

Figures-of-Merit for the Technical Development and Application of Advanced Oxidation Processes

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Advanced oxidation processes (AOPs), which involve the in-situ generation of highly potent chemical oxidants such as the hydroxyl radical ($\bullet\text{OH}$), have recently emerged as an important class of technologies for accelerating the oxidation and hence destruction of a wide range of organic contaminants in polluted water and air. We propose generally applicable standard figures-of-merit for comparing these waste treatment technologies. These figures-of-merit are based on electrical energy consumption within two phenomenological kinetic order regimes: one for high contaminant concentrations (electrical energy per mass, EE/M) and one for low concentrations (electrical energy per order of magnitude per m^3 , EE/O). We also point out that a simple understanding of the overall kinetic behavior of organic destruction in a waste stream (i.e., whether zero or first order) is necessary for describing meaningful electrical efficiencies. These standard figures-of-merit provide a direct link to the electrical efficiency (lower values mean higher efficiency) of an advanced oxidation process,

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independent of the nature of the system and therefore allow for direct comparison of widely disparate AOP technologies. We have also shown that the EE/M and EE/O parameters are inversely proportional to fundamental efficiency factors, such as the lamp efficiency, the fraction of the emitted light flux that is absorbed in the water and the quantum yield of generation of active radicals.

Introduction

Advanced Oxidation Processes (AOPs), which involve the in-situ generation of highly potent chemical oxidants, such as the hydroxyl radical ($\bullet\text{OH}$), have recently emerged (1) as an important class of technologies for accelerating the oxidation and hence destruction of a wide range of organic contaminants in polluted water and air. A partial list of these processes includes: homogeneous ultraviolet irradiation (2) (either direct irradiation of the contaminant or photolytic oxidation mediated by hydrogen peroxide (UV/H₂O₂), and/or ozone (UV/O₃), heterogeneous photocatalysis (3) using semiconductor catalysts (UV/TiO₂), electron-beam irradiation (4), X-ray or gamma-ray radiolysis, non-thermal electrical discharge (5), supercritical water (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 destruction. All of these processes, however, are electrically-driven and share the common denominator of hydroxyl radical chemistry (at least in part). Of the above AOPs, the photochemical processes are the most important industrially; hence, we shall use photochemical examples in our discussion of the application of the figures-of-merit developed in this paper.

Despite the fact that some of these AOPs have been developed to the point of full-scale commercialization, a generally applicable figure-of-merit has 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, we propose figures-of-merit that are based on electrical energy consumption within two phenomenological kinetic order regimes: one for high contaminant concentrations, and one for low concentrations. We also point out that a simple understanding of the overall kinetic behavior of organic destruction in a waste stream (i.e., whether zero

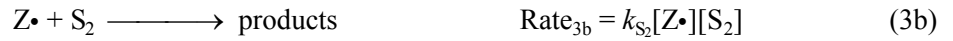
or first order) is necessary for describing meaningful electrical efficiencies. These standard figures-of-merit are valuable in that they give a direct link to the electrical efficiency of an advanced oxidation process, independent of the nature of the system and therefore allow for comparison of widely disparate AOP technologies. Such figures-of-merit are necessary not only to compare AOP technologies, 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 often can be both site- and problem-specific. We contend that a simple figure-of-merit based on electrical-energy consumption can be very useful and informative for AOPs, since these processes are often electrical-energy intensive and electrical energy can represent a major fraction of the operating costs. Moreover, electrical-energy dosage requirements also dictate the size of the capital equipment needed to generate the requisite dosage, so investment should also tend to scale with this figure-of-merit.

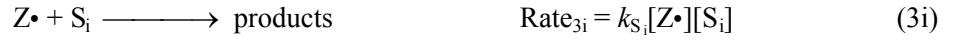
A Simple Reaction Mechanism for AOPs

Although the destruction of organic contaminants through advanced oxidation processes can be complex and involves a number of elementary chemical steps, the overall kinetics or rate of destruction of a specific component, and, more surprisingly, even the destruction 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 organic contaminant. In general, most AOPs can be modeled by the following simple mechanism:





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where c is a constant which depends on the system and the technology, P is the electrical 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), $Z\cdot$ is a highly reactive intermediate (e.g., $\bullet OH$, $H\cdot$, hydrated electron, etc.) (δ), C is a particular organic contaminant (or C can also represent the total organic carbon), and $S_1, S_2, \dots, S_i, \dots$ are a series of scavengers for the $Z\cdot$ radical. Rate_1 is the rate of formation ($M s^{-1}$) of $Z\cdot$ [For example, in the case of a photochemical process, $c = G\chi\phi_{Z\cdot}/P$, where G is the total absolute photon flow (Einsteins s^{-1}) emitted from the lamp in all directions in a useful wavelength range, χ is the fraction of those photons that are absorbed in the water and $\phi_{Z\cdot}$ is the quantum yield for the generation of $Z\cdot$]. Rate_2 is the rate of reaction of $Z\cdot$ with C with second-order rate constant k_C , and $\text{Rate}_{3a}, \text{Rate}_{3b}, \dots, \text{Rate}_{3i}, \dots$ are the rates of reaction of $Z\cdot$ with scavengers $S_1, S_2, \dots, S_i, \dots$ with second-order rate constants k_{S_1}, k_{S_2} and k_{S_i} . A steady-state analysis of this general mechanism yields the following overall rate law:

$$\text{rate} = \frac{cPk_C[C]/V}{k_C[C] + \sum_i k_{S_i}[S_i]} \qquad (4)$$

This simple mechanism illustrates why one often observes simple overall kinetics that are either zero-order 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 contaminant dominates over the scavenging of $Z\cdot$ in reaction 3), then the reaction rate will be *zero order* in C (rate = cP/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 *pseudo* first-order rate constant k_1' (min^{-1}) given by

$$k_1' = \frac{60cPk_C / V}{\sum_i k_{S_i} [S_i]} \quad (5)$$

The demarcation between "high" and "low" concentration varies considerably with the system but is often ~100 ppm (For TOC destruction, lower concentrations can still follow zero-order kinetics) (9). The kinetic order with respect to C has important ramifications for defining the parameters of the electrical-energy dosage for an AOP treatment. As described below, the dosage requirements within the zero-order regime scale with the amount of organic material to be treated (i.e., with mass); whereas, the dosage scales with the volume and treatment goals (i.e., orders of magnitude of reduction per unit volume) for the first-order regime.

Figures-of-Merit

We propose two figures-of-merit: one suitable for high organic concentrations and the other for low concentrations.

1. Electrical Energy per Unit Mass (EE/M): 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 amount of electrical energy use. The definition of EE/M is:

Electrical Energy per Kilogram (EE/M) is the electrical energy in kilowatt hours (kWh) required to bring about the degradation of a unit mass (one kilogram, kg) of a contaminant C in polluted water or air.

The EE/M value (in kWh/kg) can be calculated from the simple formula:

$$EE/M = \frac{P \times t \times 1000}{V \times M \times 60 \times (c_i - c_f)} \quad (6)$$

P is the rated power (kW) of the AOP system, V is the volume (in liters, L) of water or air treated in the time t (min), M is the molecular weight (g mol^{-1}) of C (10), c_i, c_f are the initial and final concentrations (mol L^{-1}) of C and the factor of 1000 converts g to kg. Higher EE/M values would correspond to lower

destruction efficiencies. We define electrical energy as the energy supplied to the AOP treatment system (i.e., “out-of-the-wall”) (EE). It is important that the starting concentration be stated when giving an EE/M value.

Often the EE/M can be related to more fundamental parameters of the system. For example, in the case of a photochemical process, equation 6 can be written in another way by noting that $(c_i - c_f)/t$ is the zero-order rate $60G\chi\phi_{Z\bullet}/V$ ($M \text{ min}^{-1}$)

$$EE/M = \frac{P \times 1000}{M \times 3600 \times G\chi\phi_{Z\bullet}} \quad (7)$$

Thus the EE/M 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 EE/M . Also the larger the fraction of the light absorbed ($\chi \rightarrow 1.0$) and the larger the quantum yield $\phi_{Z\bullet}$, the smaller the EE/M . Similar fundamental efficiency equations could be derived for other AOPs.

We can use Equation 7 to calculate a minimum feasible value of EE/M (i.e., maximum efficiency) for a photochemical oxidation process:

We assume that for a hypothetical contaminant with a molecular weight of 100 g mol^{-1} :

- 1) 25% of the electrical 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 contains 0.1308 kWh of energy or one kWh of electrical energy output (at 25% efficiency) would generate 1.91 Einsteins of UV photons and 1.91 moles or 191 g of the contaminant would be degraded per kWh of electricity. Under these best case assumptions, the **minimum EE/M value would be 5.2 kWh/kg**. For TOC destruction (i.e., atomic weight of 12 g mol^{-1}) and assuming only one hydroxyl radical required per carbon atom, the minimum EE/M would be 43.6 kWh/kg TOC.

More efficient photochemical processes would require more efficient light sources (unlikely, except for incremental improvements), processes that would utilize a wider range of the lamp output (now possible with some iron-based photocatalysts) or greater than unit quantum yields for oxidant production (12). Similar estimates of maximum efficiency should be definable in an analogous manner for other AOPs.

2. Electrical Energy per Order (EE/O): 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 electrical energy required to bring about a reduction by one order of magnitude in [C] is independent of [C] (13). Thus it would take the same amount of electrical energy to decrease from 10 ppm to 1 ppm in a given volume as it would to decrease from 10 ppb to 1 ppb. EE/O is defined as:

Electrical Energy per Order (EE/O) is the electrical energy in kilowatt hours (kWh) required to bring about the degradation of a contaminant C by one order of magnitude in 1 m³ (1000 L) (14) of contaminated water or air.

EE/O values (in kWh per order per m³) can be calculated using the following formulas:

$$EE/O = \frac{P \times t \times 1000}{V \times 60 \times \log(c_i / c_f)} \quad \text{Batch operation} \quad (8a)$$

$$EE/O = \frac{P}{F \times \log(c_i / c_f)} \quad \text{Flow-through operation} \quad (8b)$$

where P , V , t and c_i, c_f have the same definitions as in Equation 6 (15). F is the water flow rate (m³/h) in the flow-through system.

Note that equations 8 can only be related directly to molecular rate expressions for idealized reactors (16). Equation 8b implicitly assumes first-order kinetics, that is, $\log(c_i/c_f) = 0.4343k_1'\tau$, where τ (min) is the retention time in the reactor and k_1' is in min⁻¹. Hence, by using $F = V_r/\tau$, where V_r is the reactor volume (L), equation 8b can be rewritten as

$$EE/O = \frac{38.4 \times P}{V_r \times k_1'} \quad (9a)$$

or using equation 5

$$EE/O = \frac{0.640 P \sum_i k_{S_i} [S_i]}{G \chi \phi_{Z\bullet} k_C} \quad (9b)$$

Thus the EE/O is again inversely proportional to the three important fundamental efficiency parameters.

We can use Equation 9b to illustrate the calculation of an EE/O for a given system. Suppose that a waste water containing trichloroethylene (TCE) at 10 ppm is to be treated by a UV/H₂O₂ process, where the water has a bicarbonate concentration of 10 mM at pH 7 and with an added H₂O₂ concentration of 100 ppm (2.94 mM). The rate constants for reaction of hydroxyl radicals with H₂O₂ ($2.7 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$), HCO₃⁻ ($8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$) and TCE ($4.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) are known (17). Assume that a 1 kW lamp is used with a 25% UV power efficiency in the 200-300 nm region. If we assume that the average wavelength is 254 nm, $G = 5.31 \times 10^{-4} \text{ Einsteins s}^{-1}$. If we assume $\chi = 0.75$ and $\phi_{Z\bullet} = 1.0$, the EE/O is calculated to be 0.034 kWh/order/m³. Note that the EE/O is inversely proportional to k_C .

Examples

We present two examples of waste treatment to illustrate the use of the EE/M and EE/O figures-of-merit:

1. 2000 L of a wastewater containing 500 ppm of total organic carbon (TOC) as phenol is treated for 10 hours with an AOP rated at 30 kW to yield an effluent that is 100 ppm TOC. The mass of TOC removed is $2000 \text{ (L)} \times 0.00040 \text{ (kg/L)} = 0.8 \text{ kg TOC}$; thus the EE/M value is $(30 \times 10)/0.8 = 375 \text{ kWh/kg}$.
2. A groundwater containing 20 ppm of trichloroethylene (TCE) flowing at 8.5 m³/h is treated with an AOP rated at 25 kW. It was found that the effluent concentration of TCE had dropped to 5 ppb. The orders of removal is $\log(20/0.005) = 3.602$; thus using equation 8b, the EE/O value is $25/(8.5 \times 3.602) = 0.82 \text{ kWh/order/m}^3$.

Conclusions

The figures-of-merit proposed in this paper provide a direct link to the electrical efficiency (lower values mean a more efficient process) of an AOP system, independent of the nature of the system (i.e., effectively treating the AOP system as a "black box"). These figures-of-merit, EE/M and EE/O, allow for a rapid determination of the electrical-energy cost and an indication of the total power (and therefore equipment size as well) required for a specific application. For example, if the EE/O of a process is 3.0 kWh per order per m³, 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 per kWh, the electrical energy cost will be $3.0 \times 3 \times 0.08 = \0.72 per m³ of water. 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 destruction, at least whether phenomenologically first- or zero-order, is the key to understanding the elements and applicability of advanced waste treatment technologies.

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- (8) In a given case, the reactions are usually dominated by only one radical (e.g. •OH).
- (9) As illustrated by Equation 4, it is quite possible that for high degrees of destruction 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 $\sum_i k_{S_i}[S_i]$ 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.
- (10) To calculate EE/M values for TOC destruction, rather than a specific contaminant destruction, M is equal to the atomic weight of carbon (12 g/mole) and c_i and c_f are total carbon concentrations in moles/liter.

- (11) Electrical energy defined in this manner includes the electrical efficiencies of any transformers or power supplies, and corresponds to the electrical energy billed by the power company.
- (12) The observation of EE/M 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.
- (13) Recall that for first-order kinetics the half-life (or time for any order of reduction) is independent of the initial concentration.
- (14) EE/O is often expressed in terms of 1000 US gallons. These EE/O values are larger than those based on 1000 L by a factor of 3.785.
- (15) 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 (CSTR's). 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 EE dosage is not a constant per order so equation 8a cannot be used. The EE would need to be calculated for each destructive removal efficiency.
- (16) 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).
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