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FIGURES-OF-MERIT FOR THE TECHNICAL DEVELOPMENT AND APPLICATION OF ADVANCED OXIDATION TECHNOLOGIES FOR BOTH ELECTRIC- AND SOLAR-DRIVEN SYSTEMS[†]

(IUPAC Technical Report)

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Abstract: Advanced oxidation technologies (AOTs), which involve the *in situ* generation of highly potent chemical oxidants, such as the hydroxyl radical (•OH), have emerged as an important class of technologies for accelerating the oxidation (and hence removal) of a wide range of organic contaminants in polluted water and air. In this report, standard figures-of-merit are proposed for the comparison and evaluation of these waste treatment technologies. These figures-of-merit are based on electric-energy consumption (for electric-energy-driven systems) or collector area (for solar-energy-driven systems). They fit within two phenomenological kinetic order regimes: 1) for high contaminant concentrations (electric energy per mass, E_{EM}, or collector area per mass, A_{CM}) and 2) for low concentrations (electric energy per order of magnitude, E_{EO}, or collector area per order of magnitude, A_{CO}). Furthermore, a simple understanding of the overall kinetic behavior of organic contaminant removal in a waste stream (i.e., whether zero- or first-order) is shown to be necessary for the description of meaningful electric- or solar-energy efficiencies. These standard figures-of-merit provide a direct link to the electric- or solar-energy efficiency (lower values mean higher efficiency) of an advanced oxidation technology, independent of the nature of the system, and therefore allow for direct comparison of widely disparate AOTs. These figures-of-merit are also shown to be inversely proportional to fundamental efficiency factors, such as the lamp efficiency (for electrical systems), the fraction of the emitted light that is absorbed in the aqueous solution, and the quantum yield of generation of active radicals.

I. INTRODUCTION

Advanced oxidation technologies (AOTs), which involve the *in situ* generation of highly potent chemical oxidants, such as the hydroxyl radical (•OH), have emerged [1] as an important class of technologies for accelerating the oxidation (and hence contaminant removal) of a wide range of organic contaminants in polluted water and air. A partial list of these technologies includes: homogeneous ultraviolet irradiation [2] (either direct irradiation of the contaminant or photolytic oxidation mediated by hydrogen peroxide (UV/H$_2$O$_2$), and/or ozone (UV/H$_2$O$_2$/O$_3$ or UV/O$_3$), heterogeneous photocatalysis using semiconductor catalysts (e.g., UV/TiO$_2$) [3], electron-beam irradiation [4], X-ray or gamma-ray radiolysis, nonthermal electric discharge [5], supercritical water oxidation [6] and ultrasonic irradiation (sonolysis) [7] or electrohydraulic cavitation. These technologies involve widely different methods of activation, as well as oxidant generation, and can potentially utilize a number of different mechanisms for organic contaminant removal. Most of these processes, however, are electric-energy-driven and share the common denominator of hydroxyl radical chemistry for part of the contaminant removal. Of the above AOTs, the photochemical processes are the most important commercially; hence, photochemical examples are used in the discussion of the application of the figures-of-merit developed in this paper, including those driven by the absorption of solar energy.

Despite the fact that some of these AOTs have been developed to the point of full-scale commercialization, generally applicable figures-of-merit have yet to be established. There has been a tendency to quote or estimate treatment costs per unit volume for a particular waste stream and technology (e.g., dollars/1000 gal); however, such notation does not take into account the concentration of the contaminant nor the treatment goals. Herein, figures-of-merit are recommended that are based on electric energy consumption or solar collector area within two phenomenological kinetic order regimes: one for high contaminant concentrations, and one for low concentrations. Furthermore, a simple understanding of the overall kinetic behavior of organic contaminant removal in a waste stream (i.e., whether zero or first order) is necessary for describing meaningful energy efficiencies. These standard figures-of-merit are valuable in that they give a direct link to the electric- or solar-energy efficiency of an advanced oxidation technology, independent of the nature of the system, and therefore allow for comparison of widely disparate AOTs (see ref. 8 for an example of how these figures-of-merit have been used to evaluate three different AOTs). Such figures-of-merit are necessary not only to compare AOTs, but also to provide the requisite data for scale-up and economic analyses for comparison with conventional treatment technologies (e.g., carbon adsorption/regeneration, air stripping, and incineration).

There are a number of important factors in selecting a waste-treatment technology, including: economics, economy of scale, regulations, effluent quality goals, operation (maintenance, control, safety) and robustness (flexibility to change/upsets). Although all these factors are important, economics is often paramount. A full economic analysis of the net present cost (i.e., amortized investment, installation, and operating costs) of implementing a wide range of treatment technologies represents an arduous task and is both site- and problem-specific.

Since most AOTs are electric-energy-intensive, and electric energy can represent a major fraction of the operating costs, simple figures-of-merit based on electric energy consumption can be very useful and informative. Moreover, electric energy dose requirements also dictate the size of the capital equipment needed to generate the requisite dose, so investment should also tend to scale (inversely) with this figure-of-merit.

The use of solar energy to mineralize organic pollutants or to detoxify water or air contaminated with them has gained considerable interest in the past few years [9,10]. As this approach moves toward possible commercial application, there is a need for corresponding "solar figures-of-merit" to evaluate and to compare various solar-energy-driven systems.

Note: the authors chose not to follow all the recommendations given in the IUPAC "Green Book" [11], because this report is aimed at a specific audience used to a certain choice of units, and for whom equations containing numerical values related to specified units are more useful.

II. A SIMPLE REACTION MECHANISM FOR AOTs

Although the removal and eventual mineralization of organic contaminants through advanced oxidation processes can be complex, and involves a number of elementary chemical steps, the overall kinetics or rate of removal of a specific component, and even the reduction of the total organic carbon (TOC) content, can often be described phenomenologically by simple rate expressions that are either zero-order or first-order in the organic contaminant. In general, most processes involved in AOTs can be modeled by the following simple mechanism:

$$A \rightarrow Z\bullet \qquad v_1 = \xi P/V \tag{1}$$

$$Z\bullet + C \rightarrow products \qquad v_2 = k_C[Z\bullet][C] \tag{2}$$

$$Z\bullet + S_1 \rightarrow products \qquad v_{3a} = k_{S_1}[Z\bullet][S_1] \tag{3a}$$

$$Z\bullet + S_2 \rightarrow \text{products} \quad v_{3b} = k_{S_2}[Z\bullet][S_2] \tag{3b}$$

. . . .

$$Z\bullet + S_i \rightarrow \text{products} \quad v_{3i} = k_{S_i}[Z\bullet][S_i] \tag{3i}$$

. . . .

where v is a rate (M s^{-1}), ξ is a constant [usual unit: mol s^{-1} kW^{-1}] that depends on the system and the technology, P is the electric power [kW] input to the system, and V is the treated volume [L]. A is the initiating compound, which can be water or some added substance (e.g., H_2O_2 or O_3), Z$\bullet$ is a highly reactive intermediate (e.g., $\bullet$OH, H$\bullet$, hydrated electron, etc.) [12], C is a particular organic contaminant (or C can also represent the total organic carbon), and S_1, S_2, ..., S_i, ... are a series of scavengers for the Z$\bullet$ radical. v_1 is the rate of formation [M s^{-1}] of Z$\bullet$. (For example, in the case of an electric-driven photo-chemical process, $\xi = G\chi\Phi_{Z\bullet}/P$, where G is the total absolute photon flow [einsteins s^{-1}] [13] emitted from the lamp in all directions in a useful wavelength range, χ is the fraction of those photons that are absorbed in the solution, and $\Phi_{Z\bullet}$ is the quantum yield for the generation of Z$\bullet$.) v_2 is the rate of reaction of Z$\bullet$ with C, with second-order rate constant k_C, and v_{3a}, v_{3b} ..., v_{3i} ... are the rates of reaction of Z$\bullet$ with scavengers S_1, S_2, ..., S_i ..., with second-order rate constants k_{S_1} k_{S_2} and k_{S_i}. Note that the above general mechanism does not assume any reformation of C from the intermediates.

A steady-state analysis of this general mechanism yields the following overall rate law:

$$\text{rate} = -\frac{d[C]}{dt} = \frac{\xi P k_C[C]/V}{k_C[C] + \sum_i k_{S_i}[S_i]} \tag{4}$$

This simple mechanism illustrates why one often observes simple overall kinetics that are either zero- or first-order in the contaminant C. If [C] is high, so that $k_C[C] \gg \sum_i k_{S_i}[S_i]$ (i.e., reaction 2 with the contaminant dominates over the scavenging of Z$\bullet$ in reactions 3), then the reaction rate will be *zero-order* in C (rate = $\xi P/V$). On the other hand, if [C] is low so that $k_C[C] \ll \sum_i k_{S_i}[S_i]$, the reaction rate will be *first order* in C with the *observed* first-order rate constant k_1' [s^{-1}] given by

$$k_1' = \frac{\xi P k_C/V}{\sum_i k_{S_i}[S_i]} \tag{5}$$

The demarcation between "high" and "low" concentration varies considerably with the system but is often ~100 mg/L. (For TOC reduction, much lower concentrations can still follow zero-order kinet-ics [14].) The kinetic order with respect to C has important ramifications for defining the parameters of the electric-energy dose for an AOT treatment. As described below, the dose requirements within the zero-order regime increase linearly with the amount of organic material to be treated (i.e., with mass), whereas, for the first-order regime, the dose scales with the volume and treatment goal (i.e., orders of magnitude of reduction in concentration).

III. FIGURES-OF-MERIT FOR ELECTRIC-ENERGY-DRIVEN SYSTEMS

Two figures-of-merit are proposed: one suitable for high organic concentrations and the other for low concentrations.

III.1. Electric energy per mass (E_{EM})

This figure-of-merit is most useful when [C] is high (i.e., phenomenologically zero-order in C) because the rate of removal of the contaminant is directly proportional to the rate of electric energy use. The def-inition of E_{EM} is:

Electric energy per mass (E_{EM}) is the electric energy in kilowatt-hours [kWh] required to bring about the degradation of a unit mass (e.g., one kilogram, kg) of a contaminant C in polluted water or air.

The E_{EM} value [kWh/kg] can be calculated from the simple formulas:

$$E_{EM} = \frac{Pt1000}{VM(c_i - c_f)} \qquad \text{batch operation} \qquad (6a)$$

$$E_{EM} = \frac{P}{FM(c_i - c_f)} \qquad \text{flow-through operation} \qquad (6b)$$

P is the rated power [kW] of the AOT system, V is the volume [L] of water or air treated in the time t [h], M is the molar mass [g mol^{-1}] of C [15], F is the water or air volume flow rate [m^3/h], c_i, c_f are the initial (or influent) and final (or effluent) concentrations [M or mol L^{-1}] of C, and the factor of 1000 converts g to kg. Higher E_{EM} values correspond to lower removal efficiencies. Alternatively, if mass concentrations are used ($\gamma = m/V$) (usual unit mg/L),

$$E_{EM} = \frac{Pt10^6}{V(\gamma_i - \gamma_f)} \qquad \text{batch operation} \qquad (6c)$$

$$E_{EM} = \frac{P10^3}{F(\gamma_i - \gamma_f)} \qquad \text{flow-through operation} \qquad (6d)$$

The "electric energy" is defined as the energy supplied to the AOT treatment system (i.e., "out-of-the-wall") [16]. It is important that the starting concentration be stated when giving an E_{EM} value.

Often the E_{EM} can be related to more fundamental parameters of the system. For example, in the case of a photochemical process, $\xi P = G\chi\Phi_{Z\bullet}$ (see eq. 4), where G is the photon flow (einstein s^{-1}) from the lamp, χ is the fraction of this flow that enters the photochemical reactor, and $\Phi_{Z\bullet}$ is the quantum yield for generation of the intermediate Z$\bullet$ (see eq. 1). Under conditions where the rate is "zero-order", the zero-order rate from eq. 4 is $3600G\chi\Phi_{Z\bullet}/V$ [M h^{-1}], thus

$$E_{EM} = \frac{P1000}{M\,3600\,G\chi\,\Phi_{Z\bullet}} \qquad (7)$$

Thus, the E_{EM} is inversely proportional to the fundamental efficiency factors G, χ, and $\Phi_{Z\bullet}$. The more efficient the lamp, the larger G will be, compared to the input power P, and the lower the E_{EM}. Also, the larger the fraction of the light absorbed ($\chi \to 1.0$) and the larger the quantum yield $\Phi_{Z\bullet}$, the smaller the E_{EM}. Similar fundamental efficiency equations could be derived for other AOTs.

Equation 7 can be used to calculate a minimum feasible value of E_{EM} (i.e., maximum efficiency) for a photochemical oxidation process:

A hypothetical contaminant is assumed with a molar mass of 100 g mol^{-1}:

1. 25% of the electric energy input into a medium-pressure UV lamp system produces useful UV photons with an average wavelength of 254 nm.
2. $\Phi_{Z\bullet} = \chi = 1.0$.
3. One Z$\bullet$ radical is required to transform and remove one molecule of contaminant.

One einstein (one mole) of 254-nm photons carries an energy of 0.1308 kWh, or one kWh of electric energy output (at 25% efficiency) would generate 1.91 einsteins of UV photons so that 1.91 moles or 191 g of the contaminant would be degraded per kWh of electric energy. Under these "best-case" assumptions, the **minimum E_{EM} would be 5.2 kWh/kg.** For TOC reduction (i.e., molar mass of 12 g mol^{-1}) and **assuming only two hydroxyl radicals required per carbon atom, the minimum E_{EM} would be 87.2 kWh/kg TOC**.

More efficient photochemical processes would require more efficient light sources (unlikely, except for incremental improvements), processes that utilize a wider range of the spectral lamp output (now possible with some iron-based photocatalysts) or greater than unit quantum yields for oxidant production [17]. Similar estimates of maximum efficiency should be definable in an analogous manner for other AOTs.

III.2. Electric energy per order (E_{EO})

This figure-of-merit is best used for situations where [C] is low (i.e., cases that are overall first-order in C) because the amount of electric energy required to bring about a reduction by one order of magnitude in [C] is independent of [C] [18]. Thus, it would take the same amount of electric energy to reduce the contaminant concentration from 10 mg/L to 1 mg/L in a given volume as it would to reduce it from 10 μg/L to 1 μg/L. E_{EO} is defined as:

> Electric energy per order (E_{EO}) is the electric energy in kilowatt hours [kWh] required to degrade a contaminant C by one order of magnitude in a unit volume [e.g., 1 m^3 (1000 L)] [19] of contaminated water or air.

E_{EO} values [usual units, kWh/m^3/order] can be calculated using the following formulas:

$$E_{EO} = \frac{Pt1000}{V \lg\left(c_i / c_f\right)} \qquad \text{batch operation} \qquad (8a)$$

$$E_{EO} = \frac{P}{F \lg\left(c_i / c_f\right)} \qquad \text{flow-through operation} \qquad (8b)$$

where P, V, t, and c_i, c_f have the same definitions as in eqs. 6 [20], and lg is the symbol for the decadic logarithm. As before, F is the water or air volume flow rate [m^3/h] in the flow-through system.

Note that eqs. 8 implicitly assume first-order kinetics, that is, $\lg(c_i/c_f) = 0.4343k_1't$, where t [min] is the reaction time in the reactor and k_1' is the first-order rate constant [min^{-1}]. For example, in the case of an idealized batch reactor [21], eq. 8a becomes

$$E_{EO} = \frac{38.4P}{V k_1'} \qquad (9)$$

where V is batch reactor volume [L].

Again, the E_{EO} can be related to more fundamental parameters. For example, in the case of a photochemical reaction, the first-order rate constant k_1' [min^{-1}] is given by

$$k_1' = \frac{60\, G\chi\, \Phi_{Z\bullet} k_C / V}{\sum_i k_{S_i} [S_i]} \qquad (10)$$

and using eq. 5

$$E_{EO} = \frac{0.640 P \sum_i k_{S_i} [S_i]}{G \chi \Phi_{Z \bullet} k_C} \qquad (11)$$

Thus, the E_{EO} is again inversely proportional to the three important fundamental efficiency parameters.

Equation 11 can be used to illustrate the calculation of a theoretical E_{EO} for a given system. Suppose that a wastewater containing trichloroethene (TCE) at 10 mg/L is to be treated by a UV/H_2O_2 process, where the water has a bicarbonate concentration of 10 mM at pH 7 and an added H_2O_2 concentration of 100 mg/L (2.94 mM). The rate constants for reaction of hydroxyl radicals with H_2O_2 (2.7×10^7 M^{-1} s^{-1}), HCO$_3^-$ (8.5×10^6 M^{-1} s^{-1}) and TCE (4.2×10^9 M^{-1} s^{-1}) are known [22]. Assume that a 1-kW lamp is used with 25% UV power efficiency in the 200–300 nm region. If one assumes that the average wavelength is 254 nm ($G = 5.31 \times 10^{-4}$ einstein s^{-1}), $\chi = 0.75$ and $\Phi_{Z \bullet} = 1.0$, the E_{EO} is calculated to be 0.034 kWh/m^3/order. Note that the E_{EO} is inversely proportional to k_C.

IV. SOLAR-ENERGY-DRIVEN SYSTEMS

In solar-energy-driven systems, the electric energy [kWh] {given by $P \times t$ – the electrical power used [kW] times the treatment time [h]} is replaced by the solar energy (kWh) collected {$(E_S \times A \times t)/1000$, where E_S is the solar irradiance [W m^{-2}] incident on the collector, A is the collector area [m^2], and t is the time [h]}. While there is no cost for the solar radiation, there can be a substantial capital cost for the collector. Generally, the capital cost of a solar collector is proportional to its area; hence, figures-of-merit based on the solar collector area are appropriate.

The solar irradiance E_S anywhere on Earth's surface depends on the time of day, the season, the altitude, latitude, and the cloud cover. (The spectral distribution of E_S depends somewhat on altitude and atmospheric conditions, but these effects are small enough to be ignored for purposes of defining figures-of-merit.) With the sun directly overhead on a cloudless day, E_S is about 1000 W m^{-2}. A "standardized" irradiance, E_S^o (1000 W m^{-2} based on the AM 1.5 standard solar spectrum on a horizontal surface) [23], can be used in the definition of the solar figures-of-merit by correcting the observed irradiance to the standard. Thus, two "solar figures-of-merit" can be defined for the two kinetic regimes based on the collector area necessary to remove a given pollutant.

The average solar irradiance $\bar{E}_S$ over the time of a given treatment is given by

$$\bar{E}_S = \frac{\int_{t_i}^{t_f} E_S(t) dt}{(t_f - t_i)} \qquad (12)$$

where $E_S(t)$ is the irradiance at a given time t and t_i, t_f are the initial and final times, respectively. $\bar{E}_S$ is best determined using an integrating radiometer or an actinometer (e.g., the ferrioxalate actinometer [24]).

IV.1 Collector area per mass (A_{CM})

In the high concentration range, the appropriate figure-of-merit is the *collector area per mass* (A_{CM}), defined as

Collector area per mass (A_{CM}) is the collector area required to bring about the degradation of a unit mass (e.g., one kilogram, kg) of a contaminant C in polluted water or air in a time t_o (1 h) when the incident solar irradiance is 1000 W m^{-2}.

For a batch system treated over a certain time period t, the A_{CM} [m^2/kg] may be calculated from

$$A_{CM} = \frac{A\,\overline{E}_S\,t\,1000}{E_S^o\,t_o\,M\,V\,(c_i - c_f)} \tag{13a}$$

where A [m^2] is the actual collector area, M is the molar mass [g mol^{-1}] of the pollutant, V [L] is the volume treated, $\overline{E}_S$[W m^{-2}] is the average solar irradiance over the period t of the treatment, and c_i, and c_f are the influent and effluent pollutant concentrations [M]. Note that $E_S^o = 1000$ W m^{-2} and $t_o = 1.0$ h.

Alternatively, if mass concentrations ($\gamma = m/V$) [usual units, mg/L] are used

$$A_{CM} = \frac{A\overline{E}_S t 1000}{V(\gamma_i - \gamma_f)} \tag{13b}$$

In a flow-through system with a flow rate of F [m^3 h^{-1}], the corresponding equations are

$$A_{CM} = \frac{A\overline{E}_S}{MF(c_i - c_f)} \tag{13c}$$

where $\overline{E}_S$[W m^{-2}] is averaged over the residence time. For mass concentrations in mg/L

$$A_{CM} = \frac{A\overline{E}_S 1000}{F(\gamma_i - \gamma_f)} \tag{13d}$$

IV.2 Collector area per order (A_{CO})

In the low concentration range, the appropriate figure-of-merit is the *collector area per order* (A_{CO}), defined as

Collector area per order (A_{CO}) is the collector area required to reduce the concentration of a contaminant C in polluted water or air in a unit volume (e.g., 1 m^3) by one order of magnitude in a time t$_o$ (1 h) when the incident solar irradiance is 1000 W m^{-2}.

The A_{CO} [m^2/(m^3-order)] can be calculated from

$$A_{CO} = \frac{A\overline{E}_S t}{V \lg(c_i / c_f)} \qquad \text{batch operation} \tag{14a}$$

$$A_{CO} = \frac{A\overline{E}_S}{F \lg(c_i / c_f)} \qquad \text{flow-through operation} \tag{14b}$$

V. EXAMPLES

Three examples of waste treatment are presented to illustrate the use of the figures-of-merit:

1. 2000 L of a wastewater containing 500 mg/L of total organic carbon (TOC) as phenol is treated in a batch reactor for 10 h with an AOT rated at 30 kW to yield an effluent that is 100 mg/L TOC.

What is the E_{EM} for this system?

$P = 30$ kW; $\gamma_I = 500$ mg/L; $\gamma_f = 100$ mg/L; $V = 2000$ L; $t = 10$ h. From eq. 6c, the $E_{EM} = 375$ kWh/kg.

2. A groundwater containing 200 µg/L of trichloroethene (TCE) flowing at 20 m³/h is treated with an AOT rated at 25 kW. It was found that the effluent concentration of TCE had dropped to 5 µg/L.

    $P = 25$ kW; $\gamma_I = 200$ µg/L; $\gamma_f = 5$ µg/L; $F = 20$ m³/h. From eq. 8b, the $E_{EO} = 0.78$ kWh/m³/order.

3. A solar collector of dimensions 1×4 m is employed in a water treatment system to treat 1,4-dioxane (initial concentration 500 mg/L). The average solar irradiance was 850 W m^{-2}. The total volume of the batch system was 300 L. The 1,4-dioxane was found to decay by zero-order kinetics to 200 mg/L in 1.5 h.

    $A = 4$ m²; $\bar{E}_S = 850$ W m^{-2}; $V = 300$ L; $\gamma_i = 500$ mg/L; $\gamma_f = 200$ mg/L. From eq. 8b, the $A_{CM} = 56.7$ m²h per kg 1,4-dioxane.

VI. CONCLUSIONS

The figures-of-merit proposed in this paper provide a direct link to the efficiency (lower values mean a more efficient process) of an AOT system, independent of the nature of the system (i.e., effectively treating the AOT system as a "black box"). These figures-of-merit (E_{EM} and E_{EO} for an electric-energy-driven system and A_{CM} and A_{CO} for a solar-energy-driven system), allow for a rapid determination of the system costs and an indication of the total power and/or capital investment required for a specific application. For example, if the E_{EO} of a process is 3.0 kWh/m³/order, the treatment goal is a reduction in the concentration of the contaminant by a factor of three orders of magnitude and the cost of electricity is 0.08 USD/kWh, the electric energy cost will be $3.0 \times 3 \times 0.08 = 0.72$ USD/m³ of water treated. Of course, there are other cost factors (chemicals, operation/maintenance, capital, etc.) that go into a complete cost analysis; however, these figures-of-merit, if adopted, will allow the industry and potential users to have a standardized objective basis for comparison. Lastly, it is clear that an understanding of the kinetics of contaminant removal, at least whether phenomenologically first- or zero-order, is the key to understanding the elements and applicability of advanced waste-treatment technologies.

ACKNOWLEDGMENTS

REFERENCES AND NOTES

1. a) *Proceedings of the Symposium on Advanced Oxidation Processes for the Treatment of Contaminated Water and Air*, Toronto, Canada (June 1990); b) A. P. Jackman and R. L. Powell, *Hazardous Waste Treatment Technologies*, Noyes Publications, Park Ridge, NJ (1991).

2. J. R. Bolton and S. R. Cater. In *Surface and Aquatic Environmental Photochemistry*, G. Helz, R. Zepp, D. Crosby (Eds.), Ch. 33, pp. 467–490, CRC Press, Boca Raton, (1994).

3. (a) O. Legrini, E. Oliveros, A. M. Braun. *Chem. Rev.* **93**, 671 (1993); (b) M. R. Hoffmann, S. T. Martin, W. Choi, D. W. Bahnemann. *Chem. Rev.* **95**, 69–96 (1995).

4. W. J. Cooper, R. D. Curry, K. E. O'Shea (Eds.). *Environmental Applications of Ionizing Radiation*, Wiley, New York (1998).

5. a) A. D. Donaldson, R. P. Apa, T. L. Eddy, J. E. Flinn. *HTD (Am. Soc. Mech. Eng.)*, **161**, 41 (1991); b) L. A. Rosocha, W. H. McCulla, G. K. Anderson, J. J. Coogan, M. Kang, R. A. Tennant, P. J. Wantuck. In "Thermal Treat. Radioact., Hazard. Chem. Mixed Med. Wastes, Proc. 11th Incineration Conference," M. E. Wacks (Ed.), p. 179, University of California, Irvine (1992).

6. J. W. Tester, H. R. Holgate, F. J. Armellini, P. A. Webley, W. R. Killilea, G. T. Hong, H. E. Barner. "Supercritical water oxidation: Technology process development and fundamental research" in *Emerging Technologies in Hazardous Waste Management III*, ACS Symposium Series, Vol. 518, pp. 35–76, American Chemical Society, Washington, DC (1993).

7. a) H. M. Cheung, A. Bhatnagar, G. Jansen. *Environ. Sci. Technol.* **25**, 1510 (1991); b) S. Okouchi, O. Nojima, T. Arai. *Water Sci. Technol.* **26**, 2053 (1992).

8. J. R. Bolton, J. E. Valladares, J. P. Zanin, W. J. Cooper, M. G. Nickelsen, D. C. Kajdi, T. D. Waite, C. N. Kurucz. *J. Adv. Oxid. Technol.* **3**, 174–181 (1998).

9. J. R. Bolton, A. Safarzadeh-Amiri, S. R. Cater. "The Detoxification of Waste Water Streams Using Solar and Artificial UV Light Sources", *Alternative Fuels and the Environment*, R. Sterrett (Ed.), pp. 187–192, Lewis Publishers, Boca Raton, FL (1994).

10. *Solar Energy*, A Special Issue devoted to "Solar Detoxification", J. R. Bolton (Ed.), *Solar Energy* **56** (1996).

11. *Quantities, Units and Symbols in Physical Chemistry* (The IUPAC "Green Book"), 2nd ed., I. Mills, T. Cvitas, K. Homann, N. Kallay, K. Kuchitsu (Eds.), Blackwell, Oxford (1993).

12. In a given case, the reactions are usually dominated by only one radical (e.g., •OH).

13. One Einstein = one mole (6.023×10^{23}) photons.

14. As illustrated by eq. 4, it is quite possible that for high degrees of removal of high concentrations of a contaminant, the system could exhibit a transition from zero to first-order kinetics during the treatment. Furthermore, it is possible that neither $k_C[C]$ nor $\Sigma_i\, k_{S_i}[S_i]$ could be clearly rate-determining for a particular system. In this case, the kinetic behavior would be more complex and not described by simple first- or zero-order kinetics.

15. To calculate E_{EM} values for TOC reduction, rather than a specific contaminant removal, M is equal to the atomic weight of carbon ($12\ \text{g mol}^{-1}$) and c_i and c_f are total carbon concentrations in mol L^{-1} (M).

16. Electric energy defined in this manner includes the electric-energy efficiencies of any transformers or power supplies, and corresponds to the electric energy billed by the power company.

17. The observation of E_{EM} values lower than the maximum feasible efficiency could indicate radical-chain chemistry; however, it is also possible that it could indicate that the wrong kinetic behavior was assumed; that is, the process might actually be first order rather than assumed zero order.

18. Recall that for first-order kinetics the half-life (or time for any order of reduction) is independent of the initial concentration.

19. E_{EO} is often expressed in terms of 1000 US gallons. These E_{EO} values are larger than those based on 1000 L by a factor of 3.785.

20. Equation 8a for first-order reactions is appropriate for batch or plug-flow reactors; however, a different form is required for continuously stirred tank reactors (CSTRs). For a CSTR, $c_f/c_i = 1/(1+ k\tau)$ where τ is the hold-up time and k is the first-order rate constant. Unlike a batch or plug-flow reactor, the electrical energy dose is not a constant per order so eq. 8a cannot be used. The electrical energy would need to be calculated for each removal efficiency.
21. Equations 8 are valid only for idealized batch and flow-through situations (i.e., perfectly mixed for batch and pure plug-flow for the flow-through configuration). Actual situations need to be corrected for inefficiencies in mixing (batch) and dispersion (flow-through).

22. G. V. Buxton, C. L. Greenstock, W. P. Helman, A. B. Ross. *J. Phys. Chem. Ref. Data* **17**, 513 (1988).
23. R. Hulstrom, R. Bird, C. Riordan. *Solar Cells* **15**, 365–391 (1985).
24. S. L. Murov, I. Carmichael, G. L. Hug. *Handbook of Photochemistry*, p. 299, Marcel Dekker, New York (1993).