

WEIGHTED FLUENCE-BASED PARAMETERS for Assessing UV and UV/H₂O₂ Performance and Transferring Bench-Scale Results to Full-Scale Water Treatment Reactor Models

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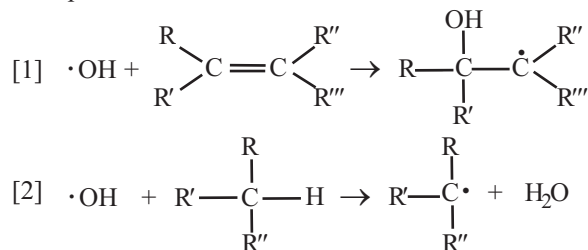
ABSTRACT

The lack of a standard approach for presenting contaminant remediation kinetics using the UV/H₂O₂ advanced oxidation process (AOP) for water treatment hampers efforts to cross-interpret results and apply literature data for the prediction of treatment efficiencies in new experimental settings. Properly weighted UV fluence rates can be used to define parameters for assessing the UV/H₂O₂ AOP that models predict to be essentially invariant with reactor geometry and lamp type. A pollutant action spectrum-weighted average fluence-based rate constant characterizes the direct photolysis portion of the reaction, while an H₂O₂ action spectrum-weighted average fluence rate-normalized ·OH concentration characterizes the indirect photolysis portion of the reaction. Experimental data for the photolysis of atrazine gathered at two different laboratories support the validity of the model. Using these parameters, a relatively simple kinetic model is presented that allows prediction of pollutant degradation rates in any reactor for which the pollutant and H₂O₂ weighted fluence rates can be calculated.

Keywords: Advanced oxidation process; water treatment; UV; hydrogen peroxide; atrazine; kinetics; photochemical modeling.

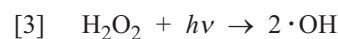
INTRODUCTION

Advanced Oxidation Processes (AOPs) continue to attract interest from academia, industry, and government for their potential to destroy hazardous air and water pollutants. There are several available AOPs, all of which have as a common feature generation of the hydroxyl radical (·OH). These radicals react rapidly and nonspecifically with organic chemicals via one of two mechanisms, addition to multiple bonds or H-atom abstraction:



These reactions generate carbon-centered radicals that undergo further reaction with molecular oxygen to destroy the organic molecule. In theory, AOPs are capable of completely mineralizing organic chemicals, with the end products being only CO₂, H₂O, and mineral acids. In practice, the amount of time and/or forcing conditions required make this goal unattainable, and best practice dictates that the reaction only be carried out until non-hazardous by-products are present.

Of the AOPs that involve ultraviolet (UV), two are particularly noteworthy for the frequency with which they appear in research journals and their practicality for application to water treatment. Semiconductor photocatalysis using UV in combination with solid TiO₂ particles has been studied for use in water and air treatment (Fujishima and Rao 1998). In water, the heterogeneous nature of the process raises several practical issues that appear to make it uneconomical on large scales. Chief among these are the limited extent to which light can penetrate the heterogeneous suspensions making it possible to treat only a relatively small volume of water per photon. Additionally, the process efficiency is closely associated with the extent to which pollutants adsorb on the semiconductor surface, and fouling of the surface by natural water constituents will disrupt the process. Finally, semiconductors also display low quantum yields of ·OH (Sun and Bolton, 1996). These limitations are not faced by another popular UV-based AOP, the UV/H₂O₂ process. Hydrogen peroxide is soluble in water and undergoes direct photolysis to produce dissolved ·OH:



Approximately 50% of the liberated ·OH radicals rapidly recombine in the water “solvent cage”. Thus, the yield of ·OH is one mole per mole of H₂O₂ photolyzed (Baxendale

and Wilson 1957). The UV/H₂O₂ process is homogenous, in contrast to the UV/TiO₂ process, and the main factors that determine its efficiency are the rate at which the pollutant reacts with ·OH and the extent to which the water matrix screens light from H₂O₂ and competes with the pollutant for ·OH. As a homogenous process, UV/H₂O₂ is especially simple to apply for treating large volumes of water. For this reason, it is in current use for full-scale water treatment and will likely see increased use in the future (Water and Wastes Digest 2003).

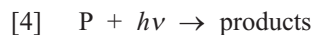
To evaluate the effectiveness of UV/H₂O₂ and to optimize its use, some researchers employ bench-scale experiments while others use pilot-scale reactors. Unfortunately, there has been little work done to facilitate interpretation of bench-scale results so that they may be used to predict reactor performance. In this regard, two issues are noteworthy. First, bench-scale researchers often present their results in terms of parameters that either are not directly transferable to full-scale reactors (e.g., time-based rate constants) or require fairly complex models to use in predicting reactor performance (e.g., quantum yields). Second, the terminology and units used by photochemists and water treatment engineers are not always consistent. For example, in current engineering practice the photonic energy delivered to solution is usually expressed in fluence units (e.g., mJ cm⁻²), while photochemists often use photon flux (einsteins L⁻¹). Thus, it is desirable to bridge the gap between these two camps and to make it simpler for water treatment engineers to use bench-scale experimental results in reactor models.

This article introduces two new parameters designed to make bench-scale UV/H₂O₂ results transferable to reactor models based on the average fluence rate in the reactor. To do this, it is necessary to specify two different fluence rates: one weighted by the pollutant action spectrum, and one weighted by the H₂O₂ action spectrum. Bench scale results that must be specified in terms of these fluence rates are the direct photolysis rate constant and the steady-state ·OH radical concentration. Given the ability to accurately model fluence rates in a reactor, these parameters can be used in a simple model to predict photodegradation rates in any reactor. Furthermore, these parameters are independent of optical pathlength and are relatively insensitive to the lamp spectrum. The major restriction is their applicability to a specific pollutant and water type.

CHARACTERIZING THE UV/H₂O₂ PROCESS PERFORMANCE

Many researchers characterize AOP performance by comparing overall rates of pollutant degradation. This can be a useful approach in some cases, but it does not allow different researchers, using different conditions, to compare their results or understand why their results may differ. For the UV/H₂O₂ process, a more thorough approach exam-

ines the rates at which two simultaneous reactions occur, direct photolysis of the target pollutant (P) and reaction of the pollutant with ·OH, or indirect photolysis.



Any scheme for characterizing the UV/H₂O₂ process performance should involve quantifying the rates (or extents of reaction) of both of these reactions, individually, under the test circumstances. While this may sound simple, it requires a bit of calculation that derives from basic photochemical theory. A thorough description of the mathematical model involved can be found elsewhere (Sharpless and Linden 2003), and only a brief outline is given here.

Reactions 4 and 5 are elementary (i.e., they show the mechanism). For low concentrations of P in a batch reactor, the overall pollutant destruction rate can be written as follows:

$$[6] \quad \frac{d[P]}{dt} = (k'_d + k_{\text{OH}}[·\text{OH}])[P] = k'_t[P]$$

Here, k'_t is the observed first-order rate constant (units are usually s⁻¹), k'_d is the pseudo-first order rate constant for direct photolysis, k_{OH} is the second order rate constant for reaction between P and ·OH (units of M⁻¹ s⁻¹), and the square brackets represent molar concentrations. This equation integrates to give first-order kinetics in the presence and absence of H₂O₂, and representative data are shown in

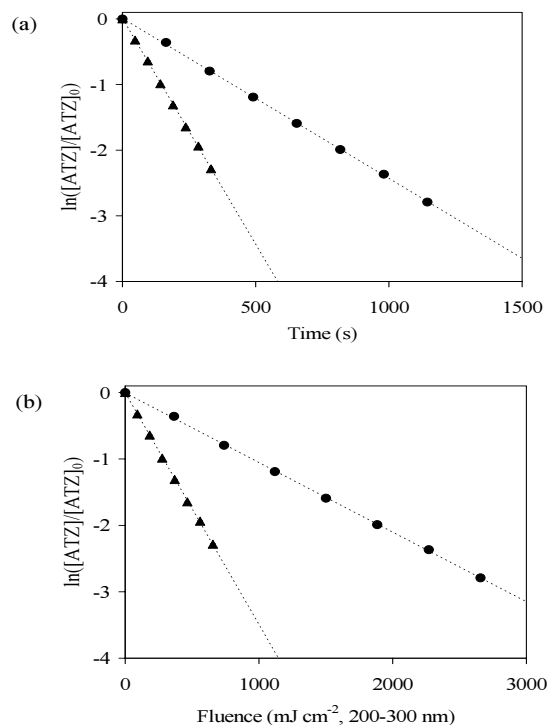


Figure 1: First order kinetic analysis for ATZ photolysis with a medium pressure Hg lamp in synthetic drinking water: direct photolysis (●), with 2.9 mM H₂O₂ (▲). (a) time-based analysis; (b) fluence-based analysis.

Figure 1a for atrazine (ATZ) photolysis with a 1 kW medium pressure mercury lamp in a synthetic drinking water.

The quantities k_d and $[\cdot\text{OH}]$ are functions of the spectral distribution of the UV light and its intensity in the water, and they can be predicted from photochemical theory using the following equations:

$$[7] \quad k_d = \sum_{\lambda} k_{a,\lambda} \Phi_{\lambda}$$

$$[8] \quad [\cdot\text{OH}] = \frac{\sum_{\lambda} k_{a(\text{H}_2\text{O}_2),\lambda} \Phi_{\text{OH},\lambda} [\text{H}_2\text{O}_2]}{\sum_i k_{s,i}}$$

Here, $k_{a,\lambda}$ is the specific rate of light absorption by P (einstains $\text{mol}^{-1} \text{s}^{-1}$), Φ_{λ} is the direct photolysis quantum yield (the fraction of molecules that absorb light and undergo photolysis, mol einstein^{-1}), $k_{a(\text{H}_2\text{O}_2),\lambda}$ is the specific rate of light absorption by H_2O_2 , $\Phi_{\text{OH},\lambda}$ is the hydroxyl radical quantum yield (1.0 in water), and $k_{s,i}$ are pseudo-first order rate constants for reaction of $\cdot\text{OH}$ with water constituents other than P. For monochromatic light the summations over wavelength do not apply.

To quantify the individual rates of reactions 4 and 5, k_t is measured experimentally. Then, k_a for P is calculated and equation 7 is used to find the value of k_d . This approach requires knowledge of the intensity and spectral distribution of the UV source, the absorption spectrum of P, the direct photolysis quantum yield(s), and the optical path-length in solution (Sharpless and Linden 2003). Once k_d is calculated, the product $k_{\text{OH}}[\cdot\text{OH}]$ is found by difference from k_t . The value of k_{OH} may be known or measured, allowing calculation of $[\cdot\text{OH}]$.

Experiments may then be compared on the basis of the rates of reactions 4 and 5 or by comparing the experimental k_d and $[\cdot\text{OH}]$ values.

FLUENCE-BASED ASSESSMENT PARAMETERS

Many reports of photodegradation kinetics express k_t and k_d in units of inverse time, leading this author to use the subscript t on the overall rate constant above. While this is a simple parameter to measure, several authors have recently emphasized its lack of value as a predictor of reaction rates that will be obtained with different reactor geometries (Bolton and Stefan 2002; Sharpless and Linden 2003); k_t is a function of solution transmittance and the incident irradiance, which vary with experimental conditions, leading to a variable rate “constant”. In an effort to facilitate comparisons of rate constants between labs, some researchers have presented results in terms of average fluence-based rate constants (k_f). These represent the extent of degradation per unit of fluence (e.g., mJ cm^{-2}) delivered to the solution over a specified wavelength range, corrected for light screening by the water matrix. The average flu-

ence rate (E'_{avg}) may be calculated from the incident fluence rate (E'_0), the solution absorption spectrum, and the optical pathlength using established procedures (Morowitz 1950). Once E'_{avg} is specified, k_t and k_f can be related by,

$$[9] \quad k_f = \frac{k_t}{E'_{\text{avg}}}$$

The data analysis with respect to fluence also leads to first-order kinetics as shown in Figure 1b, which uses the same ATZ photolysis data in Figure 1a.

For direct photolysis with *monochromatic* radiation, Bolton and Stefan (2002) have shown that k_f is invariant with experimental geometry and water transmittance. For *polychromatic* radiation, the equations involve summations over wavelength in both the numerator and denominator of equation 9. Importantly, this implies that k_f for polychromatic radiation will only be constant with changing conditions if k_a for P changes by the same percent as does E'_{avg} .

The results of an inter-laboratory study of ATZ degradation illustrate some of these points (Stefan et al., 2001). Two different labs, one at Duke University and one at Bolton Photosciences Inc. (BPI), conducted fluence-based kinetic studies of ATZ removal in the same water and in the absence and presence of 2.9 mM H_2O_2 (100 mg/L). Each lab used a different ATZ concentration and different solution depths. With the fluence rate defined over 200 to 300 nm, the results in Table 1 were obtained. With low-pressure mercury lamps (monochromatic at 254 nm), very good agreement between k_f values was obtained, in keeping with the expected invariance for monochromatic radiation. However, a large discrepancy exists between the values obtained with medium-pressure mercury lamps (polychromatic radiation).

Measurements showed that the lamp spectra differed between Duke and BPI (Figure 2a). This fact, and the different solution depths, resulted in k_a for ATZ being higher per unit E'_{avg} at BPI than at Duke. Calculated k_a values for $E'_{\text{avg}} = 2.4 \text{ mW cm}^{-2}$ are shown in Figure 2b. Under these conditions, more ATZ is destroyed per unit E'_{avg} at BPI. A similar situation holds in the presence of H_2O_2 , although

Table 1: Fluence-based rate constants for ATZ removal ($\text{cm}^2/\text{mJ} \times 10^3$, over the wavelength range 200–300 nm)

	LP	LPH	MP	MPH
Duke	0.54	4.1	1.1	3.7
BPI	0.52	3.8	1.5	5.4

LP = low pressure mercury lamp; MP = medium pressure mercury lamp.

LPH = LP + 2.9 mM H_2O_2 ; MPH = MP + 2.9 mM H_2O_2 .

in this case both equations 7 and 8 must be used to model the experimental data. This requires measurement of Φ_λ for ATZ. Estimates and direct measurements indicate that below 250 nm $\Phi_\lambda \sim 0.055$ and above 250 nm $\Phi_\lambda \sim 0.038$ (Stefan et al. 2001; Sharpless et al. 2003). Using these parameters, it is possible to model accurately the effects of H_2O_2 observed at both Duke and BPI (Stefan et al. 2001). These results show that k'_f , as defined here, may not be the best parameter for comparing UV and UV/ H_2O_2 results. Furthermore, no simple procedure emerged from these studies to quantify the indirect photolysis efficiency.

To establish a fluence-based means for assessing indirect photolysis rates, Rosenfeldt and Linden (2005) recently introduced the R_{OH} concept, which specifies the $\cdot\text{OH}$ concentration obtained for a given E'_{avg} . This quantity can be measured by using a probe chemical that reacts with $\cdot\text{OH}$ but does not undergo substantial direct photolysis under the test conditions. Application of equation 6 then allows calculation of $[\cdot\text{OH}]$, and dividing by E'_{avg} yields R_{OH} . In any water, as the H_2O_2 concentration is increased, R_{OH} will increase. Waters high in $\cdot\text{OH}$ scavengers or of low transmittance will have lower R_{OH} values than clear waters (where light absorption by H_2O_2 is high) or waters that are low in $\cdot\text{OH}$ scavengers. This concept is extremely

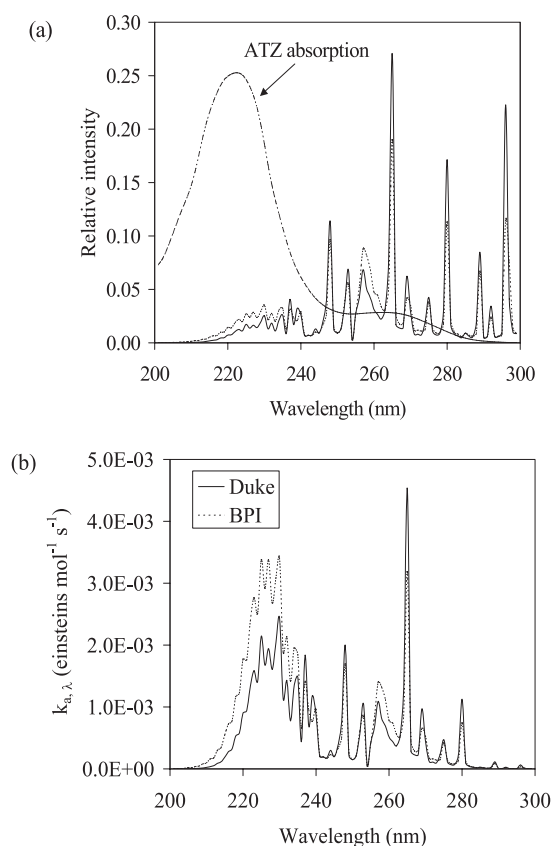


Figure 2: (a) Lamp spectra at Duke (—) and BPI (---) with ATZ absorption spectrum overlain; (b) calculated specific rates of light absorption with lamps at Duke and BPI for 1 μM ATZ for equal average irradiance levels (2.4 mW cm^{-2}).

useful in that it specifies a required fluence rate to achieve a certain $\cdot\text{OH}$ concentration for a given water. However, unless the fluence rate is properly defined, R_{OH} may be just as variable between experimental arrangements as is k'_f .

WEIGHTED FLUENCE-BASED ASSESSMENT PARAMETERS

It is possible to define k'_f and R_{OH} values for a given pollutant that are relatively invariant with experimental parameters except the water matrix. This requires specification of two different E'_{avg} values: one weighted by the pollutant action spectrum, and the other weighted by the H_2O_2 action spectrum. The first is used to determine pollutant-weighted k'_f values (k_f^w), and the second is used to determine H_2O_2 -weighted R_{OH} values (R_{OH}^w). The weighting procedure is identical to that used in UV disinfection, where E'_{avg} values are weighted by the pathogen action spectrum or the DNA absorbance spectrum (Linden and Darby 1997). To use this approach, one must know the action spectrum (the relative degradation rate versus wavelength) of the pollutant and H_2O_2 . In photochemical parlance, the absorption spectrum and the quantum yield are distinguished. The absorption spectrum specifies the strength of light absorption, usually in terms of the molar absorption coefficient, ϵ ($\text{M}^{-1} \text{ cm}^{-1}$). The quantum yield, Φ (mol einstein^{-1}) specifies the fraction of molecules that are destroyed per photon. The product $\epsilon \Phi$ versus wavelength gives the action spectrum. The action spectrum for H_2O_2 is identical to its absorption spectrum because $\Phi_{\text{OH}} = 1.0$ over the wavelength range of interest (Baxendale and Wilson 1957). In practice, one may measure both ϵ and Φ , or the action spectrum may be measured directly as the relative rate (per photon) versus wavelength.

For a given pollutant, the weighted E'_{avg} is defined here as:

$$[10] \quad E'_{\text{avg}}(\text{P}) = \frac{\sum_{\lambda} E'_{\text{avg},\lambda} \epsilon_{\lambda} \Phi_{\lambda}}{(\epsilon \Phi)_{\text{max}}}$$

A similar equation is used to obtain the H_2O_2 weighted E'_{avg} , except that the Φ values cancel (they are all 1.0) and the ϵ values are from the H_2O_2 absorption spectrum. Using the properly weighted E'_{avg} values, we define the parameters,

$$[11] \quad k_f^w = \frac{k'_t}{E'_{\text{avg}}[\text{P}]}$$

$$[12] \quad R_{\text{OH}}^w = \frac{R_{\text{OH}}}{E'_{\text{avg}}[\text{H}_2\text{O}_2]}$$

Here, k_f^w is the pollutant-weighted, average fluence-based rate constant, R_{OH}^w is the peroxide-weighted, average fluence-normalized R_{OH} value, and the other symbols have been previously defined. It is very important to note that

k_f^w must be determined from direct photolysis experiments to be useful in the model given below. The key feature of equations 11 and 12 is that the numerator and denominator vary at almost the same rate with changing optical pathlength and, within certain limits, lamp spectrum. This is because the weighted E'_{avg} values vary at almost the same rate as the k_a values making k_f^w and R_{OH}^w virtually constant.

For monochromatic radiation, a thorough derivation gives (Sharpless, manuscript in preparation):

$$[13] \quad k_f^w = \frac{\ln(10) (\varepsilon_P \Phi_P)_{\text{max}}}{U}$$

$$[14] \quad R_{\text{OH}}^w = \frac{\ln(10) [\text{H}_2\text{O}_2] (\varepsilon_{\text{H}_2\text{O}_2} \Phi_{\text{H}_2\text{O}_2})_{\text{max}}}{U \sum_i k_{s,i}}$$

Here, the subscripts P and H_2O_2 refer to the pollutant and H_2O_2 , respectively, $k_{s,i}$ values are pseudo first-order rate constants for scavenging of $\cdot\text{OH}$ by species i , and U is the photonic energy at the given wavelength (J einstein^{-1}). Equation 13 necessarily bears resemblance to the monochromatic expression for k_f presented by Bolton and Stefan (2002). In equation 13, the only parameter determining the value of k_f^w is the photon energy for a given wavelength; note that multiplying by U gives a truly invariant constant. In equation 14, only the nature of the water ($\cdot\text{OH}$ scavenging), the concentration of peroxide, and the photon energy for a given wavelength affect R_{OH}^w again, multiplying by U gives a true constant. For polychromatic radiation, the equations involve complex summations that lead to less compact final expressions. For both poly- and monochromatic radiation, these parameters vary with the photon energy for a given wavelength, unless appropriate corrections are made. However, there are few UV sources in actual application, with the result that for common lamps, the spectra are not so drastically different that major variations in k_f^w and R_{OH}^w will be seen on changing lamps.

The utility of these concepts can be seen by revisiting the Duke and BPI ATZ data. Recalculation of the direct photolysis rate constants using ATZ weighted fluence rates for the medium-pressure Hg lamps gives $k_f^w = 7.0 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$ at Duke and $7.2 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$ at BPI, a considerably better agreement than when unweighted fluence rates were used (Table 1). For the low-pressure lamps, both labs obtained $7.2 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$. Thus, the k_f^w values from both labs, with both types of lamp, are identical within the error inherent in the experiments. Note that using equation 13, the k_f^w value at 254 nm is predicted to be $7.9 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$, which is slightly higher than the experimental values. Although not shown here, k_f^w values for polychromatic radiation can also be calculated theoretically, and values of 7.5×10^{-3} and $7.4 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$ are predicted for the medium-pressure lamps at Duke and BPI, respectively, in good agreement with the experimental values.

Although $\cdot\text{OH}$ concentrations were not measured in this study, they can be estimated using equation 8. Doing so allows calculation of the R_{OH}^w values obtained in each experiment. These data, along with the k_f^w values, are summarized in Table 2. Note that k_f^w values are not given for 2.9 mM H_2O_2 because the overall rate constant in this case contains a contribution from indirect photolysis, in which case k_f^w is not an appropriate evaluation parameter.

Model studies (Sharpless, manuscript in preparation) also show that the k_f^w and R_{OH}^w values vary little with the optical pathlength for polychromatic irradiation. For example, changing the solution depth from 1 to 100 cm in a model for ATZ using the spectrum of the medium-pressure lamp at BPI changes k_f^w from 7.3×10^{-3} to $7.4 \times 10^{-3} \text{ cm}^2 \text{ mJ}^{-1}$. With the same pathlengths and 2.9 mM H_2O_2 , the model predicts R_{OH}^w values of 1.3×10^{-11} and $1.4 \times 10^{-11} \text{ M cm}^2 \text{ mW}^{-1}$.

Finally, a model study of the effect of lamp spectrum shows that these parameters should be essentially constant

Table 2: Weighted fluence-based parameters for ATZ removal. Abbreviations are given in Table 1

		LP	LPH	MP	MPH
Duke	k_f^w ($\text{cm}^2 \text{ mJ}^{-1}$)	7.2×10^{-3}	N/A	7.0×10^{-3}	N/A
	R_{OH}^w ($\text{M cm}^2 \text{ mW}^{-1}$)	—	1.4×10^{-11}	—	1.4×10^{-11}
BPI	k_f^w ($\text{cm}^2 \text{ mJ}^{-1}$)	7.2×10^{-3}	N/A	7.2×10^{-3}	N/A
	R_{OH}^w ($\text{M cm}^2 \text{ mW}^{-1}$)	—	1.4×10^{-11}	—	1.4×10^{-11}

for all common lamp types in present operation. Figure 3 shows a set of lamp spectra (low- and medium-pressure Hg and a blackbody spectrum) overlain with a water absorption spectrum. Using these spectral data, assuming 1 mM ATZ, 0.29 μM H_2O_2 , some assumptions about $\cdot\text{OH}$ scavenging, and an optical pathlength of 5 cm, calculations give the k_f^w and R_{OH}^w values shown in Table 3. Even with these drastic changes in lamp spectrum, the weighted fluence-based parameters are incredibly constant. Thus, for practical purposes k_f^w can be considered a true constant that varies only with pollutant, and R_{OH}^w values can be considered to vary only with H_2O_2 concentration and water quality.

A WEIGHTED FLUENCE-BASED TRANSFERABLE MODEL

The weighted fluence-based parameters k_f^w and R_{OH}^w offer a powerful and simple way to transfer expected kinetic results between experimental arrangements. All that is required for applying them under new experimental conditions is that the weighted fluence rates, $E'_{\text{avg}}(P)$ and $E'_{\text{avg}}(\text{H}_2\text{O}_2)$ be calculable. With these parameters, the

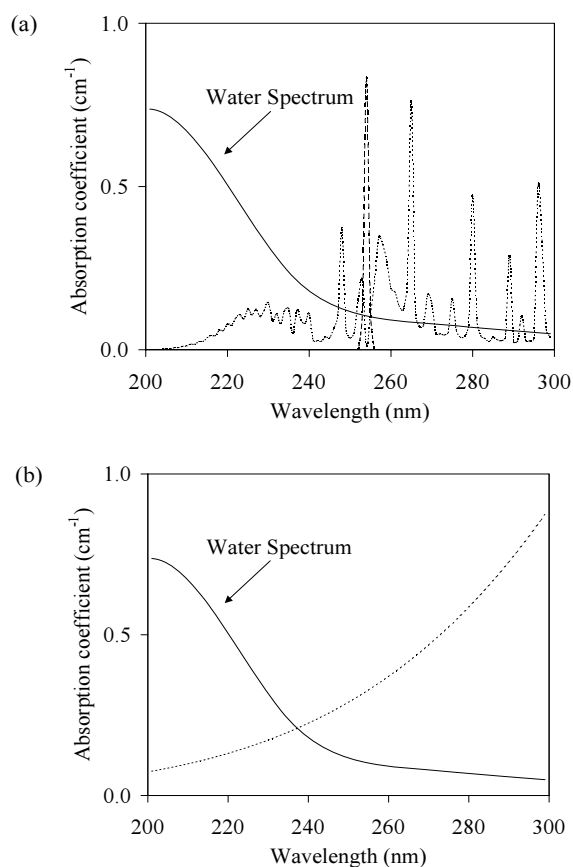


Figure 3: Model water and lamp spectra for calculating and for ATZ. Parameters described in detail in text: (a) water absorbance and low- (dashes) and medium-pressure (dots) lamp spectra; (b) water absorbance and blackbody emission spectrum

extents of pollutant degradation can be predicted for a given exposure time t using equation 15.

$$[15] \quad \ln\left(\frac{[P]_0}{[P]}\right) = \left[\left(k_f^w E'_{\text{avg}}(P) \right) + k_{\text{OH}} \left(R_{\text{OH}}^w E'_{\text{avg}}(\text{H}_2\text{O}_2) \right) \right] \times t$$

This equation accurately models the results with and without H_2O_2 for the Duke/BPI ATZ study, and further experimental tests of its validity should be conducted.

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Table 3: k_f^w ($\text{cm}^2 \text{mJ}^{-1}$) and R_{OH}^w ($\text{M cm}^2 \text{mW}^{-1}$) values calculated using spectral data in Figure 3 with $[\text{ATZ}] = 1 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 0.29 \text{ mM}$, and a 5 cm pathlength.

	LP	MP	Blackbody
k_f^w	7.9×10^{-3}	7.4×10^{-3}	7.5×10^{-3}
R_{OH}^w	2.6×10^{-12}	2.3×10^{-12}	2.5×10^{-12}

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