Comparison of Two Advanced Oxidation Processes for their production of Hydroxyl Radicals and Evaluation of a UV/Ozone AOP at Varying UV Fluence for Treating Diclofenac

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ABSTRACT

Comparison of two Advanced Oxidation Processes for their production of Hydroxyl Radicals and evaluation of a UV/Ozone AOP at varying UV fluence for treating DCF

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This study explores the efficacy of two advanced oxidation processes for generation of hydroxyl radicals to promote degradation of emerging contaminants. Drought and water shortage have become pressing issues caused by our world’s changing climate. Water reclamation and reuse are increasingly important options for relieving this water stress. Water reuse runs the risk of reintroducing recalcitrant compounds that can accumulate in our bodies and environment. Advanced treatment methods that degrade these compounds are vital to protect our health and the health of the environment while providing necessary water resources. Advanced oxidation processes (AOPs) have shown great promise for removing recalcitrant compounds through the production of highly reactive hydroxyl radicals (•OH). This study investigated two AOPs for their production of •OH as indicated by the probe compound pCBA. One of the AOPs examined was a proprietary device that utilizes ambient air and UV to generate singlet oxygen, which subsequently produces •OH in water. The other is a more common method that combines UV and ozone (O₃) to produce •OH. The proprietary method was not found to produce notable hydroxyl radicals compared to the UV/O₃ AOP. The UV dose of the UV/O₃ AOP was also altered to analyze the impact on hydroxyl radical production and removal of a representative emerging contaminant, diclofenac (DCF). The sleeves made to alter the UV dose were not found to change the UV dose enough to show a consequential difference in degradation for the fluence indicator atrazine (ATZ) or the emerging contaminant DCF. Further testing with thicker sleeves would be important to determine the necessary amounts of UV and reasonably scale this technology for a water treatment facility.

Keywords: advanced oxidation processes, emerging contaminants, ozone, UV
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Chapter 1
INTRODUCTION

Growing populations are exhausting and contaminating our limited water resources. Water reclamation and potable reuse have become opportunities of great interest to relieve water stress. However, the risk of recalcitrant compounds, such as pharmaceuticals and personal care products, remaining after conventional water reclamation treatment is a cause for concern. These recalcitrant compounds can generally be classified as contaminants of emerging concern (CECs) or emerging contaminants. The increasing presence of emerging contaminants in natural waters poses a potential risk for human and environmental health, and further development of treatment methods that remove these pollutants before they enter the environment is critical.

The health effects of these emerging contaminants are mostly unknown, but many are endocrine disrupting compounds, and their continual input into the environment makes them a long term potential risk even at low concentrations [1]. The removal of these compounds from wastewater during treatment is imperative to avoid further accumulation in the environment. The World Health Organization (WHO) along with the International Water Association (IWA) have stated that preventative risk management must be implemented so that safe drinking water may be provided to all populations [1].

Ozonation has shown promise for treating micropollutants but is limited by its high selectivity and slow kinetics [2]. Advanced oxidation processes (AOPs) pair ozone with other oxidizing agents such as hydrogen peroxide (H$_2$O$_2$) or irradiation sources like UV to produce hydroxyl radicals, the most reactive oxidant in most water systems [3]. Hydroxyl radicals have proven capable of degrading ozone recalcitrant micropollutants, but further research is needed to optimize AOPs and ensure complete mineralization of these
compounds. However, even partial degradation of organic compounds by AOPs will generally enhance their subsequent biodegradability so they could either be fully removed by an additional biological treatment, would be more likely to degrade fully in the environment, or would do less harm if released [4].

This study examined two AOPs, one that combines ozone and UV and the other uses UV and ambient air to generate singlet oxygen and consequently hydroxyl radicals.

1.1 Research Questions

This research was conducted with the support of Clear Water Tech, LLC., a division of Pentair (CWT), and the questions this study aimed to answer were shaped by their interests. CWT designs and builds ozone generators and wanted to test the efficacy of one of their ozone generators as part of an AOP system to a commercial AOP that uses a commercially-available singlet oxygen generating system. Specifically, Clear Water Tech, LLC. requested examination of a UV/ozone system compared to a singlet oxygen system for hydroxyl radical production. Additionally, they requested examination of the ability of their UV/ozone system to degrade emerging contaminants. These requests led to the formulation of the following research questions:

1. How does hydroxy radical production of a UV/ozone AOP compare to that of an AOP using singlet oxygen?

2. How is hydroxyl radical production affected by alterations to UV fluence for a UV/ozone AOP?

3. How effective is the UV/ozone AOP at degrading a recalcitrant emerging contaminant, and is that efficacy affected by alterations in UV fluence?
1.2 General Approach
This study was conducted in three phases to address the three research questions. The first phase used para-chlorobenzoic acid (pCBA) as a hydroxyl radical indicator to compare the hydroxyl radical production of the UV and ozone AOP and the singlet oxygen AOP. In the second phase, the UV fluence was altered with mesh sleeves to discern the effects of UV alterations on hydroxyl radical production. Atrazine was also used in this phase as an indicator of UV fluence. The final phase consisted of tests with an example emerging contaminant, diclofenac, to determine the UV and ozone AOP’s ability to degrade a representative recalcitrant contaminant.

Chapter 2
LITERATURE REVIEW
The presence of contaminants of emerging concern (CECs) in the environment and the use of Advanced Oxidation Processes (AOPs) to treat them are relatively new topics of discussion. Literature on CECs and current technologies relevant to their treatment were reviewed in order to discern areas requiring additional study.

2.1 Contaminants of Emerging Concern
Contaminants of emerging concern (CECs) are a new class of contaminant that have been raising concern as their prevalence in wastewater effluents, environmental waters, and source waters for drinking water treatment has been increasing [5]. Improvements in analytical methods have made even smaller concentrations of these contaminants detectable, down to the parts per trillion, augmenting interest and concern from the scientific community and the public [6]. CECs include pharmaceuticals and personal care products (PPCPs), as well as pesticides, surfactants, and gasoline additives [5]. The dominant route for PPCP and some other CECs entry into the environment is through
effluent from domestic wastewater treatment [7]. PPCPs are largely found in wastewater due to their excretion and improper disposal by humans (Figure 1) [1]. A number of these compounds are found both in the influent and effluent of wastewater treatment plants, demonstrating their resistance to conventional treatment and persistence in the environment [7]. At best a 1-log concentration unit of removal is achieved for many PPCPs at plants employing only primary and secondary treatment [7]. Pharmaceuticals especially are designed to maintain their chemical structure and are persistent against biological degradation [8]. This explains why we see pharmaceuticals traveling through various locations in Figure 1. Figure 1 also shows that in addition to human use, the agriculture industry is also a major source of pharmaceutical contamination.

Figure 1. Routes of pharmaceutical contamination into the aquatic environment. [4]
Generally the concentrations of PPCPs in the environment are low, but their continuous input makes them a long-term potential risk for aquatic and terrestrial organisms [8]. The health effects of these compounds are mostly unknown but many are endocrine disrupting compounds that can affect the functionality and production of hormones, lead to tumors, and cause reproductive problems [1]. Many of the compounds have also been proven capable of bioaccumulating in larger species including humans, again making them a long-term potential risk whose impacts will only get worse [5]. These risks are also compounded as these chemicals mix together forming so-called “cocktails” which may cause other unknown impacts [8]. Additionally, the continual presence of pharmaceuticals at low levels in the environment is directly related to bacterial resistance of antibiotics [9]. The World Health Organization (WHO) identifies antibiotic resistance in bacteria to be a major global threat to human society [10]. It is in our best interest to employ the precautionary principle and remove these compounds from our waters [1].

2.1.1 Diclofenac

Diclofenac (DCF) is a non-steroidal anti-inflammatory drug used as an analgesic in many situations, from reducing inflammation in arthritis to relieving menstrual pain [11]. DCF is one of the pharmaceuticals most detected in water sources and is found in both water treatment influent and effluent [11]. DCF is difficult to remove because it is relatively stable compound with aromatic rings (Figure 2) and is resistant to biological treatment [11]. While DCF exhibits poor biodegradation, some can be achieved in anoxic conditions and degradation also tends to be higher in acidic conditions [12]. Generally WWTPs can only achieve removal efficiencies of 21-40% [12]. However, similar to other non-steroidal anti-inflammatory drugs, DCF is photochemically active and over 90% can be removed in natural water bodies by photolytic degradation [11], [12]. The efficacy of
phototransformation especially in natural water bodies, however is unreliable due to changes in turbidity and cloud cover that can affect light penetration.

![Chemical structure of DCF](image)

**Figure 2. Chemical structure of DCF.** [13]

Concentrations of DCF up to 1.3 μg/L are frequently detected in surface water, groundwater and WWTP effluent [4]. DCF is known to harmfully affect several environmental species at concentrations less than 1μg/L [14]. Pharmaceutical residues of DCF passed through the food chain have been cited with the devastating decline of vultures in India [12]. Studies have indicated a high reactivity of DCF with ozone [4] and further investigation on the advanced oxidation of this micropollutant is vital to ensure complete mineralization.

2.1.2 Atrazine

Atrazine (ATZ) is a widely used endocrine disrupting, carcinogenic and persistent herbicide (Figure 3) [15]. A study detected ATZ in the source water of almost every DWTP tested, even those far removed from areas with agricultural ATZ application [16]. The frequent detection of ATZ in source and finished waters suggest it is recalcitrant to conventional treatment and a widespread environmental contaminant [16]. ATZ has been found in the effluent of water treatment plants and proved to be resistant to both ozonation and chlorine oxidation [16]. The difficulty to remove ATZ has led to the
interest in using AOPs [17]. Additionally, ATZ is more reactive with hydroxyl radicals \((K_{\cdot OH, ATZ} = 3 \times 10^9 M^{-1} s^{-1})\) than with ozone alone \((K_{O_3, ATZ} = 6.0 M^{-1} s^{-1})\) [18]. Catalytic ozonation that uses activated carbon to produce hydroxyl radicals has achieved up to 80% removal of ATZ in 30 minutes [18].

Figure 3. Chemical structure of ATZ. [15]

2.2 Advanced Oxidation Processes

Advanced oxidation processes (AOPs) pair oxidizing agents such as ozone and hydrogen peroxide \((H_2O_2)\) or irradiation sources like UV to produce hydroxyl radicals. Hydroxyl radicals are the most reactive oxidant in most water systems and can be used to destroy organic pollutants in water [3], [19].

2.2.1 Ultraviolet Light

Ultraviolet (UV) light on its own is becoming a popular option for disinfecting water [20]. UV effectively inactivates human pathogens such as bacteria, spores, viruses, and even protozoa. This includes the destruction of Giardia lamblia cysts and Cryptosporidium parvum oocysts [21]. It has also been found that pharmaceuticals can be degraded directly and indirectly by photochemical processes initiated by UV-A and UV-B radiation from sunlight in surface waters. The direct photochemical reaction of an organic substance that occurs when a photon is absorbed causing an electronic excitation and usually an unstable intermediate, is called photolysis. UV photons can also interact
with natural organic matter (NOM) in surface waters and generate reactive species, such as singlet oxygen, solvated electrons, superoxide anion, hydroxyl radicals and others. These reactive species can degrade anthropogenic organic compounds in an indirect photochemical process [22]. Applying UV light directly or in a combined advanced oxidation process during water treatment may allow a treatment process that capitalizes on the photodegradation potential of these contaminants in a more controlled and reliable manner. While natural UV is plentiful, relying on photolysis in natural water systems is unreliable; there are too many potential variables that can affect the efficacy of this process.

2.2.2 Ozone
The use of ozone for disinfection is also becoming increasingly common [20]. Ozone reacts with contaminants and microorganisms in aqueous systems in two ways: through direct ozonation and via hydroxyl radicals that form when dissolved ozone decomposes [20]. Direct ozone oxidation is limited by high selectivity and slow kinetics [2], [23]. Ozone mainly reacts with double bonds, activated aromatic systems and non-protonated amines [24]. Ozone is also an extremely powerful oxidant that can inactivate even the most resistant pathogenic microorganisms like protozoa, but this requires high ozone exposure [23].

Hydroxyl radicals, on the other hand, are non-selective [3]. Hydroxyl radicals are the strongest oxidants in water and the desired products of advanced oxidation processes (AOPs) [24]. Hydroxyl radicals readily react with pollutants through a number of mechanisms, including: hydrogen abstraction, radical-radical reactions, electrophilic addition, and electron transfer [25]. Hydrogen abstraction is the removal of a proton by a radical, forming a new radical [26], and radical-radical reactions proceed on potential
energy surfaces with no maximum, using collisional deactivation to create stable molecular products [27]. Electrophilic addition is when an at least slightly positive radical attacks a region of electron density on another molecule, often a double bond between carbon atoms [28]. Finally electron transfer is simply the exchange of electrons from a donor to an acceptor molecule [29]. Each of these mechanisms results in degradation of the original contaminant, typically to a simpler, less harmful molecule.

2.2.3 Combining Ozone and UV

Strong oxidizing radicals can be formed by combining ozone with other oxidizing agents such as H2O2 or irradiation sources like UV light. Such a combination is commonly called an Advanced Oxidizing Process or AOP [3]. In this study, we are focusing on the AOP combining ozone and UV. The UV photolysis of ozone results in the rapid production of hydroxyl radicals (•OH) according to the reaction mechanism shown in (Eq1-3) [30].

$$O_3 + H_2O \xrightarrow{hv} O_2 + H_2O_2$$  \hspace{1cm} \text{Eq. 1}

$$H_2O_2 \xrightarrow{hv} 2\cdot OH$$  \hspace{1cm} \text{Eq. 2}

$$2O_3 + H_2O_2 \leftrightarrow 2\cdot OH + 3O_2$$  \hspace{1cm} \text{Eq. 3}

CECs are degraded by the attack of these strong radicals as well as the direct photolysis by UV and oxidation by molecular ozone [3], [30]. This multi-level attack results in a synergy that degrades resistant CECs more effectively than either ozone or UV could on their own (Figure 4 & 5) [3]. We can see in Figure 4 that ozone was better than UV alone at degrading carbofuran, but the combination UV/O3 showed the fastest reaction rate and most complete removal. Figure 5 shows that for N-Nitrosopyrrolidine, 1 mg/L of ozone alone was comparable to the degradation power of UV on its own, but in all cases the
UV/O3 AOP provided superior removal to either O3 or UV on their own. AOPs that produce hydroxyl radicals are also better equipped at degrading lipid regulating pharmaceuticals like bezafibrate and their metabolites [4]. For example, Clorofibric acid (CBF) is a metabolite of fibrate lipid regulators clofibrate and etofibrate and was detected in domestic wastewater effluent nearly 30 years ago. CBF has a relatively small second-order rate constant (<20 M⁻¹s⁻¹) for reactions with molecular ozone. However, significant improvements in degradation have been seen when hydrogen peroxide is added, or the pH is elevated. These options suggest the importance of hydroxyl radicals in the degradation of this acidic drug metabolite and the greater removal potential via AOPs [4]. Molecular ozone is more stable in acidic conditions and the presence of OH⁻ ions in higher pH conditions triggers the decomposition of ozone and the production of •OH radicals [25], [2].

![Figure 4. The degradation of 0.2 mM CBF by three different treatment processes: UV, ozone, and combined UV and ozone. [3]](image-url)
Figure 5. The degradation of N-Nitrosopyrrolidine at an initial concentration of 1 μM by UV. The fluence rate (0.58 mW cm$^{-2}$) and the ozone concentrations (0.3, 0.5, and 1 mg/L) were tested separately and together at pH=7. [30]

Employing UV and ozone technologies requires no continuous chemical addition, just on-site generation which can require a significant energy input but reduces the hazards associated with chemical transportation and storage [31].

2.2.4 Singlet Oxygen

The method of degrading water pollutants using singlet oxygen has not been explored as much as other AOPs [32]. Singlet oxygen has a high electrophilicity and is capable of oxidizing phenols, sulfides, and amines [33]. One method for producing molecular singlet oxygen is photosensitized oxidation. This process requires molecular oxygen, light of an appropriate wavelength, and a photosensitizer capable of absorbing light and exciting oxygen to its singlet state [32]. The singlet oxygen generator used in this study is of a proprietary nature and the method of singlet oxygen generation is not disclosed; however, the photosensitized generation method is presented below to help the understanding of
singlet oxygen. Photosensitized oxidation generates the excited sensitizer triplet state ($^3\text{PS}^*$) that can react in one of two ways: Type I (radical-photo-oxidation) and Type II (photo-oxidation by singlet oxygen) (Figure 6). Similar to hydroxyl radicals in traditional AOPs, we can see the excited sensitizer triplet state ($^3\text{PS}^*$) can lead to electron transfer and remove protons.

![Figure 6. The mechanism and reaction of photosensitized oxidation.](image)

(A) Shows the mechanisms of the two types of photosensitized oxidation. (B) Gives the reaction of photosensitized oxidation (Type II).

Chapter 3

MATERIALS & METHODS

Tests for this study were set up as batch runs in a horizontal PVC chamber (Figure 7), which will henceforth be referred to as the “reactor vessel” or the “reactor”. The reactor had two openings on the top, one served as an entry point for tubing that provided gas bubbling and the other was a sampling port (Figure 8). The reactor had a quartz sleeve for the low-pressure high output UV lamp that runs through the center. The reactor also contained glass beads during that the experimental runs to help keep the tubing in place and improve the diffusion of gas bubbles. The reactor was filled with 5 L of the different experimental solutions and then sampled at varying time intervals for 20 minutes.
Depending on the contents of the reactor for a given test, the waste was either stored for hazardous waste collection or poured down the sink.

**Figure 7. Cross section illustration of the reactor.** Modified image from the Bioshield UV System’s installation and user’s guide [34].

**Figure 8. The experimental set-up inside the fume hood of lab 13-114.** The black PVC reactor vessel is on the left, the ozone generator is on the right and the ozone monitor is above.
3.1 Materials
A Pentair Bioshield UV system provided UV irradiation, and a ClearWater Tech LLC ozone generator (CD1500P) provided ozone during experiments. A singlet oxygen generator was used as well; the company name is undisclosed due to the proprietary nature of the technology.
Lab grade tert-Butanol (TBA), para-Chlorobenzoic Acid (pCBA), Sodium Sulfite Anhydrous, ATZ, DCF, and Potassium Phosphate Monobasic, HPLC grade Methanol (99.9%), acetonitrile, and acetic acid were obtained from Fisher Scientific. A Thermo Scientific Genesys 10S UV-Vis Spectrophotometer and a Rosemount 499AOZ ozone sensor were both used to measure the concentration of ozone during experiments.

3.1.1 pCBA Probe Compound
The probe compound para-chlorobenzoic acid (pCBA) was used to determine the concentrations of hydroxyl radicals in solution. The pCBA compound is used because it is very reactive with •OH, $k_{\text{OH,pCBA}} = 5 \times 10^9 \text{M}^{-1}\text{s}^{-1}$, but has low reactivity with ozone, $k_{\text{O}_3,\text{pCBA}} = 0.15 \text{M}^{-1}\text{s}^{-1}$ [35]. Previous studies have also indicated that pCBA does not undergo direct photolysis [36]. The quantum yield of pCBA has been determined as 0.026 using UV at wavelengths 250-350 nm, suggesting direct photolysis of pCBA is slow [37].

A stock solution of 10 mM pCBA was prepared in DI water. 2.5 mL of the concentrated stock solution was added to the 5 L reactor vessel during experimentation to achieve an initial pCBA concentration of 5 uM.
3.1.2 DCF Solution
A stock solution of 0.25 g/L of DCF was made in 50% DI water and 50% methanol. 200 mL of this stock solution was added to the 5 L reactor for an initial concentration of 10 mg/l.

3.1.3 ATZ Solution
An ATZ stock solution of 0.5 g/l was prepared in methanol. 15 mL of this stock was added to the reactor for experimental runs to get an initial concentration of 7 uM ATZ.

3.1.4 TBA Solution
Tert Butanol (TBA) is a necessary scavenger in hydroxyl radical experiments using pCBA as a probe compound. Without TBA, pCBA propagates •OH chain reactions and leads to overestimation of •OH exposure [38]. In this study, a 0.5 M TBA stock solution was prepared in DI water. 8 mL of this stock solution was added to the 5 L reactor vessel for each experimental run for a TBA concentration of 800 uM.

3.1.5 Phosphate buffer
A 0.5 M stock solution of phosphate buffer was prepared by adding 68 g of potassium phosphate monobasic to 1 L of DI water. The phosphate buffer solution was pH adjusted to 7 using phosphoric acid and/or sodium hydroxide. The buffer solution was then ozonated for 20 minutes to destroy any organic material. After ozonation, the solution was left open for a few hours to allow the dissolved ozone to volatize, leaving no initial dissolved ozone for the experimental runs. An amount of the stock solution was added to the 5 L reactor to obtain a concentration of 5 mM phosphate buffer for most of the experimental runs.

3.1.6 Sodium Sulfite Solution
A 50 mg/L solution of sodium sulfite was prepared before experimental runs each day. 25 uL of this solution was added to each sample vial to quench the oxidation reaction.
Without excess sodium sulfite the samples could continue to react, and give inaccurate readings of the probe compounds degradation over time [38]. Sodium sulfite was added to all samples regardless of use of ozone, for consistency.

**3.1.7 Well mixed Reactor Study**
A “well mixed study” was conducted to determine how long it would take the 5 L reactor to reach a homogenous concentration of the constituent, throughout the reactor volume. To conduct the study, pCBA stock solution was added to 4L of DI in the reactor vessel to reach a concentration of 5 uM. The red line on Figure 9 marks 5uM, the target concentration. The green line with triangle markings represents the average of two runs conducted with air bubbling through the tubing at 6 L/min, while the yellow line with circles represents a test run with the air pump running at maximum air flow.

![Figure 9. pCBA Concentration Over Time with Air Bubbling](image)

**Figure 9. pCBA Concentration Over Time with Air Bubbling.** The green line represents the average of two test runs bubbling air at 6 L/min and the yellow represents a test at maximum air flow. The red 5 uM line represents the target concentration the reactor was dosed with.
The results of the “well mixed” study demonstrate that it takes around 360 seconds or 6 minutes to reach the expected reactor concentration of 5 uM. There was not a marked difference between the runs at an airflow of 6 L/min and the run at maximum air flow. The average concentrations of the two tests at 6 L/min and the test at full air flow had standard deviations ranging from 0.54 to 0.96. Based on these results, a pre-mixing time of 6 minutes was used for the experimental tests to ensure a homogenous experimental solution before experimental treatment and sampling.

3.1.8 Ozone Monitoring
A Rosemount 499AOZ ozone sensor was used to monitor ozone concentration in the reactor vessel. Direct UV measurements of aqueous ozone using a Thermo Scientific Genesys 10S UV-Vis Spectrophotometer were also used to confirm ozone readings and calibrate the Rosemount sensor, using Beer’s Law (Equation 4) [39]:

$$A = \varepsilon lc$$

where ...

- $A$= absorbance @ 258 nm
- $\varepsilon = 2900 \text{M}^{-1}\text{cm}^{-1}$
- $l$ = path length, 1 cm
- $c$ = concentration, M

For tests with ozone, ideally, the ozone concentration would have remained stable throughout each experimental run. However, the ozone generator did not maintain a constant ozone concentration, and thus the ozone concentration at each sampling time was noted. Prior to each experiment, the ozone generator was started in 4 L of DI until the measured ozone concentration was relatively stable. The ozone generator was shut off while the fifth liter of solution with the experimental constituents (pCBA/DCF/ATZ, TBA, and phosphate buffer) was added and allowed 6 minutes to mix with air bubbling.
The ozone generator was turned again after six minutes of mixing to initiate the experiment.

3.2 Analytical Methods: HPLC
Analysis of sample concentrations was performed by a Thermo Scientific UltiMate 3000 Ultra High-Performance Liquid Chromatography (HPLC) system with an Acclaim 120 C18 column (4.6x100 mm, 5 um internal diameter).

For pCBA analysis, a 60:40 solution of 99.9% HPLC Grade methanol and DI water was pH adjusted to a pH of 2.7 using phosphoric acid [37]. Samples were analyzed at 234 nm with a flow rate of 1 mL/min. For ATZ, an eluent solution of 60% acetonitrile and 40% DI was used, with a flowrate of 1 mL/min and analyzed at a wavelength of 226 nm [18]. For DCF, an eluent solution of 10% acetic acid and 90% methanol was used. Samples were run at a flowrate of 0.25 uL/min and measured at a wavelength of 280 nm [40].

3.3 Quality Assurance and Quality Control
Quality assurance and quality control (QA/QC) is a crucial part of experimentation that checks for accuracy and precision in measurements. Several QA/QC techniques were employed during this study to ensure reliable results including controls and replicate experiment runs.

In this study, control runs without AOP treatment were performed to see if any changes in pCBA concentration occurred without treatment and to determine how long it would take for the system to become well-mixed. Control experiments consisted of bubbling air through the system instead of ozone or singlet oxygen, with no UV, and sampling at intervals for 20 minutes to monitor pCBA concentration with no reaction in the system. Control runs also included running ozone and UV each on their own. These runs helped
determine the efficacy of ozone and UV on their own at degrading pCBA, ATZ, and DCF.

Experimental runs were repeated to ensure precise results. Several runs were done in triplicate, but some were done in duplicate due to time and chemical availability constraints.

Chapter 4

RESULTS & DISCUSSIONS
The main goals of this study were to compare the efficacy of two different AOP technologies for their production of hydroxyl radicals and CEC removal. The effect of alterations to UV fluence on the efficacy of the UV/ozone AOP were also examined. Hydroxyl radical production was determined through the degradation of the probe compound pCBA and UV fluence was examined through the degradation of ATZ. Finally, the example emerging contaminant DCF was used to test the efficacy of the UV/O3 at degrading a recalcitrant contaminant.

Phase 1: Comparison of •OH Production using UV/O3 and Singlet Oxygen AOPs
Phase 1 consisted of control tests of ozone and UV on their own as well as tests of both the UV/O3 and singlet oxygen AOPs.

4.1 O3 and UV Control Tests
The controls tests of ozone and UV used individually determined the ability of each treatment mechanism to independently degrade pCBA. The results of the ozone-only test were as expected with little overall pCBA degradation (Figure 10).
Figure 10. pCBA Concentration over time with ozone bubbling and UV treatment. The initial reactor condition after 6 minutes of mixing: 5 uM pCBA, 800uM TBA and 5mM phosphate buffer (pH=7). The average of three ozone experimental runs and four UV runs are displayed with the standard deviations represented as error bars. An average of two runs with just air are also displayed.

For the ozone tests, the ozone was bubbled into the reactor at 6 L/min for 1200 seconds (20 minutes). The concentration of ozone varied widely from as 0.02 to 2.4 ppm. It should be noted that for the first ozone test, the 6 minutes of mixing was done with oxygen rather than air, and the second test was only given 5 minutes to mix. These minor differences do not appear to have been significant because the samples of the three tests had standard deviations all less than 0.1.

The ozone only controls indicate very little pCBA degradation, with an average of 26% removal over 20 minutes. This is expected since pCBA has a relatively low reactivity with ozone, \( k_{O_3,pCBA} = 0.15 \ M^{-1}s^{-1} \) [35].

The UV runs on the other hand had a surprisingly large amount of pCBA degradation, with an average pCBA removal of 78% over the 20-minute run (Figure 10). This is surprising because other studies have noted that pCBA does not undergo direct photolysis.
so it may be that the air bubbling in addition to the UV exposure was able to create hydroxyl radicals in solution [36], [37]. For the UV only tests, the solution was given the same 6-minute mixing step before the treatment began. After plugging in the UV light, it takes approximately 20 seconds to ignite giving time to prepare and take the first sample at 0 seconds when the light turns on. Samples were then taken intermittently for 1200 seconds (20 minutes). The four UV tests had measured pCBA concentrations at any given time with standard deviations ranging from 0.05 to 0.5.

The control experiments were also conducted by bubbling only air through the reactor. As expected, no pCBA degradation was noted.

4.2 AOP Tests

To test the AOPs, the same 5 L reactor set-up was used. The tubing (Figure 7) was changed depending on what gas was bubbling into the reactor, either ozone for the UV/O₃ AOP and ozone only tests or the singlet oxygen gas for the other AOP. Looking at all the results of Phase 1 together, it is clear that the UV/Ozone AOP had the highest hydroxyl radical production (Figure 11). However, the error bars on the UV/O₃ AOP suggest that the AOP may actually be similar to UV on its own. It is also interesting to note that all the lines have error bars indicating standard deviations, but they are only visible for the UV/ O₃ line since results were generally consistent across multiple experimental runs.
Figure 11. pCBA degradation over time for the UV/O3 AOP, singlet oxygen AOP, and UV, and Ozone Controls. The displayed data was averaged from duplicate, triplicate, and even quadruplicate experiments and error bars represent the standard deviations of the repeated experiments. Initial experimental conditions: 5 uM pCBA, 800 uM TBA and 5 mM phosphate buffer (pH=7).

The degradation curves from Figure 11 were fit with exponential trendlines to find the first-order reaction rate constants for the different treatments (Table 1). The reaction rate constant for the ozone experiments is significantly less than the AOP and UV coefficients. This is expected because pCBA is minimally reactive with ozone as compared to hydroxyl radicals or UV light. The UV reaction coefficient was also less than the UV/O3 AOP, demonstrating the increased hydroxyl radical production when the two methods are combined.
Table 1. Pseudo first-order reaction rate constants for pCBA degradation

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Reaction Rate Constant (x10^{-3}) (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>O3</td>
<td>0.2</td>
</tr>
<tr>
<td>UV</td>
<td>1</td>
</tr>
<tr>
<td>O3/UV AOP</td>
<td>2</td>
</tr>
</tbody>
</table>

1.3 Previous AOP Studies

A previous proprietary study with the singlet oxygen generator used pCBA as the hydroxyl radical probe compound but did not include the other experimental solution constituents (TBA and phosphate buffer). The initial single oxygen experiments for this study were done with the complete solution (pCBA, TBA, and phosphate buffer) to match the O3/UV AOP experiments described above. However, these experiments showed little to no pCBA degradation (Figure 12). This led to thinking that the additional constituents may be hindering the mechanism by which singlet oxygen produces hydroxyl radicals. Additional tests were thus run with just DI water and pCBA, similar to the aforementioned study (Figure 13A).
Figure 12. pCBA Concentration Over Time with Singlet Oxygen Treatment in Experimental Solution. The experimental solution (5 uM pCBA, 800 uM TBA and 5 mM phosphate buffer (pH=7)) was bubbled with the singlet oxygen gas and sampled for 1200 seconds (20 minutes).

The previous study with this singlet oxygen generator noted complete degradation of 3 uM pCBA in 20 minutes. The three tests conducted in this study had pCBA removal between 0 and 12%, which is significantly less degradation than found in the previous study, under similar experimental conditions.
Figure 13. pCBA Concentration Over Time with Singlet Oxygen Treatment in DI water. A) The red line gives the average of the three runs done in the complete experimental solution (5 uM pCBA, 800 uM TBA and 5 mM phosphate buffer (pH=7)). The blue line represents the average of two runs done similar to another study with just pCBA in DI water at a concentration of 3 uM. B) The graph produced by a previous study testing pCBA degradation by the same singlet oxygen generator in DI water at different pHs.

In a prepared solution of pCBA at a concentration of 3 uM in DI water the singlet oxygen generator demonstrated more degradation with percent removals of 13 and 18%. These
values are significantly less than the previous study, which demonstrated complete degradation of pCBA after 20 minutes (Figure 13B). These differences in results may be attributed to some differences in experimental set-up. The complete methods used by the previous study were not disclosed because of the proprietary nature of the equipment.

To compare the singlet oxygen AOP to the UV/O3 AOP, the UV/O3 AOP tests were repeated with the same conditions of just pCBA in DI water. These tests were done at 3 uM pCBA like the previous study and 5 uM pCBA. Both runs showed complete degradation of pCBA in ten minutes or less. The 3 uM run only had pCBA present in the first, time zero sample so preparing a graph demonstrating degradation was not feasible.

Without TBA in the experimental solution, pCBA accelerates ozone decomposition and the production of hydroxyl radicals. Yang et al. (2016) found the presence of pCBA to enhance the ozone decay rate to $3.1 \times 10^{-2}$ s$^{-1}$ as compared to the control decay rate of $1.5 \times 10^{-3}$ s$^{-1}$. An explanation for pCBA’s enhancement of ozone decay has been ascribed to the formation of H$_2$O$_2$ from the reaction of •OH with pCBA, which then reacts with ozone to again produce •OH. Another study proposed that the hydroxylated intermediates formed during ozonation of aromatic compounds with electron-withdrawn groups (e.g. benzoic acid) were capable of reacting with ozone to produce •OH [38]. Therefore, pCBA is a promoter of ozone decay and the results of the UV/ozone AOP runs in DI water without TBA do not give an accurate representation of the AOPs ability to produce hydroxyl radicals. Since pCBA is highly reactive with hydroxyl radicals it degrades quickly without the presence of TBA as a scavenger to interrupt this •OH promotion cycle.
Additional experimental runs with the UV/ozone AOP in the complete experimental solution were done in Phase 2.

**Phase 2: Effect of UV fluence alterations to hydroxyl radical production**

To examine the effect changing the amount of UV would have on contaminant degradation, two mesh sleeves were made to place over the UV quartz sleeve. One mesh sleeve was made of a single layer of mesh (SS) and the second had a double layer (DS) (Figure 14).

![Image of sleeves](image)

**Figure 14. The sleeves designed to reduce UV fluence.** The single sleeve (SS) on top and the double sleeve (DS) below are displayed with A) showing the full sleeves and B) giving a zoomed in view for a closer look at the density of the mesh.
The herbicide ATZ has been shown in previous studies to respond to UV light, and therefore is used as an indicator of UV fluence, or the total radiant UV energy applied to a system, sometimes called the UV dose [21], [41]. Initial experiments with ATZ showed that UV alone was just as effective as the UV/O3 AOP at degrading ATZ (Figure 15). This led to the focus on ATZ as a UV indicator as in previous studies rather than a hydroxyl radical indicator.

![Figure 15. Degradation of ATZ over time from UV, ozone and UV/O3 AOP treatment. Each line represents the average of two experimental runs with the error bars representing the standard deviations. The initial experimental conditions: 7 uM ATZ, 800 uM TBA and 5 mM phosphate buffer (pH=7).](image)

Figure 15 shows that UV alone was able to fully degrade ATZ and no additional benefit was really seen by adding ozone. This means UV was the main driver of degradation of ATZ in our system and ATZ makes a good fluence indicator.

To understand the effect of the sleeves on the UV fluence in the system, tests were conducted with ATZ under three conditions: unsleeved, SS, and DS (Figure 16). The rate of degradation of ATZ corresponds, as expected, with increased
fluence in the unsleeved condition compared to either sleeved condition, and the
double sleeve took the longest to fully degrade the ATZ. This correlation
between increased fluence and degradation can be seen numerically through the
first order reaction rate constants found by fitting the graph with exponential
trendlines (Table 2). While the unsleeved condition obviously has the largest
reaction rate constant, the two sleeved conditions are pretty close in value
meaning the two different sleeves did not change the UV fluence by very different
amounts.

![Graph showing degradation of ATZ under varying UV conditions.](image)

**Figure 16. Degradation of ATZ under varying UV conditions.** The experimental
solution (7 uM ATZ, 800 uM TBA and 5 mM phosphate buffer (pH=7)) was bubbled
with air for mixing while exposed to UV. Each line is an average of two experimental
runs and the error bars represent the standard deviations.
Table 2. Pseudo first order reaction rate constants for the degradation of ATZ with varying UV fluence.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Reaction Rate Constant (x10^{-3}) (s^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsleeved</td>
<td>7.88</td>
</tr>
<tr>
<td>Single Sleeve (SS)</td>
<td>6.29</td>
</tr>
<tr>
<td>Double Sleeve (DS)</td>
<td>4.83</td>
</tr>
</tbody>
</table>

Next, the sleeves were tested with ozone and UV to see the altered UV’s effect on hydroxyl radical production through pCBA degradation (Figure 17). We would expect the reduced UV to make the overall UV/O3 AOP less effective at producing hydroxyl radicals and degrading pCBA. However, all the runs had similar pCBA degradation, with first-order reaction rate constants of 2x10^{-3}. The identical reaction rate constants demonstrate the lack of significant difference between the three UV conditions.

![Graph showing degradation of pCBA with varying UV conditions](image)

**Figure 17. Degradation of pCBA by the UV/O3 AOP with varying UV conditions.**

The initial experimental condition: 5 uM pCBA, 800 uM TBA and 5 mM phosphate buffer (pH=7). The displayed data are averages of two experimental runs for each and the error bars represent the standard deviations.
While we saw some difference in the amount of UV fluence based on the ATZ tests, there was negligible difference in pCBA degradation with the reduced UV fluence. The differences in UV indicated by the altered degradations of ATZ were minor and it could be that the only minor alterations in UV combined with the inconsistent concentrations of ozone account for the lack of distinction between the different pCBA runs. The irregular ozone concentration is also most likely the cause for the large standard deviations.

**Phase 3: Evaluation of the UV/O3 AOP for removing example emerging contaminant, DCF**

As mentioned in the literature review, the non-steroidal anti-inflammatory drug DCF is one of the most detected recalcitrant pharmaceuticals found in source waters [11]. DCF has demonstrated reactivity with both UV and ozone so it was hypothesized that it would be fully degradable with the UV/O3 AOP [11], [12], [4]. Tests with 10 mg/L concentrations of DCF were run with UV, ozone and UV/O3 AOP treatments (Figure 18).
Figure 18. Degradation of DCF overtime by UV, ozone and the UV/O3 AOP. Each line shows the average of two test runs and the standard deviations are given as error bars. The initial experimental conditions were: 10 mg/L DCF, 800 uM TBA and 5 mM phosphate buffer (pH=7).

It was found that the UV/O3 AOP was most effective at degrading DCF with an average removal of 92.9%. The ozone tests had an average DCF removal of 38.0% and the UV tests had an average removal of 84.2%. The first order reaction rate constants for the degradation of DCF with UV and the AOP were found to be $1.76 \times 10^{-3}$ s$^{-1}$ and $2.30 \times 10^{-3}$ s$^{-1}$ respectively. While these rate constants are very close, we can see the AOP was the best method.

Similar to Phase Two tests, DCF degradation tests were performed with the three UV conditions of unsleeved, SS, and DS to examine the effects of varied UV fluence on DCF degradation. The unsleeved condition demonstrated the fastest initial degradation but as time went on all three conditions were relatively equal (Figure 19).
Figure 19. DCF degradation over time with altered UV fluence for the UV/O3 AOP. Each line represents the date averages of two test runs and has error bars that represent the standard deviations. The initial experimental conditions were: 10 mg/L DCF, 800 uM TBA and 5 mM phosphate buffer (pH=7).

Similar to the pCBA degradation with UV alterations (Figure 17) there was little difference observed in the effect to DCF degradation (Figure 19). All the UV conditions resulted in first order reaction rate constants of 2x10^{-3} s^{-1} (Table 3). This again is most likely because the alterations to UV fluence were not extreme and the ozone dosing was inconsistent.

Table 3. Pseudo first order reaction rate constants of DCF degradation with varied UV exposure.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Reaction Rate Constant (x10^{-3})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unsleeved</td>
<td>2.30</td>
</tr>
<tr>
<td>Single Sleeve (SS)</td>
<td>1.92</td>
</tr>
<tr>
<td>Double Sleeve (DS)</td>
<td>1.88</td>
</tr>
</tbody>
</table>
Chapter 5
CONCLUSIONS & FUTURE WORK
The three phases of this study addressed the three research questions. The first phase compared two different AOPs for their production of highly reactive hydroxyl radicals, as indicated by degradation of the probe compound pCBA. These two AOPs were combining ozone and UV (UV/O3) compared to generating singlet oxygen and in turn hydroxyl radicals. The second phase investigated how altering UV fluence would impact hydroxyl radical production for the UV/O3 AOP. Finally, the third phase studied the degradation of DCF, a representative CEC, DCF by the UV/O3 AOP with varied UV conditions.

1. How does hydroxy radical production of a UV/O3 AOP compare to that of an AOP using singlet oxygen?

This study found that the singlet oxygen AOP did not yield hydroxyl radicals. These findings did not agree with a previous study that demonstrated complete degradation of 3 μM pCBA by the singlet oxygen AOP in 20 minutes. This discrepancy gives cause for continued study to determine the mechanisms of the singlet oxygen AOP and what experimental circumstances may have been causing these varying results.

2. How is hydroxyl radical production affected by alterations to UV fluence for the UV/O3 AOP?

Tests with ATZ demonstrated the impact on fluence the two sleeves had, however the difference in degradation between the unsleeved, SS, and DS were not very large with respective degradation rate constants equal to 7.88, 6.29, and 4.83 s^{-1}. Additional tests with the different sleeve conditions and pCBA were run to see how they would affect
hydroxyl radical production. These tests with pCBA did not demonstrate the differences in fluence significantly impacting hydroxyl radical production through pCBA degradation. It is important to note that the tests with pCBA also included ozone, and the ozone generator did not maintain a consistent ozone concentration. The irregular ozone concentration and the fact that the fluence difference between sleeves was only minor, may be why similar results were seen between the different sleeve conditions. However, further investigation is necessary to determine whether these experimental conditions were the main factors or if it was due to the nature of the chemicals tested and their individual reactivities with UV.

3. How effective is the UV/O3 AOP at degrading a recalcitrant emerging contaminant, and is that efficacy affected by alterations in UV fluence?

The example emerging contaminant DCF was used to test the UV/O3 AOP for degrading a recalcitrant compound. The AOP showed the greatest removal of DCF with an average removal of 93% over 20 minutes. The UV and ozone only controls had removals of 84% and 38%, respectively. These tests demonstrate the improved removal of DCF with the combination of O3 and UV to produce hydroxyl radicals. These results also show how effective UV is on its own at removing DCF since the first order reaction rate constants of the UV and AOP tests were actually the same with both being 2x10^{-3}. More tests with the SS and DS were done with DCF to see if there would be a significant impact to degradation with alterations to the UV fluence. The unsleeved condition was found to have the best degradation initially but as time went on all three sleeve conditions seemed to be about the same and all had the same reaction rate constant of 2x10^{-3}.  

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5.1 Future Work
This study furthered the field of AOP research, but much remains to be done to fully understand and optimize these processes for full-scale implementation.

5.1.1 Altering UV fluence
The UV fluence experiments in this study were demonstrated with ATZ degradation. In future studies, these tests should be expanded and used to calculate specific fluence values. This would help compare these bench-scale experiments to full scale UV systems at water treatment facilities. It would also make it clearer how much the SS and DS impacted the fluence. It would also be better in future studies to have thicker sleeves that would have more obvious impacts on fluence. I would recommend using the DS and a four-layer sleeve.

5.1.2 Additional Emerging Contaminant
As mentioned earlier in this study, contaminants of emerging concern (CECs) are becoming increasingly prevalent in wastewater effluents, environmental waters, and source waters for drinking water treatment [5]. Additional studies testing various mixes of emerging contaminants would be interesting because this is often the case in natural waters. This would give insight into how the presence of other competing compounds affect the reaction kinetics.

5.1.3 Determining Byproducts
The experimental solution used for the DCF tests (10 mg/L DCF, 800 uM TBA and 5 mM phosphate buffer (pH=7)) developed an orange color after treatment (Figure 20).
Figure 20. **DCF effluent after UV treatment.** The 10 mg/L DCF, 800 uM TBA, and 5 mM phosphate buffer (pH=7) solution was treated with UV light for 20 minutes.

This unexpected change in the solution’s color after ozone, UV, and AOP treatment may have been due to the formation of unidentified byproducts. Other studies have found significant reduction of toxicity of DCF solutions that were irradiated with UV. They also found reduced potential for bioaccumulation as indicated by the calculated Log Kow values [42]. Therefore, it is possible that while these byproducts appear concerning in color they are actually less harmful than the parent substance. Additional testing of these byproducts is still necessary to ensure they are less toxic and whether they can be fully removed with additional treatment.
REFERENCES/WORKS CITED/BIBLIOGRAPHY


Appendix

Appendix A: HPLC Calibration Curves

Figure 21. pCBA calibration curve. Duplicates of four pCBA concentrations (0.5, 1, 2, 5 uM) were averaged and graphed against the measured HPLC areas to generate the calibration curve.
Figure 22. ATZ calibration curve. Triplicates of four ATZ concentrations (0.5, 1, 2, 5 mg/L) were averaged and graphed against the measured HPLC areas to generate the calibration curve.

Figure 23. DCF calibration curve. Triplicates of three DCF concentrations (1, 10, 100 mg/L) were averaged and graphed against the measured HPLC areas to generate the calibration curve.
Appendix B: Degradation curves fit with exponential trendlines to find reaction rate constants

Figure 24. Degradation curves for pCBA with different treatment fit with exponential trendlines. Each curve represents the average of two test runs and the standard deviations are given as error bars. The initial experimental conditions were: 10 mg/L DCF, 800uM TBA and 5mM phosphate buffer (pH=7).
Figure 25. Degradation curves for ATZ with different treatment fit with exponential trendlines. Each curve represents the average of two experimental runs with the error bars representing the standard deviations. The initial experimental conditions: 7 uM ATZ, 800 uM TBA and 5 mM phosphate buffer (pH=7).

Figure 26. Degradation curves of ATZ at varying UV fluence fit with exponential trendlines. The experimental solution (7 uM ATZ, 800 uM TBA and 5 mM phosphate buffer (pH=7)) was bubbled with air for mixing while exposed to UV. Each line is an average of two experimental runs and the error bars represent the standard deviations.
Figure 27. Degradation curves of pCBA with varying fluence fit with exponential trendlines. The initial experimental condition: 5 uM pCBA, 800 uM TBA and 5 mM phosphate buffer (pH=7). The displayed data are averages of two experimental runs for each and the error bars represent the standard deviations.

Figure 28. Degradation curves of DCF with different treatment fit with exponential trendlines. Each line shows the average of two test runs and the standard deviations are given as error bars. The initial experimental conditions were: 10 mg/L DCF, 800uM TBA and 5 mM phosphate buffer (pH=7).
Figure 29. Degradation curves of DCF with varying UV fluence fit with exponential trendlines. Each line represents the date averages of two test runs and has error bars that represent the standard deviations. The initial experimental conditions were: 10 mg/L DCF, 800 uM TBA and 5mM phosphate buffer (pH=7).