PHOTOCHEMICAL DEGRADATION OF TOTAL ORGANIC CARBON IN WASTEWATER TREATMENT

Group # 4:
Michael Sanfilippo
Gabrielle Schantz
Camille Sturdivant
Christopher You

The chemical and cost efficiency of the ozone with ultraviolet radiation (O$_3$/UV) photochemical degradation of total organic carbon (TOC) was examined. The efficiencies were compared to other commonly used wastewater purification processes, hydrogen peroxide with UV (H$_2$O$_2$/UV) and titanium dioxide with UV (TiO$_2$/UV). The O$_3$/UV process appears to be the least cost-efficient process due to high chemical costs and high-energy costs; however, it is the most efficient at removing TOC from wastewater. The associated costs for O$_3$/UV are 96.00 U.S. dollars/m$^3$ in chemical costs, a 2400 kWh/m$^3$ in energy demand leading to 374.40 US dollars/m$^3$ in energy costs, and a total cost of 470.40 U.S. dollars/m$^3$ [1]. The process is able to degrade 61% of TOC in the wastewater within 4 hours, an estimate of a larger scale degradation process [1]. The H$_2$O$_2$/UV and TiO$_2$/UV processes appear to be more cost-effective than the O$_3$/UV process; however, they are not as efficient at degrading the TOC in the wastewater.

INTRODUCTION: WATER PURIFICATION & PHOTOCHEMICAL DEGRADATION PROCESSES

A time existed when companies, such as Aquafina, Dasani, and Fiji, did not exist. Famous today for their bottled water production, these companies have all thrived in sales, along with their importance to the world. However, bottled water has not always been there to quench the thirst of a baseball player after he had just hit a home run. It has not always been there when one wakes up in the middle of the night and needs a quality serving of clean water before he or she can fall back asleep.

A time also existed when it was not necessarily easy to have any clean drinking water at all. Lakes, rivers, and ponds now contain numerous amounts of bacteria and disease that may be very toxic to the human body. Diseases, such as cholera and typhoid fever, have made their rounds in causing illness, and sometimes death, to adults and children of all ages. These deadly diseases were the main reasons that lead to the creation of numerous water filtration systems.

Many years of experimentation and studies have led to the harmless, pure drinking water that America and other parts of the world have today. Many chemical treatment processes have been practiced to obtain such a purified liquid. However, engineers are always brainstorming and trying to come up with better, more efficient processes. One of the main processes being studied today is the photochemical degradation process. There are many different methods to create such a process, including different atoms and molecules along with different starting catalysts to initialize a photochemical reaction. Some of the more common processes include: hydrogen peroxide/ultraviolet radiation (H$_2$O$_2$/UV), titanium dioxide/UV (TiO$_2$/UV), and ozone/UV (O$_3$/UV).

Radiation with Hydrogen Peroxide

The hydrogen peroxide/ultraviolet degradation process of pollutants is typically used as the last step of the water treatment, usually occurring after filtration. In the treatment of drinking water, the process is normally run within a closed vessel UV reactor because of the smaller carbon footprint,
reduction of airborne pollution, and reduced exposure to UV radiation [2]. The general reaction for the decomposition of hydrogen peroxide is

\[
\text{H}_2\text{O}_2 + \text{HO}^- \rightarrow \text{H}_2\text{O} + \text{O}_2 + \text{HO}'
\]

in which water, oxygen, and a hydroxyl radical are formed. The oxidation potential of the hydroxyl radical (2.8 V) is higher than that of ozone and chlorine, 2.07 V and 1.39 V respectively, which allows it to be able to oxidize both inorganic and organic compounds [2]. Furthermore, the hydroxyl radical is unselective when it reacts with other compounds and will react with any organic or inorganic compounds in the aqueous system [2].

In the H$_2$O$_2$/UV process, the hydroxyl radicals can react through three different mechanisms. These mechanisms include hydrogen abstraction, electrophilic addition, and electron transfer [3]. In hydrogen abstraction, an organic radical (RH') forms and reacts with dissolved oxygen to form (RHO$_2$'). Electrophilic addition occurs when the HO’ radical inserts itself into the π-bond in an organic molecule to produce an organic radical. This type of mechanism is useful in the rapid dechlorination of chlorinated phenols to produce an alcohol and chloride ions [3]. Electron transfer reactions reduce hydroxyl radicals to hydroxide anions by an organic molecule, and are useful when halogen substitution and steric hindrance make electrophilic addition and hydrogen abstraction reactions unfavorable [3]. The radicals formed by the three mechanisms then react with the desired contaminants in water and therefore remove the pollutant from the system. These processes have been effective in destroying micro-pollutants in both group water and surface water.

The key design and operating parameters for the H$_2$O$_2$/UV process include the dose of peroxide, UV lamp type and light intensity, reactor contact time, and control systems [2]. The control systems maintain or change the pH and temperature at which the reactor is run. The reaction can run under low-pressure or medium pressure continuous UV light while there is H$_2$O$_2$ present [2]. Additionally, the Electrical Energy per Order (EEO), which determines the removal efficiency of contaminants. This measurement is used to compare how well the H$_2$O$_2$/UV process is at removing certain contaminant. For example, the EEO values for benzene and methyl tertiary butyl ether (MTBE) are 2 and 10 kWh/1,000gal/order of removal. This shows that H$_2$O$_2$/UV removal of benzene is more easily accomplished that removal of MTBE [2].

Radiation with Titanium Dioxide

One of the newer, growing fields of photochemical degradation has involved titanium dioxide (TiO$_2$) as the catalyst with ultraviolet (UV) light, which degrades organic materials in wastewater into carbon dioxide and water with little to no harmful byproducts. The degradation process involved TiO$_2$ being hit by light of a certain wavelength, turning the semiconductor into a strong oxidant, which helped degrade organic materials in water [4].

Using TiO$_2$ has been popular for the degradation of organic dyes in wastewater, for example, Safranin-T, a hazardous dye used in textile that can irritate and permanently damage the human eye, with which researchers from multiple institutions in India have experimented [4]. The process of degradation of the dye was seen as the solution in which the dye was dissolved with TiO$_2$ became colorless when hit with UV light. Specifically, when the TiO$_2$ is hit by UV light, an electron is freed into the conduction band, resulting in a positively charged “hole” in the valance band, seen in Equation 2. The positively charged “hole” reactions with the surrounding water to from hydroxyl radicals ('OH), which are “powerful, indiscriminate oxidizing agents” that reacts with organic materials, in this case the dye Safranin-T [4]:

\[
\text{TiO}_2 + \text{hv} \rightarrow \text{TiO}_2 [\text{e}^- \text{(cb)} + \text{h}^+ \text{(vb)}]
\]

\[
\text{H}_2\text{O} + \text{h}^+ \rightarrow \cdot\text{OH}
\]

In the experiment, many variables, including the molarity of the dye solution and the pH of TiO$_2$ amount inserted, affected the efficiency of the process [4]. Other experiments were conducted using platinized
titanium dioxide or aqueous titanium dioxide, aiming to improve the efficiency of the absorbed light of a specific wavelength [4].

**Radiation with Ozone**

Presently, the most commonly used photochemical degradation process is the ozone/ultraviolet radiation degradation process [3]. As a method of organic material removal, this advanced oxidative process (AOP) uses a combination of ozone and UV light to purify and treat corrupted residual waters [3]. Before this process is discussed in depth, it is crucial to understand what ozone is.

Ozone was first incorporated into the water treatment process during the early 1800s, mainly in Asia and Europe [5]. This unstable gas is made up of three oxygen atoms that will willingly reduce back to oxygen. During this ozone reduction, a free radical of oxygen is formed. This radical is highly reactive and will not last long under normal conditions [5]. Because this oxygen radical is so highly reactive, it is able to react with many things, including bacteria and other forms of contamination in water. Compared to the chlorination process used to decontaminate water, ozone is much more effective against bacterial and viral pollution [5]. The properties of ozone can also lessen iron, manganese, and sulfur concentrations, and can also oust taste and odor issues [5].

In order to make the ozone gas used to conduct the $\text{O}_3$ / UV process, energy must be added along with the oxygen atoms. This energy can originate from an electric discharge field or by UV radiation [5]. For the purpose of this paper, UV radiation will be the focus source of energy. To effectively treat a small portion of waste, UV ozonators are the most practical [5]. Compared to a larger portion of waste, UV ozonation is much more efficient, as it is done using a smaller batch of wastewater. A larger batch of wastewater has much more room for error and inefficiency in the treatment and decontamination. The $\text{O}_3$ / UV process does not need any special monitoring, and thus can be carried out in a batch or continuous process [3].

Despite its high efficiency and sustainability, the $\text{O}_3$ / UV process still encounters a few issues. Ozone has a low solubility in water, which creates constraints in mass transfer [3]. However, this minor issue can be resolved without trouble. Using stirred-tank photochemical reactors, the transfer of mass increases along with the rate of ozone solubility [3]. Other forms of photochemical reactors, such as tubular and internal loops, are also just as practical [3]. Although this process is the most readily used today, it is still very expensive due to operational, equipment, and maintenance costs [5]. Scientists and engineers are constantly looking to make the process more efficient, both operation-wise and cost-wise.

**METHOD OF EXPERIMENTATION**

It may be difficult to understand exactly why the $\text{O}_3$ / UV process is currently the most practiced, due to a lack of cost efficiency. These high costs originate from the high electrical energy demand for UV lamps and ozonizers in order for the process to even be plausible [1]. However, compared to other photochemical processes discussed, this process most efficiently removes harmful chemicals from wastewater. These findings were found in an experiment that measured the rate of total organic carbon (TOC) removal from wastewater [6].

TOC is a very crucial parameter for the measure of organic pollution in wastewater because it involves all organic compounds that could possibly be contained within wastewater [6]. Rupert Bauer and Hubert Fallmann, from the Institute of Physical Chemistry in Wien, Austria, conducted an experiment
that measured both the TOC removal rate and the pH of wastewater using different AOP processes, including the \( \text{O}_3 \)/UV process combined with iron to act as a catalyst in the reaction [1]. To obtain the desired results, the, “TOC measurements (catalytic combustion/NDIR-principle) were carried out using a Shimadzu TOC 5000 analyzer with an ASI 5000 auto sampler. The pH was measured with a pH 537 pH-meter with E56 glass electrode (WTW)” [1]. Bauer and Fallmann continue in their explanation of the equipment they used in this experiment, “UV-Vis spectra were measured with a Shimadzu UV160A spectrometer in 10 mm quartz cells. Light intensities were measured with a Kipp and Zonen CC20 radiation indicator with pyranometer CM3, spectral range from 305 to 2800 nm” [1]. The equipment and apparatuses stated above were used to measure three main variables in this experiment, which are TOC concentration/removal, pH, and UV light intensity. The measurement of UV light was practiced just to make sure that it was remaining efficient throughout the entirety of the experiment.

Bauer and Fallmann begin the experiment by heating the initial wastewater solution [1]. “For the comparison of different AOP solutions were irradiated with a 150 W high pressure mercury lamp fixed in a water cooled quartz tube for direct immersion into a 750 mL reaction vessel” [1]. \( \text{O}_2 \) or \( \text{O}_3 \) was then transferred into the reaction vessel by a process known as bubbling [1]. This bubbling by a capillary glass tube provides a good blending of the wastewater solution with either \( \text{O}_2 \) or \( \text{O}_3 \) [1]. The choice of \( \text{O}_2 \) or \( \text{O}_3 \) depends on which process was being studied at the time. For the purpose of this experiment, the pH of the wastewater in each trial was fixed to a value between 2.8 and 3.0, using a sulfuric acid solution [1]. Various reactions occurred between the wastewater solution and the molecules and atoms contained within each respective AOP. The overall flow of wastewater and the reagent can be seen in Appendix A-1. The data obtained turns out to support the statement above that the \( \text{O}_3 \)/UV process does a very efficient job of removing harmful substances from wastewater solutions.

RESULTS

Mineralization of 4-CP Solution Through Advanced Oxidative Processes

In Bauer and Fallmann’s initial experiment, the AOP was tested on wastewater with “TOC of a \( 10^{-3} \) mol/L 4-CP solution,” which contains 72 ppm of TOC in the wastewater, in the environment mentioned in the methods described above. When the \( \text{O}_3 \)/UV radiation AOP was used, which also included ferrous ions in the reactor vessels, the time it took for 72 ppm of TOC to degrade in the wastewater was about 22 minutes [1]. With these results, the efficiency of the AOP was calculated for the use of \( \text{O}_3 \)/UV degradation process of a “landfill leachate,” which contains 545 ppm of TOC per m³ of wastewater prepared [1]. The amount of TOC that is degraded through the degradation process is 332 ppm, which is 61% of the total amount of TOC that was initially present in the wastewater; In addition, for that amount of TOC to be eliminated from the solution, 4 hours were needed [1]. This specific AOP using ozone was compared to other oxidative photochemical degradation processes, each resulted in a different amount of time to eliminate a certain amount of pollutant from the wastewater.

Relative Cost Estimates: Using Only \( \text{O}_3 \) Versus Using \( \text{O}_3 \) with Ultraviolet Radiation

Ozonation is not considered to be one of the most cost efficient processes for several reasons [1]. First, the energy consumption of the laboratory equipment per unit of wastewater used in a large-scale plant is fairly high and not efficient [1]. The ozonizer uses electrical power, as opposed to solar, and also with low efficiency [1]. In addition, a sizable amount of ozone escaped the reaction vessel unconsumed because the residence time was too short [1]. Furthermore, it is estimated that the mineralization of 60% of TOC would take 6 hours using only \( \text{O}_3 \) and 4 hours for \( \text{O}_3 \)/UV [1]. Also, it has been discovered that UV radiation has the ability to improve the \( \text{O}_3 \) process, however, the higher energy demand nearly eclipses the faster degradation rate [1].

In terms of numbers, ozone alone used 144 U.S. dollars/m³ in chemical costs, 2400 kWh/m³ in energy demand, and 374.4 U.S. dollars/m³ in energy costs, leading to a total cost of 518.4 U.S. dollars/m³
to degrade 59% of TOC in 6 hours [1]. When combined with UV light, ozone uses 96.0 U.S. dollars/m$^3$ in chemical costs, 2400 kWh/m$^3$ in energy demand, and 374.4 US dollars/m$^3$ in energy costs, leading to a total cost of 470.4 U.S. dollars/m$^3$ to degrade 61% of TOC in 4 hours [1]. It should be noted that these cost estimates were calculated in 1997 and that they should be adjusted for inflation.

**DISCUSSION OF PHOTOCHEMICAL DEGRADATION PROCESSES**

**Advantages and Disadvantages of Using Ozone**

The O$_3$/UV radiation process is one of the most common methods of photochemical degradation because the process of ozonation is well-known and the overall degradation process has been experimented with for a longer time, supplying more data for further research and applications [3]. Although the cost of using ozone and UV radiation is high, the process is favored because of the chemical efficiency, eliminating the majority of wastewater pollutant using less ozone and in a short amount of time [1]. The chemical efficiency originated from the radicals that form from ozone during radiation: the radical oxygen formed is very reactive and will instantly react with water to form hydroxide radicals and/or hydrogen peroxide, which are the main reacting agents for the degradation process [5]. Not accounting for the equipment cost of the O$_3$/UV radiation process, using ozone has the advantage of eliminating the highest amount of pollutants in a reasonable time period, which decreases the cost of the overall procedure.

The major disadvantages of the O$_3$/UV process are the high-energy demand and the high chemical costs. The high energy demand of 2400 kWh/m$^3$ of wastewater, which would lead to a high-energy cost and therefore a high overall cost as well [1]. Additionally, the costs of the ozone is relatively high in comparison to other processes as it cost $96.0/m$^3$ of ozone as of 1997, which adjusted for inflation would cost $142.02/m$^3$ of ozone today [1]. The high costs of the ozone would also increase the total costs of the overall process. Other than the high costs associated with energy demands and the ozone itself, there do not appear to be many disadvantages to the O$_3$/UV process. It seems that at a lab-scale setting, using ozone as the reagent would be preferred over all other methods because of the chemical efficiency, but to expand these process into large industrial-scale setting, methods that require least amount of spending on energy and supply would be preferred. However, further research in the O$_3$/UV radiation method should result in improved methods so that the process can be efficient not just chemically but also economically.

**O$_3$/UV Compared with H$_2$O$_2$ and TiO$_2$ Processes**

H$_2$O$_2$ is a safe and efficient chemical that has been used in wastewater treatment, originally to reduce odor [7]. Hydrogen peroxide can be shipped in bulk and stored at a concentration of 35% while remaining extremely stable and having a rate loss between 1-2% depending on the size of the storage container [8]. This allows it to be readily available and economically favorable for use within water treatment process, which require large amounts of reagent. Furthermore, the cost of hydrogen peroxide and UV light processes tend to be less than those incurred with ozonation processes [7]. However, the H$_2$O$_2$/UV process is slightly less efficient at degrading some compounds, such as chlorophenols, when compared to ozonation processes. It should also be noted that the process requires high concentration of H$_2$O$_2$ and/or a significantly longer UV-exposure time in comparison to the O$_3$ concentrations and UV exposure time in the O$_3$/UV process [8]. Overall using hydrogen peroxide as an alternative to ozone is reasonable: in addition to the chemical itself being inexpensive, it is also a liquid that will mix well with any wastewater solutions. Hydrogen peroxide does not need to be bubbled through nor need advanced technology to suspend it in the solution.

Similarly, using titanium dioxide with ultraviolet radiation is favored economically because, as the chemical is a solid, it can be recycled if used in its powder form, in addition to the availability of UV lamps used in these processes. However, when experimenting with aqueous TiO$_2$,
which is much more efficient, the process becomes much more expensive as the particles need to be separated out of the treated liquid through centrifuges or microfiltration techniques [1]. Because of this obstacle, there have not been many experiments using TiO$_2$ as the substrate and is less common in industry. However, with more advancements in removing TiO$_2$ particles from solution, this process would become the most efficient method of removing certain pollutants from wastewater. Ultimately, the main difference between the O$_3$ process and the TiO$_2$ process is that one deals with a gas, which does not dissolve easily in liquids, and the other a solid. However, the mechanism in the process of photochemical degradation is similar in that the radical hydroxide group is produced and used as the main oxidizing agent. Both O$_3$ and TiO$_2$ process produce a positive region through UV radiation, which reacts with the surround water to form hydroxide radicals [1]. Both processes are also impacted by the concentration of the substrate, the pH, and the wavelength of UV radiation used when experimented on [4] [1].

**CONCLUSION**

Many processes to clean and purify water exist, from the distillation of tap water to the desalination of seawater to the degradation of chemicals from wastewater. Photochemical degradation is one of the more recent processes to clean water and research today is trying to improve the efficiency of degradation and lower the cost of proceeding with these processes in large, industrial scales. Three photochemical degradation processes, also called advanced oxidative processes because of the reactions that take place, that have been experimented with uses titanium dioxide, hydrogen peroxide, or ozone as the initial reagents, which are all radiated with ultraviolet light for the reaction to occur and to initialize the degradation process.

The O$_3$/UV process was described in detail, with the methods extracted from the experiment of Rupert Bauer and Hubert Fallmann of the Institute of Physical Chemistry in the Technical University of Vienna, in which a solution containing total organic carbon (TOC) went through the process of photochemical degradation through multiple methods, with the method containing ozone emphasized in the description [5]. It was seen that using ozone as the reagent in the degradation process is chemically efficient, eliminating the small, test amount of TOC in a very short amount of time, compared to other chemical methods. These results were then scaled-up to industrial data, and estimated that 61% of TOC in a landfill would be eliminated in 4 hours using the O$_3$/UV degradation process. However, the energy and supply costs of ozone were shadowed by the chemical efficiency of ozone [5]. This advanced oxidative process, in addition to using hydrogen peroxide and titanium dioxide, are still being studied so that one day polluted rivers caused by industrial wastewater could be easily and safely cleaned.
REFERENCES


APPENDIX A-1
FLOW DIAGRAM OF O\textsubscript{2}/UV PROCESS

(These values are estimates using the results of the lab experiments conducted by Bauer and Fallmann.)

*batch process; single cycle; per m\textsuperscript{3} wastewater