Development of Simplified Models for Advanced Oxidation Processes

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1. Introduction

Advanced oxidation processes (AOPs) that produce highly reactive hydroxyl radicals at ambient temperature and atmospheric pressure are attractive and promising water and wastewater treatment technologies. In sustainable development of water and wastewater treatment technologies, AOPs can play significant roles. For example, AOPs can potentially mineralize toxic organic compounds via radical involved chain reactions and do not leave any hazardous wastes if adequate design is applied. In water reuse and water reclamation areas, it is a common practice to employ a combination of ultraviolet with hydrogen peroxide (UV/H_2O_2) AOP for the removal of specific organic contaminants (e.g., 1,4-dioxane, NDMA) after the RO process. The energy consumption of UV/H_2O_2 contributes approximately 7% of overall energy usages in the water reclamation process, and therefore, AOP is a competitive technology with other water treatment technologies (e.g., RO, MF, and UF). Although in design of AOPs we maximize removal efficacy of organic compounds and minimize energy usage in AOPs per removal of order of the target compound, there is a trade-off between these parameters. For example, in UV/H_2O_2, increasing the dosage of hydrogen peroxide increases the removal efficacy of target compound by absorbing more fraction of UV light to produce hydroxyl radicals, while an excess dosage of hydrogen peroxide might decrease the removal efficacy and energy efficiency by increasing the scavenging of hydroxyl radical by hydrogen peroxide. Accordingly, there is a need to develop a tool to evaluate these treatment design parameters at first place.

Simplified pseudo-steady state model and pseudo-steady state model are useful tools to optimize these design and operational parameters in AOPs. Although there are some limitations that result from the steady-state assumptions, they are precise enough to examine the feasibility of the AOPs. In the simplified pseudo-steady analysis, steady-state concentrations of radicals do not change with time and are

equal to the initial steady-state concentrations. The steady-state hydroxyl radical concentration can be solved analytically. The pseudo-steady state model assumes net zero of the rate of radical species that are involved in AOPs but radical concentrations change with time. Accordingly, an ordinary differential equation (ODE) should be solved numerically to obtain time-dependent concentration profile of hydroxyl radical. Although several models for AOPs have already been developed in peer-reviewed research articles (Glaze *et al.*, 1995; Lay, 1989; and Stefan *et al.*, 1996), none of them developed a learning module or actual tools for users to calculate and optimize their AOP design.

In this module, we develop tools that are easy to use for the purpose of designing AOPs. In these tools, we include two AOPs simulation models: 1) simplified pseudo-steady state model and 2) pseudo-steady state model for ozone with hydrogen peroxide and ultraviolet photolysis with hydrogen peroxide AOPs, respectively. We consider flow conditions in various reactors that include completely mixed batch reactor (CMBR), completely mixed flow reactor (CMFR), plug flow reactor (PFR), tanks-in-series (TIS) reactors, and dispersed flow reactor (DFR). Users can estimate and optimize their design of AOPs with respect to removal efficacy and energy efficiency by calculating the effluent concentration of a target compound of interest and the energy efficiency per removal order (EE/O) values (Bolton and Cater, 1994). In addition, users can also learn how to develop AOPs models from this module by reading the contents in section 2 and Appendix A, where background knowledge and development processes for various AOPs models in various reactors are presented. A Microsoft Excel spread sheet associated with simplified pseudo-steady state models and MathCAD files associated with pseudo-steady state models are provided. In the sample problem section, examples about how AOPs can be designed from the sustainable water and wastewater treatment point of view by removing target contaminants and minimizing overall energy usage are given.

Because this module requires students to have some background knowledge of advanced oxidation processes with process principles and reaction kinetics, students are referred to read the book *Water Treatment Principles and Design* (3rd edition), written by Crittenden *et al.* (2012). It is also noted that MathCAD might not be a standard practical tool to obtain for graduate student, the MathCAD files are voluntarily practice for pseudo-steady state models.

2. Simplified Pseudo-Steady State Models

In this module, the simplified pseudo-steady state models include: 1) H_2O_2/O_3 model; 2) H_2O_2 added after O_3 addition model; 3) UV/H_2O_2 model; and 4) O_3 - R_c model. The reactor types include: 1) tanks-in-series (TIS) reactor; 2) completely mixed batch reactor (CMBR); 3) completely mixed flow reactor (CMFR); 4) plug flow reactor (PFR); and 5) dispersed flow reactor (DFR) in closed systems. Table 2.1 lists important elementary reactions that are involved in these models. It is noted that we excluded reactions that occur less likely than above reactions (e.g., HO· + HO·). In the following part, the development processes of all these four simplified pseudo-steady state models are described separately.

Table 2.1. Important elementary reactions that are involved in the AOPs

No.	Reactions	Rate constants, $M^{-1}s^{-1}$	Source
Reactions specifically for H_2O_2/O_3 process			

1	$HO_2^- + O_3 \rightarrow O_3^-\bullet + HO_2\bullet$	$k_1 = 2.8 \times 10^6$	a
2	$OH^- + O_3 \rightarrow HO_2^- + O_2$	$k_2 = 70$	a
3	$O_2^-\bullet + O_3 \rightarrow O_3^-\bullet + O_2$	$k_3 = 1.6 \times 10^9$	b
4	$O_3^-\bullet + H^+ \rightarrow HO_3\bullet$	$k_4 = 5.2 \times 10^{10}$	b
5	$HO_3\bullet \rightarrow HO\bullet + O_2$	$k_5 = 1.1 \times 10^5 \text{ s}^{-1}$	b
6	$O_3 + R \rightarrow Products$	$k_6 = ?$	
7	$O_3 + HO\bullet \xrightarrow{k_7} HO_2\bullet + O_2$	$k_7 = 2.6 \times 10^8$	a

Reactions specifically for H₂O₂/UV process			

8	$H_2O_2 + h\nu \rightarrow 2HO\bullet$	$r_{UV,H_2O_2} = -r_{HO\bullet}/2 = -\Phi_{H_2O_2} P_{U-V} f_{H_2O_2} \left(1 - e^{-A}\right)$ $A = 2.303b\left(\varepsilon_{H_2O_2} C_{H_2O_2} + \varepsilon_{HO_2^-} C_{HO_2^-} + \varepsilon_R C_R + \varepsilon_{NOM} C_{NOM}\right)$ $f_{H_2O_2} = 2.303b\left(\varepsilon_{H_2O_2} C_{H_2O_2} + \varepsilon_{HO_2^-} C_{HO_2^-}\right)\Big/A$ $\varepsilon_{H_2O_2,254nm} = 17.9 \sim 19.6 \text{ M}^{-1}\text{cm}^{-1}$ $\Phi_{H_2O_2} = \Phi_{HO_2^-} = 0.5$	
9	$R + h\nu \rightarrow Products$	$r_{UV,R} = -\Phi_R P_{U-V} f_R \left(1 - e^{-A}\right)$ $f_R = 2.303b\varepsilon_R C_R /A$	

Reactions common for both H₂O₂/O₃ and H₂O₂/UV processes			

10	$HO\bullet + HO_2^- \rightarrow OH^- + HO_2\bullet$	$k_{10} = 7.5 \times 10^9$	c
11	$HO\bullet + H_2O_2 \rightarrow H_2O + HO_2\bullet$	$k_{11} = 2.7 \times 10^7$	d
12	$HO\bullet + HCO_3^- \rightarrow CO_3^-\bullet + H_2O$	$k_{12} = 8.5 \times 10^6$	d
13	$HO\bullet + R \rightarrow Products$	k_{13} (See *GCM)	
14	$HO\bullet + NOM \rightarrow Products$	$k_{14} = 1.39 \times 10^8$ to 4.53×10^8 (average = 2.23×10^8)	e
15	$HO\bullet + Cl^- \rightarrow Products$	$k_{15} = 4.3 \times 10^9$	d
16	$HO\bullet + CO_3^{2-} \rightarrow CO_3^-\bullet + OH^-$	$k_{16} = 3.9 \times 10^8$	d
17	$HO\bullet + Fe^{2+} \rightarrow Products$	$k_{17} = 2.3 \times 10^8$	d
18	$HO\bullet + Mn^{2+} \rightarrow Products$	$k_{18} = 1.4 \times 10^8$	d

Acid dissociation constants			

19	$H_2CO_3^* \rightleftarrows H^+ + HCO_3^-$	$pK_{a1} = 6.3$	f

20	$HCO_3^- \rightleftarrows H^+ + CO_3^{2-}$	$pK_{a2} = 10.3$	f
21	$H_2O \rightleftarrows H^+ + OH^-$	$pK_{a3} = 14$	f
22	$H_2O_2 \rightleftarrows H^+ + HO_2^-$	$pK_{a5} = 11.75$	g
23	$HO_2 \cdot \rightleftarrows H^+ + O_2^- \cdot$	$pK_{a6} = 4.8$	a

References: (a) Staehelin and Hoigne, 1982; (b) Buhler *et al.*, 1984; (c) Christensen *et al.*, 1982; (d) Buxton and Greenstock, 1988; (e) Westerhoff *et al.*, 2007; (f) Stumm and Morgan, 1981; (g) Behar *et al.*, 1970.

2.1   Ozone with Hydrogen Peroxide Model

The H_2O_2/O_3 model is a process in which gaseous ozone is injected in water and hydrogen peroxide is added simultaneously. The gaseous ozone is transferred into water via mass transfer process. Accordingly, initial chemical reactions take place in the presence of hydrogen peroxide.

2.1.1   Elementary Reactions

The elementary reactions of H_2O_2/O_3 process involved in this model are reactions 1-7 and 10-18 in Table 2.1.

The overall reaction for the H_2O_2/O_3 process is:

$$H_2O_2 + 2O_3 \rightarrow 2HO \cdot + 3O_2 \tag{2-1}$$

From the reaction above, we can see that 0.5 mole of H_2O_2 is required for each mole of O_3 in order to produce a mole of HO·, or a mass ratio of 0.354 kg of H_2O_2 is needed per kilogram of O_3.

From all of the elementary reactions involved in this model as listed in Table 2.1, net formation rates of various radicals can be obtained as below:

$$\begin{aligned} r_{HO \cdot} = &k_5[HO_3 \cdot] - k_{10}[HO \cdot][HO_2^-] - k_{11}[HO \cdot][H_2O_2] - k_{12}[HO \cdot][HCO_3^-] - k_{13}[HO \cdot][R] \\ &- k_{14}[HO \cdot][NOM] - k_{15}[HO \cdot][Cl^-] - k_{16}[HO \cdot][CO_3^{2-}] - k_{17}[HO \cdot][Fe^{2+}] - k_{18}[HO \cdot][Mn^{2+}] \end{aligned} \tag{2-2}$$

$$r_{HO_3 \cdot} = k_4[O_3^- \cdot][H^+] - k_5[HO_3 \cdot] \tag{2-3}$$

$$r_{O_3^- \cdot} = k_1[O_3][HO_2^-] + k_3[O_2^- \cdot][O_3] - k_4[O_3^- \cdot][H^+] \tag{2-4}$$

$$r_{HO_2 \cdot / O_2 \cdot} = k_1[HO_2^-][O_3] + k_{10}[HO \cdot][HO_2^-] + k_{11}[HO \cdot][H_2O_2] - k_3[O_3][O_2^- \cdot] \tag{2-5}$$

where $r_{HO \cdot}$ = net formation rate of hydroxyl radical formation, mole/L•s

$r_{HO_3 \cdot}$ = net formation rate of ozonide radical formation, mole/L•s

$r_{O_3^- \cdot}$ = net formation rate of ozonide ion radical formation, mole/L•s

$r_{HO_2 \cdot / O_2 \cdot}$ = total formation rate of superoxide radical formation, mole/L•s

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k_{12} = second order rate constant between hydroxyl radical and bicarbonate, L/mole•s

k_{13} = second order rate constant between hydroxyl radical and target organic compound R, L/mole•s

k_{14} = second order rate constant between hydroxyl radical and NOM, L/mole•s

k_{15} = second order rate constant between hydroxyl radical and Cl⁻, L/mole•s

k_{16} = second order rate constant between hydroxyl radical and carbonate, L/mole•s

k_{17} = second order rate constant between hydroxyl radical and Fe(II), L/mole•s

k_{18} = second order rate constant between hydroxyl radical and Mn(II), L/mole•s

$[HO_3\bullet]$ = concentration of ozonide radical, mole/L

$[HO\bullet]$ = concentration of hydroxyl radical, mole/L

$[HO_2^-]$ = concentration of conjugate base or anion of hydrogen peroxide, mole/L

$[H_2O_2]$ = concentration of hydrogen peroxide, mole/L

$[HCO_3^-]$ = concentration of bicarbonate, mole/L

$[R]$ = concentration of target organic compound, mole/L

$[NOM]$ = concentration of NOM, mole/L

$[Cl^-]$ = concentration of chloride ion, mole/L

$[CO_3^{2-}]$ = concentration of carbonate, mole/L

$[Fe^{2+}]$ = concentration of two value iron ion, mole/L

$[Mn^{2+}]$ = concentration of two value manganese ion, mole/L

$[O_3^-\bullet]$ = concentration of ozonide ion radical, mole/L

$[H^+]$ = concentration of hydrogen ion, mole/L

$[O_2^-\bullet]$ = concentration of superoxide anion radical, mole/L

$[O_3]$ = concentration of ozone, mole/L

At pseudo–steady state approximation (i.e., all of the net formation rates of radicals (Eq. 2-2 to Eq. 2-5) are set to be zero), the following expression of the concentration of the hydroxyl radical (Eq. 2-6) can be obtained.

$$[HO\bullet]_{ss} = \frac{2k_1[HO_2^-][O_3]}{k_{12}[HCO_3^-]+k_{13}[R]+k_{14}[NOM]+k_{15}[Cl^-]+k_{16}[CO_3^{2-}]+k_{17}[Fe^{2+}]+k_{18}[Mn^{2+}]} \qquad (2\text{-}6)$$

where $[HO\bullet]_{ss}$ = pseudo-steady-state concentration of hydroxyl radical, mole/L.

The pseudo–steady state assumption is also invoked for the formation rate of ozone in the liquid phase and the reaction rate of ozone can be written as below:

$$r_{O_3} = k_L a \left(\frac{P_{O_3}}{H_{O_3}} - [O_3] \right) - k_1[HO_2^-][O_3] - k_3[O_2^-\bullet][O_3] = 0 \qquad (2\text{-}7)$$

where k_{La} = overall mass transfer coefficient for ozone, s^{-1}

P_{O3} = partial pressure of ozone in inlet gas, atm

H_{O3} = Henry's law constant for ozone, atm·L/mole

Substituting equation 2-5 and 2-7 into equation 2-6, the following expression is obtained:

$$[HO\bullet]_{ss} = \frac{k_L a \left(\dfrac{P_{O_3}}{H_{O_3}} \right)}{k_{10}[HO_2^-]+k_{11}[H_2O_2]+k_{12}[HCO_3^-]+k_{13}[R]+k_{14}[NOM]+k_{15}[Cl^-]+k_{16}[CO_3^{2-}]+k_{17}[Fe^{2+}]+k_{18}[Mn^{2+}]}$$

$$(2\text{-}8)$$

The model can be further simplified with the assumption that the concentration of the hydroxyl radical does not change with time and is equal to the initial value expressed as below:

$$[HO\bullet]_{ss,0} = \frac{k_L a \left(\dfrac{P_{O_3}}{H_{O_3}} \right)}{k_{10}[HO_2^-]_0+k_{11}[H_2O_2]_0+k_{12}[HCO_3^-]_0+k_{13}[R]_0+k_{14}[NOM]_0+k_{15}[Cl^-]_0+k_{16}[CO_3^{2-}]_0+k_{17}[Fe^{2+}]_0+k_{18}[Mn^{2+}]_0}$$

$$(2\text{-}9)$$

where $[HO\bullet]_{ss,0}$ = initial steady-state concentration of HO•, mole/L

$[HO_2^-]_0$ = initial concentration of conjugate base or anion of hydrogen peroxide, mole/L

$[H_2O_2]_0$ = initial concentration of hydrogen peroxide, mole/L

$[HCO_3^-]_0$ = initial concentration of bicarbonate, mole/L

$[R]_0$ = initial concentration of target organic compound, mole/L

$[NOM]_0$ = initial concentration of NOM, mole/L

$[Cl^-]_0$ = initial concentration of chloride ion, mole/L

$[CO_3^{2-}]_0$ = initial concentration of carbonate, mole/L

$[Fe^{2+}]_0$ = initial concentration of two value iron ion, mole/L

$[Mn^{2+}]_0$ = initial concentration of two value manganese ion, mole/L

Thus, a pseudo–first-order consumption rate law of the target compound can be obtained:

$$r_R = -k_R[R] \tag{2-10}$$

$$k_R = k_{13}[HO\bullet]_{ss,0} \tag{2-11}$$

where k_R is the pseudo–first-order reaction rate constant of target compound R, s^{-1}, and k_{13} is the second order rate constant between target compound R and the hydroxyl radical, L/mole•s. This model, termed the simplified pseudo–steady state (Sim-PSS) model, may overestimate the consumption rate of the target compound, because it assumes that the hydroxyl radical concentration is constant and equal to the initial value. For a more comprehensive model of the AOP that does not assume pseudo–steady state or a constant pH, users can refer to the AdOx^{TM} (version 1.0), developed by Crittenden *et al.*(1999).

There is a tool available to calculate the aqueous phase hydroxyl radical reaction rate constant, which is k_{13} in Table 2.1. Users can refer to the Group Contribution Method developed by Minakata *et al.* (2009). This method can predict a large variety of aqueous phase hydroxyl radical reaction rate constants. A Microsoft Excel spread sheet and a compiled FORTRAN program are given for this purpose. This material is available free of charge via the Internet at http://pubs.acs.org/doi/suppl/10.1021/es900956c.

2.1.2   Reactors

Effluent concentration of the target compound can be written from mass balances for the target compound in tanks-in-series (TIS) reactor, completely mixed batch reactor (CMBR), completely mixed flow reactor (CMFR), plug flow reactor (PFR), and dispersed flow reactor (DFR) in a closed system.

$$[R] = \frac{[R]_0}{(1 + k_R \dfrac{\tau}{n})^n} \qquad \text{(TIS)} \tag{2-12}$$

$$[R] = [R]_0 e^{-k_R t} \qquad \text{(CMBR)} \tag{2-13}$$

$$[R] = \frac{[R]_0}{(1 + k_R \tau)} \qquad \text{(CMFR)} \tag{2-14}$$

$$[R] = [R]_0 e^{-k_R \tau} \qquad \text{(PFR)} \tag{2-15}$$

$$[R] = \frac{[R]_0 \, 4a \exp(Pe/2)}{(1+a)^2 \exp(aPe/2) - (1-a)^2 \exp(-aPe/2)} \qquad \text{(DFR)} \qquad (2\text{-}16)$$

$$(a = \sqrt{1 + 4k_R\tau/\text{Pe}})$$

where $[R]_0$ is the influent concentration of the target compound, $[R]$ is the effluent concentration of the target compound, τ is the hydraulic retention time of the reactor, k_R is the pseudo–first-order reaction rate constant of the target compound, n is the number of tanks for TIS, and Pe is the Peclet number for DFR.

2.1.3 Energy Efficiency per Removal of Order

The energy efficiency per removal of order (EE/O) values of the batch system (i.e., CMBR) and the flow system (i.e., TIS, CMFR, PFR, DFR) can be calculated from the equations below, respectively.

For batch system

$$\text{EE/O} = \frac{\dfrac{k_L a \times \dfrac{P_{O_3}}{H_{O_3}} \times V \times \dfrac{10^3 \text{ liter}}{\text{meter}^3} \times M_{O_3} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{O3} \times t \times \dfrac{60 \text{ seconds}}{\text{minutes}}}{\eta} + C_{H2O2} \times V \times E_{H2O2} \times \dfrac{0.0022 \text{ lb}}{\text{gram}}}{V \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad (2\text{-}17)$$

where k_{La} = overall mass transfer coefficient for ozone, s^{-1}

P_{O3} = partial pressure of ozone in inlet gas, atm

H_{O3} = Henry's law constant for ozone, atm·L/mole

V = reactor volume, m^3

M_{O3} = molecular weight of ozone, g/mole

E_{O3} = energy use to produce O_3, kWh/lb

t = reaction time for batch reactor, minute

η = transfer efficiency of ozone contactor , dimensionless

C_{H2O2} = total concentration of H_2O_2 added into the reactor, mg/L

E_{H2O2} = energy use to produce H_2O_2, kWh/lb;

C_i = influent concentration of the target compound, mg/L

C_f = effluent concentration of the target compound, mg/L

For flow system

$$EE/O = \frac{\dfrac{k_L a \times \dfrac{P_{O_3}}{H_{O_3}} \times V \times \dfrac{10^3 \text{ liter}}{\text{meter}} \times M_{O_3} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{O3}}{\eta} + C_{H2O2} \times Q \times E_{H2O2} \times \dfrac{0.0022 \text{ lb}}{\text{gram}}}{Q \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad (2\text{-}18)$$

where $Q = $ flow rate of the reactor, m^3/s

2.2 H₂O₂ Added after O₃ Addition Model

There is occasion where gaseous ozone is injected at first place and solely ozonation takes place for obtaining Ct disinfection credits and then hydrogen peroxide is added for the destruction of target organic compound. The waste water will continuously flow through an ozone contactor for disinfection and a H_2O_2/O_3 reactor for the degradation of target compound. In this model, we only simulate the H_2O_2/O_3 reactor, where hydrogen peroxide is added to water that has a certain concentration of ozone (i.e., $[O_3]_{res}$).

2.2.1 Elementary Reactions

The elementary reactions involved, the formation rates of radicals and the calculation process of the concentration of the hydroxyl radical are the same with the simplified pseudo-steady state H_2O_2/O_3 model. The steady state hydroxyl radical concentration is given by the following equation using $[O_3]_{res}$:

$$[HO\bullet]_{ss} = \frac{2k_1[HO_2^-][O_3]_{res}}{k_{12}[HCO_3^-] + k_{13}[R] + k_{14}[NOM] + k_{15}[Cl^-] + k_{16}[CO_3^{2-}] + k_{17}[Fe^{2+}] + k_{18}[Mn^{2+}]} \qquad (2\text{-}19)$$

The model can be further simplified with the assumption that the concentration of the hydroxyl radical does not change with time and is equal to the initial value, expressed as below:

$$[HO\bullet]_{ss,0} = \frac{2k_1[HO_2^-]_0[O_3]_{res}}{k_{12}[HCO_3^-]_0 + k_{13}[R]_0 + k_{14}[NOM]_0 + k_{15}[Cl^-]_0 + k_{16}[CO_3^{2-}]_0 + k_{17}[Fe^{2+}]_0 + k_{18}[Mn^{2+}]_0} \qquad (2\text{-}20)$$

Thus a pseudo–first-order reaction rate of the target compound can be same as in equations (2-10) and (2-11), respectively.

2.2.2 Reactors

The mass balance equations for the target compound in various types of reactors are the same with the simplified pseudo-steady state H_2O_2/O_3 model. The process where hydrogen peroxide is added in the presence of dissolved ozone is for particularly flow reactors, and therefore, we only consider flow system (i.e., CMFR, TIS, PFR, and DIS) for this process.

2.2.3 Energy Efficiency per Removal of Order

As mentioned above, we only consider flow system for the EE/O calculations. The EE/O value for the flow system can be calculated by

$$EE/O = \frac{\dfrac{Q \times C_{O3} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{O3}}{\eta} + Q \times C_{H2O2} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{H2O2}}{Q \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad (2\text{-}21)$$

where Q = flow rate of the reactor, m³/s

C_{O3} = concentration of ozone in liquid phase, mg/L

E_{O3} = energy use to produce O_3, kWh/lb

η = transfer efficiency of the ozone contactor, dimensionless

C_{H2O2} = total concentration of H_2O_2 added into the reactor, mg/L

E_{H2O2} = energy use to produce H_2O_2, kWh/lb

C_i = influent concentration of the target compound, mg/L

C_f = effluent concentration of the target compound, mg/L

2.3 Ultraviolet with Hydrogen Peroxide Model

The H_2O_2/UV is a process in which hydrogen peroxide is injected into a reactor equipped with UV light. The photolysis of hydrogen peroxide will produce hydroxyl radical that can degrade target compounds.

2.3.1 Elementary Reactions

The elementary reactions of the H_2O_2/UV process involved in this model are reactions 8-18 in Table 2.1. From the elementary reactions involved in this model, the net formation rate of the hydroxyl radical can be obtained as below:

$$r_{HO\bullet} = 2\Phi_{H_2O_2} P_{U\text{-}V} f_{H_2O_2} - k_{10}[HO\bullet][HO_2^-] - k_{11}[HO\bullet][H_2O_2] - k_{12}[HO\bullet][HCO_3^-]$$
$$- k_{13}[HO\bullet][R] - k_{14}[HO\bullet][NOM] - k_{15}[HO\bullet][Cl^-] - k_{16}[HO\bullet][CO_3^{2-}] \qquad (2\text{-}22)$$
$$- k_{17}[HO\bullet][Fe^{2+}] - k_{18}[HO\bullet][Mn^{2+}]$$

where $r_{HO\bullet}$ = net formation rate of hydroxyl radical, mole/L•s

Φ_{H2O2} = quantum yield of hydrogen peroxide, mole/einstein

$P_{U\text{-}V}$ = UV light intensity at wavelength λ, einstein/(L•s)

f_{H2O2} = fraction of light absorbed by hydrogen peroxide, dimensionless

A = absorbance, dimensionless

k_{10} = second order rate constant between hydroxyl radical and anion of hydrogen peroxide,

L/mole•s

k_{11} = second order rate constant between hydroxyl radical and hydrogen peroxide, L/mole•s

k_{12} = second order rate constant between hydroxyl radical and bicarbonate, L/mole•s

k_{13} = second order rate constant between hydroxyl radical and target organic compound R, L/mole•s

k_{14} = second order rate constant between hydroxyl radical and NOM, L/mole•s

k_{15} = second order rate constant between hydroxyl radical and chloride ion, L/mole•s

k_{16} = second order rate constant between hydroxyl radical and carbonate, L/mole•s

k_{17} = second order rate constant between hydroxyl radical and Fe(II), L/mole•s

k_{18} = second order rate constant between hydroxyl radical and Mn(II), L/mole•s

$[HO•]$ = concentration of hydroxyl radical, mole/L

$[HO_2^-]$ = concentration of anion of hydrogen peroxide, mole/L

$[H_2O_2]$ = concentration of hydrogen peroxide, mole/L

$[HCO_3^-]$ = concentration of bicarbonate, mole/L

$[R]$ = concentration of target compound R, mole/L

$[NOM]$ = concentration of NOM, mole carbon/L

$[Cl^-]$ = concentration of chloride ion, mole/L

$[CO_3^{2-}]$ = concentration of carbonate, mole/L

$[Fe^{2+}]$ = concentration of Fe^{2+}, mole/L

$[Mn^{2+}]$ = concentration of Mn^{2+}, mole/L

After invoking the pseudo–steady state approximation, steady-state hydroxyl radical concentration is:

$$[HO•]_{ss} = \frac{2\Phi_{H_2O_2} P_{U-V} f_{H_2O_2}}{k_{10}[HO_2^-] + k_{11}[H_2O_2] + k_{12}[HCO_3^-] + k_{13}[R] + k_{14}[NOM] + k_{15}[Cl^-] + k_{16}[CO_3^{2-}] + k_{17}[Fe^{2+}] + k_{18}[Mn^{2+}]}$$

(2-23)

This model can be further simplified with the assumption that the concentration of the hydroxyl radical does not change with time and is equal to the initial value expressed as below:

$$[HO\bullet]_{ss,0} = \frac{2\Phi_{H_2O_2} P_{U\text{-}V} f_{H_2O_2}}{k_{10}[HO_2^-]_0 + k_{11}[H_2O_2]_0 + k_{12}[HCO_3^-]_0 + k_{13}[R]_0 + k_{14}[NOM]_0 + k_{15}[Cl^-]_0 + k_{16}[CO_3^{2-}]_0 + k_{17}[Fe^{2+}]_0 + k_{18}[Mn^{2+}]_0}$$

(2-24)

where $[HO\bullet]_{ss,0}$ = initial pseudo–steady state concentration of hydroxyl radical, mole/L

$[H_2O_2]_0$ = initial concentration of hydrogen peroxide, mole/L

$[HCO_3^-]_0$ = initial concentration of bicarbonate, mole/L

$[R]_0$ = initial concentration of target compound R, mole/L

$[NOM]_0$ = initial concentration of NOM, mole/L

$[Cl^-]_0$ = initial concentration of chloride ion, mole/L

$[CO_3^{2-}]_0$ = initial concentration of carbonate, mole/L

$[Fe^{2+}]_0$ = initial concentration of Fe^{2+}, mole/L

$[Mn^{2+}]_0$ = initial concentration of Mn^{2+}, mole/L

The photolysis of the target compound can be neglected because of the low reaction rate. Thus a pseudo–first-order reaction rate of the target compound can be same as in equations (2-10) and (2-11), respectively.

2.3.2 Reactors

The mass balance equations for the target compound in various reactors are the same with the simplified pseudo-steady state H_2O_2/O_3 model. The effluent concentrations of target compound can be estimated using equations from (2-12) to (2-16) for reactor types of TIS, CMBR, CMFR, PFR, and DFR, respectively.

2.3.3 Energy Efficiency per Removal of Order

The EE/O values of the flow system and the batch system can be calculated by

$$EE/O = \frac{P + Q \times \dfrac{3600 \text{ seconds}}{\text{hours}} \times C_{H2O2} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{H2O2}}{Q \times \dfrac{3600 \text{ seconds}}{\text{hours}} \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad \text{(For flow system)} \qquad (2\text{-}25)$$

$$EE/O = \frac{P \times t \times \dfrac{1 \text{ hour}}{60 \text{ minutes}} + V \times C_{H2O2} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{H2O2}}{V \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad \text{(For batch system)} \qquad (2\text{-}26)$$

where P = total lamp power, kW

13

Q = flow rate of the reactor, m^3/s

C_{H2O2} = total concentration of H_2O_2 added into the reactor, mg/L

E_{H2O2} = energy use to produce H_2O_2, kWh/lb

V = reactor volume, m^3

t = reaction time for the batch system, min

C_i = influent concentration of the target compound, mg/L

C_f = effluent concentration of the target compound, mg/L

2.4 Ozone Rc Model

During ozonation, hydroxyl radical will be produced when aqueous phase ozone reacts with NOM. Since hydroxyl radical is a highly reactive oxidant for degradation of target compound, the target compound will be degraded by two ways: direct reacting with ozone and reacting with hydroxyl radical produced by ozone and NOM. It is important to simulate both degradation pathways for the purpose of adequate prediction of degradation and optimization of the process.

2.4.1 Elementary Reactions

The destruction rate of the target compound can be expressed as below:

$$r_R = -k_{O3}[R][O_3] - k_{HO\bullet}[HO\bullet][R] \tag{2-27}$$

where r_R = rate of disappearance of the target compound R, mole/L · s

$[O_3]$ = concentration of ozone in aqueous phase, mole/L

$[R]$ = concentration of target compound R, mole/L

$[HO\cdot]$ = concentration of hydroxyl radical, mole/L

$k_{HO\bullet}$ = second order rate constants between hydroxyl radical and target compound, L/mole · s

k_{O3} = second order rate constants between ozone and target compound, L/ mole · s

It is reported that the ratio of the concentration of the hydroxyl radical to the concentration of ozone in aqueous phase, termed as R_c (=$[HO\bullet]/[O_3]$), is relatively constant (10^{-7}-10^{-9}) during the decomposition process in the presence of NOM (Elovitz and von Gunten, 1999).

The loss of ozone and the decomposition of the target compound can be described by pseudo–first-order reaction and second order reaction, respectively:

$$r_{O_3} = -k[O_3] \tag{2-28}$$

$$r_R = -(k_{O_3} + k_{HO\bullet}R_c)[O_3][R] \tag{2-29}$$

where r_{O3} = rate of loss of ozone in aqueous phase, mole/L·s

k = pseudo-first-order rate constant for ozone, s^{-1}

r_R = rate of disappearance of target compound R, mole/L·s

R_c = ratio of hydroxyl radical concentration to aqueous phase ozone concentration, dimensionless

$k_{HO\cdot}$ = second order rate constants between hydroxyl radical and target compound, L/mole·s

k_{O3} = second order rate constants between ozone and target compound, L/mole·s

2.4.2 Reactors

The mass balance equations for ozone and target compound in various reactors are the same with the simplified pseudo-steady state H$_2$O$_2$/O$_3$ model. The effluent concentrations of target compound can be estimated using equations from (2-12) to (2-16) for reactor types of TIS, CMBR, CMFR, PFR, and DFR, respectively.

2.4.3 Energy Efficiency per Removal of Order

The EE/O values of the batch system and the flow system can be calculated by

$$EE/O = \frac{Q \times C_{O3} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{O3}}{\eta \times Q \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad \text{(For flow system)} \qquad (2\text{-}30)$$

$$EE/O = \frac{V \times C_{O3} \times \dfrac{0.0022 \text{ lb}}{\text{gram}} \times E_{O3}}{\eta \times V \times \log\left(\dfrac{C_i}{C_f}\right)} \qquad \text{(For batch system)} \qquad (2\text{-}31)$$

where Q = flow rate of the liquid stream of the reactor for flow system, m^3/s

V = volume of the reactor, m^3

C_{O3} = ozone concentration in the liquid phase, mg/L

E_{O3} = energy use to produce O$_3$, kWh/lb

η = transfer efficiency of the ozone contactor, dimensionless

C_i = influent concentration of the target compound, mg/L

C_f = effluent concentration of the target compound, mg/L

3. Instruction for Microsoft Excel Spread Sheet

This part gives an instruction of the supplemental Microsoft Excel spread sheet associated with the simplified pseudo-steady state models.

3.1 Input Data

To run a simulation, some properties or operational parameters should be directly entered into the appropriate places. The following discussion will elaborate on how to enter the parameters and the information necessary for a model simulation run.

There are three steps for entering inputs: (1) entering general inputs in general input column on the "Input Page", (2) choosing one kind of model and entering relative parameters for a specific model type in corresponding column on the "Input Page", (3) choosing one type of reactor and entering relative parameters for a specific reactor type in corresponding page following the "Input Page".

3.1.1 Inputs for All Types of Reactors

This part has five columns divided by general inputs and inputs for different kinds of models applied.

(1) General inputs for four models

This column contains background parameters and properties which can be used by all of the four models. The general inputs include alkalinity, DOC, the reaction rate constant of DOC with the hydroxyl radical, the concentration of chloride ion, the concentration of Fe(II), the concentration of Mn(II), pH, the concentration of the target compound, the molecular weight of the target compound, the HO· reaction rate constant with the target compound, the total reactor volume, and the flow rate of the reactor (this input can be neglected when users use completely mixed batch reactor(CMBR)).

General Inputs For Four Models	
pH	7.5
Concentration of target compound, mg/L	0.1
Molecular weight of target compound, g/mole	131
$k_{HO·}$ with target compound, $M^{-1}s^{-1}$ (See *GCM)	4.20E+09
Concentration of chloride ion, mg/L	2.00
Concentration of iron ion (II), mg/L	0.05
Concentration of manganese ion (II), mg/L	0.10
Alkalinity, mg/L as $CaCO_3$	400
DOC, mg/L	0.7
$k_{HO·}$ with DOC, $M^{-1}s^{-1}$	3.90E+08
Total reactor volume, m^3	10
Flow rate, m^3/s (Can be neglected when using CMBR)	0.025

Figure 3.1. General inputs of simplified pseudo-steady state models.

(2) Inputs for H₂O₂/O₃ model

When using the H_2O_2/O_3 model, you should enter the total H_2O_2 dosage, the overall mass transfer coefficient for O_3, the partial pressure of ozone, the energy use for O_3 production, the energy use for H_2O_2 production, and the transfer efficiency of ozone contactor, apart from entering the general inputs. (Users can refer to Appendix B for recommended values of the transfer efficiency of ozone contactor and the energy use for H_2O_2 production and O_3 production.)

Inputs For H₂O₂/O₃ Model	
Total H_2O_2 dosage, mg/L	1
Overall mass transfer coefficient for O_3, s^{-1}	0.00060
Partial pressure of ozone, atm	0.07
Energy use for O_3 production, kWh/lb	5
Transfer efficiency of ozone contactor	0.8
Energy use for H_2O_2 production, kWh/lb	4.9

Figure 3.2. Inputs for H₂O₂/O₃ model.

(3) Inputs for H₂O₂ added after O₃ addition model

For this model, you should specify the total H_2O_2 dosage, the initial ozone concentration at the point of H_2O_2 addition, the transfer efficiency of ozone contactor, the energy use for O_3 production, and the energy use for H_2O_2 production. (Users can refer to Appendix B for recommended values of the transfer efficiency of ozone contactor and the energy use for H_2O_2 production and O_3 production.)

Inputs For H₂O₂ Added After O₃ Addition Model	
Total H2O2 dosage, mg/L	1.4
Initial ozone concentration at the point of H_2O_2 addition, mg/L	5.5
Transfer efficiency of ozone contactor	0.8
Energy use for O_3 production, kWh/lb	5
Energy use for H_2O_2 production, kWh/lb	4.9

Figure 3.3. Inputs for H₂O₂ added after O₃ addition model.

(4) Inputs for H₂O₂/UV model

For this kind of model, you should specify the total H_2O_2 dosage, the wavelength of light used in this model, the number of lamps, the lamp power, the lamp efficiency, the energy use for H_2O_2 production (users can refer to Appendix B for a recommended value of the energy use for H_2O_2 production), and the absorbance of NOM at 254 nm for a cell path length of 1 cm.

Inputs For H$_2$O$_2$/UV Model	
Total H$_2$O$_2$ dosage, mg/L	85
Wavelength of light, nm	254
Number of lamps	12
Lamp power, kW	15
Electronical efficiency	0.2
Energy use for H$_2$O$_2$ production, kWh/lb	4.9
Absorbance of NOM at 254 nm for a cell path length of 1 cm	0.300

Figure 3.4. Inputs for H$_2$O$_2$/UV model.

(5) Inputs for O$_3$ R$_c$ model

For this kind of model, you should specify the initial ozone concentration, the second order reaction rate constant between ozone and the target compound (which can be ignored for the most part because the direct oxidation of ozone is usually negligible as compared to hydroxyl radical), the R$_c$ value (users can refer to Appendix B for a recommended value of the R$_c$), the ozone pseudo–first-order reaction rate constant, the transfer efficiency of ozone contactor, the energy use for ozone production (users can refer to Appendix B for a recommended value of the transfer efficiency of ozone contactor and the energy use for O$_3$ production).

Inputs For O$_3$ R$_c$ Model	
Initial ozone concentration, mg/L	1.3
k_{O3} with target compound, M^{-1}s^{-1}	17
R$_c$(=[HO•]/[O$_3$])	1.00E-07
Ozone pseudo-first-order reactioin rate constant, min^{-1}	0.1
Transfer efficiency of ozone contactor	0.8
Energy use for O$_3$ production, kWh/lb	5

Figure 3.5. Inputs for O$_3$ R$_c$ model.

3.1.2 Inputs for Specific Reactors

This spread sheet contains five kinds of reactors: completely mixed batch reactor (CMBR), plug flow reactor (PFR), completely mixed flow reactor (CMFR) as ideal reactors and tanks in series (TIS) reactor, dispersed flow reactor (DFR) in closed systems as non-ideal reactors. You should enter reactor parameters in the corresponding pages following the "Input Page."

For the CMBR, you should specify the reaction time for CMBR on the "CMBR Page".

Inputs of complete mixing batch reactor(CMBR)
reaction time for CMBR(min)	3

Figure 3.6. Input for CMBR.

For the TIS reactor, you should specify the number of completely mixed flow reactors on the "TIS Page".

Inputs of Tank-in-series(TIS) reactor

number of completely mixed flow reactors	4

Figure 3.7. Input for TIS.

For the DFR reactor, you should specify the Peclet number on the "DFR Page".

Inputs of dispersed flow model closed system(DFR)

Peclet number(Pe)	35

Figure 3.8. Input for DFR.

3.2   Output Data

The output data of each kind of reactor can be found on the corresponding page, which contains the effluent concentrations of the target compound and EE/O values for all four models.

Outputs of Tanks-in-series (TIS) Reactor

Types of models	Effluent concentration of target compound, mg/L	EE/O, kWh/m^3 . order of removal	EE/O, kWh/kgal . order of removal
H_2O_2/O_3 model	0.057	0.165	0.624
H_2O_2 added after O_3 addition model	0.091	0.263	0.997
H_2O_2/UV model	0.010	0.601	2.275
O_3 R_c model	0.041	0.026	0.098

Figure 3.9. Outputs for TIS.

4.   Instruction for MathCAD Files

This part gives an instruction of the supplemental MathCAD files associated with the pseudo-steady state models.

4.1   Input Data

To run a simulation, some properties or operational parameters should be directly entered in the appropriate places. The following discussion will elaborate on how to enter the parameters and information necessary for a model simulation run.

There are four steps for entering inputs: (1) choosing one kind of model and opening relative MathCAD file, (2) entering general inputs in the general inputs column, (3) entering inputs specific to the chosen model in the corresponding model column, (4) choosing one type of reactor and entering relative parameters in the corresponding reactor column.

4.1.1 General Inputs for Four Models

This column contains background parameters and properties which can be used by all of the four models. The general inputs include alkalinity, DOC, reaction rate constant of DOC with hydroxyl radical, concentration of chloride ion, concentration of Fe(II), concentration of Mn(II), pH, concentration of target compound, molecular weight of target compound, HO· reaction rate constant with target compound, and total reactor volume.

General Inputs:

pH	$pH := 7.5$
Concentration of target compound, mg/L	$\rho := 0.2$
Molecular weight of target compound, g/mole	$M := 131.389$
$k_{HO\cdot}$ with target compound, $M^{-1}S^{-1}$ (see *GCM)	$k9 := 4.2 \cdot 10^9$
Concentration of chloride ion, mg/L	$Clm := 35.5 \cdot 10^{-3}$
Concentration of Fe(II), mg/L	$Fem := 56 \cdot 10^{-3}$
Concentration of Mn(II), mg/L	$Mnm := 55 \cdot 10^{-3}$
Alkalinity, mg/L as $CaCO_3$	$Alk := 400$
DOC, mg/L	$DOC := 0.7$
$k_{HO\cdot}$ with DOC, $M^{-1}s^{-1}$	$k10 := 3.9 \cdot 10^8$
Total reactor volume, m^3	$v := 5.5$

Figure 4.1. General Inputs of pseudo-steady state models.

4.1.2 Inputs for H_2O_2/O_3 Model

When using the H_2O_2/O_3 model, you should enter the total H_2O_2 dosage, overall mass transfer coefficient for O_3, partial pressure of ozone, energy use for O_3 production, energy use for H_2O_2 production, and transfer efficiency of ozone contactor, apart from entering the general inputs. (Users can refer to Appendix B for recommended values of the transfer efficiency of ozone contactor and the energy use for H_2O_2 production and O_3 production.)

```
Inputs For H₂O₂/O₃ Model:

Total H₂O₂ dosage, mg/L                          H2O2t := 3

Overall mass transfer coefficient for O₃, s⁻¹    KLa := 0.0007

Partial pressure of ozone, atm                   PO3 := 0.1

Energy use for O₃ production, kWh/lb             E1 := 5

Energy use for H₂O₂ production, kWh/lb          E3 := 4.9

Transfer efficiency of ozone contactor           η := 0.8
```

Figure 4.2. Inputs for H_2O_2/O_3 model.

4.1.3 Inputs for H_2O_2 Added after O_3 Addition Model

When using the H_2O_2 added after O_3 addition model, you should specify the total H_2O_2 dosage, the initial ozone concentration at the point of H_2O_2 addition, the transfer efficiency of ozone contactor, the energy use for O_3 production, and the energy use for H_2O_2 production. (Users can refer to Appendix B for recommended values of the transfer efficiency of ozone contactor and the energy use for H_2O_2 production and O_3 production.)

```
Inputs For H₂O₂ Added After O₃ Addition Model

Total H₂O₂ dosage, mg/L                          H2O2t := 3.81

Initial ozone concentration at the point of      O3res := 12
H₂O₂ addition, mg/L

Energy use for O₃ production, kWh/lb             E1 := 5

Energy use for H₂O₂ production, kWh/lb          E3 := 4.9

Transfer efficiency of ozone contactor           η := 0.8
```

Figure 4.3. Inputs for H_2O_2 added after O_3 addition model.

4.1.4 Inputs for H_2O_2/UV Model

When using the H_2O_2/UV model, you should specify the wavelength of light used in this model, the number of lamps, the lamp power, the lamp efficiency, the absorbance of NOM at 254 nm for a cell path length of 1cm, and the energy use for H_2O_2 production (users can refer to Appendix B for a recommended value of the energy use for H_2O_2 production).

Inputs For H₂O₂/UV Model

Total H₂O₂ dosage, mg/L	$H2O2t := 40$
Wavelength of light, nm	$\lambda := 254$
Number of lamps	$nlamp := 20$
Lamp power, kW	$P := 15$
Lamp efficiency	$\eta := 0.3$
Absorbance of NOM at 254 nm for a cell length of 1cm	$a := 0.0137$
Energy use for H₂O₂ production, kWh/lb	$E3 := 4.9$

Figure 4.4. Inputs for H₂O₂/UV model.

4.1.5 Inputs for O₃ Rₒ Model

When using O₃ Rₒ model, you should specify the initial ozone concentration, the reaction rate constant between ozone and target compound (which can be ignored for the most part because the direct oxidation of ozone is usually negligible as compared to hydroxyl radical), the Rₒ value (users can refer to Appendix B for a recommended value of the Rₒ), the ozone pseudo-first-order reaction rate constant, the transfer efficiency of ozone contactor, and the energy use for O₃ production (users can refer to Appendix B for a recommended value of the transfer efficiency of ozone contactor and the energy use for O₃ production).

Inputs For O₃ Rₒ Model

Initial ozone concentration, mg/L	$O3init := 4$
k_{O3} with target compound, M⁻¹s⁻¹	$kO3 := 17$
R_c (=[HO·]/[O₃])	$C := 10^{-7}$
Ozone pseudo-first-order reaction rate constant, min⁻¹	$k := 0.1$
Energy use for O₃ production, kWh/lb	$E1 := 5$
Transfer efficiency of ozone contactor	$\eta := 0.8$

Figure 4.5. Inputs for O₃ Rₒ model.

4.1.6 Inputs for Specific Reactors

These MathCAD files contain three kinds of reactors: CMBR, PFR and CMFR. You should enter reactor parameters in the corresponding columns.

For CMBR, you should specify the reaction time for CMBR on "CMBR" column.

CMBR
Reaction time for CMBR, min   tCMBR := 0.58

Figure 4.6. Inputs for CMBR.

For CMFR or PFR, you should specify the flow rate of the reactor on "CMFR or PFR" column.

CMFR or PFR
Flow rate, m³/s   Q := 0.025

Figure 4.7. Inputs for CMFR or PFR.

4.2 Calculation
The calculation part lists detailed calculation process.

3. Calculation:

$HO2_0 := H2O2t \div 34 \div 10^3 \cdot 10^{(pH-pKa3)}$ $HO2_0 = 1.323 \times 10^{-9}$ $NOM_0 := DOC \div 12 \div 10^3$ $NOM_0 = 5.833 \times 10^{-5}$

$H2O2_0 := H2O2t \div 34 \div 10^3 - HO2_0$ $H2O2_0 = 2.353 \times 10^{-5}$ $Cl_0 := Clm \cdot 10^{-6} \div 35.5$ $Cl_0 = 1 \times 10^{-8}$

$HCO3_0 := \dfrac{\left(Alk \div 50 \div 10^3\right)}{\left(1 + 2 \cdot \dfrac{10^{-pKa2}}{10^{-pH}}\right)}$ $HCO3_0 = 3.987 \times 10^{-3}$ $Fe_0 := Fem \cdot 10^{-6} \div 56$ $Fe_0 = 1 \times 10^{-8}$

$Mn_0 := Mnm \cdot 10^{-6} \div 55$ $Mn_0 = 1 \times 10^{-8}$

$CO3_0 := \dfrac{\left(Alk \div 50 \div 10^3 - HCO3_0\right)}{2}$ $CO3_0 = 6.32 \times 10^{-6}$ $A := \left(k2 + k3 \cdot \dfrac{10^{-pKa3}}{10^{-pH}}\right)$

$R_0 := \dfrac{\rho \cdot 10^{-6}}{M}$ $R_0 = 1.522 \times 10^{-6}$ $B := \left(k7 + k6 \cdot \dfrac{10^{-pKa2}}{10^{-pH}}\right)$

$C := \left(k4 + k5 \cdot \dfrac{10^{-pKa3}}{10^{-pH}}\right)$

$x_0 := H2O2_0$ $x_1 := R_0$ $x_2 := NOM_0$ $x_3 := Fe_0$ $x_4 := Mn_0$ $x_5 := Cl_0$ $x_6 := HCO3_0$

Figure 4.8. Calculation part.

4.3 Output Data
The output data of each kind of reactor can be found on corresponding part, which contains the effluent concentration profiles of main species and the EE/O value profiles for the chosen process.
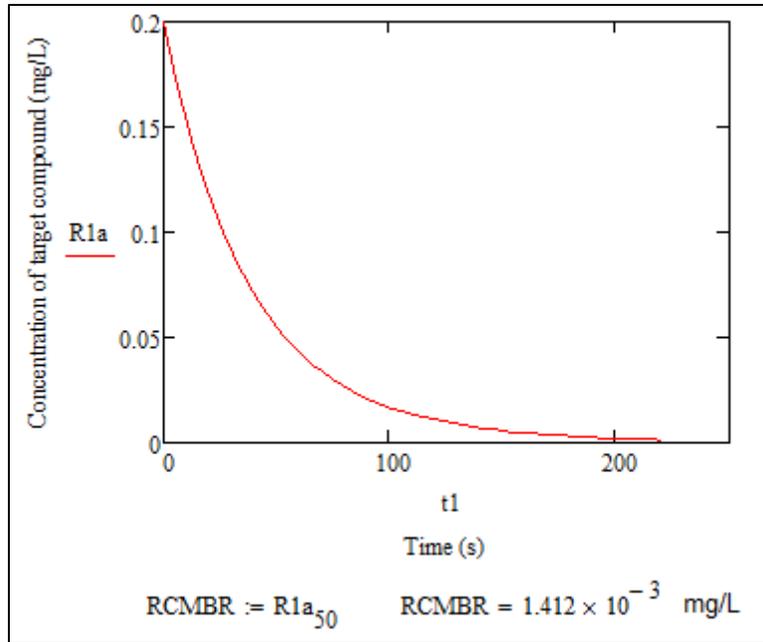
(a)
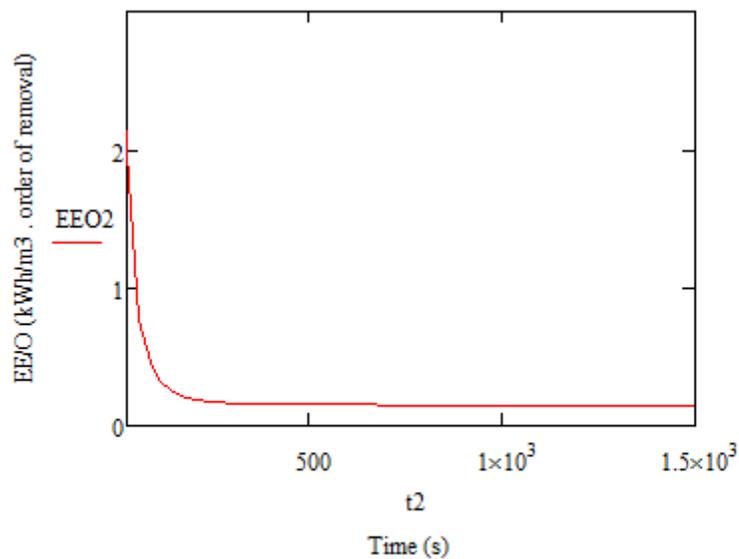
$$EEOCMFR := EEO2_{50} = 0.151 \quad kWh/m^3 . \text{ order of removal}$$

$$EEOCMFR1 := EEOCMFR \div 264.2 \cdot 10^3 = 0.571 \quad kWh/10^3 \, gal . \text{ order of removal}$$

(b)

Figure 4.9. Outputs part. (a) Effluent concentration profile of target compound. (b) EE/O value profile.

5. Sample Problems

In this section, we will give several sample problems to aid users to understand how to use our models to optimize the designs of AOPs. The optimization processes of using simplified pseudo-steady state models and pseudo-steady state models are similar. For simplicity, in this part we only give three samples for the pseudo-steady state models, which include H_2O_2/O_3 model, H_2O_2 added after O_3 addition model, and UV/H_2O_2 model.

5.1 Sample Problem for Pseudo-Steady State H_2O_2/O_3 Model

5.1.1 Problem Statement

A small city discovered that one of its well was contaminated with 200 μg/L TCE. In order to use the well as drinking water source, the TCE needs to be reduced below its maximum contaminant level (MCL), which is 5 μg/L. During normal pumping operations, the well produces about 0.025 m³/s water. The pH, alkalinity and DOC concentration are 7.5, 400 mg/L as $CaCO_3$, and 0.7 mg/L, respectively.

Compound	Influent concentration		HO• Rate Constant, $k_{HO•}$, L/mole•s
	(μg/L)	(μmol/L)	
TCE	200	1.52	4.20×10^9
DOC	700		3.90×10^8

In this case, we will design a H_2O_2/O_3 process that can remove the target compound below its MCL and determine the optimum operational parameters including H_2O_2 dosage and overall mass transfer coefficient for O_3. A plug flow reactor (PFR) will be designed, considering the follow information: (1) the partial pressure of ozone is 0.1 atm, (2) the Henry's law constant for O_3 at 23° C is 83.9 atm·L/mole, (3) the influent concentration of chloride ion is 2 mg/L, (4) the influent concentration of iron ion(II) is 0.05 mg/L, (5) the influent concentration of manganese ion(II) is 0.1 mg/L, (6) the energy use for O_3 production is 5 kWh/lb, (7) the energy use for H_2O_2 production is 4.9 kWh/lb, and (8) the transfer efficiency of the ozone contactor is 80%.

5.1.2 Solution

Before we optimize our design of the H_2O_2/O_3 process, we should determine our treatment objective of the target pollutant, TCE. According to the MCL of TCE, which is 5 μg/L, we will set the treatment objective to be 3 μg/L, which is below the MCL. A plug flow reactor (PFR) will be designed in this example. For simplicity, we will use a fixed hydraulic retention time of 4 min. However, in practice, users can use different hydraulic retention times and determine the optimum value by comparing the EE/O for each retention time.

To determine the optimum operational parameters, we will find different pairs of H_2O_2 dosages and overall mass transfer coefficient for O_3 that can achieve the desired removal of TCE. By comparing the calculated EE/O values for all pairs, we will get the optimum H_2O_2 dosages and overall mass transfer coefficient for O_3. The detailed way of determining the operational parameters is shown as below.

(1) Determine the reactor volume

With a hydraulic retention time of 4 min, the volume of the reactor can be calculated by
$V = Q \times \tau = 0.025 \times 4 \times 60 = 6$ m³,
where Q is the flow rate and τ is the hydraulic retention time.

(2) Determine the overall mass transfer coefficient for O_3

To evaluate the impact of ozone mass transfer on the performance of H_2O_2/O_3 process, we will model overall mass transfer coefficients for O_3 (k_La) ranging from 5.6×10^{-4} s^{-1} to 10^{-3} s^{-1} as listed in Table 6.1.

(3) Determine the H_2O_2 dosage for each overall mass transfer coefficient for O_3

For each k_La value, the proper H_2O_2 dosage to achieve the treatment objective is determined and the corresponding EE/O value is calculated, which are listed in Table 6.1. We should notice that the proper H_2O_2 dosage mentioned above might not be easily found. Users can first try a relatively large range of H_2O_2 dosage and then gradually narrow the searching range of H_2O_2 dosage until users find the proper H_2O_2 dosage with a satisfied accuracy. At the same time, with an ozone partial pressure of 0.1 atm, the molar ratio of H_2O_2 dosage to the ozone dosage that transfers from the gas phase to the liquid phase can also be calculated by

$$r_{[H_2O_2]/[O_3]} = \frac{C_{H_2O_2} \times \dfrac{1 \text{ gram}}{10^3 \text{ milligram}}}{M_{H2O2} \times k_La \times \dfrac{P}{H} \times \tau \times \dfrac{60 \text{ seconds}}{\text{minutes}}}$$

where $r_{[H2O2]/[O3]}$ is the molar ratio of H_2O_2 dosage to the ozone dosage transferred to liquid phase, mM/mM; C_{H2O2} is the concentration of H_2O_2 in the liquid phase, mg/L; k_La is the overall mass transfer coefficient for O_3, s^{-1}, P is the partial pressure of ozone in the gas phase, atm; H is the Henry's law constant for O_3, atmL/mol; and τ is the hydraulic retention time for PFR, min. From Table 5.1, we can see that the $r_{[H2O2]/[O3]}$ are modeled ranging from 0.39 to 1.08.

Table 5.1. Simulation results of various operational conditions for H_2O_2/O_3 process that achieves the treatment objective

Run NO.	k_La (10^{-4}s^{-1})	H_2O_2 dosage (mM)	$R_{[H2O2]/[O3]}$ (mM/mM)	EE/O (kWh/m^3. order of removal)
1	5.6	0.17	1.08	0.092
2	5.7	0.15	0.94	0.089
3	6.0	0.13	0.76	0.088
4	6.5	0.12	0.64	0.090
5	7.0	0.11	0.57	0.096
6	7.5	0.11	0.53	0.101
7	8.0	0.11	0.49	0.105
8	9.0	0.11	0.44	0.117
9	10.0	0.11	0.39	0.127

To give users a detailed instruction about how to use our supplied MathCAD file for H_2O_2/O_3 process to get the effluent concentration of target compound and EE/O values for a single run, we will run NO.3 in Table 5.1 as an example in the following part.

Get start
Open the MathCAD file for H_2O_2/O_3 process and the main window will appear.

1. Inputs

General Inputs:

pH	$pH := 7.5$
Concentration of target compound, mg/L	$\rho := 0.2$
Molecular weight of target compound, g/mole	$M := 131.389$
$k_{HO\cdot}$ with target compound, $M^{-1}S^{-1}$ (see *GCM)	$k9 := 4.2 \cdot 10^{9}$
Concentration of chloride ion, mg/L	$Clm := 0.355 \cdot 10^{-3}$
Concentration of Fe(II), mg/L	$Fem := 0.56 \cdot 10^{-3}$
Concentration of Mn(II), mg/L	$Mnm := 0.55 \cdot 10^{-3}$
Alkalinity, mg/L as CaCO$_3$	$Alk := 400$
DOC, mg/L	$DOC := 0.7$
$k_{HO\cdot}$ with DOC, $M^{-1}s^{-1}$	$k10 := 3.9 \cdot 10^{8}$

Inputs For H$_2$O$_2$/O$_3$ Model:

Total H$_2$O$_2$ dosage, mg/L	$H2O2t := 20$
Overall mass transfer coefficient for O$_3$, s^{-1}	$KLa := 0.0007$
Partial pressure of ozone, atm	$PO3 := 0.17$
Energy use for O$_3$ production, kWh/lb	$E1 := 5$
Ozone flow rate, mL/min	$QO3 := 4 \cdot 10^{4}$
Energy use for H$_2$O$_2$ production, kWh/lb	$E3 := 4.9$

Figure 5.1. Main window of H$_2$O$_2$/O$_3$ model.

General input

The general inputs are specified in the left corner of the input part shown in Figure 5.1. The pH is 7.5; the concentration of target compound (TCE) is 200 µg/L; the molecular weight of target compound (TCE) is 131.389 g/mole; $k_{HO\cdot}$ with target compound is $4.20 \times 10^9\ M^{-1}s^{-1}$; concentrations of chloride ion, iron ion(II), and manganese ion(II) is 2 mg/L, 0.05 mg/L, and 0.1 mg/L, respectively; alkalinity is 400 mg/L as CaCO$_3$; DOC concentration is 0.7 mg/L; $k_{HO\cdot}$ with DOC is $3.9 \times 10^8\ M^{-1}s^{-1}$; and the total reactor volume is 6 m^3.

General Inputs:

pH	$pH := 7.5$
Concentration of target compound, mg/L	$\rho := 0.2$
Molecular weight of target compound, g/mole	$M := 131.389$
$k_{HO\cdot}$ with target compound, $M^{-1}S^{-1}$	$k9 := 4.2 \cdot 10^9$
(see *GCM)	
Concentration of chloride ion, mg/L	$Clm := 2$
Concentration of Fe(II), mg/L	$Fem := 0.05$
Concentration of Mn(II), mg/L	$Mnm := 0.1$
Alkalinity, mg/L as $CaCO_3$	$Alk := 400$
DOC, mg/L	$DOC := 0.7$
$k_{HO\cdot}$ with DOC, $M^{-1}s^{-1}$	$k10 := 3.9 \cdot 10^8$
Total reactor volume, m^3	$v := 6$

Figure 5.2. General input portion.

Inputs for H_2O_2/O_3 model

The inputs for H_2O_2/O_3 model are specified in the middle part of the main window shown in Figure 5.1. The total H_2O_2 dosage is 0.13 mM (4.4 mg/L); the overall mass transfer coefficient for O_3 is $6 \times 10^{-4} s^{-1}$; the partial pressure of ozone is 0.1 atm; the energy use for O_3 production is 5 kWh/lb O_3; the transfer efficiency of ozone contactor is 0.8; and the energy use for H_2O_2 production is 4.9 kWh/lb.

Inputs For H_2O_2/O_3 Model:

Total H_2O_2 dosage, mg/L	$H2O2t := 4.4$
Overall mass transfer coefficient for O_3, s^{-1}	$KLa := 0.0006$
Partial pressure of ozone, atm	$PO3 := 0.1$
Energy use for O_3 production, kWh/lb	$E1 := 5$
Energy use for H_2O_2 production, kWh/lb	$E3 := 4.9$
Transfer efficiency of ozone contactor	$\eta := 0.8$

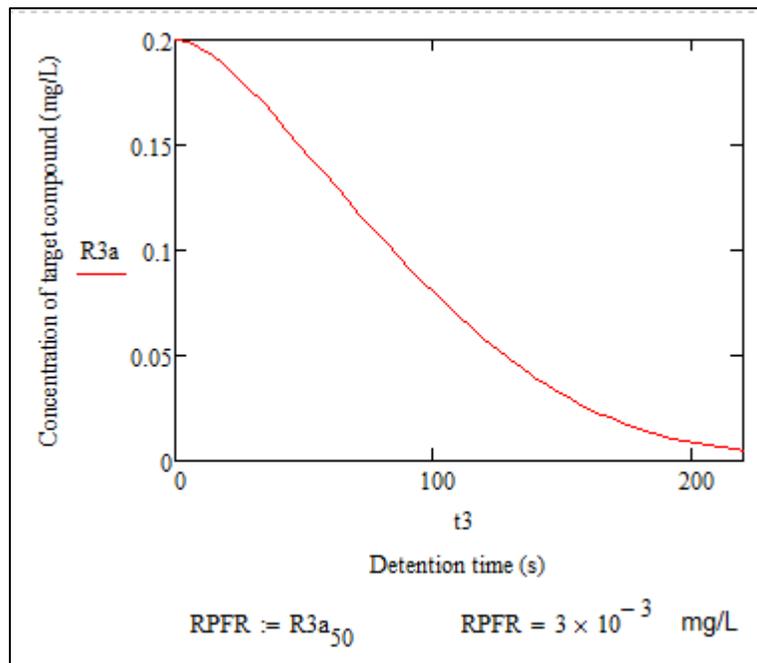**Figure 5.3. H_2O_2/O_3 model input portion.**

Inputs for reactor properties

In this solution, a PFR system will be designed. The inputs for PFR are specified in CMFR or PFR column of inputs portion. The flow rate is 0.025 m³/s.

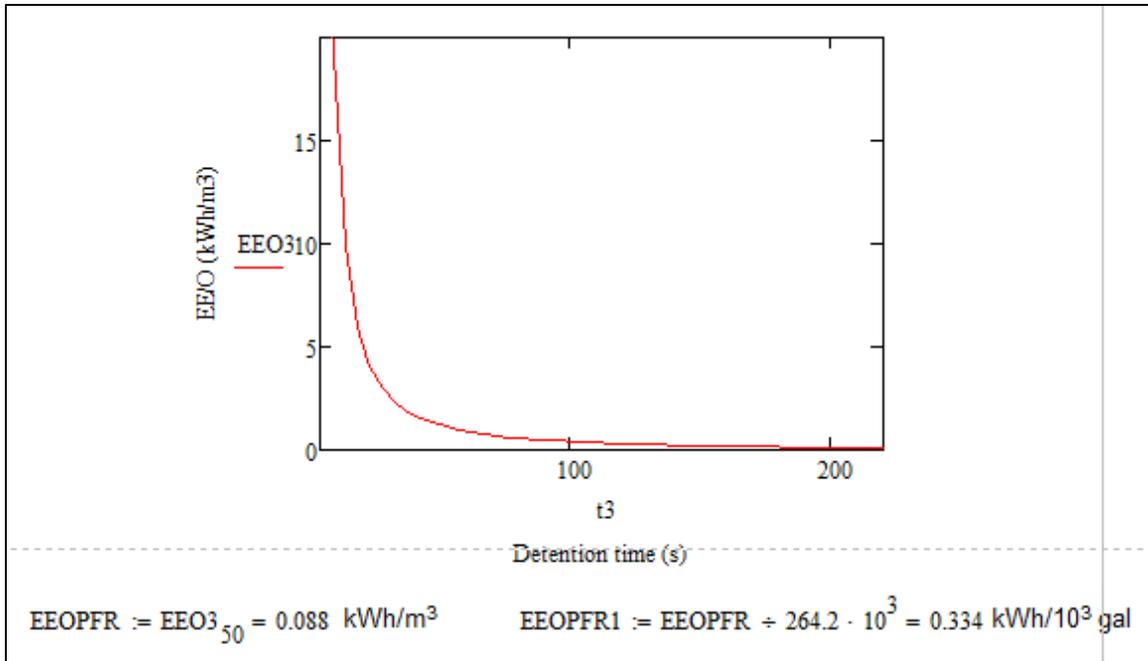| CMFR or PFR	
Flow rate, m³/s	$Q := 0.025$

Figure 5.4. PFR input portion.

Viewing results

We can obtain the effluent concentration profile of target compound and EE/O value of the process from the "output of PFR" part. In this solution, the effluent concentration of TCE is 3 µg/L and the EE/O for H_2O_2/O_3 model is 0.088 kWh/m³ or 0.334 kWh/kgal.

$$RPFR := R3a_{50} \qquad RPFR = 3 \times 10^{-3} \quad mg/L$$

(a)

$$EEOPFR := EEO3_{50} = 0.088 \ kWh/m^3 \qquad EEOPFR1 := EEOPFR \div 264.2 \cdot 10^3 = 0.334 \ kWh/10^3 \ gal$$

(b)

Figure 5.5. H$_2$O$_2$/O$_3$ model output portion of PFR. (a) Effluent concentration profile of target compound. (b) EE/O value profile.

(4) Determine the optimum overall mass transfer coefficient of O$_3$ and H$_2$O$_2$ dosage

We can compare the EE/O to get the optimum H$_2$O$_2$ dosages and overall mass transfer coefficients for O$_3$. The EE/O values of all cases in Table 5.1 are plotted in Figure 5.6. We can see that increasing the $r_{[H2O2]/[O3]}$ value will decrease the EE/O value at low $r_{[H2O2]/[O3]}$ levels and increase the EE/O values at high $r_{[H2O2]/[O3]}$ levels. The lowest EE/O value is achieved in run NO.3, when $r_{[H2O2]/[O3]}$ is 0.76, H$_2$O$_2$ dosage is 0.13 mM (4.4 mg/L), and k_La is 0.0006 s^{-1}.
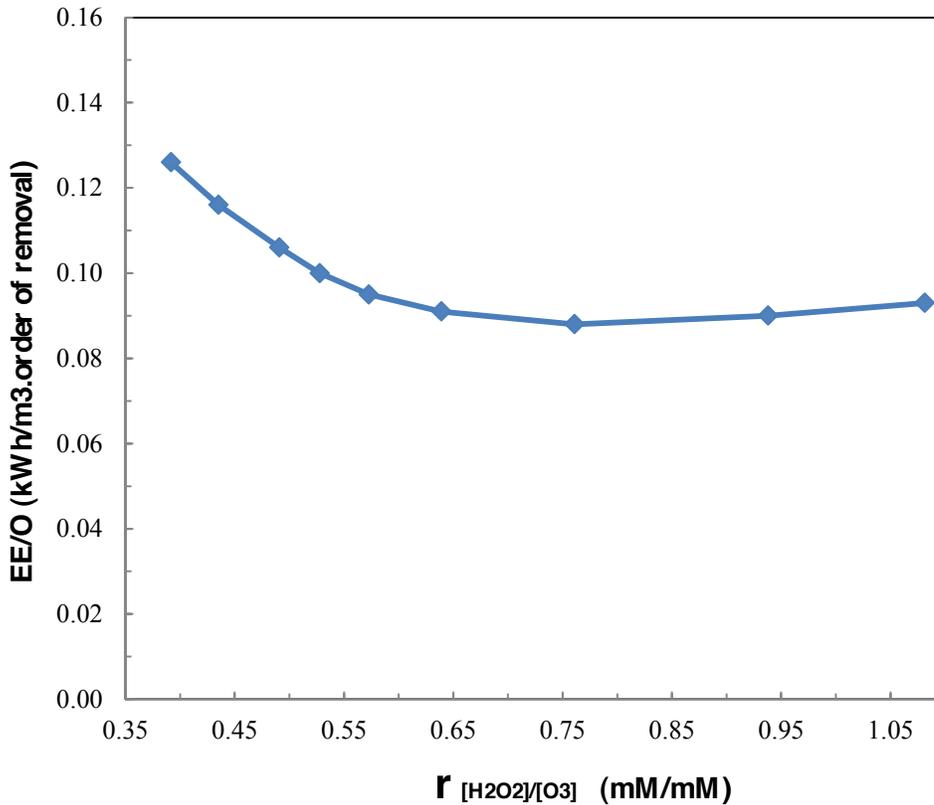
30

Figure 5.6. The impact of $r_{[H2O2]/[O3]}$ on the EE/O values of H_2O_2/O_3 process.

(5) Conclusion

In this example, a PFR will be designed.
The optimized design parameters are as below:

Volume of reactor: 6 m^3
Overall mass transfer coefficients for O_3: 0.0006 s^{-1}
H_2O_2 dosage: 4.4 mg/L

5.2 Sample Problem for Pseudo-Steady State H_2O_2 Added after O_3 Addition Model

5.2.1 Problem Statement

A small city discovered that one of its well was contaminated by some chemical pollutants. Ozone was first added to the water to disinfect it, and when certain Ct disinfection credit was obtained, it is useful to estimate the potential of adding H_2O_2 to remove target pollutant, TCE. The concentration of TCE is 50 μg/L. In order to use the water as drinking water, the TCE needs to be reduced below its maximum contaminant level (MCL), which is 5 μg/L. During normal pumping operations, the well produces about 0.025 m^3/s water. The pH, alkalinity and DOC concentration are 7.5, 400 mg/L as $CaCO_3$, and 0.7 mg/L, respectively.

Compound	Influent concentration		HO• Rate Constant, $k_{HO•}$, L/mole•s
	(μg/L)	(μmol/L)	
TCE	50	0.38	$4.20×10^9$
DOC	700		$3.90×10^8$

In this example, we will design a H_2O_2 added after O_3 addition system that can remove the target compound below its MCL and determine the optimum operational parameters including initial dissolved O_3 concentration at the point of H_2O_2 addition and the H_2O_2 dosage. A plug flow reactor (PFR) will be designed, considering the follow information: (1) the influent concentration of chloride ion is 0.5 mg/L, (2) the influent concentration of iron ion(II) is 0.05 mg/L, (3) the influent concentration of manganese ion(II) is 0.1 mg/L, (4) the energy use for O_3 production is 5 kWh/lb, (5) the energy use for H_2O_2 production is 4.9 kWh/lb, and (6) the transfer efficiency of ozone contactor is 80%.

5.2.2 Solution

Before we optimize our design of the H_2O_2 added after O_3 addition process, we should determine our treatment objective of the target pollutant, TCE. According to the MCL of TCE, which is 5 μg/L, we will set the treatment objective to be 3 μg/L, which is below the MCL. A plug flow reactor (PFR) will be designed in this example. For simplicity, we will use a fixed hydraulic retention time of 4 min. However, in practice, users can use different hydraulic retention times and determine the optimum value by comparing the EE/O for each retention time.

To determine the optimum operational parameters, we will find different pairs of H_2O_2 dosages and initial dissolved O_3 concentration that can achieve the desired removal of TCE. By comparing the calculated EE/O values for all pairs, we will get the optimum H_2O_2 dosages and initial dissolved O_3 concentration. The detailed way of determining the operational parameters is shown as below.

(1) Determine the reactor volume

With a hydraulic retention time of 4 min, the volume of the reactor can be calculated by
$V = Q × \tau = 0.025 × 4 × 60 = 6 \text{ m}^3$,
where Q is the flow rate and τ is the hydraulic retention time.

(2) Determine initial dissolved O_3 concentration

We will model the initial dissolved O_3 concentration at the point of H_2O_2 addition ($[O_3]_{diss}$) ranging from 1.5 mg/L (0.03 mM) to 5.0 mg/L (0.10 mM) as listed in Table 6.2.

(3) Determine the H_2O_2 dosage for each initial dissolved O_3 concentration

For each $[O_3]_{diss}$, the proper H_2O_2 dosage to achieve the treatment objective is determined and the corresponding EE/O value is calculated, which are listed in Table 5.2. We should notice that the proper H_2O_2 dosage mentioned above might not be easily found. Users can first try a relatively large range of H_2O_2 dosage and then gradually narrow the searching range of H_2O_2 dosage until users find the proper H_2O_2 dosage with a satisfied accuracy. At the same time, we can calculate the molar ratio of H_2O_2 dosage to $[O_3]_{diss}$ ($[H_2O_2]/[O_3]_{diss}$). From Table 5.2, we can see that we simulate the $[H_2O_2]/[O_3]_{diss}$ value ranging from 0.14 to 1.32.

Table 5.2. Simulation results of various operational conditions for H_2O_2 added after O_3 addition process that achieves the treatment objective

Run NO.	$[O_3]_{diss}$	H_2O_2 dosage	$[H_2O_2]/[O_3]_{diss}$	EE/O

	(mg/L)	(mg/L)	(mM/mM)	(kWh/m^3.order of removal)
1	1.5	1.4	1.32	0.0284
2	1.6	1.2	1.06	0.0272
3	1.7	1.1	0.91	0.0265
4	1.8	1.0	0.78	0.0264
5	1.9	0.9	0.67	0.0274
6	2.0	0.8	0.56	0.0294
7	2.5	0.6	0.34	0.0338
8	3.0	0.6	0.28	0.0369
9	3.5	0.5	0.20	0.0427
10	4.0	0.5	0.18	0.0487
11	4.5	0.5	0.16	0.0549
12	5.0	0.5	0.14	0.0604

To give users a detailed instruction about how to use our supplied MathCAD file for H_2O_2 added after O_3 addition process to get the effluent concentration of target compound and EE/O values for a single run, we will run the NO.6 in Table 5.2 as an example in the following part.

Get start
Open the MathCAD file for H_2O_2 added after O_3 addition process and the main window will appear.

1. Inputs

General Inputs:

pH	pH := 7.5
Concentration of target compound, mg/L	ρ := 0.2
Molecular weight of target compound, g/mole	M := 131.389
k_{HO}. with target compound, M-1S-1	k9 := 4.2 · 10^9
(see *GCM)	
Concentration of chloride ion, mg/L	Clm := 0.355 · 10^{-3}
Concentration of Fe(II), mg/L	Fem := 0.56 · 10^{-3}
Concentration of Mn(II), mg/L	Mnm := 0.55 · 10^{-3}
Alkalinity, mg/L as CaCO$_3$	Alk := 400
DOC, mg/L	DOC := 0.7
k_{HO}. with DOC, M-1s-1	k10 := 3.9 · 10^8

Inputs For H_2O_2 Added After O_3 Model

Total H_2O_2 dosage, mg/L	H2O2t := 25
Residual ozone concentration at the point of H_2O_2 addition, mg/L	O3res := 37
Overall mass transfer coefficient for O_3, s-1	KLa := 0.0007
Partial pressure of ozone, atm	PO3 := 0.07
Ozone flow rate, mL/min	QO3 := 4 · 10^4
Energy use for O_3 production, kWh/lb	E1 := 5
Energy use for H_2O_2 production, kWh/lb	E3 := 4.9

Figure 5.7. Main input window of H_2O_2 added after O_3 addition model.

General input
The general inputs are specified in the left corner of the main window shown in Figure 5.7. The pH is 7.5; the concentration of target compound (TCE) is 50 µg/L; the molecular weight of target compound is 131.389 g/mole; k_{HO}. with target compound is 4.20×10^9 M^{-1}s^{-1}; concentrations of chloride ion, iron ion(II), and manganese ion(II) are 0.5 mg/L, 0.05 mg/L, and 0.1 mg/L, respectively; alkalinity is 400 mg/L as CaCO$_3$; DOC concentration is 0.7 mg/L; k_{HO}. with DOC is 3.90×10^8 M^{-1}s^{-1}; and the total reactor volume is 6 m^3.

General Inputs:

pH	$pH := 7.5$
Concentration of target compound, mg/L	$c := 0.05$
Molecular weight of target compound, g/mole	$M := 131.389$
$k_{HO\cdot}$ with target compound, $M^{-1}S^{-1}$	$k9 := 4.2 \cdot 10^9$
(see *GCM)	
Concentration of chloride ion, mg/L	$Clm := 0.5$
Concentration of Fe(II), mg/L	$Fem := 0.05$
Concentration of Mn(II), mg/L	$Mnm := 0.1$
Alkalinity, mg/L as $CaCO_3$	$Alk := 400$
DOC, mg/L	$DOC := 0.7$
$k_{HO\cdot}$ with DOC, $M^{-1}s^{-1}$	$k10 := 3.9 \cdot 10^8$
Total reactor volume, m^3	$v := 6$

Figure 5.8. General input portion.

Inputs for H_2O_2 added after O_3 addition model

The inputs for H_2O_2 added after O_3 addition model are specified in the middle part of the main window shown in Figure 5.7. The H_2O_2 dosage is 0.8 mg/L; the initial ozone concentration at the point of H_2O_2 addition is 2 mg/L; the transfer efficiency of ozone contactor is 0.8; the energy use for O_3 production is 5 kWh/lb; and the energy use for H_2O_2 production is 4.9 kWh/lb.

Inputs For H_2O_2 Added After O_3 Addition Model

Total H_2O_2 dosage, mg/L	$H2O2t := 0.8$
Initial ozone concentration at the point of H_2O_2 addition, mg/L	$O3res := 2$
Energy use for O_3 production, kWh/lb	$E1 := 5$
Energy use for H_2O_2 production, kWh/lb	$E3 := 4.9$
Transfer efficiency of ozone contactor	$\eta := 0.8$

Figure 5.9. H_2O_2 added after O_3 addition model input portion.

Inputs for reactor properties

In this solution, a PFR system will be designed. The inputs for PFR are specified in CMFR or PFR
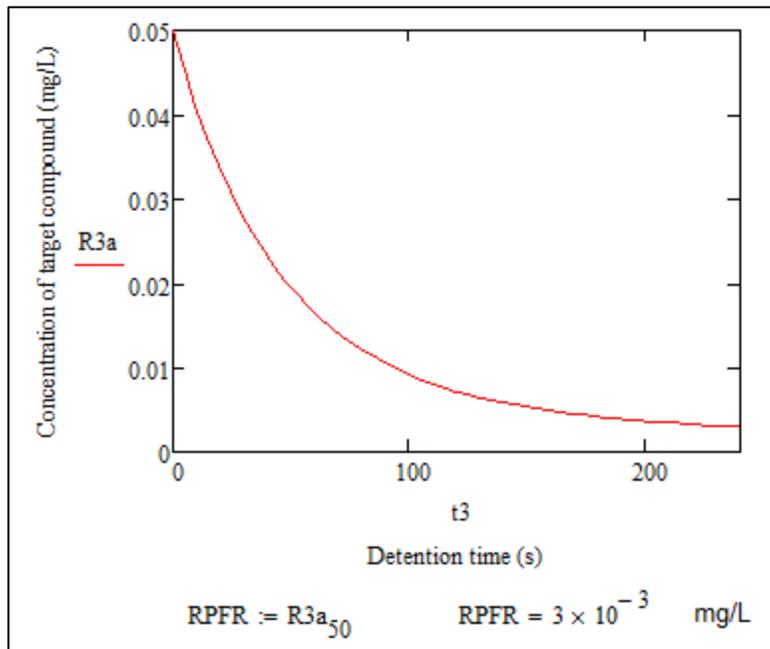
column of inputs portion. The flow rate is 0.025 m^3/s.

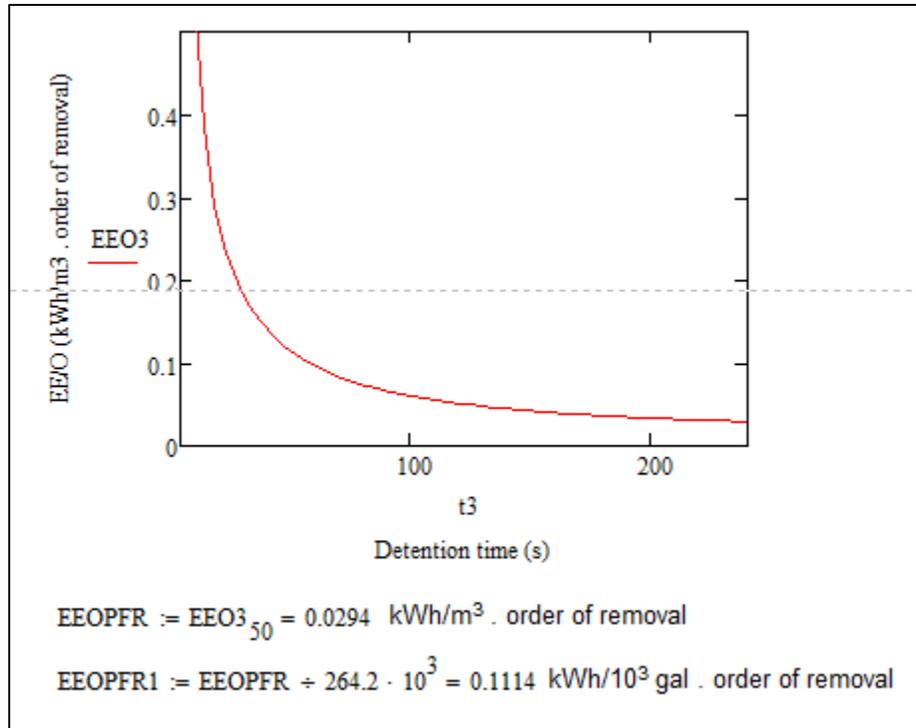| CMFR or PFR	
Flow rate, m^3/s	$Q := 0.025$

Figure 5.10. PFR input portion.

Viewing results

We can obtain the effluent concentration profile of target compound and EE/O value of the process from the "output of PFR" part. In this solution, the effluent concentration of TCE is 3 µg/L. The EE/O for H$_2$O$_2$ added after O$_3$ addition model is 0.0294 kWh/m^3.order of removal or 0.1114 kWh/kgal.order of removal.

$$RPFR := R3a_{50} \qquad RPFR = 3 \times 10^{-3} \quad mg/L$$

(a)

$EEOPFR := EEO3_{50} = 0.0294 \ kWh/m^3 \cdot order \ of \ removal$

$EEOPFR1 := EEOPFR \div 264.2 \cdot 10^3 = 0.1114 \ kWh/10^3 \ gal \cdot order \ of \ removal$

(b)

Figure 5.11. H_2O_2 added after O_3 addition model output portion of PFR. (a) Effluent concentration profile of target compound. (b) EE/O value profile.

(4) Determine the optimum initial dissolved O_3 concentration and H_2O_2 dosage

We can then compare the EE/O to get the optimum H_2O_2 dosages and initial dissolved O_3 concentration at the point of H_2O_2 addition. The EE/O values of all cases in Table 5.2 are plotted in Figure 5.12. We can see that increasing the $[H_2O_2]/[O_3]_{diss}$ value will decrease the EE/O value at low $[H_2O_2]/[O_3]_{diss}$ levels and increase the EE/O values at high $[H_2O_2]/[O_3]_{diss}$ levels. The lowest EE/O value is achieved in run NO.4, when $[H_2O_2]/[O_3]_{diss}$ is 0.78, H_2O_2 dosage is 1.0 mg/L, and initial dissolved O_3 concentration is 1.8 mg/L.
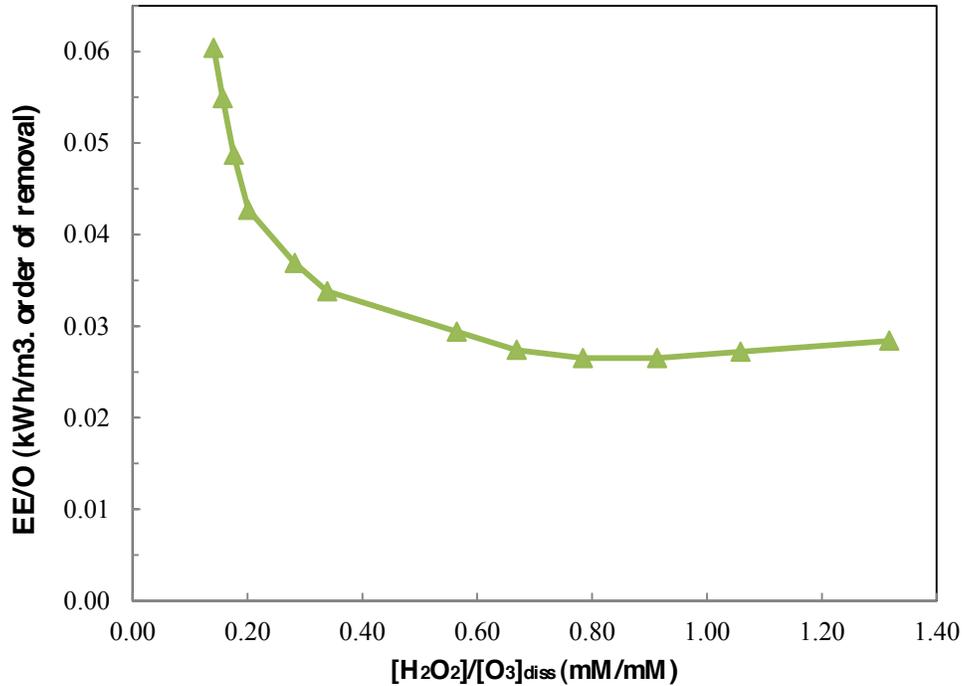
Figure 5.12. The impact of molar ratio of H_2O_2 dosage to initial dissolved ozone concentration on the EE/O values of H_2O_2 added after O_3 addition process.

(5) Conclusion

In this example, a PFR will be designed.
The design parameters are as below:

Volume of reactor: 6 m^3
Initial dissolved O_3 concentration at the point of H_2O_2 addition: 1.8 mg/L
H_2O_2 dosage: 1.0 mg/L

5.3 Sample Problem for Pseudo-Steady-State H_2O_2/UV Model

5.3.1 Problem Statement

A small city discovered that one of its well was contaminated with 200 μg/L TCE. In order to use the well as drinking water source, the TCE needs to be reduced below its maximum contaminant level (MCL), which is 5 μg/L. The pH, alkalinity, and DOC concentration are 6.8, 400 mg/L as $CaCO_3$, and 0.7 mg/L, respectively. The following table shows some important physicochemical properties of H_2O_2, TCE and NOM.

Compound	MW, g/mole	OH Radical rate constant, k_{OH}, L/mole•s	Extinction coefficient, ε, L/mole•cm	Quantum yield, ϕ
TCE	131.389	4.20×10^9	Ignored	0

NOM	NA	3.90×10^8	0.0196	0
H_2O_2	34.015	-	19.6	0.5

In this example, we will design a UV/H_2O_2 system that can remove the target compound below its MCL and determine the optimum operational parameters including H_2O_2 dosage, and total lamp power. A plug flow reactor (PFR) will be designed, considering the follow information: (1) for simplicity, the UV-light intensity is monochromatic at 254 nm and that the lamps are 20% efficient, (2) the influent concentration of chloride ion is 2 mg/L, (3) the influent concentration of iron ion(II) is 0.05 mg/L, (4) the influent concentration of manganese ion(II) is 0.1 mg/L, (5) the absorbance of NOM at 254 nm for a cell path length of 1cm is 0.014, and (6) the energy use for H_2O_2 production is 4.9 kWh/lb.

5.3.2   Solution

Before we optimize our design of the UV/H_2O_2 process, we should determine our treatment objective of the target pollutant, TCE. According to the MCL of TCE, which is 5 μg/L, we will set the treatment objective to be 3 μg/L, which is below the MCL. A plug flow reactor (PFR) will be designed in this example. For simplicity, we will use a fixed hydraulic retention time of 4 min. However, in practice, users can use different hydraulic retention times and determine the optimum value by comparing the EE/O for each retention time.

To determine the optimum operational parameters, we will find different pairs of H_2O_2 dosages and total lamp power that can achieve the desired removal of TCE. By comparing the calculated EE/O values for all pairs, we will get the optimum H_2O_2 dosages and total lamp power. Because the residual H_2O_2 for the UV/H_2O_2 process might be detrimental to the environment if they are directly discharged into the public water system, we should also consider the residual H_2O_2 concentration for all simulation when we optimize our operational parameters. The detailed way of determining the operational parameters is shown as below.

(1) Determine the reactor volume

With a hydraulic retention time of 4 min, the volume of the reactor can be calculated by
$V = Q \times \tau = 0.025 \times 4 \times 60 = 6 \text{ m}^3$,
where Q is the flow rate and τ is the hydraulic retention time.

(2) Determine the total lamp power

We will model the total lamp power ranging from 20 kW to 45 kW as listed in Table 5.3. With a reactor volume of 6 m³, the total lamp power is related to the UV intensity by the equation below

where P_{U-V} is the UV intensity, einsteins/L·s; P is the total lamp power, kW; η is the lamp efficiency, dimensionless; N_{av} is the Avogadro's number, mole^{-1}; V is the reactor volume, m³; h is the Planck's constant, J/Hz; and ν is the light frequency, Hz. We should notice that in practice, the lamp efficiency may vary for different options of UV lamp. However, in this sample problem, we assume the lamp efficiency is 20% for simplicity. We can calculate the UV intensity corresponding to each total lamp power as shown in Table 5.3.

Table 5.3 The UV intensity corresponding to various total lamp power

Run NO.	Total lamp	UV intensity

	power (kW)	(10^{-6} eins./L·s)
1	20	0.39
2	21	0.41
3	22	0.43
4	24	0.47
5	30	0.59
6	40	0.79
7	45	0.89

(3) Determine the H_2O_2 dosage for each total lamp power

For each total lamp power, the proper H_2O_2 dosage to achieve the treatment objective is determined, and the corresponding residual H_2O_2 concentration and EE/O value are recorded in Table 5.4. We should notice that the proper H_2O_2 dosage mentioned above might not be easily found. Users can first try a relatively large range of H_2O_2 dosage and then gradually narrow the searching range of H_2O_2 dosage until users find the proper H_2O_2 dosage with a satisfied accuracy.

Table 5.4. Simulation results of various operational conditions for UV/H_2O_2 process that achieves the treatment objective

Run NO.	Total lamp power (kW)	UV intensity (10^{-6} eins./L·s)	H_2O_2 dosage (mg/L)	Residual H_2O_2 concentration (mg/L)	EE/O (kWh/m^3.order of removal)
1	20	0.39	26.9	21.2	0.281
2	21	0.41	24.2	18.6	0.271
3	22	0.43	22.1	16.5	0.265
4	24	0.47	19.0	13.5	0.258
5	30	0.59	13.8	8.5	0.264
6	40	0.79	10.0	4.9	0.303
7	45	0.89	8.8	3.9	0.327

To give users a detailed instruction about how to use our supplied MathCAD file for UV/H_2O_2 process to get the effluent concentration of target compound and EE/O values for a single run, we will run the NO.5 in Table 5.4 as an example in the following part.

Get start
Open the MathCAD file for UV/H_2O_2 process and the main window will appear.

1. Inputs

General Inputs:

pH	$pH := 6.8$
Concentration of target compound, mg/L	$\rho := 0.2$
Molecular weight of target compound, g/mole	$M := 131.389$
$k_{HO\cdot}$ with target compound, $M^{-1}S^{-1}$ (see *GCM)	$k9 := 4.2 \cdot 10^{9}$
Concentration of chloride ion, mg/L	$Clm := 2$
Concentration of Fe(II), mg/L	$Fem := 0.05$
Concentration of Mn(II), mg/L	$Mnm := 0.1$
Alkalinity, mg/L as $CaCO_3$	$Alk := 400$
DOC, mg/L	$DOC := 0.7$
$k_{HO\cdot}$ with DOC, $M^{-1}s^{-1}$	$k10 := 3.9 \cdot 10^{8}$

Inputs For H_2O_2/UV Model

Total H_2O_2 dosage, mg/L	$H2O2t := 13.77$
Wavelength of light, nm	$\lambda := 254$
Number of lamps	$nlamp := 2$
Lamp power, kW	$P := 15$
Lamp efficiency	$\eta := 0.2$
Absorbance of NOM at 254 nm for a cell length of 1cm	$a := 0.014$
Energy use for H_2O_2 production, kWh/lb	$E3 := 4.9$

Figure 5.13. Main input window.

General input

The general inputs are specified in the upper left corner of the main input window, as shown in Figure 5.13. The pH is 6.8; the concentration of the target compound (TCE) is 200 µg/L; the molecular weight of the target compound is 131 g/mole; the $k_{HO\cdot}$ with target compound is $4.20 \times 10^{9}\,M^{-1}s^{-1}$; the concentrations of chloride ion, iron ion(II), and manganese ion(II) are 2 mg/L, 0.05 mg/L, and 0.1 mg/L, respectively; the alkalinity is 400 mg/L as $CaCO_3$; the DOC concentration is 0.7 mg/L; the $k_{HO\cdot}$ with DOC is 3.90×10^{8} $M^{-1}s^{-1}$; the total reactor volume is 6 m^3.

General Inputs:

pH	$pH := 6.8$
Concentration of target compound, mg/L	$\rho := 0.2$
Molecular weight of target compound, g/mole	$M := 131.389$
k_{HO^-} with target compound, $M^{-1}S^{-1}$ (see *GCM)	$k9 := 4.2 \cdot 10^9$
Concentration of chloride ion, mg/L	$Clm := 2$
Concentration of Fe(II), mg/L	$Fem := 0.05$
Concentration of Mn(II), mg/L	$Mnm := 0.1$
Alkalinity, mg/L as $CaCO_3$	$Alk := 400$
DOC, mg/L	$DOC := 0.7$
k_{HO^-} with DOC, $M^{-1}s^{-1}$	$k10 := 3.9 \cdot 10^8$
Total reactor volume, m^3	$v := 6$

Figure 5.14. General input portion of the main input window.

Inputs for H_2O_2/UV model

The inputs for the H_2O_2/UV model are specified in the middle of the main input window, as shown in Figure 5.13. The H_2O_2 dosage is 13.8 mg/L; the wavelength of light is 254 nm; the number of lamps is 2; the lamp power is 15 kW; the lamp efficiency is 0.2; the energy use for H_2O_2 production is 4.9 kWh/lb; and the absorbance of NOM at 254 nm for a cell path length of 1cm is 0.014.

Inputs For H_2O_2/UV Model

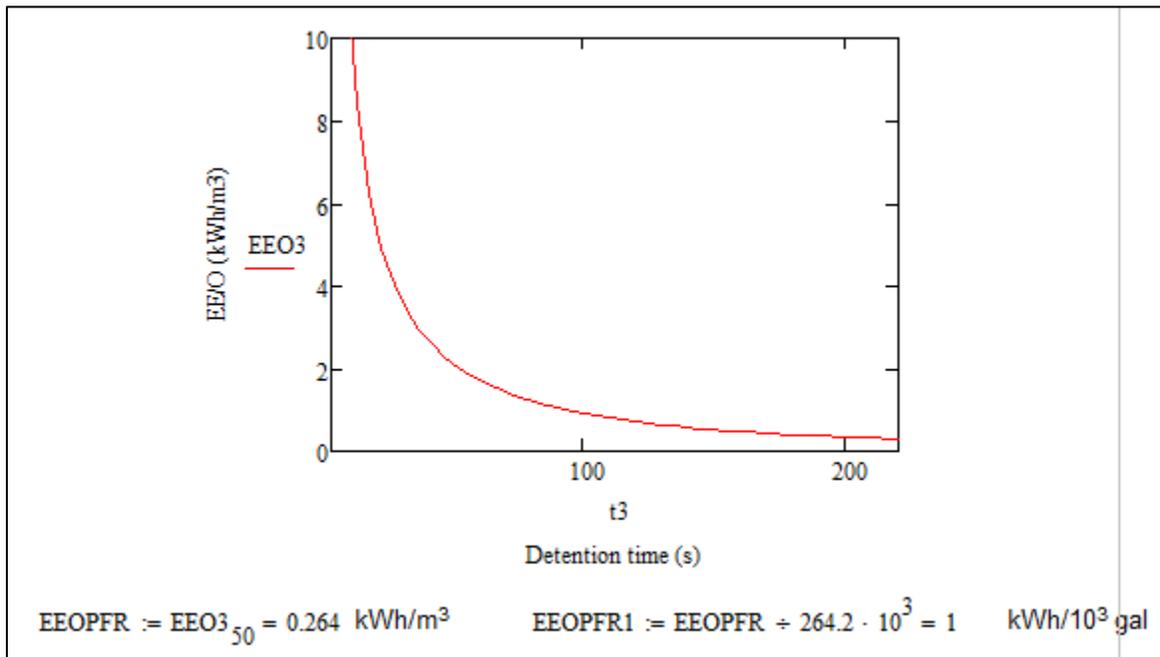|	
Total H_2O_2 dosage, mg/L	$H2O2t := 13.8$
Wavelength of light, nm	$\lambda := 254$
Number of lamps	$nlamp := 2$
Lamp power, kW	$P := 15$
Lamp efficiency	$\eta := 0.2$
Absorbance of NOM at 254 nm for a cell length of 1cm	$a := 0.014$
Energy use for H_2O_2 production, kWh/lb	$E3 := 4.9$

Figure 5.15. H_2O_2/UV model input portion of the main input window.

Viewing results

We can obtain the effluent concentration profile of target compound and EE/O value of the process from the "output of PFR" part. In this solution, the effluent concentration of TCE is 3 μg/L. The EE/O for H_2O_2/O_3 model is 0.264 kWh/m³ or 1.000 kWh/kgal.

$$RPFR := R3a_{50} \qquad RPFR = 3 \times 10^{-3} \quad mg/L$$

(a)

$$EEOPFR := EEO3_{50} = 0.264 \ kWh/m^3 \qquad EEOPFR1 := EEOPFR \div 264.2 \cdot 10^3 = 1 \quad kWh/10^3 \ gal$$

(b)

42
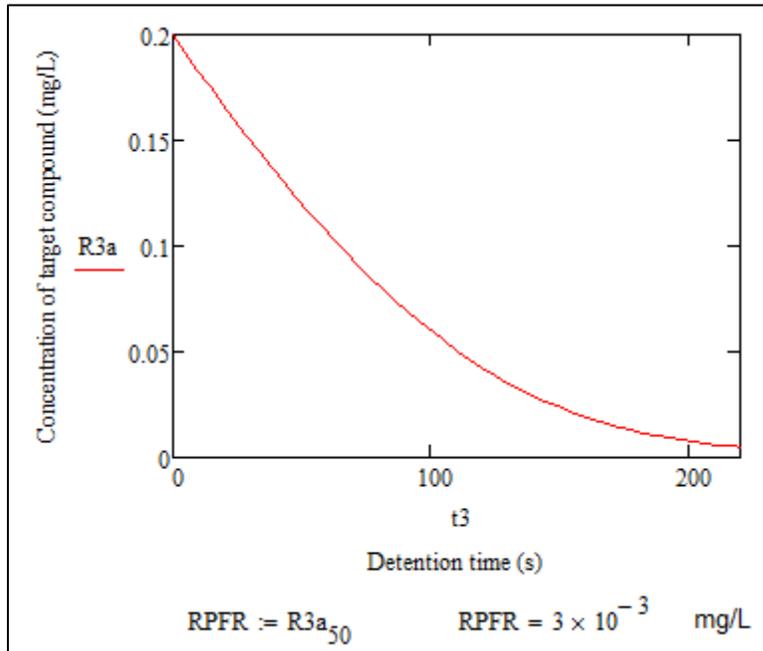
Figure 5.16. UV/H$_2$O$_2$ model output portion of PFR. (a) Effluent concentration profile of target compound. (b) EE/O value profile.

We can also predict the residual H$_2$O$_2$ concentration from the "output of PFR" part. In this solution, the residual H$_2$O$_2$ concentration is 8.5 mg/L.

$$\text{H2O2tPFR} := \text{H2O23a}_{50} \qquad \text{H2O2tPFR} = 8.5 \quad \text{mg/L}$$
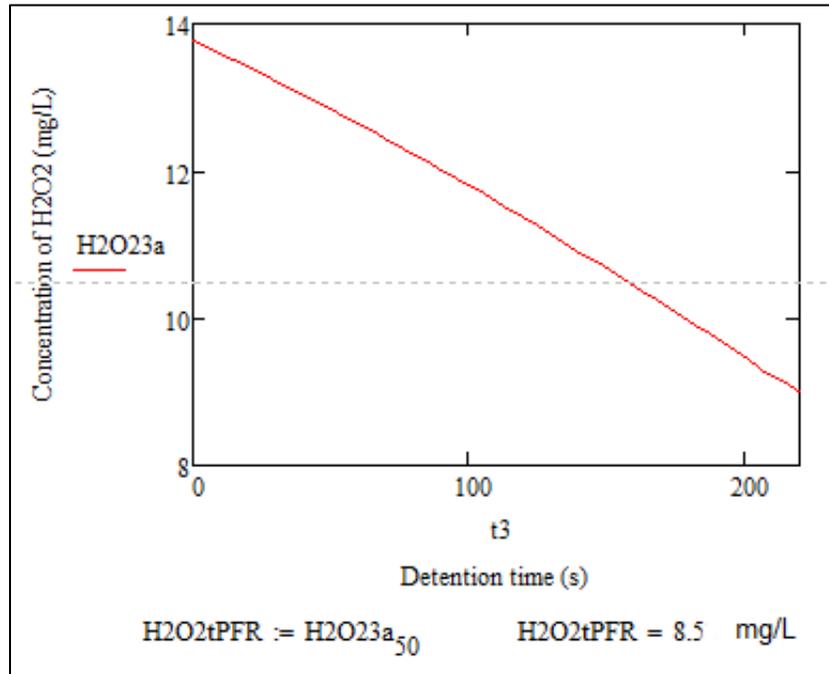
Figure 5.17. The residual H$_2$O$_2$ concentration of UV/H$_2$O$_2$ model

(4) Determine the optimum H$_2$O$_2$ dosage and total lamp power

We can then compare the EE/O to get the optimum H$_2$O$_2$ dosages and total lamp power. The EE/O values of all cases are plotted in Figure 5.17. From Table 5.4 and Figure 5.17, we can see that at low H$_2$O$_2$ dosage levels, the EE/O values are high even though the residual H$_2$O$_2$ concentrations are low and at high H$_2$O$_2$ dosage levels, both the EE/O values and residual H$_2$O$_2$ concentration are high. Both of these two H$_2$O$_2$ dosage levels might not be a good choice to design a cost effective UV/H$_2$O$_2$ process. At middle level of H$_2$O$_2$ dosage, the EE/O values are relatively low and the residual H$_2$O$_2$ concentrations are not very high, which might be an ideal region to choose the operational variables. The lowest EE/O value is achieved in run NO.4, when H$_2$O$_2$ dosage is 19.0 mg/L, the residual H$_2$O$_2$ concentration is 13.5 mg/L, and the total light power is 24 kW.
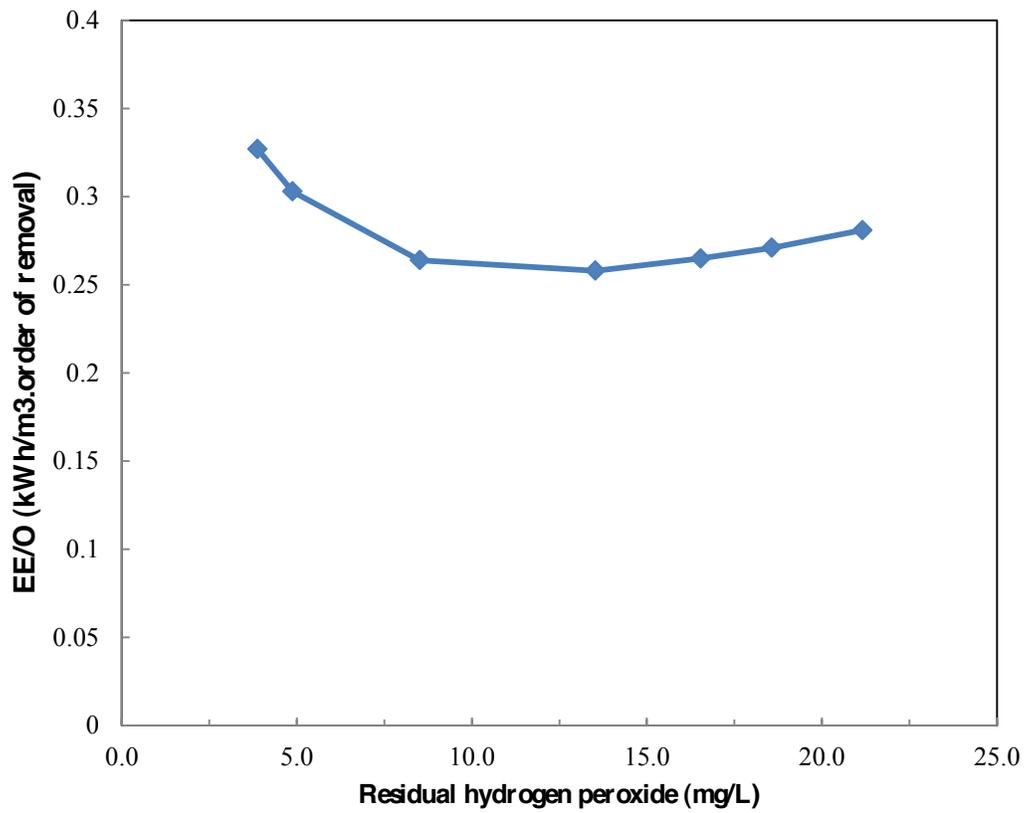
Figure 5.17. The relation between the residual hydrogen peroxide and the EE/O values of H_2O_2/UV process.

(5) Conclusion

In this example, a PFR will be designed.
The design parameters are as below:

Volume of reactor: 6 m^3
Total light power: 24 kW
H_2O_2 dosage: 19.0 mg/L

Appendix A. Development process of pseudo-steady state model

In this module, the pseudo-steady state models include: 1) H_2O_2/O_3 model; 2) H_2O_2 added after O_3 addition model; 3) UV/H_2O_2 model; and 4) O_3 - R_c model. The reactor types include: 1) completely mixed batch reactor (CMBR); 2) completely mixed flow reactor (CMFR); and 3) plug flow reactor (PFR). The elementary reactions involved in the pseudo-steady state models are the same with the simplified pseudo-steady state models as listed in Table 2.1.

1. Ozone with Hydrogen Peroxide Model

1.1 Elementary Reactions

The elemental reactions of H_2O_2/O_3 process involved in this model are the same with the simplified pseudo-steady state H_2O_2/O_3 model. From all of the elementary reactions involved, net formation rates of main species, including H_2O_2/HO_2^-, R, NOM, Fe^{2+}, Mn^{2+}, Cl^-, HCO_3^-/CO_3^{2-}, O_3, can be obtained as below:

$$\frac{d[H_2O_2/HO_2^-]}{dt} = -k_1[HO_2^-][O_3] - k_{10}[HO\bullet][HO_2^-] - k_{11}[HO\bullet][H_2O_2]$$

(A-1)

$$\frac{d[R]}{dt} = -k_9[HO\bullet][R]$$

(A-2)

$$\frac{d[NOM]}{dt} = -k_{14}[HO\bullet][NOM]$$

(A-3)

$$\frac{d[Fe^{2+}]}{dt} = -k_{17}[HO\bullet][Fe^{2+}]$$

(A-4)

$$\frac{d[Mn^{2+}]}{dt} = -k_{18}[HO\bullet][Mn^{2+}]$$

(A-5)

$$\frac{d[Cl^-]}{dt} = -k_{15}[HO\bullet][Cl^-]$$

(A-6)

$$\frac{d[HCO_3^-/CO_3^{2-}]}{dt} = -k_{12}[HO\bullet][HCO_3^-] - k_{16}[HO\bullet][CO_3^{2-}]$$

(A-7)

$$\frac{d[O_3]}{dt} = k_La\left(\frac{P_{O_3}}{H} - [O_3]\right) - k_1[HO_2^-][O_3] - k_3[O_2^-\bullet][O_3]$$

(A-8)

The net formation rates of radicals, including HO•, HO₃•, O₃⁻•, and O₂⁻•, are the same with simplified pseudo-steady state H_2O_2/O_3 model and can be calculated with the equations from (2-2) to (2-5), respectively.

The following equilibrium relationships are considered:

$$[HCO_3^-] = \frac{K_{a1}[H_2CO_3^*]}{[H^+]} \tag{A-9}$$

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} \tag{A-10}$$

$$[HO_2^-] = \frac{K_{a3}[H_2O_2]}{[H^+]} \tag{A-11}$$

The following expressions of radical concentrations are obtained once the pseudo–steady state approximation is applied to all radical intermediates, which means all of the net formation rates of radicals are set to be zero.

$$[HO\bullet]_{ss} = \frac{k_5[HO_3\bullet]}{k_{10}[HO_2^-]+k_{11}[H_2O_2]+k_{12}[HCO_3^-]+k_{13}[R]+k_{14}[NOM]+k_{15}[Cl^-]+k_{16}[CO_3^{2-}]+k_{17}[Fe^{2+}]+k_{18}[Mn^{2+}]} \tag{A-12}$$

$$[HO_3\bullet]_{ss} = \frac{k_4[O_3^-\bullet][H^+]}{k_5} \tag{A-13}$$

$$[O_3^-\bullet]_{ss} = \frac{k_1[HO_2^-][O_3]+k_3[O_2^-\bullet][O_3]}{k_4[H^+]} \tag{A-14}$$

$$[O_2^-\bullet]_{ss} = \frac{k_1[HO_2^-][O_3] + k_{10}[HO\bullet][HO_2^-]+k_{11}[HO\bullet][H_2O_2]}{k_3[O_3]} \tag{A-15}$$

1.2 Reactors

Pseudo-steady state H_2O_2/O_3 model considers following reactors: 1) completely mixed batch reactor (CMBR), 2) completely mixed flow reactor (CMFR), and 3) plug flow reactor (PFR). The mass balance equations for all of these reactors are listed as below:

$$\frac{dC_a}{dt} = r_a \qquad \text{(CMBR)} \tag{A-16}$$

$$\frac{dC_a}{dt} = \frac{1}{\tau}(C_{ao}-C_a)+r_a \qquad \text{(CMFR)} \tag{A-17}$$

$$\frac{dC_a}{d\tau} = r_a \qquad \text{(PFR)} \qquad \text{(A-18)}$$

where C_{ao} is the influent concentration of species A; C_a is the concentration of A at time t; t is the reaction time; τ is the hydraulic retention time; and r_a is the net formation rate of the species A. The ordinary differential equations (ODEs) resulting from the substitution of net formation rates of main species and concentrations of radicals into the mass balances equations are solved by 4th-order Runge-Kutta method.

1.3　Energy Efficiency per Removal of Order

The calculation of the EE/O values for both flow systems and batch systems are the same with the simplified pseudo-steady state H_2O_2/O_3 model.

2.　H_2O_2 Added after O_3 Addition Model

2.1　Elementary Reactions

The elementary reactions and development processes of pseudo-steady state H_2O_2 added after O_3 addition model are the same with pseudo-steady state H_2O_2/O_3 model except that the net formation rate of aqueous phase O_3 doesn't include mass transfer process of O_3 from gas phase to aqueous phase, which is expressed as below:

$$\frac{d[O_3]}{dt} = -k_1[HO_2^-][O_3] - k_3[O_2^-\bullet][O_3]$$

(A-19)

2.2　Reactors

The process where hydrogen peroxide is added in the presence of dissolved ozone is for particularly flow reactors, and therefore, we only consider CMFR and PFR for this process. The mass balance equations for main species in various reactors are the same with the pseudo-steady state H_2O_2/O_3 model. The ordinary differential equations (ODEs) resulting from the substitution of formation rates of main species and concentrations of radicals into the mass balances equations are solved by 4th-oder Runge-Kutta method.

2.3　Energy Efficiency per Removal of Order

The calculations of the EE/O values for flow system are the same with the simplified pseudo-steady state H_2O_2 added after O_3 addition model.

3.　Ultraviolet with Hydrogen Peroxide Model

3.1　Elementary Reactions

The elementary reactions of H_2O_2/UV process involved in this model are the same with the simplified pseudo-steady state H_2O_2/UV model. From all of the elementary reactions involved, the net formation rates of main species, including H_2O_2/HO_2^-, R, NOM, Fe^{2+}, Mn^{2+}, Cl^-, HCO_3^-/CO_3^{2-}, can be obtained as below:

$$\frac{d[H_2O_2/HO_2^-]}{dt} = -\Phi P_{U-V}f(1-e^{-A})-k_{10}[HO\bullet][HO_2^-]-k_{11}[HO\bullet][H_2O_2] \tag{A-20}$$

$$\frac{d[R]}{dt} = -k_{13}[HO\bullet][R] \tag{A-21}$$

$$\frac{d[NOM]}{dt} = -k_{14}[HO\bullet][NOM] \tag{A-22}$$

$$\frac{d[Fe^{2+}]}{dt} = -k_{17}[HO\bullet][Fe^{2+}] \tag{A-23}$$

$$\frac{d[Mn^{2+}]}{dt} = -k_{18}[HO\bullet][Mn^{2+}] \tag{A-24}$$

$$\frac{d[Cl^-]}{dt} = -k_{15}[HO\bullet][Cl^-] \tag{A-25}$$

$$\frac{d[HCO_3^-/CO_3^{2-}]}{dt} = -k_{12}[HO\bullet][HCO_3^-]-k_{16}[HO\bullet][CO_3^{2-}] \tag{A-26}$$

The net formation rate of HO• is the same with simplified pseudo-steady state H_2O_2/UV model, which can be found in (2-24). The following equilibrium relationships are considered:

$$[HCO_3^-] = \frac{K_{a1}[H_2CO_3^*]}{[H^+]} \tag{A-27}$$

$$[CO_3^{2-}] = \frac{K_{a2}[HCO_3^-]}{[H^+]} \tag{A-28}$$

$$[HO_2^-] = \frac{K_{a3}[H_2O_2]}{[H^+]} \tag{A-29}$$

The following expressions of steady state HO• concentrations is obtained once the pseudo–steady state approximation is applied, which means the net formation rate of HO• is set to be zero.

$$[HO\bullet]_{ss} = \frac{2\Phi P_{U-V}f(1-e^{-A})}{k_{10}[HO_2^-]+k_{11}[H_2O_2]+k_{12}[HCO_3^-]+k_{13}[R]+k_{14}[NOM]+k_{15}[Cl^-]+k_{16}[CO_3^{2-}]+k_{17}[Fe^{2+}]+k_{18}[Mn^{2+}]} \tag{A-30}$$

3.2 Reactors

The mass balance equations for main species in various reactors are the same with the pseudo-steady state H_2O_2/O_3 model. The ordinary differential equations (ODEs) resulting from the substitution of formation rates of main species and concentrations of radicals into the mass balances equations are solved by 4th-oder Runge-Kutta method.

3.3 Energy Efficiency per Removal of Order

The calculation of EE/O value for both flow systems and batch systems are the same with the simplified pseudo-steady state H_2O_2/UV model.

4. Ozone R_c model

4.1 Elementary Reactions

The elementary reactions in this model are the same with the simplified pseudo-steady state O_3 R_c model. The net formation rates of main species, including O_3, R, NOM, Fe^{2+}, Mn^{2+}, Cl^-, HCO_3^-/CO_3^{2-}, can be obtained:

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

(A-31)

$$\frac{d[R]}{dt} = -(k_{O_3} + k_{13}R_c)[O_3][R]$$

(A-32)

$$\frac{d[NOM]}{dt} = -k_{14}R_c[O_3][NOM]$$

(A-33)

$$\frac{d[Fe^{2+}]}{dt} = -k_{17}R_c[O_3][Fe^{2+}]$$

(A-34)

$$\frac{d[Mn^{2+}]}{dt} = -k_{18}R_c[O_3][Mn^{2+}]$$

(A-35)

$$\frac{d[Cl^-]}{dt} = -k_{15}R_c[O_3][Cl^-]$$

(A-36)

$$\frac{d[HCO_3^-/CO_3^{2-}]}{dt} = -k_{12}R_c[O_3][HCO_3^-] - k_{16}R_c[O_3][CO_3^{2-}]$$

(A-37)

4.2 Reactors

The mass balance equations for ozone and main species in various reactors are the same with the pseudo-steady state H_2O_2/O_3 model. The ordinary differential equations (ODEs) resulting from the substitution of

formation rates of main species into the mass balances equations are solved by 4th-order Runge-Kutta method.

4.3 Energy Efficiency per Removal of Order

The calculation of EE/O value for both flow systems and batch systems are the same with the simplified pseudo-steady state O_3 R_c model.

Appendix B. Typical Values of Certain Inputs

Inputs		Values	Reference
$k_{HO\bullet}$ with DOC, $M^{-1}s^{-1}$		1.39×10^8 to 4.53×10^8	a
Overall mass transfer coefficient for O_3, s^{-1}		7×10^{-4}	b
Energy use for O_3 production, kWh/lb	Air feed	6 to 8	c
	O_2 feed	4 to 6	c
Energy use for H_2O_2 production, kWh/lb		4.9	d
Transfer efficiency of ozone contactor		$\geq 80\%$	e
R_c for O_3 R_c model, dimensionless		10^{-9} to 10^{-7}	f

References: (a) Westerhoff *et. al.* 2007; (b) Glaze *et. al.* 1989; (c) Kerwin, 2005; (d) Rosenfeldt *et. al.* 2006; (e) DeMers *et al.* 1992; (f) Elovitz *et. al.* 1999.

Appendix C. References

1. Behar, D.; Czapski, G.; Duchovny, I. *J. Phys. Chem.* **1970**, *74*, 2206-2210.
2. Bolton, J. R.; Cater, S. R. *Aq. Surf. Photochem.* **1994**, *0*, 467-490.
3. Buhler, R. F.; Staehelin, J.; Hoigne, J. *J. Phys. Chem.* **1984**, *8* (12), 2560-2564.
4. Buxton, G. V.; Greenstock, C. L. *J. Phys. Chem. Ref. Data.* **1988**, *17* (2), 513-586.
5. Christensen, H. S.; Sehested, K.; Corftizan, H. *J. Phys. Chem.* **1982**, *86*, 15-88.
6. Crittenden, J. C.; Hu, S.; Hand, D. W.; Green, S. *Water Res.* **1999,** *33* (10), 2315-2328.
7. Crittenden, J. C.; Trussell, R. R.; Hand, D. W.; Howe, K. J.; Tchobanoglous, G. *Water Treatment Principles and Design,* 3rd ed.; John Wiley & Sons. Ltd.: New York, 2012; pp 1415-1472.
8. DeMers, L.D. and R.C. Renner. *Alternative Disinfection Technologies for Small Drinking Water Systems.*; AWWARF and AWWA, Denver, CO. 1992.
9. Draganic, Z. D.; Negron-mendoza, A.; Sehested, K.; Vujosevic, S. I.; Navarro-Gonzales, R.; Albarran-Sanchez, M. G.; Draganic, I. G. *Radiat. Phys. Chem.* **1991**, *38* (3), 317-321.
10. Elovitz, M. S.; Von Gunten, U. *Ozone: Sci. Eng.* **1999,** *21* (3), 239-260.
11. Glaze, W. H.; Kang, J.-W. *Ind. Eng. Chem. Res.* **1989**, *28* (11), 1573-1580.
12. Glaze, W. H.; Lay, Y.; Kang, J.W. *Ind. Eng. Chem. Res.* **1995**, 34, 2314-2323.
13. Kerwin, R. L. *Ozone in Drinking Water Treatment - Process Design, Operation, and Optimization,* 1st ed.; American Water Works Association (AWWA), 2005.
14. Lay, Y.S. Ph.D. dissertation. **1989**.
15. Minakata, D.; Li, K.; Westerhoff, P.; Crittenden, J. C. *Environ. Sci. Technol.* **2009,** *43* (16), 6220 - 6227.
16. Rosenfeldt, E. J.; Cononica, S.; Linden, K. G.; von Gunten, U. *Water Res.* **2006**, *40* (20), 3695-3704.
17. Staehelin, J.; Hoigne, J. *Environ. Sci. Technol.* **1982**, *16* (10), 676-681.
18. Stefan, M.I.; Hoy, A.R.; Bolton, J.R. *Environ. Sci. Technol.* **1996**, 30, 2382-2390.
19. Stumm, W.; Morgan, J. J. *Aquatic chemistry: An Introduction Emphasizing Chemical Equilibria in Natural Waters*; Wiley-Interscience: New York, 1981.
20. Westerhoff, P.; Mezyk, S. P.; Cooper, W. J.; Minakata, D. *Environ. Sci. Technol.* **2007**, *41* (13), 4640-4646.