water treatment; Kinetic model

INTRODUCTION

A number of models have been presented to characterize the ultraviolet (UV) plus hydrogen peroxide (H_2O_2) advanced oxidation process, termed UV/ H_2O_2 (1-4). Some of these models applied the assumption of pseudo steady-state hydroxyl radical ($\bullet OH$) concentration while others consider all species dynamic, including radicals. Existing models incorporate the $\bullet OH$ scavenging potential of natural organic matter (NOM) while few model the transformation of NOM. Those that do consider changes in NOM primarily target the mineralization of NOM and so, do not address its partial degradation under practical operation conditions.

In commercial drinking water UV/ H_2O_2 applications, the oxidation conditions (i.e., fluences and/or H_2O_2 concentrations) are not strong enough to mineralize NOM. Instead, significant partial oxidation of NOM takes place, leading to changes in water characteristics that in turn affect process efficacy and water quality (5,6). For example, the reduction in the absorbance of water at 254 nm UV leads to an increase in the photolysis of H_2O_2 , thereby increasing the rate of $\bullet OH$ production.

The focus of this research has been the development of a model that predicts partial degradation of NOM by incorporating a surrogate parameter, the absorbance of 254 nm UV, representing structural transformation of NOM (from aromatic to aliphatic) attributable to $\bullet OH$ attack. The portion of NOM that absorbs at 254 nm has been defined as chromophoric natural organic matter (CNOM). The

model treats all species (including radicals) under non-steady state conditions and predicts system parameters, such as components' concentration and absorbance trajectory.

MATERIALS AND METHODS

Experiments were conducted using "synthetic waters" in which isolated Suwannee River NOM (SRNOM) (International Humic Substances Society) was added to MilliQ water. UV/ H_2O_2 treatment was performed using a low pressure high output lamp (Trojan Technologies) housed in a collimated beam apparatus. Experiments were conducted at different irradiation times, initial H_2O_2 concentrations, and NOM concentrations (conditions presented in Table I).

A calibrated radiometer (IL1700, sensor SED240 for 254 nm, International Light Inc.) was used to determine the incident photon fluence rate following the actinometry method given by (7). TOC was measured using a Sievers 900 TOC analyzer. The degradation of CNOM was monitored using a spectrophotometer (Cary 100, Varian Inc.). H_2O_2 concentration was measured by reaction with iodide catalyzed by molybdate (8). The scavenging rate of the NOM was determined by competition kinetics with the $\bullet OH$ probe 4-chloro-benzoic acid (pCBA), which was measured by HPLC (Waters 600-MS) with Waters 996 photodiode array detector and Supelcosil LC-18 column.

The following system of equations was used to model the reactions (Table II) of UV/H₂O₂ system:

$$[1] \frac{d[H_2O_2]}{dt} = k_{a,H_2O_2,254} \cdot H_2O_2 \cdot OH [H_2O_2] - k_2[\bullet OH][H_2O_2] - [H_2O_2] - k_3[\bullet OH][HO_2^-] - k_7[O_2^{\bullet-}][H_2O_2] - k_{10}[HO_2^{\bullet}][H_2O_2] - k_6[\bullet OH]^2 + k_8[O_2^{\bullet-}][HO_2^{\bullet}] + k_9 [HO_2^{\bullet}]^2$$

where

$$[2] k_{a,H_2O_2} = \frac{E_p^z \cdot \epsilon_{H_2O_2} [1 - 10^{-aZ}] \times 1000}{aZ}$$

In Equation [2], E_p^z is the incident photon fluence rate (Es cm⁻² s⁻¹) and Z is the pathlength (2.95 cm).

$$[3] a = [H_2O_2] \epsilon_{H_2O_2} + CNOM$$

In Equation [4], a is the total water absorption coefficient at 254 nm (cm⁻¹), $\epsilon_{H_2O_2}$ was the decadic molar absorption coefficient of H₂O₂ at 254 nm (19.6 M⁻¹ cm⁻¹) and CNOM was adsorption coefficient of chromophoric NOM which, by definition, only absorbed at 254 nm.

$$[4] [HO_2^-] = \frac{K_a [H_2O_2]}{[H^+]}$$

$$[5] \frac{d[\bullet OH]}{dt} = -k_2[\bullet OH][H_2O_2] - k_3[\bullet OH][HO_2^-] - k_4[\bullet OH][HO_2^{\bullet}] - k_5[\bullet OH][O_2(\bullet-)] - [(2k) 6[\bullet OH]_2 - k_{OH,TOC9Hsystem}$$

$$[6] \frac{d[O_2^{\bullet-}]}{dt} = k_4[\bullet OH][HO_2^{\bullet}] - k_5[\bullet OH][O_2^{\bullet-}] - k_7[O_2^{\bullet-}][H_2O_2] - k_8[HO_2^{\bullet}] - 2k_9 [HO_2^{\bullet}]^2 - k_{10}[HO_2^{\bullet}][H_2O_2] + k_2[\bullet OH][H_2O_2] + k_3[\bullet OH][HO_2^-]$$

$$[7] [HO_2^{\bullet}] = \frac{[H^+][O_2^{\bullet-}]}{K_{a2}}$$

$$[8] \frac{d[pCBA]}{dt} = -k_{OH,pCBA}[\bullet OH][pCBA]$$

$$[9] \frac{dCNOM}{dt} = -k_{OH,CNOM}[\bullet OH]CNOM$$

All the reaction rate constants (Table II) were given except for $k_{OH,CNOM}$ and $k_{OH,TOC9Hsystem}$. These two parameters were numerically estimated by maximum likelihood estimation.

RESULTS AND DISCUSSION

The experimental results from UV/H₂O₂ treatment of SRNOM synthetic water are given in Figure 1. Using this experimental data and the set of model expressions given above, the two unknown rate parameters $k_{OH,CNOM}$, and $k_{OH,TOC9Hsystem}$, were estimated simultaneously using maximum likelihood estimation. Given as lines in Figure 1 are model predictions using the estimated rate parameters.

Scavenging of hydroxyl radical by natural organic matter

The observed rate of degradation of pCBA increased with increasing the initial H₂O₂ concentration (Figure 1). As an increase in H₂O₂ yielded a greater concentration of •OH, the increase in the degradation of the pCBA was expected. Further, as TOC was increased, there was a reduction in the observed rate of degradation of pCBA. Again, this was expected as a greater concentration of NOM would lead to greater scavenging of •OH by NOM, in turn reducing observed rate of degradation of pCBA.

From the parameter estimation, the reaction rate constant for the reaction between •OH and TOC, $k_{OH,TOC9Hsystem}$, was estimated at 1.14E4 L mg⁻¹ s⁻¹. Literature reports for $k_{OH,TOC9Hsystem}$ for SRNOM fractions and isolated NOM originating from different sources are presented in Table II. The $k_{OH,TOC9Hsystem}$ estimated in this study for SRNOM agreed reasonably well with literature reports for $k_{OH,TOC9Hsystem}$ for fulvic and humic fractions of SRNOM. The estimated value, 1.14E4 L mg⁻¹ s⁻¹, was within error of the value reported by Westerhoff et al. (9) for SRNOM fulvic acid using pulse radiolysis with competition kinetics and direct transient growth (1.33±0.2 E4 L mg⁻¹ s⁻¹). Slightly higher were the



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values for SRNOM humic acid reported by Goldstone et al. (10) using γ -radiolysis with competition kinetics ($1.9 \pm 0.05 \text{ E4 L mg}^{-1} \text{ s}^{-1}$). About three-fold the value estimated in this study were the values reported by Goldstone et al. (10) for SRNOM fulvic acid ($2.7 \pm 0.05 \text{ E4 L mg}^{-1} \text{ s}^{-1}$) and by Westerhoff et al. (11) for SRNOM fulvic acid ($3.08 \text{ E4 L mg}^{-1} \text{ s}^{-1}$) using ozonation with competition kinetics. This variation between reported $k_{\bullet\text{OH},\text{TOC}9\text{Hsystem}}$ values demonstrates that estimation of the parameter is subject to the method used for $\bullet\text{OH}$ production (i.e. ozonation, UV/ H_2O_2 , pulse radiolysis, γ -radiolysis, or nitrate-induced solar driven photolysis), as well as the type of NOM employed (i.e., aquatic isolate, fulvic or humic isolates). Yet, it is apparent that $k_{\bullet\text{OH},\text{TOC}9\text{Hsystem}}$ has been estimated to fall within a range from roughly 1E4 to $4\text{E4 L mg}^{-1} \text{ s}^{-1}$ (Table III). The $k_{\bullet\text{OH},\text{TOC}9\text{Hsystem}}$ estimated in this work lies within this range.

Degradation of chromophoric natural organic matter

It was observed that as the initial H_2O_2 concentration was increased, the observed rate of degradation CNOM increased. As discussed earlier, an increase in H_2O_2 would

yield a greater concentration of $\bullet\text{OH}$ thereby increasing the degradation of CNOM. From parameter estimation, $k_{\bullet\text{OH},\text{CNOM}}$ was estimated at $3.04\text{E8 L mol}^{-1}\text{s}^{-1}$. Future research will present the ability of the model, using the two parameters estimated for synthetic water, to predict changes in CNOM for natural waters.

Prediction of the change in CNOM is deemed important since in the UV/ H_2O_2 system CNOM is often the major absorber of photons. Any change in CNOM would have an impact on water absorption coefficient, a (Equation [3]), the photolysis of H_2O_2 (Equation [2]), and subsequently the concentration of $\bullet\text{OH}$. A reduction in CNOM would lead to greater absorption of photons by H_2O_2 thus improving photolysis and $\bullet\text{OH}$ production. Therefore, it was clear that by considering the change in CNOM, prediction of H_2O_2 degradation would be more accurate.

Hydrogen peroxide degradation

Interestingly, the observed rate of degradation of H_2O_2 was not greatly affected by the change in TOC. That is, about 20% degradation of H_2O_2 was observed for all three concentrations of TOC. Also, the model did not accurately

Figure 1: Experimental results (points) and model predictions (lines) for pCBA, CNOM, and H_2O_2 for synthetic water treated by UV/ H_2O_2 are varying levels of TOC, initial H_2O_2 concentration, and irradiation time.

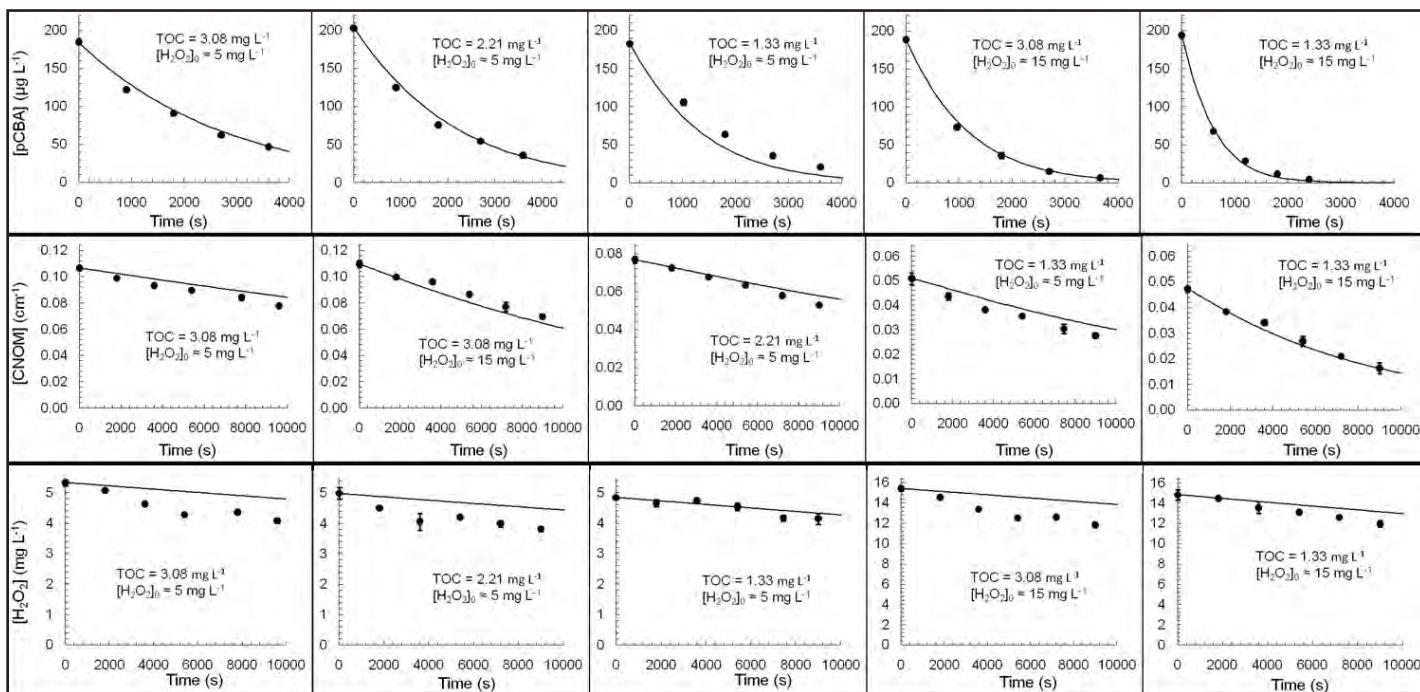


Table I. Experimental conditions for UV/ H_2O_2 treatment of synthetic water

NOM Source	Suwannee River
Total organic carbon (mg L ⁻¹)	1.33, 2.21, 3.08
A254 (cm ⁻¹)	0.049, 0.065, 0.108
Irradiation time (min)	0, 30, 60, 90, 120, 150
Initial H_2O_2 concentration (mg L ⁻¹)	5, 15

Table II. Series of reactions and corresponding rate constants for kinetics model

Reaction	Rate constant	Reference
1 $\text{H}_2\text{O}_2 + h\nu \rightarrow 2\cdot\text{OH}$	$\Phi^{H_2O_2 \rightarrow \cdot OH} = 0.5$ (primary quantum yield)	(12)
2 $\cdot\text{OH} + \text{H}_2\text{O}_2 \rightarrow \text{O}_2\cdot^- + \text{H}_2\text{O} + \text{H}^+$	$k_2 = 2.7\text{E}7 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
3 $\cdot\text{OH} + \text{HO}_2^- \rightarrow \text{O}_2\cdot^- + \text{H}_2\text{O}$	$k_3 = 7.5\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
4 $\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_4 = 6.6\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
5 $\cdot\text{OH} + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O} + \text{O}_2$	$k_5 = 8.0\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
6 $\cdot\text{OH} + \cdot\text{OH} \rightarrow \text{H}_2\text{O}_2$	$k_6 = 5.5\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
7 $\text{O}_2\cdot^- + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{OH}^- + \text{O}_2$	$k_7 = 0.13 \text{ L mol}^{-1} \text{ s}^{-1}$	(14)
8 $\text{O}_2\cdot^- + \text{HO}_2\cdot + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{OH}^- + \text{O}_2$	$k_8 = 9.7\text{E}7 \text{ L mol}^{-1} \text{ s}^{-1}$	(13)
9 $\text{HO}_2\cdot + \text{HO}_2\cdot \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$	$k_9 = 8.6\text{E}5 \text{ L mol}^{-1} \text{ s}^{-1}$	(15)
10 $\text{HO}_2\cdot + \text{H}_2\text{O}_2 \rightarrow \cdot\text{OH} + \text{H}_2\text{O} + \text{O}_2$	$k_{10} = 3.7 \text{ L mol}^{-1} \text{ s}^{-1}$	(14)
11 $\text{H}_2\text{O}_2 \leftrightarrow \text{H}^+ + \text{HO}_2^-$	$k_{a1} = 10^{-11.6}$	(16)
12 $\text{HO}_2\cdot \leftrightarrow \text{H}^+ + \text{O}_2\cdot^-$	$k_{a2} = 10^{-4.8}$	(16)
13 $\cdot\text{OH} + \text{pCBA} \rightarrow \text{products}$	$k_{\cdot\text{OH}, \text{pCBA}} = 5\text{E}9 \text{ L mol}^{-1} \text{ s}^{-1}$	(17)
14 $\cdot\text{OH} + \text{TOC} \rightarrow \text{products}$	$k_{\cdot\text{OH}, \text{TOC}} = ? \text{ L mg}^{-1} \text{ s}^{-1}$	
15 $\cdot\text{OH} + \text{CNOM} \rightarrow \text{products}$	$k_{\cdot\text{OH}, \text{CNOM}} = ? \text{ L mol}^{-1} \text{ s}^{-1}$	

Table III. Literature reported values for $k_{\cdot\text{OH}, \text{TOC}9\text{Hystem}}$

NOM Source	$k_{\cdot\text{OH}, \text{TOC}9\text{Hystem}}$ ($\text{L mg}^{-1} \text{ s}^{-1}$)	Determination Method	Reference
Suwannee River NOM Isolate	1.14E4	UV/H ₂ O ₂ : competition kinetics	Present work
Suwannee River Fulvic Acid	(1.33±0.2)E4	Pulse radiolysis: competition kinetics and direct transient growth	(9)
Suwannee River Fulvic Acid	3.08E4	Ozonation: competition kinetics	(11)
Suwannee River Fulvic Acid	(2.7±0.04)E4	γ-radiolysis: competition kinetics	(10)
Suwannee River Humic Acid	(1.9±0.04)E4	γ-radiolysis: competition kinetics	(10)

predict H₂O₂ degradation, under predicting the actual concentrations (**Figure 1**). Similar to the UV/H₂O₂ models presented in the literature, the model presented here assumed photolysis to be the primary pathway for H₂O₂ degradation. If this assumption were to be correct, an increased TOC would lead to slower degradation of H₂O₂ since TOC increase would lead to higher CNOM and subsequently the water absorbance. This would result in additional screening of UV and a reduction in the number of photons absorbed by H₂O₂.

This limitation was to some extent addressed in our model which included the change in water absorbance which affects the modelling of H₂O₂ degradation. Despite improving model predictions to some extent, the model developed here, as have past models, under predicted H₂O₂ degradation. Higher observed degradation of H₂O₂ is hypothesized to be due to H₂O₂ reaction with carbon-centred radicals that are formed when $\cdot\text{OH}$ reacts with

NOM. Future research is clearly needed to define expressions to more accurately predict H₂O₂ degradation during UV/H₂O₂ advanced oxidation of water in which NOM is present.

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