Calculating UV Dose for UV/AOP Reactors Using Dose/Log as a Water-Quality Metric

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Abstract
A method for scale up of UV/AOP reactors is outlined that uses bench scale testing to determine the UV dose required per log destruction ($D_L$) of a particular contaminant. This can then be used in CFD modeling to size a full-scale UV reactor and to test the reactor in performance trials. Methods for calculating dose based on the path length distribution in a UV reactor are given.

Keywords: Advanced Oxidation; AOP; Pilot Testing; Scale up; CFD; Geosmin; MIB; Ultraviolet; UV; UV/Peroxide; UV/Chlorine; Direct photolysis; Dose per Log; $D_L$

Background
Traditional methods using Electrical Energy per Order ($E_{EO}$) (Bolton et al., 2001) to compare the performance of various full scale AOP technologies, while useful, are not effective in translating collimated beam or bench testing to full-scale. While most parameters that affect the $E_{EO}$ of a reactor (lamp output, lamp efficiency, path length) can be scaled up from laboratory scale to full-scale without much difficulty, Computational Fluid Dynamic modeling (CFD) is needed to predict the hydraulic or mixing efficiency of a flow-through UV reactor. This article describes a method that has been developed that uses bench-scale testing to determine the UV dose required per log destruction of a particular contaminant ($D_L$) and methods for calculating the dose applied.

UV dose for Medium Pressure (MP) UV/H$_2$O$_2$ reactors is defined as the integral, by wavelength, of the UV dose, weighted by the peroxide (or other photoactive reactant) absorption coefficient relative to its value at 254 nm (H$_2$O$_2$ weighted UV dose). This is similar to UV dose in disinfection reactors, which is weighted by the germicidal (DNA) absorption spectrum relative to that at 254 nm, or by the action spectra of specific microbes (germicidal dose). As in disinfection UV reactors, and unlike the $E_{EO}$, $D_L$ is independent of the lamp spectral output, the UV transmittance and the path length that UV traverses in a reactor. Unlike disinfection reactors, however, $D_L$ in AOP reactors is dependent on the H$_2$O$_2$ concentration and the scavenging potential of the water. Therefore tests must be performed on a representative sample of water at one or more H$_2$O$_2$ concentrations to determine the scavenging potential, or better still, if the contaminant(s) of concern are used in the bench testing, the $D_L$ of the contaminant. This can then be used in CFD modeling to determine the destruction of the contaminant at each point in the reactor, and hence the full-scale performance incorporating the hydraulic efficiency can be determined. This empirical method greatly simplifies the CFD modeling of an AOP reactor where otherwise the simultaneous chemical reactions would need to be modeled.

Calculation of Average Dose in a UV Reactor
The average UV dose imparted to water passing through a UV reactor or over time in a batch reactor can be calculated from the average irradiance in the reactor, the volume in the reactor and the flow rate. However, calculating the average irradiance is complex requiring the use of computer modeling, such as UVCalc (Bolton Photosciences Inc.), and has to be done at all UV transmittances of interest. In addition, issues of shading by adjacent quartz tubes and reflection of those same tubes and the reactor wall add complexity.

An alternate simpler technique to calculate UV dose has been developed based on the path length distribution of the photons, the radiant flux of UV entering the water and the UV transmittance of the water. The equation for this calculation can be derived from first principles, but in this derivation the well known collimated beam dose calculation equation will be used as a starting point. The principle of the collimated beam calculator is that the irradiance is integrated over the column of water that the UV passes through, taking into consideration the attenuation of the UV. The depth of this column of water ($d$) is the path length that the UV is afforded. Not all the UV penetrates through this column but this “path length” is the maximum distance that the UV can travel. The dose is calculated from this path length, the time of exposure and the absorbance of the water by the following equation:

$$ D = E_s P_t (1 - R) \frac{L}{(d + L)} (1 - 10^{-a_{254}d}) t $$

where:

- $D$ = UV dose (mJ/cm$^2$)
- $E_s$ = UV irradiance at the center of the surface where UV enters the water
- $P_t$ = Transmission of water
- $L$ = Path length
- $a_{254}$ = Absorption coefficient at 254 nm
- $t$ = Exposure time (sec)
\begin{equation}
P_f = \text{the Petri Factor}
\end{equation}

\begin{equation}
R = \text{Reflectance at the air water interface}
\end{equation}

\begin{equation}
\frac{L}{d + L} = \text{Divergence Factor}
\end{equation}

\begin{equation}
d = \text{depth of suspension (cm)}
\end{equation}

\begin{equation}
L = \text{the distance (cm) from the surface of water to UV lamp}
\end{equation}

\begin{equation}
a_{254} = \text{UV absorption coefficient (cm}^{-1}\text{)} \text{ at 254 nm}
\end{equation}

\begin{equation}
t = \text{Exposure time(s)}
\end{equation}

For a perfect collimated beam, the Petri factor and \( \frac{L}{d + L} = 1 \), and if \( E_e \) is the UV irradiance entering the water, or

\begin{equation}
D = E_e \frac{(1-10^{-a_{254}d})}{a_{254}d \ln(10)}
\end{equation}

Or, for \( P_e \) the total radiant power entering the water spread over area \( A \), \( \bar{E}_e = \frac{P_e}{A} \)

\begin{equation}
D = \frac{P_e}{A} \frac{(1-10^{-a_{254}d})}{a_{254}d \ln(10)}
\end{equation}

Batch reactor

For a batch reactor of Volume \( V = A \times d \),

\begin{equation}
D = \frac{P_e}{V} \frac{(1-10^{-a_{254}d})}{a_{254} \ln(10)} \quad [4]
\end{equation}

Therefore the UV dose is a function of the radiant power entering the water, the path length, the volume, the exposure time and the UV absorption coefficient.

For a flow-through reactor the Flow rate \( Q = \frac{\text{Volume}}{\text{Time}} \), therefore:

\begin{equation}
D = \sum_{d_i} \frac{P_e F_i (1-10^{-a_{254}d_i})}{V a_{254} \ln(10)} \quad [5]
\end{equation}

where \( F_i \) is the fraction of UV with path length \( d_i \).

Flow-through reactor

However, caution must be used for the UV dose calculated for a flow-through reactor, as it does not include the hydraulic efficiency resulting from the UV dose distribution. CFD modeling should be used to determine the delivered dose or “Reduction Equivalent Dose”.

Calculating path length

The path length distribution in a UV reactor can be calculated from reactor geometry, where all the UV emits from the quartz in an arc approximately +/- 45 deg to the normal (the UV coming out of a quartz tube is limited to a +/- 45 degree angle due to internal reflection and refraction by the quartz tube). If the lamps are transverse to the flow a significant proportion of the UV shines up and down the pipe approaching the reactor. These much longer path lengths are only important at very high UV transmittance.

The graph shows UV dose vs. path length for a \( P_e F_i / V \) ratio of 1.

As can be seen, the UV dose is relatively independent of path length, especially at lower UVT’s (<90%T) and higher path lengths (> 20 cm). That is because substantially all the UV is gone by 20 cm at 90%T and so providing extra path length for it
to traverse does not result in an additional UV dose contribution. Conversely, at very high UVT’s (>97%T) the UV can penetrate beyond 100 cm and consequently larger diameter reactors and the UV that shines up and down the inlet/outlet piping can add substantially to the UV dose. However, in general, an error in the calculated path length only impacts the UV dose provided by the UV that travels beyond the lower bound of this error, and this is small compared to the total UV dose calculated; therefore being very accurate in the determination of the path length distribution is usually not critical.

Summing over 10 path length groupings, each representing 10% of the photons, is usually sufficient. One technique is to use the reactor geometry to obtain a rough estimate of the path lengths of the 10 (or more) groupings. CFD modeling can then be used to calculate the “mass average UV dose” of the water passing through the reactor at four or five different UVT’s. The equation above is then used to adjust the path lengths to obtain the best fit to the CFD model results. In this manner, the UV dose calculated by the equations will match the CFD results over all UVT’s, spectral distributions, etc.

Polychromatic light
The UV dose for Medium Pressure (MP) UV/H₂O₂ reactors is defined as the integral, by wavelength, of the dose, weighted by the H₂O₂ absorption coefficient relative to its value at 254 nm (H₂O₂ weighted UV dose). This is similar to UV dose in disinfection reactors, which is weighted by the germicidal (DNA) absorption spectrum (germicidal dose) or by the action spectra of specific microbes. As in disinfection UV reactors, Dₜ is independent of the lamp spectral output, the UV transmittance and the path length that UV traverses in a reactor. Therefore results from testing using a low-pressure (LP) lamp (254 nm) in a collimated beam or batch reactor can be used to scale up to a medium pressure (polychromatic) reactor and vice versa.

The UV dose for a batch reactor is therefore calculated by dividing the spectral output typically into 20 or 100 wavebands (5 nm or 1 nm intervals) and summing over all wavelengths

\[
D = \sum_{\lambda=200nm}^{300nm} \sum_{d_i} \frac{P_{\lambda} r_{\lambda} F_i}{V} \left(1 - 10^{-a_{\lambda}d_i}\right) t \quad [7]
\]

where:
- \(P_{\lambda}\) is the total radiant power at waveband \(\lambda\) entering the water.
- \(r_{\lambda}\) is the relative absorption coefficient of the oxidant or photoactive species at wavelength \(\lambda\) to that at 254 nm.
- If the quantum yield varies with UV wavelength, then this factor should be multiplied by the relative quantum yield at wavelength \(\lambda\) to that at 254 nm.
- \(a_{\lambda}\) is absorption coefficient (cm⁻¹) of the water at wavelength \(\lambda\).

The wavelength range (200 to 300 nm above) should be sufficient to encompass the entire absorption band of the oxidant or photoactive species. The relative absorption coefficient is used because that determines the photons absorbed at wavelength \(\lambda\) relative to those absorbed at 254 nm and thereby converts the UV dose to a 254 nm equivalent dose (as is done for disinfection reactors).

The UV dose in a flow through reactor can be calculated by

\[
D = \sum_{\lambda=200nm}^{300nm} \sum_{d_i} \frac{P_{\lambda} r_{\lambda} F_i}{Q} \left(1 - 10^{-a_{\lambda}d_i}\right) a_{\lambda} \ln(10) \quad [8]
\]

Bench test results
The results from laboratory testing can be plotted as the log of

![Graph showing UV dose vs. path length](image)

![Graph showing UV dose vs. UVT](image)
the contaminant concentration vs. the UV dose calculated by the above equations.

The inverse slope of the curves is calculated as the dose per log or \( D_L \) (ml/cm²/log destruction). As can be seen, for first order kinetics, the \( D_L \) is independent of concentration.

**CFD Modeling to Predict Full-Scale Performance**

As mentioned earlier, the results from collimated beam or “perfectly mixed” batch reactor testing do not include the hydraulic inefficiency that results from the uneven UV dose distribution in a full-scale reactor.

**Hydrogen Peroxide Weighted Dose**

For full-scale, UV Intensity modeling (UVI) is used to calculate the hydrogen peroxide (or other photo-active species) weighted UV dose in each of the meshed CFD cells (the UV reactor is divided into approximately 3 million cells).

\[
D_{\text{H}_2\text{O}_2} = \sum_{\lambda=200nm}^{300nm} E_{\lambda} \cdot r_{\lambda} \cdot t \quad [9]
\]

where \( D_{\text{H}_2\text{O}_2} \) is the hydrogen peroxide (or other photoactive species) weighted UV dose in the CFD cell

\( E_{\lambda} \) is the total UV irradiance (fluence rate) at waveband \( \lambda \) at the CFD cell

\( r_{\lambda} \) is the relative absorption coefficient of hydrogen peroxide (or other photoactive species) at wavelength \( \lambda \) to that at 254 nm

\( t \) is residence time of the water in the CFD cell

The \( D_L \) above (from the batch testing) is multiplied by the hydrogen peroxide weighted UV dose in each CFD cell to compute the destruction of the target contaminant in each mesh cell, and hence in the reactor as a whole as the water passes through. This way any hydraulic inefficiencies are accounted for as the greater destruction in the higher intensity field close to the UV lamps is mixed back with the lower destruction in water further away from the UV lamps.

**Contaminant Destruction**

A typical CFD plot of the Geosmin destruction through the reactor (Bircher et al., 2011) is shown below.

**Validation of Method for Scale-Up of AOP Reactors**

Validation testing has been performed using both the Sentinel Chevron 48 inch reactor with 18 x 20 kW lamps and the 24 inch reactor with 9 x 10 kW lamps. The former was reported on (Bircher et al., 2011) and showed that the \( D_L \) obtained from batch reactor tests on the same water as the full-scale tests can be used in CFD modeling to accurately predict the full-scale performance.

**Direct UV Photolysis**

This approach can be used in direct photolysis (e.g., NDMA destruction) with the absorption coefficient of the target substituted for that of hydrogen peroxide in all instances.

If the destruction of the contaminant is primarily by direct photolysis (NDMA) then the \( D_L \) is constant regardless of water quality and hydrogen peroxide concentration and CFD alone can be used to predict performance since \( D_L \) is known.

**UV/Chlorine**

The photolysis of chlorine is complicated by the fact that chlorine in water dissociates into HClO and ClO⁻ depending on the pH (pKₐ = 7.49). Both compounds absorb UV powerfully with ClO⁻ showing particularly strong absorbance up to 350 nm.

As such, the output of medium pressure lamps between 280 and 320 nm can be used very efficiently owing to the typically low background absorbance of waters at these wavelengths. In fact, MP lamp systems would require similar total lamp power as low pressure lamp systems at pH’s between 5.5 and 7 and less
total lamp power at pH’s greater than 7.

This is in stark contrast to disinfection systems where MP systems typically require two to three times the total lamp power of LP systems.

However, ClO⁻ reacts very fast with the hydroxyl radicals, negating the higher absorption by ClO⁻ at high pH. The net result is that the UV/chlorine AOP is more efficient at pH < 6.5, where HClO is the predominant species.

Calculating UV dose with the UV/Chlorine AOP is done in the same way as with hydrogen peroxide except this very strong pH dependence must be considered; it must be summed for both chlorine species normalized for their respective quantum yields at 254 nm and the integration must be carried out to 360 nm.

Discussion
The hydrogen peroxide weighted UV dose per log inactivation ($D_L$) derived from empirical performance data generated from bench-scale testing can be used in CFD modeling to accurately predict the performance of full-scale UV AOP systems. Using this method, the performance of a full-scale system can be reliably predicted from bench-scale testing of a representative sample of water.

The $D_L$ water quality metric can be used to specify the performance requirements of UV AOP systems and then be checked in performance testing of the installed system, reducing the risk for both purchasers and suppliers of UV AOP systems.

$D_L$ is inversely proportional to the reaction rate constant with the hydroxyl radical for compounds that do not react signifi-
cantly to direct photolysis.

Therefore, it can be measured for one compound or surrogate in a water matrix and then derived for all other compounds of interest, provided their individual reaction rate constant with \( \cdot \text{OH} \) is known. In addition, the impact of all hydroxyl scavengers in the tested water (such as carbonate/bicarbonate, TOC, \( \text{H}_2\text{O}_2 \), etc.) can be calculated, and from that, a \( D_L \) can be specified having been adjusted for design water quality conditions.

This approach has benefits to all parties in an AOP purchase and installation.

References

