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Standard reporting of Electrical Energy per Order (E_{EO}) for UV/H$_2$O$_2$ reactors (IUPAC Technical Report)

Abstract: The concept of Electrical Energy per Order (E_{EO}) was introduced in 2001 as a figure of merit for evaluating the energy requirements of ultraviolet-based advanced oxidation processes (UV AOPs) used for the degradation of various organic contaminants. The E_{EO} parameter represents the energy input into the reactor that can achieve an order of magnitude decrease in the concentration of a target contaminant in a unit volume. Since the introduction of this parameter, it has become increasingly popular among UV AOP researchers and practitioners. However, the E_{EO} is often reported without important details that affect the parameter, making its interpretation difficult. The E_{EO} depends on a variety of factors (*e.g.* the concentration and identity of the target contaminant and the amount of hydrogen peroxide added). Therefore, the E_{EO} parameter needs to be reported in the literature with several other experimental details affecting the reactor performance and in a way that proper comparisons can be made between reactors across studies or manufacturers. This paper discusses the proper application of the E_{EO} parameter for bench-, pilot-, and full-scale studies. Sucralose (artificial sweetener, C$_{12}$H$_{19}$Cl$_3$O$_8$) is proposed as a standard substance for reactor comparison.

Keywords: environmental chemistry; oxidation; photochemistry; water.

CONTENTS

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1 Introduction

The Electrical Energy per Order (E_{EO}) parameter was introduced in 1996 to evaluate advanced oxidation processes by Bolton *et al.* [1] and later published as a report by the IUPAC Photochemistry Commission [2]. A recently published book [3] includes an extensive section on the E_{EO}. The E_{EO} is defined as the electrical energy necessary to reduce the concentration of a contaminant by one order of magnitude (90 % reduction) in a unit volume of water. It is important to note that the E_{EO} involves only the electrical energy input to a process to achieve the degradation target. The parameter does not explain anything about the mechanism or details of the process; however, changes in the process can affect the E_{EO}, as discussed further in this paper.

The E_{EO} was proposed as a new figure of merit (a numeric descriptor of process efficiency and a valuable design parameter) for UV reactors to replace or complement more ambiguous performance parameters, such as cost per unit volume. It is a more fundamental concept than these previous parameters and, if properly reported, could be used to compare different systems based on reports and papers from different years and laboratories, regardless of the energy costs in a given year or the different experimental setups used. However, the usability of the E_{EO} values reported by researchers is undermined by incomplete reporting. This paper discusses the parameters that affect the E_{EO} outcome and that need to be reported along with the E_{EO} values, as well as methods to adjust the results of the different studies for comparison. Ways to standardize reactor testing are also proposed.

This paper focuses on using E_{EO} to characterize UV/H$_2$O$_2$ advanced oxidation processes (AOPs), since this technology has been reported as one of the most commercially-viable UV-based AOPs for waters with sufficient UV transmittance (65 % or higher) [4]. Many studies show the promising abilities of UV/H$_2$O$_2$ AOP for treating a wide range of organic contaminants in water [5–13]. Applications cover most current drinking water, water reuse, and remediation uses of AOPs. The process is based on the generation of hydroxyl radicals (HO˙) by homolytic cleavage of H$_2$O$_2$ after absorption of UV radiation. Due to the absorption properties of H$_2$O$_2$, lamps emitting wavelengths in the UVC range are necessary for the process.

The paper also focuses on E_{EO} rather than on E_{EM} (electrical energy per mass), another figure of merit proposed in the original IUPAC report [2]. E_{EM} is used for contaminants at high concentrations, where a zero-order reaction is observed. Most of the UV/H$_2$O$_2$ applications target trace-level contaminants, such as compounds that cause taste and odour issues, algal toxins, and pesticides [4], where first-order kinetics is almost always observed [14]. For these applications, E_{EO}, rather than E_{EM}, is of relevance.

The generation of HO˙ is governed by the following model (Eq. 1) [15]:

$$[\text{HO}^{\bullet}]_{SS} = \frac{[\text{H}_2\text{O}_2]\sum_{\lambda_1}^{\lambda_n}\dfrac{E_{\lambda}\varepsilon_{\text{H}_2\text{O}_2,\lambda}\Phi_{\text{HO}^{\bullet},\lambda}}{U_{\lambda}}}{\sum_{S_1}^{S_n}k_S[\text{S}]} \tag{1}$$

where

$[\text{HO}^{\bullet}]_{SS}$ = steady-state hydroxyl radical concentration, mol L^{-1}

$[\text{H}_2\text{O}_2]$ = concentration of hydrogen peroxide, mol L^{-1}

E_{λ} = average irradiance at wavelength, λ, mW cm^{-2}

$\varepsilon_{\text{H}_2\text{O}_2,\lambda}$ = H$_2$O$_2$ molar absorption coefficient at wavelength λ, L mol^{-1} cm^{-1}

$\Phi_{\text{HO}^{\bullet},\lambda}$ = quantum yield of HO˙, production from H$_2$O$_2$ at wavelength λ, mol einstein^{-1}

U_{λ} = energy per einstein at wavelength λ, J einstein^{-1}

k_S = reaction rate constant of a hydroxyl radical scavenging compound with HO˙, L mol^{-1} s^{-1}

[S] = concentration of the corresponding scavenging compound, mol L^{-1}

Note that Eq. 1 contains implied conversion factors of 1 W = 1000 mW and 1000 cm^3 = 1 L, which cancel out numerically. The units used here reflect the units commonly used for measuring and reporting the parameters of this equation. Wavelength-dependent parameters are integrated over the wavelength range for polychromatic sources [14], but the integration is shown as a summation for practical application purposes. A recent summary of wavelength-dependent quantum yield values can be found in the literature [16].

The average irradiance can be calculated by the integration of the Lambert-Beer law over the water path length, with the result given in Eq. 2.

$$E_\lambda = E_{0,\lambda} \frac{1 - \exp(-\ln(10)a_\lambda l)}{\ln(10)a_\lambda l} \tag{2}$$

where

$E_{0,\lambda}$ = incident irradiance measured at the interface between the UV source and water, mW cm^{-2}
a_λ = decadic absorption coefficient of water at wavelength λ, cm^{-1}
l = average path length of a photon through the reactor, cm

It must be noted that the average path length l is merely a conceptual parameter for full-scale reactors and cannot be easily measured, as it depends on a number of parameters (*e.g.* reactor hydraulics, position of the lamps, *etc.*). The average irradiance can be determined experimentally via reactor testing with biological or chemical indicators with known UV reaction kinetics, *i.e.* biological or chemical actinometry.

Based on Eqs. 1 and 2, the generation of HO˙ is influenced by a number of user-defined parameters, as well as other operational parameters. The user defined parameter is, in this case, the amount of H$_2$O$_2$ added to the reactor. Other variable operational parameters depend on the specific reactor configuration (average path length) and water quality (absorbance and concentrations of specific HO˙ scavenging compounds).

The reaction between a given contaminant and HO˙ is a second-order elementary reaction where HO˙ is at approximately steady state in a typical UV AOP application. Equation 3 gives the general rate expression for this reaction [3].

$$r = k_{HO,C}[HO˙]_{SS}[C] \tag{3}$$

where:

r = reaction rate, mol L^{-1} s^{-1}
$k_{HO,C}$ = second-order reaction rate constant of the given contaminant C with HO˙, L mol^{-1} s^{-1}
[HO˙]$_{SS}$ = steady-state concentration of HO˙, mol L^{-1}
[C] = concentration of the contaminant C, mol L^{-1}

Because of the approximately constant concentration of HO˙ maintained in the process, the observed reaction of decay for the target contaminant is pseudo-first-order with the reaction rate constant equal to $k_{HO,C}$[HO˙]$_{SS}$. This observed first-order decay rate for the target contaminant depends on the concentration of HO˙ that can be generated in a specific reactor at a given H$_2$O$_2$ concentration and water quality. The decay rate, in turn, determines the residence time in the reactor that leads to one order of magnitude removal of the contaminant, ultimately determining the amount of electrical energy it takes for an order of magnitude decrease of a contaminant in a unit volume – the definition of the E_{EO} parameter.

2 Discussion

Some of the aspects of E_{EO} are intrinsic to the reactor: a) the efficiency of the conversion of electrical energy supplied to the reactor to the UV energy transferred to the water; b) the reactor configuration that determines what portion of that UV energy can be used efficiently (reflective surface, mixing, *etc.*); and c) the reactor volume. However, many other aspects that are not intrinsic to the reactor can affect the E_{EO} and are discussed in the sections below. The amount of energy that needs to be supplied to a UV/H$_2$O$_2$ AOP to achieve certain
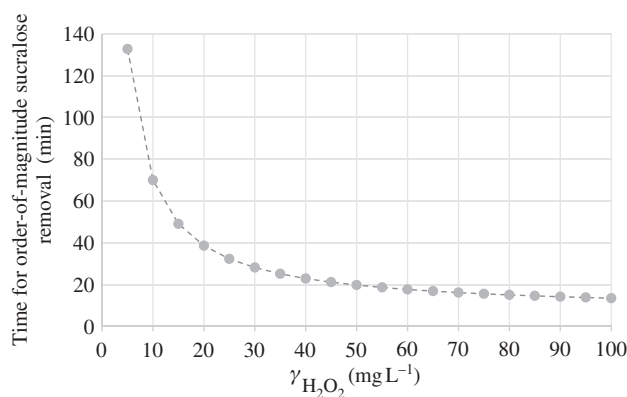
Fig. 1: Residence time as a function of $\gamma_{H_2O_2}$ for a plug-flow reactor with 1 mW cm^{-2} average irradiance treating water with 2 mg L^{-1} of TOC and 50 mg L^{-1} of alkalinity as CaCO$_3$.

contaminant removal in a given reactor depends on the amount of generated HO$^\cdot$, which in turn depends on the following parameters:

2.1 The amount of H$_2$O$_2$ used in the process

H$_2$O$_2$ concentration is a term in both the numerator and the denominator (as part of the sum of the scavenging compounds) of Eq. 1 describing the steady-state hydroxyl radical concentration. As a result, [HO$^\cdot$]$_{SS}$ has a non-linear relationship with [H$_2$O$_2$]. As [H$_2$O$_2$] increases, [HO$^\cdot$]$_{SS}$ increases, but the incremental increase in [HO$^\cdot$]$_{SS}$ becomes smaller with each incremental increase of [H$_2$O$_2$] until [HO$^\cdot$]$_{SS}$ eventually plateaus. A sensible range of H$_2$O$_2$ mass concentration ($\gamma_{H_2O_2}$) used in full-scale applications is (5–40) mg L^{-1}. The E_{EO} can be greatly affected by $\gamma_{H_2O_2}$ within this range. For example, consider a hypothetical reactor delivering 1 mW cm^{-2} average irradiance and treating water with 2 mg L^{-1} of total organic carbon (TOC) and 50 mg L^{-1} of alkalinity as CaCO$_3$. Using sucralose as a hypothetical target compound C ($k_{HO,C} = 1.56 \times 10^9$ L mol^{-1} s^{-1} [17]), at $\gamma_{H_2O_2} = $ (10 and 40) mg L^{-1}, the residence times to achieve one order-of-magnitude decrease in sucralose in the specified reactor are 70 min and 23 min, respectively. These times are directly proportional to the E_{EO}, since the energy input is constant over time. Therefore, the E_{EO} of the same reactor treating the same compound in the same water matrix will be 3 times higher if tested with $\gamma_{H_2O_2} = 10$ mg L^{-1} than if tested with $\gamma_{H_2O_2} = 40$ mg L^{-1}. These calculations are based on Eq. 1 used to calculate [HO$^\cdot$]$_{SS}$ and then used to determine the first order reaction rate in the reactor using Eq. 3. The reactor is assumed to have plug-flow conditions typical for UV reactors.

In general, the lower the concentration of H$_2$O$_2$, the more effect its variation will have on the E_{EO}. In the hypothetical reactor described above, the effect of the H$_2$O$_2$ concentration on the required residence time to achieve one order-of-magnitude decrease in the contaminant concentration is shown in Fig. 1. The effect of H$_2$O$_2$ concentration on the E_{EO} has been previously discussed and experimentally demonstrated [6].

2.2 Water quality parameters

Bicarbonate alkalinity and background organic matter are of particular importance in drinking water and wastewater applications, with $k_S = 8.5 \times 10^6$ L mol^{-1} s^{-1} [18] and 3.6×10^8 L mol^{-1} s^{-1} [19], respectively. For organic matter, mol L^{-1} in the units of the constant refers to molar concentration of organic carbon, and the molecular weight of 12 g mol^{-1} can be used for conversions. Bicarbonate alkalinity and organic matter constitute the bulk of the collective HO$^\cdot$ scavenging rate, Σk_S[S] of Eq. 1. The HO$^\cdot$ scavenging rate has units of s^{-1}. Within the typical range of water quality parameters for drinking water (approximately (1–5) mg L^{-1} of TOC and (50–200) mg L^{-1} of alkalinity as CaCO$_3$), the scavenging rate can vary from under 50 000 s^{-1} to almost 200 000 s^{-1} (a factor of 4).
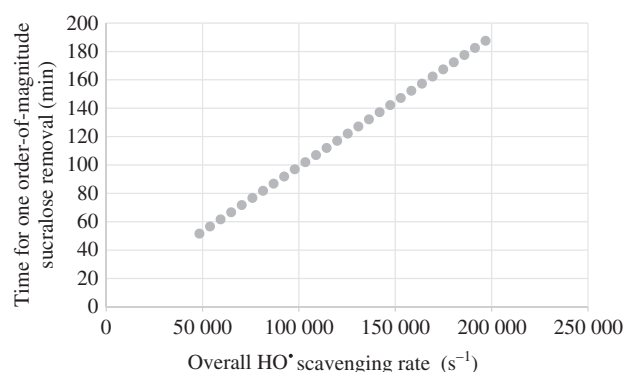
Fig. 2: Residence time as a function of background scavenging rate for a plug-flow reactor with 1 mW cm^{-2} average irradiance treating water with 10 mg L^{-1} of H$_2$O$_2$ and 5 µg L^{-1} of sucralose.

The corresponding residence time in a plug-flow reactor delivering 1 mW cm^{-2} average irradiance and using $\gamma_{H_2O_2} = 10$ mg L^{-1} is shown in Fig. 2. The residence time was calculated for one order-of-magnitude decrease in sucralose concentration as in the previous section and is directly proportional to the E_{EO}. The scavenging rate in Fig. 2 takes into account the scavenging by H$_2$O$_2$ (7900 s^{-1} for $\gamma_{H_2O_2} = 10$ mg L^{-1}) and sucralose (2000 s^{-1} at 5 µg L^{-1}). As can be seen in Fig. 2, depending on the water quality, the E_{EO} of the reactor can vary by over a factor of 4. It is important to understand that the E_{EO} is affected by the composition of the water matrix for which it was tested. Often, the E_{EO} is calculated in pure water, where only H$_2$O$_2$ and the HO$^\bullet$ probe (a chemical added to indirectly measure [HO$^\bullet$]$_{SS}$ via monitoring the chemical reaction between the probe and HO$^\bullet$) are the HO$^\bullet$-scavenging compounds. In order to estimate the process energy consumption for practical applications, it is important to understand how this value will change once applied to a real water matrix.

It must be noted that the linear relationship between HO$^\bullet$ scavenging rate and the E_{EO} presumes that changes in water quality that affect the scavenging rate do not affect the average irradiance in the reactor. In reality, this is an oversimplification. Increasing TOC, for example, will increase the absorbance of the water and will lower the average irradiance (Eq. 2) in the reactor, which was assumed to be constant in this illustration. The effect of water absorbance on average irradiance depends on the average path length in the reactor, which depends on the reactor hydraulics.

2.3 Test compound

Several aspects of the test compound identity can affect the E_{EO}:
- The absorbance of the test contaminant affects the fraction of photons that can reach H$_2$O$_2$, which in turn affects the [HO$^\bullet$]$_{SS}$ that can be generated in the process.
- The concentration of the test contaminant and its reaction rate with HO$^\bullet$ affects [HO$^\bullet$]$_{SS}$ that can be generated in the process by contributing to HO$^\bullet$ scavenging.
- The susceptibility of the contaminant to direct photolysis affects the residence time needed to achieve certain level of removal in different reactors depending on average irradiance and H$_2$O$_2$ concentration.

The test compound is commonly added at a concentration that allows monitoring the compound by analytical determination without any additional processing, such as solid phase extraction. This typically means concentrations on the order of µg L^{-1} or mg L^{-1}. For example, 4-chlorobenzoic acid, commonly used in research for measuring [HO$^\bullet$]$_{SS}$, has a molar absorption coefficient on the order of 3000 L mol^{-1} cm^{-1} at 254 nm (emission wavelength of low pressure mercury vapor lamps common in UV AOP reactors). This translates to an absorption coefficient of approximately 0.02 cm^{-1} at 1 mg L^{-1}. Depending on the background matrix of the water being evaluated, the addition of a probe compound could result in a significant decrease in the average irradiance delivered to the water. For example, most drinking waters have 85–95 % transmittance at 254 nm wavelength,
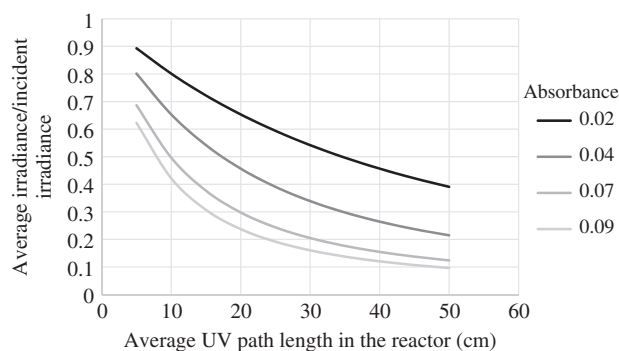
Fig. 3: Effect of incremental changes in absorbance on average irradiance in reactors with different average UV path length. Average irradiance is directly proportional to the E_{EO}.

which translates to an absorption coefficient of (0.071–0.022) cm^{-1}. Using 1 mg L^{-1} of 4-chlorobenzoic acid can double the absorption coefficient of the water with the original transmittance of 95 %, which can significantly affect the average irradiance E and the E_{EO} as the result. The effect is most prominent for high transmittance (low absorbance) waters (Fig. 3). This can be even more prominent with medium pressure mercury vapor lamps. Many organic chemicals have higher absorbance at lower wavelengths and could even more dramatically affect the fraction of photons that reach H$_2$O$_2$ and the resulting HO$^{\cdot}$ formation.

The contribution from a probe compound (also a HO$^{\cdot}$ scavenger) to the overall scavenging rate is another important factor. The reactor is often used to address contaminants at trace levels that are part of the overall background organic matter. Adding a probe increases the overall organic content. Often, the probe is more reactive than the bulk organic matter and can change the scavenging rate considerably. For example, in a study by Keen *et al.* (2014) [20], the authors used methylene blue at 5 µmol L^{-1} to measure the background HO$^{\cdot}$ scavenging rate of wastewater effluent samples and reported that the probe compound accounted for 25–50 % of the overall HO$^{\cdot}$ scavenging rate in the sample (corresponding to approximately 30–100 % change in overall scavenging rate). The scavenging rate is higher in wastewater effluent samples than in drinking water samples; therefore, adding 5 µmol L^{-1} of methylene blue as a probe to a drinking water matrix would result in an even higher percent change. As it can be seen in Fig. 2, doubling the scavenging rate would approximately double the measured E_{EO}.
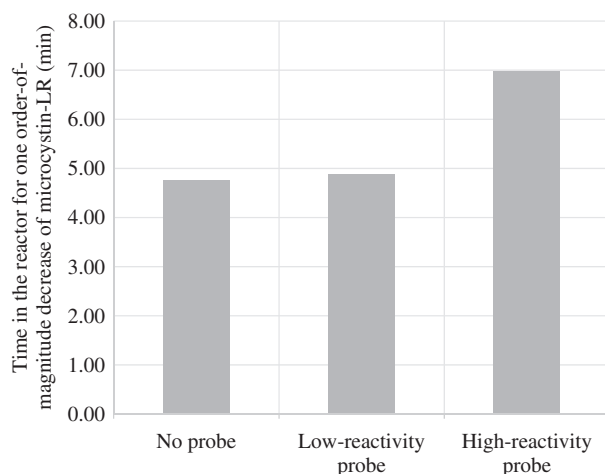

Fig. 4: Residence time in a hypothetical reactor (1 mW cm^{-2} average irradiance, 2 mg L^{-1} of TOC and 50 mg L^{-1} of alkalinity as CaCO$_3$ using 10 mg L^{-1} of H$_2$O$_2$ and 500 µg L^{-1} of HO$^{\cdot}$ probe concentration) to decrease the concentration of microcystin-LR by one order of magnitude: actual (no probe) and measured by spiking a probe with relatively low or high HO$^{\cdot}$ reactivity.

It must be noted that methylene blue is highly reactive with hydroxyl radicals, with a reaction rate constant of 2.1×10^{10} L mol^{-1} s^{-1} [18]). The reactivity of the probe determines how much it affects the E_{EO} measurement. For example, Fig. 4 shows the calculated time it takes to decrease by one order of magnitude the concentration of the algal toxin microcystin-LR in a hypothetical reactor with 1 mW cm^{-2} average irradiance, 2 mg L^{-1} of TOC and 50 mg L^{-1} of alkalinity as CaCO$_3$ using 10 mg L^{-1} of H$_2$O$_2$ and 500 µg L^{-1} of HO$^\bullet$ probe concentration. The probe options are either using the target compound microcystin-LR (high HO$^\bullet$ reactivity, $k_{HO,M-LR} = 2.3 \times 10^{10}$ L mol^{-1} s^{-1} [21]) or using an alternative lower-reactivity probe, for example sucralose ($k_{HO,sucralose} = 1.56 \times 10^9$ L mol^{-1} s^{-1}). For the given theoretical reactor, using microcystin-LR spike as a probe, the time to oxidize 90 % of the compound would be measured as 7.0 min. Based on the [HO$^\bullet$]$_{SS}$ that this reactor can generate when the scavenging rate excludes the probe compound (the actual operating conditions), 90 % oxidation of microcystin-LR is achievable in 4.8 min. Because the residence time in the reactor for one order-of-magnitude decrease in a contaminant is directly proportional to the E_{EO} of the reactor for the given contaminant and water quality, the test with microcystin-LR would result in a measured E_{EO} that is 46 % higher than the actual E_{EO}. With sucralose used to determine [HO$^\bullet$]$_{SS}$, the calculated residence time required for 90 % oxidation of microcystin-LR is 4.9 min, only a 2 % difference from the actual value.

It is possible to back-calculate the performance of the reactor by factoring out the contribution of the probe to the scavenging rate, but an estimation of the average irradiance to be used in Eq. 1 would be necessary, and this can be a complex task for a full-scale reactor. Therefore, the use of a lower-reactivity probe can provide a good estimate of the actual E_{EO} for a given reactor, water quality, and target contaminant. The times to achieve one order-of-magnitude removal for the probe compound and for the target compound are related through their second-order reaction rate constants with HO$^\bullet$ (Eq. 4), and thus the E_{EO} can be calculated for the specific target compound relative to the probe used.

$$k_{HO,probe} \times t_{1\text{-log,probe}} = k_{HO,target} \times t_{1\text{-log,target}} \tag{4}$$

The third property of the probe compound relevant for evaluating the E_{EO} of the reactor is its susceptibility to direct photolysis. The photolysis rate constant for a compound is determined from the observed first-order decay in the reactor. It is reported in either time-based units (*e.g.* s^{-1}) or fluence-based units (*e.g.* cm^2 mJ^{-1}). The time-based rate constant can be divided by the average irradiance to convert it to the fluence-based rate constant [22]. The influence of photolysis is particularly relevant for determining the effect of the parameters that affect the HO$^\bullet$ production on the E_{EO} of the reactor (*e.g.* H$_2$O$_2$ concentration or background HO$^\bullet$ scavenging rate). Depending on the relative contribution of direct photolysis vs. HO$^\bullet$ oxidation to the contaminant decrease in the reactor, this phenomenon may or may not have a pronounced effect on the E_{EO} estimation. A prime example of a compound for which this caution would be relevant is *N*-nitrosodimethylamine (NDMA). NDMA is highly susceptible to photolysis ($k_{phot,NDMA} = 2.3$ cm^2 J^{-1}), but has a comparatively
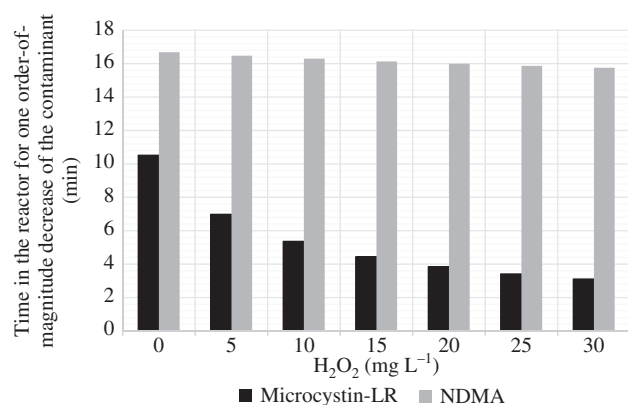
Fig. 5: Residence time as a function of H$_2$O$_2$ concentration in a hypothetical reactor with 1 mW cm^{-2} average irradiance treating water with 2 mg L^{-1} of TOC and 50 mg L^{-1} of alkalinity as CaCO$_3$. Microcystin-LR and NDMA are assumed to be at trace levels and do not affect the calculated [HO$^\bullet$]$_{SS}$.

low reaction rate constant with HO$^{\bullet}$ ($k_{HO,NDMA} = 3.3 \times 10^8$ L mol^{-1} s^{-1}) [23]). For example, the effect of increasing the H$_2$O$_2$ concentration on the E_{EO} of the UV/H$_2$O$_2$ AOP will not be the same for NDMA as, for example, for microcystin-LR, a compound much more reactive with HO$^{\bullet}$ and about as susceptible to photolysis as NDMA ($k_{HO,M\text{-}LR} = 2.3 \times 10^{10}$ L mol^{-1} s^{-1}; $k_{phot,M\text{-}LR} = 3.65$ cm^2 J^{-1} [21, 24]). This concept is illustrated in Fig. 5: the E_{EO} for treating microcystin-LR would decrease rapidly with H$_2$O$_2$ addition, but it would stay relatively unaffected by the H$_2$O$_2$ for NDMA.

3 Examples

This section contains practical examples of E_{EO} applications, what to report to make the E_{EO} useable to others, and examples of how to compare data from different studies.

3.1 Selecting the optimal H$_2$O$_2$ concentration

Mathematically, the E_{EO} will decrease indefinitely as the H$_2$O$_2$ concentration increases. For practical purposes, the [HO$^{\bullet}$]$_{SS}$ will plateau. This concept is illustrated in Fig. 1. In treating sucralose in the hypothetical reactor as illustrated in the figure, an increase of H$_2$O$_2$ concentration from 5 mg L^{-1} to 10 mg L^{-1} would decrease E_{EO} by a factor of 1.9. A further increase of the H$_2$O$_2$ concentration by another 5 mg L^{-1} from 10 to 15 mg L^{-1} would drop the E_{EO} by an additional factor of 1.4. For every next incremental increase of 5 mg L^{-1}, the energy saving will become smaller. The cost of additional H$_2$O$_2$ will at some point exceed the cost of the saved energy. The E_{EO} vs. H$_2$O$_2$ concentration can be mapped out for the specific application (specific to the water quality and the contaminant) and the optimal H$_2$O$_2$ concentration can be selected with consideration of the costs for both H$_2$O$_2$ and electrical energy.

The optimal H$_2$O$_2$ concentration for contaminants not susceptible to photolysis is not affected by the k_{HO} of the specific contaminant, as the H$_2$O$_2$ concentration directly affects the [HO$^{\bullet}$]$_{SS}$, and the E_{EO} for the given contaminant is directly related to the [HO$^{\bullet}$]$_{SS}$. For contaminants that rely mainly on direct photolysis and less on the reaction with HO$^{\bullet}$ (*e.g.* NDMA), the optimal H$_2$O$_2$ concentration would be different for each specific contaminant. The relative contribution of the direct photolysis and HO$^{\bullet}$ reaction to the overall contaminant degradation will affect the incremental decrease in E_{EO} for every additional 5 mg L^{-1} of H$_2$O$_2$. For example, a compound X, 10 times as reactive with HO$^{\bullet}$ as sucralose ($k_{HO,X} \approx 1 \times 10^{10}$ L mol^{-1} s^{-1}), but not susceptible to photolysis, would still have a 1.9 times decrease in the E_{EO} when the H$_2$O$_2$ concentration is increased from 5 to 10 mg L^{-1} and a 1.4 times decrease as the H$_2$O$_2$ concentration goes from 10 to 15 mg L^{-1}, all other parameters being constant. For a substance like microcystin-LR, which is fairly susceptible to photolysis and has a fast reaction with HO$^{\bullet}$, the E_{EO} decrease in the same reactor treating water with the same quality would be 1.5 and 1.3 for a H$_2$O$_2$ concentration increase from 5 to 10 mg L^{-1} and from 10 to 15 mg L^{-1}, respectively. For NDMA, highly susceptible to photolysis and reacting slowly with HO$^{\bullet}$, those values would be 1.0 for each increment (<5 % improvement), indicating that the E_{EO} would be virtually unaffected by any increase in the H$_2$O$_2$ concentration. These theoretical calculations for NDMA are confirmed by the experimental data from the literature [23].

The average irradiance in the reactor is directly proportional to the [HO$^{\bullet}$]$_{SS}$. Therefore, the discussion in the previous paragraph holds for any reactor treating water of a given quality. Water quality, however, would have an effect on the optimal H$_2$O$_2$ concentration. The greater the background scavenging rate, the greater will be the incremental improvement in the E_{EO} with every incremental increase in H$_2$O$_2$ concentration. However, the effect is not very dramatic within the range of water quality values. For example, for very low TOC and alkalinity water (0.5 mg L^{-1} and 50 mg L^{-1} as CaCO$_3$, respectively), the incremental decrease in E_{EO} would be 1.7 times and 1.3 times as the H$_2$O$_2$ concentration is increased from 5 to 10 mg L^{-1} and from 10 to 15 mg L^{-1}. For a water matrix with higher amounts of HO$^{\bullet}$ scavenging substances (5 mg L^{-1} of TOC and 200 mg L^{-1} of alkalinity as CaCO$_3$), those values are 2.0 and 1.5. The optimal H$_2$O$_2$ concentration for matrices with higher HO$^{\bullet}$ scavenging potential is likely to be higher than for matrices with lower scavenging potential. However, the difference

is not great within the range of water quality in the typical UV/H$_2$O$_2$ AOP process, and, depending on the costs of energy and H$_2$O$_2$, the range of optimal H$_2$O$_2$ concentrations is likely to be narrow and somewhere in the (10–30) mg L^{-1} range for most applications.

3.2 Evaluating the energy use by a specific reactor for a specific purpose

This is the most straightforward application of the E_{EO}, and it should be reported with the specifics, such as water quality, H$_2$O$_2$ concentration used, and the target contaminant identity. This value would not be transferrable to other applications or comparable with the use of other reactors. This can be considered akin to the reactor validation used in disinfection, where a reactor is tested for a range of water transmittances and flow rates to span the range of those variables in the actual field placement of the reactor. For example, a utility can use this information to estimate the energy use for the process for a range of water quality fluctuations. The value can be adjusted to a desired level of contaminant removal. For example, the electrical energy required to achieve two orders of magnitude of contaminant degradation will be twice the electrical energy for one order of magnitude.

Another example where such evaluations may be useful is in determining the placement of the UV/H$_2$O$_2$ reactor in the treatment train or to evaluate the cost-effectiveness of different pre-treatment technologies for UV/H$_2$O$_2$. For example, the E_{EO} can be calculated for the oxidation of taste- and odour-forming compounds in drinking water applications, comparing sand filtration and membrane filtration as pre-treatment. The energy savings calculated based on the E_{EO} can then be compared with the energy expenditure/costs of the pre-treatment options.

3.3 Comparing reactor performance for different contaminants

The E_{EO} values for a range of potential contaminants can be calculated for a specific reactor with specific water quality and H$_2$O$_2$ concentration. However, it is important to understand that these relative E_{EO} values are affected by the water quality and the H$_2$O$_2$ concentration in a given reactor. For example, as shown in Fig. 5, in the same hypothetical reactor, the ratio of the E_{EO} values for NDMA and microcystin-LR varies from 2.4 to 5.1 as the H$_2$O$_2$ concentration increases from 5 to 30 mg L^{-1}. While these ratios are likely to be similar for different reactors based on the relative susceptibility of each compound to direct UV photolysis vs. HO$^{\cdot}$ reaction, the results are not transferrable between reactors, and the practical utility of such information is limited.

3.4 Comparing the performance of various reactors

The electrical energy used by the reactor to achieve one order-of-magnitude decrease in the contaminant per unit volume (the definition of E_{EO}) is directly related to the ability of the reactor to transfer efficiently that energy to H$_2$O$_2$, which depends on the reactor hydraulics, configuration, reflective wall material, *etc*. This ability is quantified by the portion of Eq. 1 shown in Eq. 5 below. This quantity (ξ) has units of s^{-1} and represents the rate by which H$_2$O$_2$ absorbs energy and converts it to HO$^{\cdot}$.

$$\xi = \sum_{\lambda} \frac{E_{\lambda} \varepsilon_{\lambda} \Phi_{\lambda}}{U_{\lambda}} \tag{5}$$

To compare two reactors, the comparison should be essentially on their ξ, or, more specifically, on the efficiency of converting electrical energy to ξ. Comparison of reactors on their ability to convert electrical energy to E_{λ} is possible for monochromatic UV reactors emitting the same wavelength. Using ξ allows comparison between reactors using different wavelengths and polychromatic spectra. Energy use vs. ξ essentially shows the efficiency of converting electrical energy into HO$^{\cdot}$.

For example, reactor A is reported to have an E_{EO} of 7.1 kWh m^{-3} per order of magnitude change in the concentration of a target component when tested with caffeine concentration $= 20$ mg L^{-1} and $\gamma_{H_2O_2} = 25$ mg L^{-1} [25]. Because caffeine is susceptible to direct photolysis, it is important to know the photolysis rate in the units of s^{-1} and the overall observed decay rate in the same units. If the rates are reported in units of cm^2 mJ^{-1}, average irradiance in cm^2 mW^{-1} should be reported as well. In the cited example, the respective values for caffeine were 0.006 ± 0.003 and 0.19 ± 0.02 min^{-1}. The observed first-order decay rate is therefore $(0.19 - 0.01)$ min$^{-1} = 0.18$ min$^{-1} = 0.0030$ s^{-1}. From here, the [HO$^{\bullet}$]$_{SS}$ achieved in the reactor can be calculated knowing the k_{HO} for caffeine (4.1×10^9 L mol^{-1} s^{-1} as measured by using competition kinetics with 4-chlorobenzoic acid [25]). Based on this, it can therefore be determined that the [HO$^{\bullet}$]$_{SS}$ generated in the reactor was 0.0030 s$^{-1}/4.1 \times 10^9$ L mol^{-1} s$^{-1} = 7.3 \times 10^{-13}$ mol L^{-1}. The quantity described in Eq. 5 can now be calculated using the experimental data ([HO$^{\bullet}$]$_{SS}$, [H$_2$O$_2$], k_{HO,H_2O_2}, [caffeine], $k_{HO,caffeine}$) and Eq. 1. ξ is thus determined to be 4.4×10^{-4} s^{-1}. The ξ for the reactor is directly related to the ability of the reactor to generate HO$^{\bullet}$. It is also directly related to the photolysis rate if the contaminant is susceptible to it, as the E in the ξ term directly affects the time it takes to achieve a specific UV dose in a given reactor. Therefore, the E_{EO} is directly related to energy use divided by ξ.

Another hypothetical reactor B was tested with $\gamma_{sucralose} = 0.5$ mg L^{-1} and $\gamma_{H_2O_2} = 10$ mg L^{-1}, and the E_{EO} was calculated to be 5.5 kWh m^{-3} per order. It is impossible to directly compare the two reactors A and B, as they were tested with different compounds under different conditions. Although the E_{EO} of the hypothetical reactor B is lower, it is not necessarily a better reactor than reactor A described above. Knowing the time-based observed (reactor-specific) first-order reaction rate constant and the reaction rate constant for direct photolysis (not applicable for sucralose), ξ for the reactor can be calculated. That value in this hypothetical reactor B was calculated to be 1.43×10^{-3} s^{-1}. This can now be used with other target compounds and H$_2$O$_2$ concentrations to calculate [HO$^{\bullet}$]$_{SS}$, which is directly related to the E_{EO}.

To properly compare the two reactors (A and B), caffeine should be considered as a potential reactant in the hypothetical reactor B, or sucralose can be modelled as a probe in the reactor A, described in [25]. Because sucralose has no photolysis component that needs to be considered, it is easier to compare the two reactors by modelling the performance of the reactor A described in [25] for sucralose and comparing the results with the results of the other (hypothetical) reactor B. Using the H$_2$O$_2$ and sucralose concentrations from the hypothetical reactor B, with ξ from the reactor A, we can estimate that, under the hypothetical test conditions of $\gamma_{H_2O_2} = 10$ mg L^{-1} and $\gamma_{sucralose} = 0.5$ mg L^{-1}, the reactor A described in [25] would achieve [HO$^{\bullet}$]$_{SS} = 1.3 \times 10^{-11}$ mol L^{-1} (Eqs. 1 and 5). Using the $k_{HO,sucralose}$, the observed first-order reaction rate constant k_{obs} can be calculated to be 0.020 s^{-1}. If in the original experiment, the E_{EO} for caffeine with $k_{obs} = 0.19$ min$^{-1} = 0.0032$ s^{-1}, and the E_{EO} was calculated to be 7.1 kWh m^{-3} per order, then for sucralose with $k_{obs} = 0.020$ s^{-1}, the E_{EO} will be proportionately less, that is, if k_{obs} for sucralose is 6.25 times higher than k_{obs} for caffeine, the E_{EO} for sucralose will be 6.25 times lower, namely 1.1 kWh m^{-3} per order. This rests on the fact that the log[C]/[C$_0$], which goes into the E_{EO} calculations, has a linear relationship between the first order reaction rate constant and the residence time in the reactor. Therefore, even though the E_{EO} for reactor A, tested with caffeine, was 7.1 kWh m^{-3} per order, and the value for the hypothetical reactor B, tested with sucralose, was 5.5 kWh m^{-3} per order, reactor A had better energy efficiency, because when adjusted to sucralose, the E_{EO} was calculated to be 1.1 kWh m^{-3} per order.

Such a difference in the E_{EO} values for a single reactor with two different test compounds is not surprising, as the scavenging rate in each test is entirely different and greatly affects the test outcome, as discussed in Section 2.2. The background HO$^{\bullet}$ scavenging rate due to 20 mg L^{-1} of caffeine and 25 mg L^{-1} of H$_2$O$_2$ is 440 000 s^{-1}, while the scavenging rate due to 0.5 mg L^{-1} of sucralose and 10 mg L^{-1} H$_2$O$_2$ is only 9900 s^{-1}. For practical purposes, it is important that the background scavenging rate is as close to the actual application as possible.

Alternatively, the E_{EO} of the hypothetical reactor B could be calculated for the caffeine test conditions reported for reactor A. In this case, the k_{obs} would need to be estimated based on its two components: the first-order reaction of photolysis (k_{phot}) and the first-order reaction with HO$^{\bullet}$ ($k_{radical}$). $k_{radical}$ is equal to $k_{HO,caffeine}$[HO$^{\bullet}$]$_{SS}$ and is easily calculated using the reactor ξ and the H$_2$O$_2$ and caffeine concentrations (see Eq. 1 and Eq. 5). k_{phot} is more difficult to transfer between reactors and requires that both studies report the conversion between the time units and the fluence in mJ cm^{-2}. In the paper describing reactor A [25], that conversion can be obtained from the fluence-based rate constants reported in units of cm^2 mJ^{-1} along with the time-based counterparts. k_{phot} in units of cm^2 mJ^{-1} should be converted to units of s^{-1} using the specifics of the hypothetical reactor. Since

in previous sections the hypothetical reactor was discussed to have the average irradiance of 1 mW cm^{-2}, the conversion for the k_{phot} for caffeine is $(0.02 \times 10^{-3}$ cm^2 mJ$^{-1}) \times (1$ mW cm$^{-2}) = 0.02 \times 10^{-3}$ s^{-1}.

Therefore, it can be concluded that the following parameters need to be reported along with the E_{EO} for comparing values for reactors tested under different conditions: H$_2$O$_2$ concentration, probe compound and concentration, second-order k_{HO} of the probe (with source referenced), HO˙ scavenging by the water matrix (if tested in natural water), the observed overall reaction rate for the test compound, and the reaction rate for direct photolysis, both in units of cm^2 mJ^{-1} and in units of s^{-1} (or other time-based units). This approach does not take into account the change in absorbance with each compound and its corresponding effect on ξ. Any comparison between the E_{EO} values reported in different sources is only approximate. Use of the ξ term allows for the comparison of reactors that use different wavelengths, as well as polychromatic sources.

3.5 Evaluating the process at bench scale for full-scale application

The ability to compare bench-scale results with full-scale results relies on the ability to match the average irradiance in the bench-scale reactor with that of the full-scale reactor. If such conditions can be achieved, then the *relative* (not absolute) E_{EO} values measured at bench scale for various contaminants, H$_2$O$_2$ concentrations, and water quality parameters should be transferrable to the full scale. Transmittance of water and average path length also need to be considered and can lead to significant overestimation of E_{EO} from bench to full scale if not taken into account [22]. Additionally, the actual E_{EO} for the full-scale reactor would still have to be calculated with respect to a reference E_{EO} measured at full scale. For example, if the ratio of the E_{EO} at 5 and 10 mg L^{-1} of H$_2$O$_2$ is equal to 1.7 in a bench-scale reactor, the same ratio will be observed at these H$_2$O$_2$ concentrations in a full-scale reactor, as long as the reactors have the same average irradiance.

3.6 Common mistakes when applying the E_{EO} parameter

3.6.1 Using the E_{EO} with a non-submerged lamp

The distance from the lamp to the surface of the water would affect the order of magnitude removal for the same exposure time (and hence the same energy use). This is often seen in bench-scale studies and is not to be confused with open-channel full-scale reactors, where the E_{EO} is applicable and the effect of the water level is likely minor because the lamps are typically submerged. If an open-channel process has a configuration with lamps placed above the water, then the E_{EO} will be affected by the water level. However, this is an atypical configuration for a full-scale UV reactor, as most of them have submerged lamps.

3.6.2 Using the E_{EO} as a single intrinsic value for a given reactor

The E_{EO} for the UV/H$_2$O$_2$ AOP depends on the water quality, H$_2$O$_2$ concentration, and the target contaminant. The E_{EO} should be reported with those parameters in mind or it should be tested for a range of conditions and reported as a range.

3.6.3 Using the E_{EO} to conclude that one AOP is better than another

Often seen in bench-scale studies, for example comparing UV/H$_2$O$_2$ vs. UV/TiO$_2$ vs. UV/O$_3$ for a specific contaminant and determining the best process for this contaminant on the basis of E_{EO}. At full scale, the ability of the reactor to transfer UV radiation to solution and to transfer ozone to the solution may be different, and the relative performance of each process could be affected as a result.

3.6.4 Using incorrect notation

Additionally, the notation used in the literature is disparate. The following versions of the notation can be found: E_{EO}, EE/O, E-EO, E-Eo, EEO, EEo, E$_{Eo}$. The standard notation proposed in the original IUPAC report is E_{EO}, as E is the symbol for energy and the subscript "$_{EO}$" qualifies the energy as electrical, per order.

4 Conclusions

The E_{EO} is greatly affected by the operational parameters, such as the H$_2$O$_2$ concentration, background water quality, and the nature of the target compound. Therefore, it may be worthwhile to standardize the conditions for testing the E_{EO} of the reactor if it is to be used as an intrinsic property of the reactor for comparison and improvement of reactor design. For example, the reactor E_{EO} could be tested at 10 mg L^{-1} of H$_2$O$_2$ with sucralose as a standard target. This value may also be determined and reported for high and low HO$^{\bullet}$ scavenging rate by background water matrix constituents achieved by using a standard substance to change the alkalinity (*e.g.* sodium bicarbonate) and a standard substance to change the organic carbon content that has approximately the scavenging rate of bulk organic matter [19], the value typically used in models. Using sucralose as a standard probe offers several major advantages. First, it has virtually no absorbance at the concentrations that would be used for a test and would not affect the average irradiance in the reactor. Second, it has a comparatively low reaction rate constant with HO$^{\bullet}$, and therefore it can be added at a higher concentration without considerably affecting the overall scavenging rate of HO$^{\bullet}$. Third, it is not susceptible to direct photolysis at wavelengths equal or larger than 200 nm, which simplifies the HO$^{\bullet}$ measurements, as photolysis control is not required. Fourth, it can be detected at low concentrations even in complex water matrices and will not require a high-concentration spike. Finally, it is a safe substance that can be used even in full-scale reactors.

The background HO$^{\bullet}$ scavenging rate and the E_{EO} are linearly related (if the effect of scavenging compounds on the average absorbance is ignored), and the E_{EO} for the reactor can be reported with the plot similar to Fig. 2, allowing the given utility to estimate the E_{EO} for their own water quality based on background HO$^{\bullet}$ scavenging rate. The HO$^{\bullet}$ background scavenging rate of the water can be measured in properly designed bench-scale tests with a collimated beam apparatus.

Some of the novel UV AOP processes, such as UV/Cl$_2$, are gaining considerable traction in engineering practice as a result of its ease of use by utility operators compared with the UV/H$_2$O$_2$ process. Due to increased interest, the UV/Cl$_2$ process has been in the spotlight of recent research efforts [26–29]. However, the chemistry of the process is not understood fully enough to determine every factor influencing the E_{EO} for UV/Cl$_2$ reactors. The process generates two major reactive species, HO$^{\bullet}$ and Cl$^{\bullet}$, and the factors affecting the relative formation of one vs. the other need to be fully understood. Another example of the additional complexity of the process is that UV/Cl$_2$ relies on HOCl and OCl$^-$ pH-dependent speciation (HOCl p$K_A = 7.6$), unlike the UV/H$_2$O$_2$ process, which uses only one molecular species for HO$^{\bullet}$ generation at pH < 9 (H$_2$O$_2$ p$K_A = 11.7$), which spans the typical water/wastewater treatment pH range. Similar efforts to standardize the reporting, and possibly the measurement of E_{EO} for UV/Cl$_2$ reactors are worth pursuing in the future.

Additionally, it is recommended that factors affecting the E_{EO} for other AOPs (for example, ozone-based AOPs and titanium dioxide photocatalysis) should be investigated in a similar manner.

Membership of the sponsoring body

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