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RESEARCH ARTICLE

A photolysis coefficient for characterizing the response of aqueous constituents to photolysis

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Abstract UV photolysis and UV based advanced oxidation processes (AOPs) are gaining more and more attention for drinking water treatment. Quantum yield (ϕ) and molar absorption coefficient (ε) are the two critical parameters measuring the effectiveness of photolysis of a compound. The product of the two was proposed as a fundamental measure of a constituent's amenability to transformation by photolysis. It was shown that this product, named the photolysis coefficient, k_p, can be determined using standard bench tests and captures the properties that govern a constituent's transformation when exposed to light. The development showed the photolysis coefficient to be equally useful for microbiological, inorganic and organic constituents. Values of k_p calculated by the authors based on quantum yield and molar absorption coefficient data from the literature were summarized. Photolysis coefficients among microorganisms ranged from 8500 to more than 600000 and are far higher than for inorganic and organic compounds, which varied over a range of approximately 10 to 1000 and are much less sensitive to UV photolysis than the microorganisms.

Keywords UV photolysis, disinfection, advanced oxidation, *N*-nitrosodimethylamine, quantum yield, absorption coefficient

1 Introduction

Photolysis is a tool that environmental engineers are finding increasingly useful in addressing the need for transformation of environmental pollutants and inactivation of pathogens. Photolysis occurs when a target constituent (a pollutant or an organism) absorbs a photon of appropriate energy, enters an excited state, and undergoes a chemical reaction, which transforms it. To achieve higher removal efficiency, chemicals such as hydrogen peroxide, titanium dioxide, and free chlorine, can be introduced into the UV system to produce hydroxyl radicals, a powerful oxidant that removes constituents by what is termed advanced oxidation processes [1].

The application of ultraviolet light to water for disinfection purposes has a long history. During the course of that history, methods have been developed for expressing reaction rates and conducting bench-scale testing. Standards have been developed for the design, specification and operation of full-scale equipment for water disinfection [2]. Yet, kinetic models may be necessary for the prediction of system performance especially when the background water matrix is complex or variant. For the purpose of kinetic modeling of the process, quantum yield (ϕ) and molar absorption coefficient (ε) are the two critical parameters measuring the effectiveness of photolysis of a compound. While molar absorption coefficient quantifies the UV light available for photolysis, quantum yield refers to the number of moles of constituent transformed per einstein of photons absorbed by a constituent. Based on these two parameters and first principle derivation, kinetic models have been successfully developed for the modeling of both photolysis and UV based advanced oxidation processes for system design and mechanistic study [3,4].

However, application of these models could be limited due to the difficulties of finding the quantum yield and molar absorption coefficient for each constituent in the water matrix. In practice, the two coefficients are not readily available for pathogens and emerging contaminants, especially when a multi-wavelength light source, e.g. medium pressure mercury lamp, is used. In addition, reversibility of the hydrolysis mechanism complicates the evaluation of photolysis efficiency using kinetic models. A

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well-known example of UV photolysis is the dimerization of two adjacent thymines in a DNA molecule during UV exposure [5] and UV disinfection [6]. The formation of dimer during UV exposure of DNA is a reversible process. For example, the reaction reaches equilibrium when the sum of the thymine-containing dimers (i.e., thymine-thymine plus thymine-cytosine) of the DNA reaches approximately 7% of the total thymine content. This steady-state indicates that there is a dynamic equilibrium state between the rates of dimer formation (pseudo-zero order) and reversal (first order in dimer content) [7]. This effect can not be easily reflected by the quantum yield of DNA.

The concern over emerging contaminants has grown and many treatment facilities have UV for disinfection purposes. Converting UV photolysis alone into advanced oxidation processes (AOPs) could be an option to meet more stringent regulations in the future. An effective method for evaluating efficiency under both UV photolysis and AOP conditions is necessary.

The purpose of this discussion is to propose a photolysis coefficient, k_p, that can be used to uniquely characterize the response of any constituent to the process. Based on the first principle derivation, the photolysis coefficient represents the product of quantum yield and molar absorption coefficient at each wavelength. It describes the overall vulnerability of a pollutant upon exposure to the UV light, therefore enabling kinetic modeling without getting into the details of quantum yield and absorbance at different wavelengths. It can be used for the calculation of hydroxyl radical generation in AOPs, therefore providing a potential approach to compare UV photolysis with UV based AOPs.

Equations for both single and multiple constituents and light wavelengths were derived although the applications focused on individual constituents due to the availability of data. Also, it should be recognized that photolysis sometimes triggers a chain of reactions involving free radicals of other kinds, which can cause the rate of chemical transformation as a result of photolysis to be influenced by the chemistry of the surrounding water. The discussion is confined to the direct photolysis mechanism itself where constituents are transformed by UV light alone.

2 Methodologies

2.1 Development of the photolysis coefficient

According to the Beer Lambert law for constituent mixtures in solution, the total absorbance is given as the sum of their individual absorbency. That is, $a = \sum_{i=1}^{n} \varepsilon_i C_i$. Consequently, the Beer Lambert law can be written for a multi constituents system as $I = I_0 e^{-a'x}$ and the light absorbed by a constituent i at an infinitely small unit volume is $I_{local,i} = \frac{dI_i}{dx} = I_0 \varepsilon_i C_i e^{-a'x}$. The local rate of photolysis per unit volume at a point in a photolysis reactor is $r_{R,i} = -I_0 \varphi_i \varepsilon_i' C_i e^{-a'x}$. Integrating this local reaction rate over the whole effective pathlength, l, will give the average rate as:

$$r_{avg,i} = -I_0 \phi_i \frac{\varepsilon_i' C_i}{a'} (1 - e^{-a'l}). \quad (1)$$

For the purposes of clarity, equations in this development are written using the molar absorption coefficient in the base e (ε'); whereas, most molar absorption coefficients are found in the literature expressed as base 10 (ε) and conversion between the two, $\varepsilon' = \varepsilon \times \ln(10)$, is often a source of confusion. An einstein is a mole of photons (6.02×10^{23} photons), named in honor of Albert Einstein, who first postulated the existence of the photon [8,9]. The derivation of equations above assumes that the concentration is uniform and this may not be the case if photolysis occurs at a rapid rate and mixing is not adequate.

It is useful to view the pseudo-first order rate constant, k, for the target compound when irradiated with light as the product of two roots:

$$k = \frac{r_{avg,i}}{C_i} = -I_0 \phi_i \frac{\varepsilon_i'}{a'} (1 - e^{-a'l})$$

$$= -\phi_i \varepsilon_i' \frac{I_0 (1 - e^{-a'l})}{a'} = -k_p' \times \frac{I_0 (1 - e^{-a'l})}{a'}. \quad (2)$$

The first root, $\phi_i \varepsilon_i'$, herein named the photolysis coefficient, k_p', characterizes the interaction of the target constituent with light, with these properties, quantum yield and absorption coefficient, determining how sensitive a constituent is to photolysis. Since the overall degradation of constituents is the main interest of the study, the introduction of photolysis coefficient would significantly simplify the data needs but still accurately describe the kinetics of the system. Constituents with a small k_p' value are difficult to address with photolysis. Constituents with a large k_p' value are more easily addressed. Put another way, the photolysis coefficient can be used to determine if a particular constituent is amenable to photolysis. As will be shown later, k_p' can be determined from bench-scale experiments and a catalog of data are beginning to become available in the literature. In Eq. (2), the units of k_p' are $L \cdot einstein^{-1} \cdot cm^{-1}$.

The second root of the pseudo-first order rate constant, $\frac{I_0 (1 - e^{-a'l})}{a'}$, represents the influence of the intensity of the incident light, the absorbance of the water matrix and the distance between the light source and the target constituent. All these affect the rate at which the photons of UV light strike the target constituent in the context of a water in

a UV reactor. Whereas the first root represents the properties of the target constituent, this second root represents the properties of the external circumstances that influence the reaction; that is, the parameters engineers can influence through ingenuity of design. The treatment train selected by the process engineer to prepare the water for the UV reactor can influence the absorbance of the water matrix. For example the absorbance of a secondary effluent may be as high as 0.3 to 0.4 cm^{-1}, but the absorbance of a reverse osmosis (RO) permeate can be as low as 0.01 to 0.03 cm^{-1}. Also, the design of the UV reactor itself will determine the intensity and uniformity of UV light to which the target constituent is exposed and for how long.

If UV lamps other than low-pressure mercury lamps are used in the photo-oxidation process, (e.g., medium-pressure mercury lamps) the spectral distribution of the lamp must be considered. Usually the incident UV light intensity is measured at specific wavelength intervals (e.g., 5 nm) within the effective UV radiation range. The UV-light intensity can be assumed to be monochromatic within such a small wavelength band. The quantum yield and the molar extinction coefficient of a chromophore changes for different wavelengths, and requires measurement as a function of wavelength. Knowing the UV-light intensity, I_{01}, I_{02}, I_{03}, …, I_{0m}, at every m^{th} wavelength band (represented as λ_1, λ_2, λ_3, …, λ_m), as well as ϕ_1, ϕ_2, ϕ_3, …, ϕ_m, and ε_1, ε_2, ε_3,…, ε_m, the photolysis rate can be calculated as follows:

$$r_{avg,i} = -\sum_{j=1}^{m} I_{0,j}\phi_{i,j}\frac{\varepsilon'_{i,j}C_i}{a'_j}(1-e^{-a'_j l}), \quad (3)$$

In general, photolysis follows pseudo-first order kinetics; therefore, the photolysis rate constant may be written:

$$k = \frac{r_{avg,i}}{C_i} = -\sum_{j=1}^{m} I_{0,j}\phi_{i,j}\frac{\varepsilon'_{i,j}}{a'_j}(1-e^{-a'_j l}), \quad (4)$$

In this case, the photolysis coefficient of constituent i is $\sum_{j=1}^{m}\phi_{i,j}\varepsilon'_{i,j}$.

2.2 Calculating the photolysis coefficient for the constituent of interest

The photolysis coefficient can be determined through standard bench-scale tests. Normally these bench-scale photolysis experiments are done using a quasi-collimated beam apparatus [10,11]. The intensity of irradiance is measured in these experiments as an energy flux incident to the sample E_0 ($W \cdot cm^{-2}$) and photon flow must be converted to this form. For photons at a wavelength of λ: $I_0 = \frac{E_0}{U_\lambda}$, where U_λ is the energy embedded in an Einstein of photons and $U_\lambda = \frac{A_v hc}{\lambda}$.

Many photolysis applications are conducted with low-pressure UV light, and many full-scale designs as well. The wavelength of low-pressure UV light is 253.7 nm. At this wavelength, U_λ becomes 471527 $J \cdot einstein^{-1}$.

In bench-scale experiments, the photon flux is assessed by measuring the incident irradiance at the center of the sample surface, E_0 ($W \cdot cm^{-2}$). For a collimated beam arrangement, the light source can be assumed to be a flat plate with a light intensity constant in the y-z plane, perpendicular to the photonic flux. Assuming the reactor beneath the collimated beam is completely mixed and the depth of the sample is ℓ, the performance of the bench scale batch reactor then can be characterized as follows:

$$\int_{C_0}^{C}\frac{dC}{C} = \int_{0}^{t} -\frac{I_0 k'_p}{a'\ell}(1-e^{-a'\ell})dt, \quad (5)$$

Integrating Eq. (5), and expressing the molar absorption coefficient of the constituent, the overall absorptivity of the solution, and the photolysis coefficient in base 10, we obtain:

$$\log\frac{C}{C_0} = -\frac{k_p}{U_\lambda}E_{avg}t, \quad (6)$$

Most commonly, bench-scale results are expressed as a plot of the log removal versus the Fluence or UV dose ($mJ \cdot cm^{-2}$), where the Fluence is defined as the product of the average irradiance, E_{avg}, and the time of exposure, t. It follows that k_p in Eq. (6) (the product, $\phi \times \varepsilon$) may be determined from the slope of a plot of bench-scale collimated beam test results. As shown in Eq. (4), k_p for a medium pressure lamp can be obtained in a similar way by changing the light source for experiment.

Conducting a more detailed analysis addresses the correction factors required to accurately characterize a real-world quasi-collimated beam arrangement. Information on determining these correction factors may be found in the Ultraviolet Applications Handbook [2].

3 Results

The sensitivity of various materials in nature varies over a wide range and Schwarzenbach et al. [12] discusses some of the reasons as well as the types of chemical bonds that are most likely to be sensitive to UV light at various wavelengths. Because low pressure UV is so readily available, sensitivity to light of this wavelength is of particular importance. Tables 1-3 summarize the sensitivity of a variety of organisms, inorganic compounds and organic compounds to low pressure UV (LPUV) light using data gathered from a number of sources in the literature.

Table 1 A summary of photolysis rates of microorganisms at 253.7 nm

organism	slope[a] base 10/($cm^2 \cdot mJ^{-1}$)	k_p/($L \cdot einstein^{-1} \cdot cm^{-1}$)	Ref.
Adenovirus ST2, 15, 40, 41	−0.024	11317	[13]
Adenovirus ST40	−0.018	8487	[13]
B40-8	−0.14	66014	[13]
Bacillus subtilis	−0.059	27820	[13]
Calicivirus feline, canine	−0.106	49982	[13]
Calicivirus, bovine	−0.19	89590	[13]
Campylobacter jejuni	−0.88	414944	[13]
Cryptosporidium parvum	−0.225	106094	[13]
CVB2	−0.119	56112	[14]
Escherischia coli	−0.506	238593	[13]
Escherischia coli O157	−0.642	302720	[13]
φX174	−0.396	186725	[13]
Giardia muris	−0.122	57526	[13]
Hepatitis A	−0.181	85346	[13]
MS2 phage	−0.055	25934	[13]
Poliovirus type 1	−0.135	63656	[13]
PRD1	−0.128	60355	[13]
Qβ	−0.084	39608	[13]
Rotavirus SA-11	−0.102	48096	[13]
Salmonella typherium	−0.515	242836	[13]
Shigella dysenteriae	−1.308	616757	[13]
Shigella sonnei	−0.466	219732	[13]
Streptococcus faecalis	−0.312	147116	[13]
T7	−0.232	109394	[13]
vibrio choleae	−1.341	632318	[13]
Yersinia entrocoliticaa	−0.889	419188	[13]

Note: a) slope = $-k_p / U_{253.7} = -k_p / 471527$

Table 2 Summary of photolysis rates of inorganic chemicals at 253.7 nm

constituent	formula	slope[a] base 10/($cm^2 \cdot mJ^{-1}$)	k_p/($L \cdot einstein^{-1} \cdot cm^{-1}$)	Ref.
nitrate	NO_3^-	−0.00003	14	[15]
hypochlorous acid	HOCl	−0.00109	514	[16]
hypochlorite ion	OCl^-	−0.00065	306	[16]
monochloramine	NH_2Cl	−0.00027	127	[16]
monochloramine	NH_2Cl	−0.00046	217	[17]
monochloramine	NH_2Cl	−0.00039	184	[18]
monochloramine	NH_2Cl[b]	−0.00042	198	[19]
monochloramine	NH_2Cl[c]	−0.00022	104	[19]
dichloramine	$NHCl_2$	−0.00039	184	[18]
dichloramine	$NHCl_2$[b]	−0.00022	104	[19]
dichloramine	$NHCl_2$[c]	−0.00022	104	[19]
trichloramine	NCl_3	−0.0011	519	[18]
hydrogen peroxide	H_2O_2	−0.000046	21.8	[20]

Notes: a) slope = $-k_p / U_{253.7} = -k_p / 471527$; b) experiments conducted in the absence of oxygen; c) experiments conducted in the presence of oxygen

Table 3 Summary of photolysis rates of organic chemicals at 253.7 nm

constituent	slope[a)] base 10/($cm^2 \cdot mJ^{-1}$)	k_p /($L \cdot einstein^{-1} \cdot cm^{-1}$)	Ref.
alachlor	−0.00024	113	[21]
atrazine	−0.00034	160	[21]
bisphenol a	−0.000017	8	[22]
carbamazepine	−0.000014	7	[23]
chlorfenvinphos	−0.00103	486	[21]
clofibric acid	−0.00059	278	[23]
diclofenac	−0.005330	2513	[22]
diphenhydramine	−0.000087	41	[24]
diuron	−0.00065	306	[21]
ibuprofen	−0.000087	41	[24]
iohexol	−0.0024	1130	[23]
isoproturon	−0.000026	12	[21]
N-nitrosodimethylamine (NDMA)	−0.000980	462	[25]
naproxen	−0.00018	85	[23]
pentachlorophenol	−0.00039	184	[21]
phenazone	−0.00109	514	[24]
phenytoin (dilantin)	−0.00083	391	[24]
sulfadiazine	−0.000572	270	[22]
sulfamethazine	−0.000787	371	[22]
sulfamethoxazole	−0.002240	1056	[22]
trimethoprim	−0.000017	8	[22]

Note: a) slope = $-\ k_p$ / $U_{253.7}$ = $-\ k_p$ / 471527

The removal of a selected group of some of the more interesting environmental constituents in these tables is displayed in Fig. 1. The form of Fig. 1 represents a common way that removal by photolysis is expressed in the literature. Examination of these data will reveal that the photolysis coefficients among microorganisms, ranging from 8487 to more than 600000, are far higher than those observed for other environmental constituents of interest. For example, the adenoviruses are much more resistant to photolysis than are other microorganisms and yet, even these are much less resistant than the most sensitive of organic and inorganic compounds listed. The photolysis coefficients for inorganic and organic compounds in these data vary over a similar range of approximately 10 to 1000. It should be noted that only compounds that show some sensitivity to photolysis are listed. Most constituents show less sensitivity.

4 Discussion of the application of photolysis rate

In the field of environmental engineering and science, photolysis reactors are used for two main purposes: disinfection and destruction of undesirable environmental contaminants. Each of these will be demonstrated by example.

4.1 Disinfection

In general, the rates of photolysis reactions in disinfection are much higher than the rates normally observed in the photolysis of other environmental contaminants; hence the values of k_p for these reactions are also characteristically high. MS2, a bacterial virus or phage that uses *E. coli* as its host, has been studied by a number of researchers and it has become one of the standards used in the calibration of UV disinfection units. The data of Havelaar et al. [14] are representative of the organism's behavior. The Havelaar data are shown in Fig. 2 along with a best fit through them.

The fit is not forced through zero because there is no assurance that the assessment of the N_0 value is any more accurate than that of the rest of the data set. The slope of the plot is −0.0416 (base 10). Using Eq. (6) the following relationship is obtained:

$$\frac{k_p}{U_\lambda} = 0.0416 \rightarrow k_p = (0.0416)(471527) = 19618 \text{ at } \lambda = 253.7 \text{ nm}. \quad (7)$$

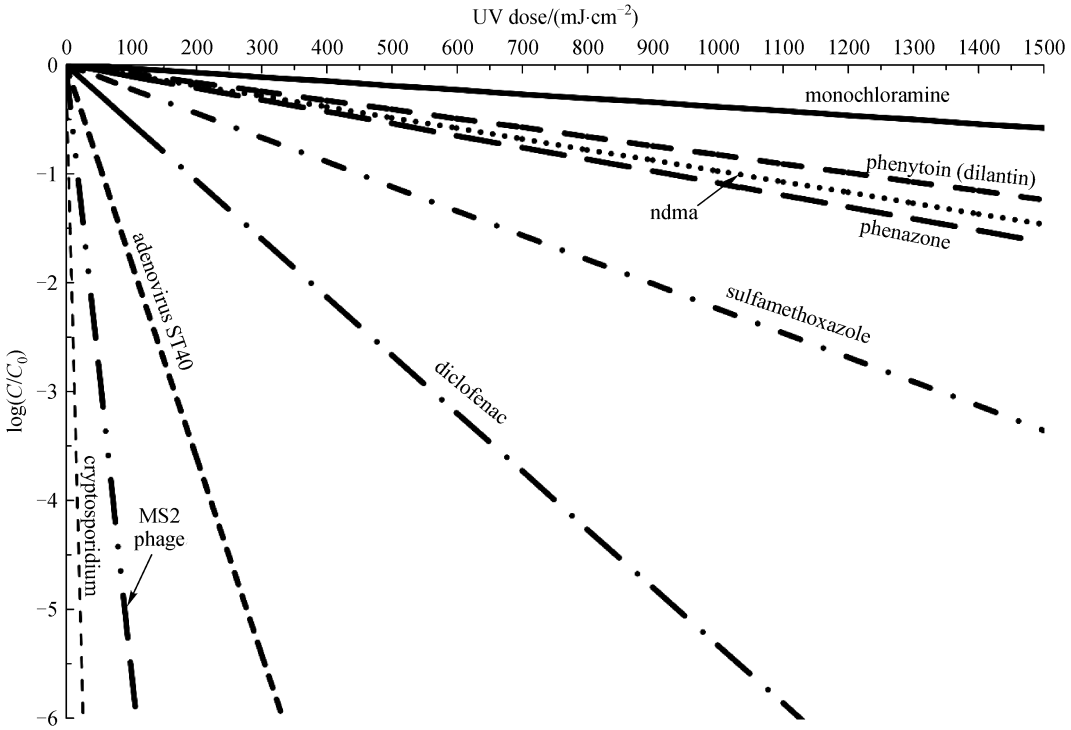

Fig. 1 Photolysis of selected constituents with increasing UV dose (based on photolysis rates of various constituents shown in Tables 1, 2, and 3)

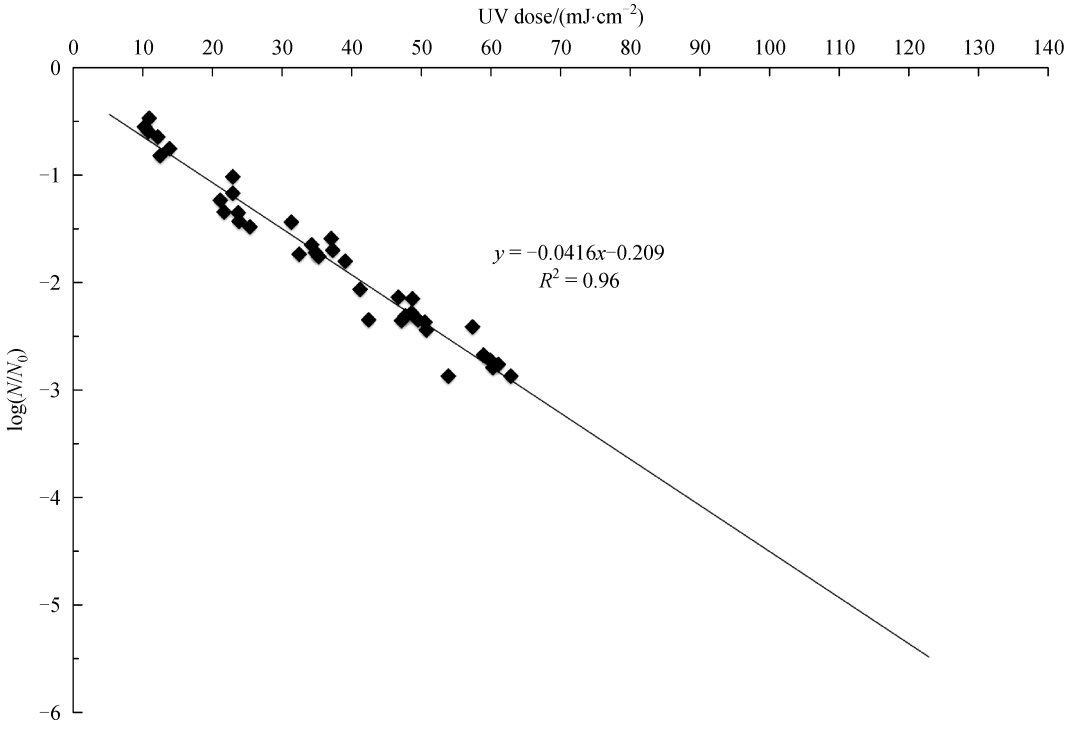

Fig. 2 Semilog plot of the inactivation of MS2 coliphage (data from [14])

In 1965, Rauth [25] reported estimates of the absorption cross-section and quantum yield for MS2 at a wavelength of 253.7 nm. The absorption cross section was reported as 0.91×10^{-13} cm$^2\cdot$molecule^{-1}. The absorption cross section can be converted to the molar absorption coefficient in the following manner:

$$\varepsilon = \frac{\sigma A_v}{1000 \times \ln(10)} = 2.38 \times 10^7 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}. \quad (8)$$

Rauth estimated the quantum yield for MS2 exposed to UV light of wavelength 253.7 nm to be 0.0012 mol $\cdot$einstein^{-1}. Thus Rauth's data would suggest a k_p value of approximately 28560 L$\cdot$einstein$^{-1}\cdot$cm^{-1}. Although the same order of magnitude, these values do not correlate precisely with Havelaar's data [14]. If it is assumed that Rauth's molar absorption coefficient is correct, the quantum yield would be factor of 1.47 lower. Havelaar's data compare well with other published data, so it seems likely that k_p is reasonably accurate. While a more precise breakdown between absorptivity and quantum yield remains elusive, the disinfection kinetics are well-characterized and it's clear that the MS2 absorbs UV light exceptionally well, but the quantum yield is not exceptionally high.

4.2 Photolysis of organic contaminants

N-nitrosodimethylamine (NDMA) is among the more significant environmental contaminants where photolysis is often employed in its removal. Several references have reported the quantum yield of NDMA at a wavelength of 253.7 nm to be approximately 0.3 mol$\cdot$einstein^{-1} [12,14,15]. Stefan and Bolton report the molar absorption coefficient for NDMA at a wavelength of 253.7 nm to be 1470 L$\cdot$mol$^{-1}\cdot$cm^{-1} [26]. Thus k_p would have a value of approximately 441. The removal can be calculated as:

$$\log\left(\frac{C}{C_0}\right) = -\left(\frac{441}{471527}\right)H' = -0.00094H'. \quad (9)$$

In Fig. 3 the results of this model are compared with the collimated beam data from the low pressure (LP) lamp at 254 nm without peroxide.

4.3 Fluence required for a one log removal based on their k_p

The photolysis coefficient itself, like most rate constants, is an abstract concept. As a result, to provide greater accessibility, data on the relative rates of reaction are often shown as the half-life or the time required for a 50 percent reduction. Where sensitivity to photolysis is concerned, a useful analogy is the 90 percent fluence, which represents the fluence of UV light required to accomplish a 90 percent transformation of the target compound. Equation (7) can be rewritten to illustrate this concept.

$$(E_{avg}t)_{90\%} = \frac{U_\lambda}{k_p}, \quad (10)$$

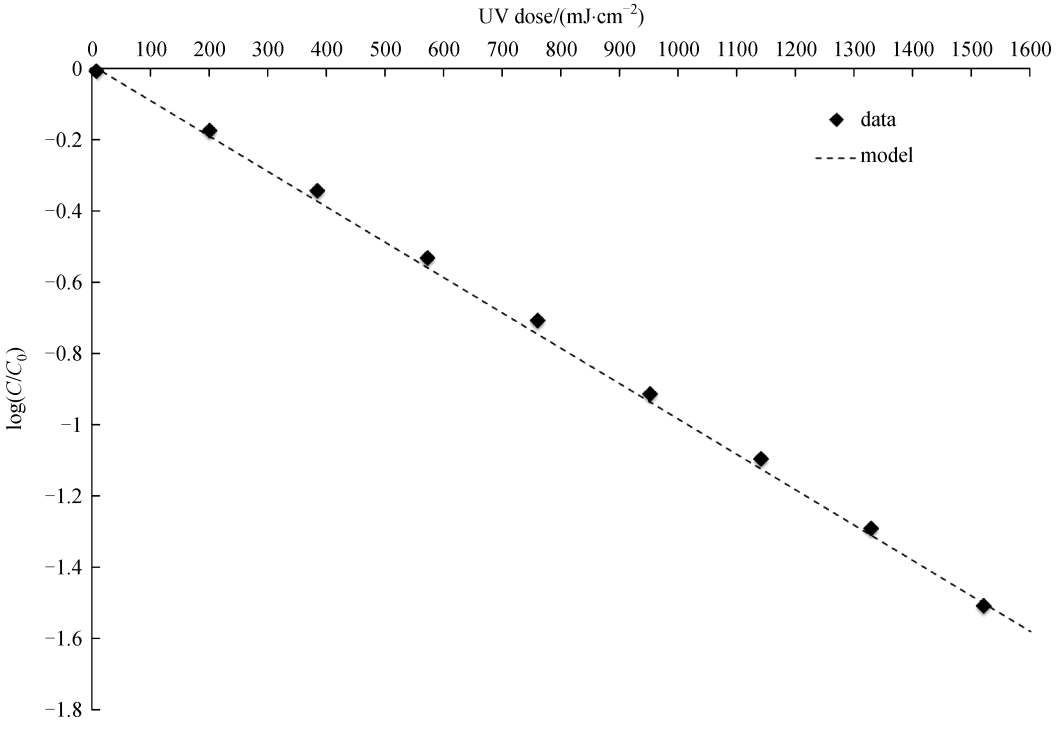

Fig. 3 Semilog plot of the destruction of NDMA via exposure to low pressure UV (data from Sharpless and Linden [27])

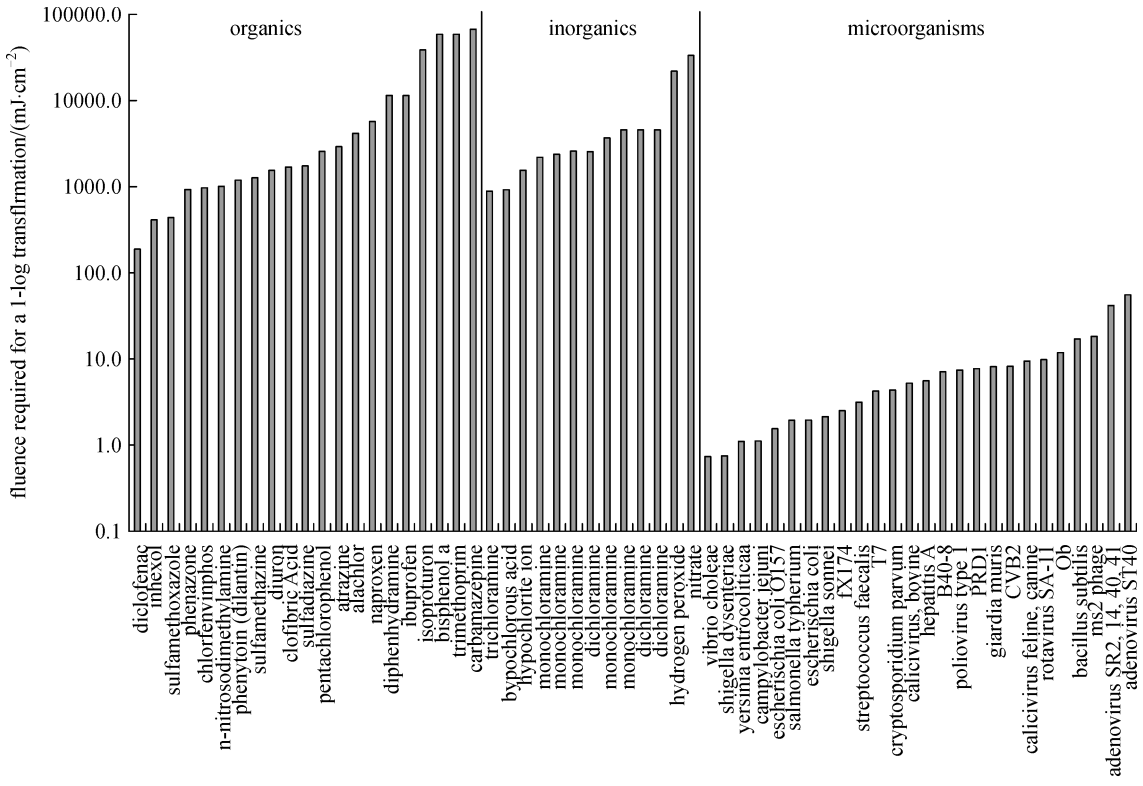

Fig. 4 Overview of fluence required for 1-log reduction in a variety of target constituents

where $(E_{avg}t)_{90\%}$ = Fluence required for a 1-log reduction.

Figure 4 illustrates results of the application of Eq. (8) to find the $(E_{avg}t)_{90\%}$ for all the constituents listed in Tables 1, 2, and 3. Once again, microorganisms show much greater sensitivity and where the design of photo reactors are concerned, even many of the compounds which show some susceptibility may be out of reach at reasonable cost unless free radicals can also be brought to bear.

5 Conclusions

A photolysis coefficient, k_p, has been proposed to capture the properties of any constituent at all irradiation wavelengths, which governs its sensitivity in photolysis reactions. It can be easily obtained from standard bench scale testing. The procedure for obtaining this coefficient for multi-wavelength light sources is as simple as for the single wavelength light source. The k_p provides a potential tool for complex kinetic modeling that avoids getting into the detail of the quantum yields and molar absorption coefficients of each constituent at each wavelength, collection of which could be time consuming and costly. Examination of several dozen k_p values developed from the literature reveals that microbiological constituents are much more sensitive to UV light than are other organic and inorganic compounds, which explains the early success of UV in disinfection. Nevertheless, there are additional constituents besides microorganisms that show UV sensitivity. The photolysis coefficient is a useful tool for use in judging which constituents are most amenable to transformation by UV processes and for scaling the design of UV photolysis processes. The concept of k_p proves that the same principles and the same types of data can be utilized in both UV and UV based AOP applications. It can be potentially used to assess the feasibility and requirements for modifying a UV system to a UV based AOP system.

Nomenclature

a = the absorptivity of the solution, base 10 (cm^{-1});

a' = the absorptivity of the solution, base e (cm^{-1});

a'_j = the absorptivity of the solution at wavelength j, base e (cm^{-1});

A_v = Avogadro's number, 6.02214×10^{23} photons·einstein^{-1};

c = speed of light, 2.99792×10^{8} m·s^{-1};

λ = wavelength of light (m);

C = the concentration of the target compound (mol·L^{-1});

C_i = the concentration of constituent i (mol·L^{-1});

C_0 = the initial concentration of the target compound (mol·L^{-1});

E_0 = energy flux incident to the sample, a measure of the intensity of irradiance (milliwatts·cm^{-2});

E_{avg} = average irradiance = $\frac{(1-10^{-a\,\ell})E_0}{\ln(10)a\,\ell}$ (milliwatts·cm^{-2});

h = Planck's constant, 6.62607×10^{-34} joules·s·photon^{-1} (or joules-s·quanta^{-1});

H' = average UV dose (millijoules·cm^{-2});

i = the index of a constituent;

I_0 = the flux of photons incident to the solution (einstein·cm^{-2}·s^{-1});

I = the flux of photons transmitted through the solution (einstein·cm^{-2}·s^{-1});

$I_{01}, I_{02}, I_{03},\ldots, I_{0m}$, = the flux of photons incident to the solution as a function of wavelength at wavelengths $\lambda_{01},\lambda_{02},\lambda_{03},\ldots,\lambda_{0m}$ for a polychromatic light source (einstein·cm^{-2}·s^{-1});

$I_{\text{local},i}$ = the light absorbed by a constituent i at an infinitely small volume (einstein·cm^{-2}·s^{-1});

n = the number of constituents;

j = the index of wavelengths;

k = pseudo-first order rate constant for target compound irradiated with light (s^{-1});

k_p = photolysis coefficient, base 10 = k'_p / ln(10) (L·einstein^{-1}·cm^{-1});

k'_p = photolysis coefficient, base e (L·einstein^{-1}·cm^{-1});

ℓ = depth of the sample (cm);

l = the effective pathlength in a reactor (cm);

m = the total number of wavelengths;

N = number of microorganisms;

N_0 = number of microorganisms at time zero;

$r_{avg,i}$ = average rate of photolysis for constituent i (mol·cm^{-3}·s^{-1});

r_R = localized rate of photolysis (mol·cm^{-3}·s^{-1});

$r_{R,i}$ = localized rate of photolysis for constituent i (mol·cm^{-3}·s^{-1});

t = time of exposure (s);

x = the distance traveled by the light (cm);

U_λ = energy per einstein for photons of wavelength λ (joules·einstein^{-1});

ϵ = the molar absorption coefficient of constituents base 10 (L·mol^{-1}·cm^{-1});

ϵ_i = the molar absorption coefficient of constituent i base 10 (L·mol^{-1}·cm^{-1});

$\varepsilon_1,\varepsilon_2,\varepsilon_3,\ldots,\varepsilon_m$ = the molar absorption coefficient of constituents base 10 at wavelengths $\lambda_{01},\lambda_{02},\lambda_{03},\ldots,\lambda_{0m}$ (L·mol^{-1}·cm^{-1});

ε' = the molar absorption coefficient of constituents base e (L·mol^{-1}·cm^{-1});

$\varepsilon'_{i,j}$ = the molar absorption coefficient of constituent i at wavelength j base e (L·mol^{-1}·cm^{-1});

ϕ = quantum yield, mole of constituent transformed per einstein of photons absorbed by constituent (mol·einstein^{-1});

ϕ_i = quantum yield of constituent i, moles transformed per einstein of photons absorbed (mol·einstein^{-1});

$\phi_1,\phi_2,\phi_3,\ldots,\phi_m$ = quantum yield of constituent i at wavelengths $\lambda_{01},\lambda_{02},\lambda_{03},\ldots,\lambda_{0m}$, moles transformed per einstein of photons absorbed (mol·einstein^{-1});

$\phi_{i,j}$ = quantum yield of constituent i at wavelength j, moles transformed per einstein of photons absorbed (mol·einstein^{-1});

λ = wavelength (nm);

$\lambda_{01},\lambda_{02},\lambda_{03},\ldots,\lambda_{0m}$ = wavelengths of light for polychromatic light source (nm);

σ = inactivation cross-section (cm^2·molecule^{-1}).

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