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Advanced Oxidation of Tartrazine and Brilliant Blue with Pulsed Ultraviolet Light Emitting Diodes

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Abstract

This study investigated the effect of ultraviolet light-emitting diodes (UVLEDs) coupled with hydrogen peroxide as an advanced oxidation process (AOP) for the degradation of two test chemicals. Brilliant Blue FCF consistently exhibited greater degradation than tartrazine, with 83 % degradation after 300 minutes at the 100 % duty cycle compared with only 17 % degradation of tartrazine under the same conditions. These differences are attributable to the structural properties of the compounds. Duty cycle was positively correlated with the first-order rate constants (k) for both chemicals but, interestingly, negatively correlated with the normalized first-order rate constants (k/duty cycle). Synergistic effects of both hydraulic mixing and LED duty cycle were manifested as novel oscillations in the effluent contaminant concentration. Further, LED output and efficiency were dependent upon duty cycle and less efficient over time perhaps due to heating effects on semiconductor performance.

Keywords

Ultra Violet light-emitting diodes (UV LED); advanced oxidation; tartrazine; brilliant blue; pulsing; rate constants

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Introduction

Advanced oxidation processes (AOPs) are important to the water sector because they can destroy toxic or refractory water pollutants (Crittenden et al., 2012). This study is focused on the ultraviolet/peroxide (UV/H₂O₂)-based AOP. In this process, hydrogen peroxide is exposed to UV light and transformed into hydroxyl radicals, which react rapidly and non-selectively with many electron-rich organic pollutants and their byproducts (Crittenden et al., 2012; Andreozzi et al., 1999). Hydroxyl radicals can attack organic pollutants by: (1) hydrogen abstraction (i.e. removing a hydrogen atom from a saturated hydrocarbon), (2) hydroxylation (i.e. adding the hydroxyl group to an unsaturated hydrocarbon), or (3) oxidation without transfer of atoms (Buxton et al., 1988). Reactions with hydroxyl radicals are among the fastest aqueous phase reactions known, with rates close to the diffusion limited reaction rate (Dorfman and Adams, 1973). Further, this kinetic advantage can be observed at ambient temperature and pressure, unlike other processes such as wet oxidation and supercritical oxidation. At present there are a variety of configurations that can be used to implement UV/H₂O₂-based AOPs, as well as a growing number of applications for them (Shu and Huang, 1994; Beltran et al., 1997; Rodrigues et al., 2008; Rosario-Ortiz et al., 2010; Cao and Mehrvar, 2011).

Currently, mercury-based fluorescent lamps are the leading source of UV light for water treatment. These lamps are large, fragile, require high voltage and power, and contain mercury, which prompts stringent requirements related to the handling of hazardous materials. UV radiation can now be delivered using light emitting diodes (LEDs) instead of conventional mercury lamps. UVLEDs exhibit many advantages including: small size, light weight, physical durability, and lack of hazardous components (Ibrahim, 2012). UVLEDs can also be powered by low, direct current voltage, which allows the use of portable power sources such as batteries or photovoltaic cells (Ibrahim, 2012; Crystal, 2013). However, these semiconductor devices require further development in order to have the lifetimes and performance characteristics necessary to compete as direct replacements of mercury lamps. One strategy for achieving longer UVLED lifetimes is by using pulsed UV (PUV), an alternate drive technique in which the light is periodically turned on and off, as opposed to being left on continuously (i.e. CUV). PUV appears to lower power consumption and to possibly extend the life of UVLEDs. These benefits may result, in part, because pulsing the UVLEDs helps prevent elevated temperatures which are known to cause damage (Lenk and Lenk, 2011).

Little data is available on the use of PUV/H₂O₂ for the destruction of soluble organics. Liang et al. (2003) used PUV to remove 98% of influent N-Nitrosodimethylamine (NDMA) from groundwater and found that rate constants increased with more frequent pulsing. Duckworth et al. (2015) investigated the effect of duty cycle on the degradation of methylene blue and found that the normalized rate constants were greater for 5% and 10% duty cycles than for larger duty cycles and approximately 1.6 times higher than CUV operation. Unfortunately, methylene blue is a cationic dye that adsorbed to the surface of the LEDs' quartz lenses, thereby reducing LED power output and complicating data interpretation.

This study seeks to expand upon PUV-LED AOP treatment and the effect of duty cycles for the degradation of soluble organic compounds. Tartrazine (TAR) and Brilliant Blue FCF (BB) were the target compounds. These chemicals are relevant to this study because (1) they are both anionic dyes that are not expected to adsorb to the LEDs, (2) they are, like other food dyes, capable of causing negative health impacts (Rowe and Rowe, 1994; Abd and Moram, 2013; Kus and Eroglu, 2015; CSPI, 2008, 2016), and (3) they have structural features (e.g. aromatic rings) that are common to many organic water pollutants.

Materials and Methods

Apparatus

A UV LED reactor was constructed as described by Duckworth et al., (2015). The reactor includes 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 (see Supplemental Figure S1). The solution contained hydrogen peroxide (30% in water from Fisher Scientific, Pittsburgh, PA), deionized water, and either TAR or BB (Fisher Scientific, Pittsburgh, PA). Each experiment was conducted with approximately 5 mM hydrogen peroxide and 0.01 mM BB or 0.05 mM TAR. Hydroxyl radicals were produced by exposing the hydrogen peroxide to UV light inside a cylindrical reactor (height and diameter of 7.62 cm) made of electro-polished 316L stainless steel. Seven 240 nm LEDs (Sensor Electronic Technology, Incorporated, Columbia, SC) 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. 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) were employed to move the solution through the reactor at a rate of 1.4 mL per minute (except where noted). The absorbance of the effluent at 630 nm (for BB, Vidotti et al., 2006) or 430 nm (for TAR, Maslowska and Janiak, 1996; Vidotti et al., 2006) was measured using an Agilent Technologies Cary 60 UV-Vis Spectrophotometer (Santa Clara, California). This spectrophotometer was capable of scanning a wide wavelength range (190 to 1100 nm) with a scan rate up to 24 000 nm per minute. Effluent solutions were passed through a small glass tube located inside the spectrophotometer (i.e. no grab sampling), and either TAR or BB was determined every 5 minutes. Control AOP experiments were conducted with both TAR and BB but without either UV light or H₂O₂, and they confirmed that TAR and BB were not removed in the presence of either UV or H₂O₂ alone (see Supplemental Figures S2–S5).

The PUV operating strategy involves implementing a duty cycle, which is defined as the percentage of time the signal is “ON”. The duty cycle was controlled with a laptop running DASyLab (DASyLab, version 12, Stamford, CT). This signal included one of six duty cycles with a frequency of 9.09 hertz. The duty cycles included five percent (5.5 milliseconds (ms) on, 104.5 ms off), ten percent (11 ms on, 99 ms off), thirty percent (33 ms on, 77 ms off), fifty percent (55 ms on, 55 ms off), seventy percent (77 ms on, 33 ms off) and one hundred percent (a constant drive signal). An integrating sphere and spectral radiometer (Labsphere, North Sutton, NH) were used to measure the optical power of the

LEDs. The 240 nm LEDs were selected for this study had a peak output at 247 nm (see Figure S6) and were selected because peroxide absorbs light energy well in this wavelength range (Beers and Sizer, 1952).

Data Analysis

A model for the degradation of TAR or BB in a UV-LED reactor was derived from a mass balance equation for a complete-mix reactor including a reaction:

$$\frac{C}{C_0} = \frac{\tau k_s e^{-(k_s + \frac{1}{\tau})} + 1}{\tau k_s + 1} \quad (1)$$

In eq 1, C_0 is the influent concentration, C is the concentration flowing out of the reactor, τ is the ratio of the volume of the reactor to the volumetric flow rate, and k_s is the apparent reaction rate constant. This equation was then used to fit the data from the experiment, permitting only k_s to vary. Best-fit k_s values were determined for each experimental run using the Microsoft Excel Solver. Additionally, Durbin-Watson statistical tests were conducted to confirm that the data sets were independent (i.e. p -value > 0.05).

Normalized rate constants were calculated by dividing k_s by the duty cycle (expressed as a fraction). This parameter was a measure of the relative impact of the light energy that is used. In the context of the current study, this normalized rate constant is a measure of the relative energy efficiency observed at each duty cycle.

Results and Discussion

The Effect of Operating Conditions on the Removal of BB and TAR

Figure 1 shows the effect of duty cycle on the relative concentration (C/C_0) of BB. As expected, higher duty cycles yielded greater removal of BB because the lights were on more frequently. The relative concentration decreased by 77% over the course of 300 minutes when the duty cycle was 100%. Lower duty cycles produced profiles showing far less degradation than the 100% duty cycle. For example, the 30% duty cycle resulted in 61% BB removal, the 20% duty cycle resulted in 43% BB removal, and the lowest duty cycles removed only small fractions of the BB. These results are consistent with the findings of Duckworth et al. (2015) for the degradation of MB in a UV LED AOP of the same design. The first-order degradation model fit the data generated at 100% and 10%, and 5% duty cycles well with $R^2 > 0.95$ for 100% and 10%, $R^2 = 0.87$ for 5%. The 20% and 30% duty cycles exhibited significant data scattering leading to poorer model fits with $R^2 < 0.67$.

Very little TAR was removed for all duty cycles (Figure 2). The relative concentration of TAR decreased by only 17% for the 100% duty cycle over 300 minutes, by 13% for the 70% duty cycle, and even less for the lowest duty cycles. The first-order degradation model fit well for both high and low duty cycles with $R^2 > 0.96$ for the 100%, 70%, and 20% duty cycles. $R^2 = 0.84$ for the 10% duty cycle. The 5% duty cycle and the intermediate duty cycles, 30% and 50%, exhibited significant data scatter leading to a poorer model fit with $R^2 < 0.75$. These results confirm that higher duty cycles result in greater TAR degradation,

though they also demonstrate that TAR is more resistant to advanced oxidation than BB. Duplicate experiments confirmed these findings for both BB and TAR (see Supplemental Figures S7–S9).

The R^2 values for the fits in Figures 1 and 2 were calculated using the best fit lines as a reference. Part of the deviation is simply experimental error associated with the absorbance measurement. However, upon closer examination, an interesting aspect of this deviation is that, in many cases, it seems to oscillate from above to below the best fit line. This oscillation is more pronounced for some conditions than for others. Oscillations in chemical reaction are often attributed to the role of stable and unstable steady states, and have been widely reported for water treatment unit operations (Marek and Svobodova, 1975; Benjamin and Lawler, 2013; Bodin et al., 2012; IAEA, 2011; Martinov et al., 2010; Qi et al., 2012; Wols et al., 2010). These oscillations arise from non-ideal mixing conditions, reactor hydraulics leading to multiple flow paths, and variations in radiation intensity (Wols et al., 2010). Thus, for a given duty cycle, the effluent consists of fluid parcels that received a discrete UV dose (i.e. the product of radiation intensity and hydraulic residence time) intermixed with, or followed by those that have received a different dose. If the CSTR is not ideal, the UV dose received by each fluid parcel would greatly vary, leading to instability in the effluent contaminant concentration. Consider the 100% duty cycle profiles for both BB (Figure 1) and TAR (Figure 2) where the UV radiation pulsing is not a factor because the LEDs were constantly on (i.e. duty cycle was 100%). The concentration profiles from these experiments exhibit notable oscillations at 130, 170, 250 min for BB and 100, 150, 200 min for TAR. These oscillations may indicate variations in the hydraulic residence time of the fluid parcels. The lowest duty cycle profiles also had subtle but noticeable oscillations, whereas the amplitude of these oscillations was larger at intermediate duty cycles. At these intermediate duty cycles, the greater amplitude of the oscillations may be a combination of fluid parcels receiving greater variations in radiation intensities at intermediate duty cycles while also experiencing a distribution of hydraulic residence times.

To further investigate the effects of mixing, TAR experiments were repeated with mechanical mixing of the PUV LED reactor. The results still exhibited small oscillations (see Supplemental Figure S10), but the mixing resulted in 8% greater TAR removal in 300 minutes with mixing than without mixing for the 100% duty cycle. These results also suggest that the wave pattern observed may, in part, be caused by incomplete mixing, with the mixing essentially serving to create a stable steady state throughout the reactor. Thus, the oscillatory behavior illustrates the synergistic effect of both mixing and duty cycle distribution functions on the reactor's effluent compound concentration due to the range of UV dosages that are applied to the treated water. This could be a consideration when selecting duty cycles and reactor conditions. In particular, using intermediate duty cycles may result in more variable effluent compound degradation than using higher or lower duty cycles. However, as these oscillations were also observed for continuous UV operation and as well as a stirred reactor (albeit to a lesser extent), they may be important to consider in designing and operating UV LED water treatment systems.

Chemical Mechanisms Influencing Degradation Rates

As may be expected, BB and TAR degraded at comparatively different rates. One potential factor affecting the degradation rates is that hydrogen abstraction reactions tend to occur more quickly for larger compounds than smaller ones (Dorfman and Adams, 1973). BB has a higher MW and more aromatic rings than TAR (Supplemental Figure S11), so it may be expected to degrade faster than TAR. It is important to note that size is not the sole factor for hydrogen abstraction, these reactions are also influenced by the location of the hydrogen atoms which in turn influences the shape of the pre-reactive complexes. Another potential cause for the difference is that hydroxyl radical addition reaction rates tend to increase with the number of double bonds present in organic structural groups (Kwok and Atkinson, 1995). BB has more double bonds than TAR, potentially contributing to the faster reaction rates for BB. Lastly, hydroxyl radical addition to aromatic rings does not readily occur at functional groups located at the ipso- position (Minakata et al., 2014). Although a previous study reported the possibility of adding a hydroxyl group to the ipso- position (Razavi et al., 2009), this mechanism appears to be negligible for aromatic rings that are not filled with functional groups at all possible positions. BB has 3 aromatic rings that do not have functional groups at the ipso- position, while TAR has two aromatic rings with sulfonic groups at this position. This means that the BB aromatic rings provide an easier target for hydroxyl radical addition reactions and more potential reaction sites than that of TAR. These three underlying chemical mechanisms are consistent with the observation that BB is more reactive with hydroxyl radicals than TAR.

The first-order degradation rate constants increased as the duty cycle increased for BB (Figure 3) and TAR (Figure 4) removal, but interestingly the normalized first-order degradation rate constants were highest at the lowest duty cycle. These trends in rate constants show that PUV advanced oxidation at low duty cycles is slower but more energetically effective than CUV operation. The mechanistic explanation for this observation is unclear but there are two hypotheses that have been mentioned in literature. The first is that PUV discharges a broader wavelength spectrum of light, including both the visible and infrared region (Anderson et al., 2000; Wekhof et al., 2001), which has been used to explain why PUV may inactivate pathogens more efficiently than CUV at low duty cycles.

However, this does not appear to explain differences in the transformation of organic chemicals or the increased production of hydroxyl radicals because the LEDs used in the current study always emit in both the UV and visible range. Further, the previous studies utilized pulsed mercury lamps, not UV LEDs; the broader spectrum may be more applicable for mercury lamps than for LEDs due to the way light is generated. The second hypothesis is related to the mechanism and rate of photon generation in LEDs, which is proportional to the applied current. During PUV, there is a sharp increase in applied current, which would cause a proportional increase in photons generated during pulsing. The PUV peak photon discharge is likely higher than that of continuous UV, a subtlety that may become more noticeable at lower duty cycles since the dye concentrations are relatively high, permitting faster kinetics for first-order reactions. This kinetic nuance is a possible subject for future research, and may have an impact on application of UV LEDs.

Effect of Staining and Operating Time on LED Performance

LED lens staining was observed in Duckworth et al. (2015) with a similar PUV reactor for the degradation of MB. In that study, the power output of the LEDs was gradually reduced because MB adsorbed to the surface of the quartz lenses. In the current study the impact of possible BB and TAR dye adsorption on LED power output was studied for three LEDs (Supplemental Figure S12). The measured power outputs of the LEDs before and after cleaning were observed to be very similar. This result was expected because, unlike MB, both TAR and BB are anionic dyes, so they were not expected to adsorb to the negatively charged quartz lenses of the LEDs. These findings not only demonstrate the suitability of BB and TAR for UV LED studies but also call attention to adsorption issues reducing LED power output. This adsorption may have implications on LED reactor design based on characteristics of the dissolved target substances and background matrixes. Interestingly, the effects of duty cycle on the observed and normalized reaction rate constants for BB and TAR were in good agreement with the results of Duckworth et al. (2015) for MB, in spite of MB adsorption onto LED lenses. Thus, even though dye adsorption reduced the LED output in the Duckworth et al. study, their overall conclusions were upheld by the results of the current study, including their conclusions about the implications of pulsing on UV LED reactor design.

Finally, the normalized apparent first-order rate constant was determined at different time points throughout the study, and the results are shown in Figure 5. The x-axis shows the operating time, or service time, at each duty cycle. In this illustration, the normalized apparent first-order rate constant is used as an indication of how the LED output changed over time. The efficiency of the LEDs declined steadily with operating time for all duty cycles. The performance decline could be due to heat buildup, which degrades the LED. Heat breaks down the crystalline structure of the device, leading to deteriorating performance. According to Schubert (2006), as much as 90% of the energy being generated may be converted to heat. The LED can deteriorate due to both heating during the “on” condition and due to switching the LED on and off. The latter is caused by mechanical stress from thermal expansion during the heating and cooling cycle. This helps explain why the normalized rate constants can decline even when the lights are not constantly on; there are combined effects of heat buildup from both being ‘on’ and switching. The temporal trends in Figure 5 demonstrate the need to improve the quality of the LED devices. Future efforts should improve the durability and performance of these devices and lead toward more consistent and successful applications.

Conclusions

Advanced oxidation with pulsed UV LEDs was used to degrade BB and TAR in laboratory scale experiments. Nonlinear, first-order degradation of both TAR and BB was observed in 300-minute experiments for both PUV and CUV. BB degradation resulted in faster rate constants than those observed with TAR degradation, likely because structural features of BB more readily facilitated hydroxyl radical addition and hydrogen abstraction reactions. Duty cycles were positively correlated with the first-order rate constants (k_s) for both compounds but negatively correlated with the normalized first-order rate constants (k_s/duty)

cycle) indicating that pollutant removal was more efficient at lower duty cycles. Oscillations in observed BB and TAR concentration profiles were more prominent at intermediate duty cycles and were likely due to hydraulic and duty cycle effects, perhaps leading to unstable steady states. These results demonstrate the potential of UV LED treatment for contaminated water and call attention to factors that may impact UV LED system performance, such as mixing, duty cycle, chemical structure, LED staining, and operating time.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. The effect of duty cycle on the removal of Brilliant Blue (BB). The initial concentration was 0.01 mM BB. Model results are based on a mass balance for a CSTR reactor with first order degradation.

Figure 2.

The effect of duty cycle on the removal of Tartrazine (TAR). The initial concentration was 0.05 mM TAR. Model results are based on a mass balance for a CSTR reactor with first order degradation.

Figure 3.
The effect of duty cycle on rate constants for BB removal.

Figure 4.
The effect of duty cycle on rate constants for TAR removal.

Figure 5.

The effect of operating time on the apparent first-order rate constant for TAR removal. The operating time is the effective time that the LEDs are 'ON'.