Advanced oxidation degradation kinetics as a function of ultraviolet LED duty cycle
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ABSTRACT
Ultraviolet (UV) light emitting diodes (LEDs) may be a viable option as a UV light source for advanced oxidation processes (AOPs) utilizing photocatalysts or oxidizing agents such as hydrogen peroxide. The effect of UV-LED duty cycle, expressed as the percentage of time the LED is powered, was investigated in an AOP with hydrogen peroxide, using methylene blue (MB) to assess contaminant degradation. The UV-LED AOP degraded the MB at all duty cycles. However, adsorption of MB onto the LED emitting surface caused a linear decline in reactor performance over time. With regard to the effect of duty cycle, the observed rate constant of MB degradation, after being adjusted to account for the duty cycle, was greater for 5 and 10% duty cycles than higher duty cycles, providing a value approximately 160% higher at 5% duty cycle than continuous operation. This increase in adjusted rate constant at low duty cycles, as well as contaminant fouling of the LED surface, may impact design and operational considerations for pulsed UV-LED AOP systems.

Key words | hydrogen peroxide, light emitting diode, methylene blue, ultraviolet

INTRODUCTION
Personnel, facilities, or equipment can become contaminated with hazardous chemicals for reasons ranging from a terrorist attack to an unintentional release. Remediation activities often include washing contaminated surfaces with water. The resulting wastewater can require pretreatment before entering a wastewater treatment plant, to avoid damaging the plant. Advanced oxidation processes (AOPs), which utilize highly reactive hydroxyl radicals, may provide a means for oxidizing organic compounds in water, potentially rendering these compounds inert. The degradation capability of AOPs employing ultraviolet light (UV) has been widely researched for contaminants including taste and odor compounds, trichloroethylene, antibiotics and pharmaceutical intermediates (Lopez et al. 2003; Jung et al. 2012; Wang et al. 2012a, b; Zoschke et al. 2012).

Traditionally, low or medium pressure mercury lamps provide the UV light source for UV-based AOP. UV light emitting diodes (LEDs) have the potential to provide an alternative UV light source for disinfection and chemical degradation. Advantages of LEDs include the ability to create arrays according to purpose, instant on/off capability, physical durability and the lack of hazardous materials. As UV LEDs are in the early stages of development, limited research has been conducted using UV LEDs for AOP with hydrogen peroxide. Past experiments successfully decomposed phenol by an AOP using UV LEDs of various wavelengths and hydrogen peroxide.
McDonald et al. (2000) demonstrated that a pulsed UV light source in conjunction with hydrogen peroxide was more effective at inactivating *Bacillus subtilis* var. *niger* than a continuous UV source with hydrogen peroxide. While hydroxyl radical production is expected to be proportional to the time-integrated UV power, it is unclear whether the improved effectiveness of the pulsed UV light source demonstrated by McDonald and colleagues originated from the direct effect of the pulsed UV light source on the *Bacillus subtilis* var. *niger* or by providing enhanced production of hydroxyl radicals. The application of pulsed, as compared to continuous, UV radiation has been demonstrated to be more effective for inactivating other pathogens (Wang et al. 2005; Bohrerova et al. 2008) when comparing alternative pulsed light sources to continuously driven mercury lamps. While the authors are unaware of other research involving hydroxyl radical formation from hydrogen peroxide in the presence of a pulsed source, research involving the photocatalytic oxidation of organic materials by the controlled periodic illumination of titanium dioxide with UV energy has indicated that the quantum efficiency of this reaction is inversely related to pulse duration (Szczechowski et al. 1993; Tokode et al. 2012; Korovin et al. 2015).

Radical production in an AOP is hypothesized to be proportional to the integrated optical power of the LEDs, regardless of pulse rate or width. However, results such as those produced by McDonald and colleagues (McDonald et al. 2000) provide evidence that the inactivation of organisms in the presence of an oxidizing agent is not proportional to the time-integrated optical power for a pulsed UV light source and that this effect is more pronounced in the presence of hydrogen peroxide. Further, McDonald et al. indicate that it is not known whether the temporal effect occurs due to a direct interaction of the pulsed UV light source with the organisms or the formation of radicals. Further, photocatalytic oxidation studies have demonstrated that effective quantum efficiency is inversely related to pulse duration. Therefore, the current experiments investigated the rate of radical production from hydrogen peroxide, indicated by methylene blue (MB) destruction, as a function of the duty cycle for pulsed UV LEDs.

### MATERIALS AND METHODS

#### Apparatus

A UV-LED reactor was constructed to assess the rate of radical production as a function of duty cycle. The reactor included drive electronics to control the duty cycle of the LEDs, a flow through water reactor containing 240 nm LEDs, and a pump to provide a continuous flow of solution. The solution contained hydrogen peroxide (50% in water from Fisher Scientific, Pittsburgh, PA, USA), deionized water, and MB (Fisher Scientific, Pittsburgh, PA, USA). The final solution contained approximately 5 mM hydrogen peroxide and 0.01 mM MB for each trial. This system permitted the creation of hydroxyl radicals by exposing the hydrogen peroxide to UV light. The hydroxyl radicals then reacted with the dye, reducing its absorption. The reduced absorption of the dye served as an indirect measure of hydroxyl radical production (Satoh et al. 2007).

The reactor was cylindrical (height and diameter of 7.62 cm) and made of electro-polished 316 L stainless steel. Seven 240 nm LEDs (Sensor Electronic Technology, Incorporated, Columbia, SC, USA) were placed in an end plate of the reactor so that the emitting surfaces of the LEDs were in physical contact with the solution. The solution entered the reactor from the bottom near one end plate and exited from the top near the end plate housing the LEDs. More information regarding the reactor design is available in the Supplementary Material, online at http://www.iwaponline.com/wst/071/108.pdf.

A MasterFlex Console Drive peristaltic pump (model number 77521-50, Gelsenkirchen, Germany) and PharMed® BPT tubing (inner diameter of 0.8 mm, Valley Forge, PA, USA) were employed to move the solution through the reactor at a rate of 1.4 mL per minute. The absorbance of the effluent at 664 nm was measured using an Agilent Technologies Cary 60 UV–visible light spectrophotometer (Santa Clara, CA, USA). A five-point calibration curve of absorbance and MB concentration ranging from 0.005 to 0.05 mM was applied to convert absorbance to MB concentration.

A control signal for the LEDs was generated on a laptop running DASYLab (DASYLab, version 12, Stamford, CT, USA). This signal included one of six duty cycles with a frequency of 9.09 Hz. The duty cycles included 5% (5.5 milliseconds (ms) on, 104.5 ms off), 10% (11 ms on, 99 ms...
off), 30% (33 ms on, 77 ms off), 50% (55 ms on, 55 ms off), 70% (77 ms on, 33 ms off) and 100% (a constant drive signal). These signals were provided over a USB bus to a driver box (measurement computing device: USB-2408-2AO, Norton, MA, USA), which provided a voltage signal to a custom-built LED control board. This control board included a power supply and an operational amplifier to provide current to the LEDs at a voltage that followed the input voltage. A LUXdrive DynaOhm (4006-020 1338, Randolph, VT, USA) was placed in series with each LED to maintain 20 mA to each LED. The voltage drop across the LED was approximately 8 V. An oscilloscope (OWON PDS5022T, Zhangzhou, China) was used to verify the timing of the pulse frequency at each LED. An integrating sphere and spectral radiometer (Labsphere, North Sutton, NH, USA) were used to measure the optical power of the LEDs across a wavelength range from 210 to 400 nm as a function of duty cycle. Measurements verified that the optical power increased proportionally with duty cycle.

**Experimental procedure**

In Experiment 1, efficiency of the reaction (e.g., the ratio of the degradation rate constant to time-integrated current) was monitored to determine when the performance of the reactor stabilized, with new dye solution added for each run and the reactor emptied after each run. This stabilization period was included because LED optical output is known to degrade exponentially as a function of time (Burmen et al. 2008), and therefore the LEDs potentially require a period of exposure to current to achieve relatively constant output over a time period consistent with the duration of the experiment. Duty cycle was then varied to demonstrate that the reactor’s performance was stable across a range of duty cycles.

In Experiment 2, the reactor was cleaned with methanol, fitted with new LEDs, and permitted to stabilize by running a first replicate of all experimental duty cycles. The order of the duty cycle conditions was then systematically varied to permit the loss of reactor efficiency with time to be analyzed. Specifically, the order of the duty cycle was randomized in the second replicate, and this order was reversed during the third replicate. As such, the average exposure time of the LEDs to MB was approximately equal for the duty cycle conditions across the second and third replicates. To decrease the rate of adsorption during this experiment, the reactor was filled with deionized water at the end of each experimental trial and clean deionized water flowed through the reactor between experimental trials.

**Data analysis**

A model for the degradation of MB in a UV-LED reactor was derived from a mass balance equation, as shown in the Supplementary Material (available online at http://www.iwaponline.com/wst/071/108.pdf), for a complete-mix reactor including a reaction, as:

\[
\frac{C}{C_0} = \frac{e^{-(k_s + \frac{1}{d} + \frac{1}{d} d_c)}}{k_s + 1}.
\]

In Equation (1), \( C_0 \) is the concentration of MB flowing into the reactor, \( C \) is the concentration of MB flowing out of the reactor, \( r \) is the ratio of the volume of the reactor to the volumetric flow rate and \( k_s \) is the apparent reaction rate constant. The parameter \( k_s \) was fit to minimize the sums of squared errors between the equation and the data. Best-fit equations were determined for each experimental run using the ‘fit’ function in Matlab 2015a (The Mathworks, Inc., Natick, MA, USA).

The production of hydroxyl radicals, and the resulting destruction of MB, is expected to be proportional to the applied UV dose, which was proportional to the duty cycle. To explore the relationship between the UV dose and the duty cycle, the apparent rate constants (\( k_s \)) calculated from Equation (1) were adjusted (\( k_{adj} \)) by the duty cycle according to

\[
k_{adj} = \frac{k_s}{d_c}.
\]

where \( d_c \) represents the duty cycle. Statistical analyses of \( k_s \) or \( k_{adj} \) included t-tests for comparing means and regression methods for determining the statistical effect of independent variables. These analyses were completed in JMP 10 (SAS Institute, Cary, NC, USA).

**RESULTS AND DISCUSSION**

**Stabilization of reactor: effects of LED activation time and MB adsorption on reactor performance**

To assess the stability of the reactor, initial trials were conducted, each at the 100% duty cycle, and rate constants were fitted to Equation (1). This model fits the data from each trial, having an \( R^2 \) value of between 0.87 and 0.98 for all conditions. The rate constants for the first three trials were above 0.020. However, the apparent rate constants for the remaining five trials were between 0.012 and 0.016. A t-test indicated the mean of the apparent rate
The mean rate constant declined linearly with time during the full duration of each replicate. Under these operational conditions, the rate of MB removal decreased in Experiment 2 included three replicates of all duty cycle conditions. Each replicate was completed before beginning the following replicate. Under these operational conditions, the rate constant declined linearly with time during the full 100 hours necessary to conduct the experiment. The mean of the $k_s$ values, averaged across duty cycle, decreased linearly among the replicates from 0.00544 to 0.00407, to 0.00294 minute$^{-1}$. Further, a linear model fitting $k_{adj}$ as a function of reaction time indicated that $k_{adj}$ decreased at a rate of 0.0000824 hour$^{-1}$. As this rate was less than the rate for the previous experiment, filling the reactor with distilled water between experimental conditions reduced the adsorption rate but did not eliminate the adsorption of MB on the LEDs.

The optical power of each LED was measured after Experiment 2, the LEDs were cleaned with methanol, and the optical power was measured again. The average optical power of the seven LEDs was 0.32 mW before cleaning and 0.51 mW after cleaning, indicating that MB buildup on the LEDs did not degrade when driven at a constant current of 20 mA, but their optical output may have slightly increased beyond the 4% error of the optical power measurement apparatus.

**Determination of observed rate constants for MB treatment**

Figure 1 shows representative plots of the mean normalized concentrations of MB as a function of time from Experiment 1. Mean normalized concentrations were determined by normalizing the initial concentration to 1 and computing the average across the three to five replicates for each condition in Experiment 1. As shown, the ratio of the observed MB concentration, $C$, to $C_0$ was stable when the reaction rate is consistent with the 12 hour equilibration time reported for adsorption of MB on titanium dioxide (Houas et al. 2003). The fact that MB can be dimerized also suggests that adsorption could have occurred throughout the entirety of the experiment. To test this hypothesis, a linear model was fitted to the adjusted rate constant as a function of time. The resulting linear model was significant, indicating that the adjusted rate constant was reduced at a rate of 0.000118 hour$^{-1}$. Interestingly, the adsorption of MB on the emitting surface of the LED, rather than the decay in LED performance, might be responsible for initial decrease in MB removal rate over time.

To compensate for the effects of MB adsorption, Experiment 2 included three replicates of all duty cycle conditions. Each replicate was completed before beginning the following replicate. Under these operational conditions, the rate constant declined linearly with time during the full 100 hours necessary to conduct the experiment. The mean of the $k_s$ values, averaged across duty cycle, decreased linearly among the replicates from 0.00544 to 0.00407, to 0.00294 minute$^{-1}$. Further, a linear model fitting $k_{adj}$ as a function of reaction time indicated that $k_{adj}$ decreased at a rate of 0.0000824 hour$^{-1}$. As this rate was less than the rate for the previous experiment, filling the reactor with distilled water between experimental conditions reduced the adsorption rate but did not eliminate the adsorption of MB on the LEDs.

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MB + peroxide solution was not exposed to UV energy. Similarly, the concentration was stable when the MB solution without peroxide was exposed to the UV LEDs at 100% duty cycle. However, when the MB + peroxide solution was exposed to UV light, the MB concentration declined over time and then stabilized. As expected, the LEDs at all duty cycles degraded the MB, showing first-order degradation before approaching a steady state. Also, shown in Figure 1 are curves fitted to these mean values using Equation (1). $R^2$ values are between 0.92 and 0.98. Similar behavior was observed for the six duty cycles in Experiment 2. Coefficients of determination for the fits of data from individual trials were generally above 0.9. However, a few trials exhibited values as low as 0.7.

**Effect of duty cycle on adjusted rate constant**

The effect of duty cycle on the resulting $k_{adj}$ values is shown in Figure 2 for the last two replicates from Experiment 2. The effect of duty cycle was statistically significant ($t(1,9) = -2.91, p < 0.0155$). Figure 2 shows $k_{adj}$ is statistically larger for the 5 and 10% duty cycle conditions than the higher duty cycle conditions. The average $k_{adj}$ value for the 5 and 10% duty cycle conditions is 165% larger than for the other duty cycles.

In summary, the adjusted rate constants for the 5 and 10% duty cycle conditions are statistically larger than adjusted rate constants for the higher duty cycle conditions. Further, there is relatively little variation among the average adjusted rate constant values for the higher duty cycles. It is possible that short-duration pulsed UV light sources may be more effective in producing radicals from peroxide, as alluded to by McDonald et al. (2000). Unfortunately, it is difficult to compare our results to those of McDonald and colleagues as their pulsed lamp operated at 100 Hz with an unspecified duty cycle. In the study of photocatalytic oxidation, both Tokode et al. (2012) and Korovin et al. (2015) demonstrated that the quantum efficiency of these reactions are inversely related to pulse duration within the range of the current study, rather than the sudden increase in efficiency as the pulse duration decreases from 33 to 11 ms as observed in this experiment.

Other possible causes also exist, including the degradation of peroxide in localized regions of the reactor for higher duty cycles, making peroxide a limiting reagent for the high duty cycle conditions. Yet another explanation could include secondary competitive reactions between hydroxyl radicals and MB degradation products, similar to those demonstrated by Houas et al. (2001). More specifically, because the initial solution contains primarily MB to react with the hydroxyl radicals, when the duty cycle is lower, fewer byproducts are produced to participate in competing reactions with hydroxyl radicals. However, as the duty cycle increases, the MB is degraded to a greater extent, producing higher concentrations of byproducts in the reactor. Because OH radicals are ‘non-selective’ when degrading organic contaminants, it is possible that the lower relative reaction rate with MB molecules at higher duty cycles occurs as the available hydroxyl radicals react with the byproducts. Thus, there are fewer hydroxyl radicals to react with MB, lowering the observed rate.

Regardless of the cause, this effect merits further study. Opportunities exist to improve the reactor if a peroxide-limited reaction is occurring. However, if the reduction in reaction rate is due to the reaction of the hydroxyl radicals with MB byproducts, the measurement of only MB may reflect contaminant degradation but may not provide an accurate proxy for hydroxyl radical production in the AOP system.

**CONCLUSIONS**

UV-LEDs operated with various duty cycles degraded MB in an AOP with hydrogen peroxide. All drive configurations resulted in first-order degradation kinetics for MB. However, when pulsing the LEDs, the adjusted first-order degradation rate constant was significantly higher for the 5 and 10% duty cycle conditions as compared to the higher duty cycle conditions. This effect could indicate that short-duration UV pulses are more effective in producing hydroxyl radicals from peroxide. However, this same result could be caused by peroxide limitations, which indicate a need for an
improved reactor design, especially at higher duty cycles. This effect could also be caused by scavenging of hydroxyl radicals by MB byproducts, indicating that the degradation of MB may not accurately reflect hydroxyl radical production in an AOP.

The MB adsorbed onto the LEDs during the experiment, reducing their optical output. Fouling of optical surfaces is a common feature of all UV systems, and the adsorption of MB to the LED optical surfaces is no exception. In practice, this fouling must be dealt with through engineering or operational controls. The fouling also complicates data analysis when performing experimentation into UV-LED performance. This adsorption will be related to the properties of the contaminants being studied. Cationic compounds, in particular, are likely to be more affected than anionic or nonionic compounds because the LED windows are composed of quartz, which may have a negative charge at typical slightly alkaline pH values.

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