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Sara Ann Fast

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Holistic analysis of emerging contaminant removal using advanced oxidation processes

By

Sara Ann Fast

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Holistic analysis of emerging contaminant removal using advanced oxidation processes

By

Sara Ann Fast

Approved:

Veera Gnaneswar Gude
(Major Professor)

Dennis D. Truax
(Co-Major Professor)

Benjamin S. Magbanua Jr.
(Committee Member)

James L. Martin
(Committee Member, Graduate Coordinator)

Jason M. Keith
Interim Dean
Bagley College of Engineering

Name: Sara Ann Fast

Date of Degree: May 8, 2015

Institution: Mississippi State University

Major Field: Civil Engineering

Major Professor: Veera Gnaneswar Gude

Title of Study: Holistic analysis of emerging contaminant removal using advanced oxidation processes

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Candidate for Degree of Master of Science

The presence of pollutants known as emerging contaminants in water and wastewater is a topic of growing interest. Emerging contaminants, which include endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs), are compounds that remain relatively unknown, although their adverse effects have been proven. Emerging contaminants are not satisfactorily removed by traditional treatment methods; therefore, there is a need for innovative techniques. Advanced oxidation processes (AOPs) have been recognized as successful removal methods for these problematic pollutants. However, technical success is not the only factor that must be considered. Process engineering, environmental, and economic and social parameters were considered. A holistic analysis was completed using a ranking system to determine the performance of several AOPs (ozonation, UV, photocatalysis, the Fenton reaction, and integrated processes). Ultimately, H_2O_2/O_3 presented the highest average ranking (3.45), with the other processes showing similar performance, with the exception of TiO_2 photocatalysis (2.11).

DEDICATION

This work is dedicated to the most important people in my life: my family. I would not be where I am today without each and every one of them. They have encouraged and guided me through every step of my life. I am unconditionally grateful for the love and support of my parents; Joe and Shelly Fast; my sisters; Kayla, Emily, and Shelby; and my grandparents; Myron and Helen Fast, Nichole Dirksen, John and Shirley Dirksen, and Randy Peterson. My thanks also go out to my soon-to-be-family-members Payne Stuart and John Besh. I would be amiss if I did not thank my dog Winnie as well, who is always willing to help me with my school work, even if it just means sitting in my lap.

Next I dedicate this thesis to my friends. I am extremely thankful for the time I had together with my college roommates: Maria Duenas, Daniela Bonilla, Robyn Chunn, and Rebecca Roland. I cannot imagine my time in graduate school without the friendship of my many classmates and colleagues notably, Edith Martinez-Guerra and Hugo Guerra.

"And He said to me, 'My grace is sufficient for you, for my strength is made perfect in weakness.' Therefore most gladly I will rather boast in my infirmities that the power of Christ may rest upon me. Therefore I take pleasure in infirmities, in reproaches, in needs, in persecutions, in distresses, for Christ's sake. For when I am weak, then I am strong." (2 Corinthians 9-10)

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INTRODUCTION

1.1 Purpose of Research

The wellbeing of humans and wildlife is a crucial factor that must be considered in the midst of all design and innovation. The American Society of Civil Engineers (ASCE) Code of Ethics states, “Engineers shall hold paramount the safety, health, and welfare of the public and shall strive to comply with the principles of sustainable development in the performance of their professional duties” (ASCE, 2015). This implies that while the development and improvement of technologies and processes are essential, it is also vital that the effect on humans and the environment be monitored. Novel designs are not only necessary for the improvement of current environmental conditions, but also for the improvement of existing designs. A design that solves one problem while creating another is not an appropriate solution. A technology is not truly effective based only on technical standards; many other aspects must be considered as well.

Water and wastewater treatment processes are designed to remove unwanted and potentially harmful materials from the influent, or incoming water, to produce an effluent, or discharged water, that meets all necessary standards. The goal of these treatments is to prevent the introduction of undesirable products into sources such as rivers, streams, and drinking water. The overall welfare of the public can be improved if these processes are successful. Further advancements can be made as removal efficiencies and process quality are improved.

However, not all situations can be simplified in this manner. While one process may be effective for removing one type of contaminant, it may not be capable of removing others. Pollutants known as emerging contaminants are subject to this dilemma. Emerging contaminants are compounds that are often difficult to remove. Furthermore, standards are not always in place to regulate the amounts that are legally permitted to enter a waterbody for many of these pollutants. Most importantly, emerging contaminants are known to have adverse effects on both humans and wildlife.

1.2 Research Objectives and Scope

It is essential that effective means of removing emerging contaminants from both water and wastewater be identified. Moreover, the best technology must be recognized. This entails that a process is selected that is not only effective technically, meaning that it successfully removes contaminants, but that meets multiple other requirements as well. An ideal process will not produce adverse effects, while also performing well in other areas. Factors such as impact on human health, economic feasibility, energy consumption, and contribution to climate change must be taken into account.

The purpose of this research is to complete a holistic analysis of advanced oxidation technologies. This class of treatment methods has been shown to successfully remove emerging contaminants when other methods were not capable of producing the desired results. This review will incorporate the many facets that have been mentioned previously. In order to compare each parameter, the success that each process portrays must first be quantified. A ranking system was created and applied to represent the amount that each process reflects positive performance in each field of interest. This allows for an equal comparison to take place across all parameters for all treatment processes. It is assumed that each process is capable of producing high percent removals of emerging contaminants, so it is their performance in other categories that sets them apart. Ultimately, the processes with the highest overall ranking represent the processes that are successful not only technically, but also in a variety of essential fields.

CHAPTER II

BACKGROUND

2.1 Emerging Contaminants

2.1.1 Introduction to emerging contaminants

Throughout the history and development of the water and wastewater treatment industries, numerous pollutants and toxics have been scrutinized and investigated. The removal and degradation processes and technologies have been fine-tuned and optimized in order to achieve the highest percentage of contaminant removal at the lowest chemical and energy consumption values possible. Furthermore, standards have been developed to manage the amounts of certain compounds that are legally permitted to enter a waterbody (U.S. EPA, 2015). This is accomplished through the National Pollutant Discharge Elimination System (NPDES). However, not all contaminants are easily removed by traditional methods, and many remain relatively unknown.

Chemicals such as these are classified as “emerging contaminants” because many are not currently regulated and have the potential to cause serious health concerns (Esplugas, et al., 2007). Many of these contaminants are actually derivatives of manufactured products, making their removal particularly complicated (Guo, et al., 2009). Emerging contaminants have the potential to cause major effects on aquatic environments, surface water, drinking water, and soil (Miranda-García, et al., 2010). The removal of emerging contaminants from water and wastewater is of growing interest due to the unfamiliar nature of the compounds. In addition, the threat posed to the health of both humans and wildlife is a troubling matter. Some of the most well-known compounds among these emerging contaminants are endocrine disrupting chemicals (EDCs) and pharmaceutical and personal care products (PPCPs) (Esplugas, et al., 2007).

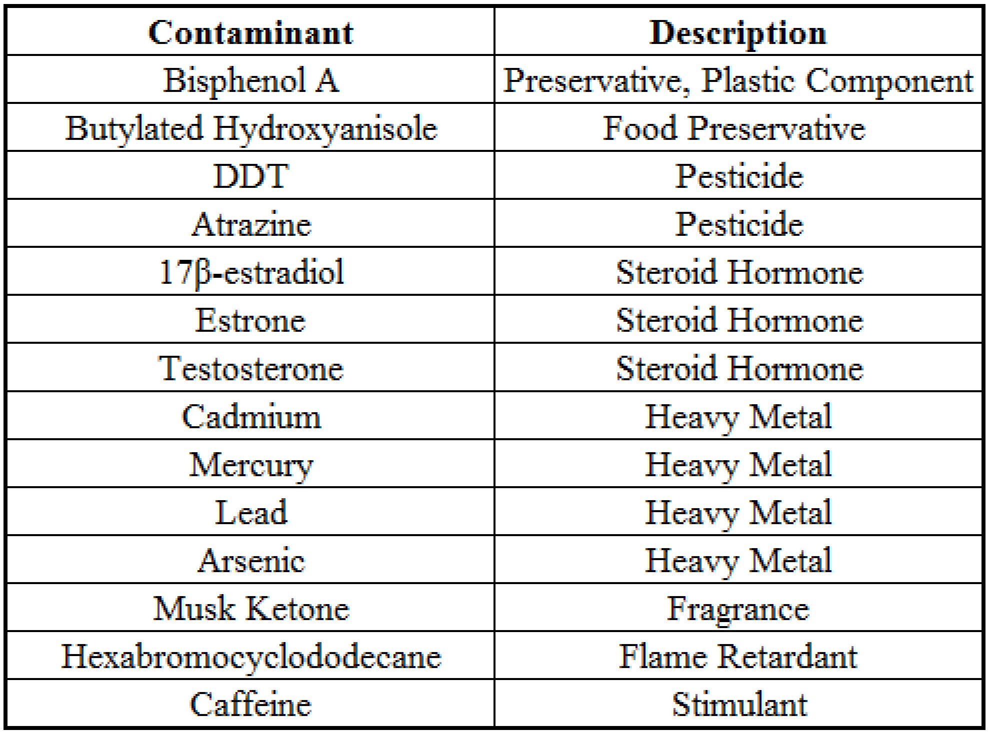
2.1.2 Endocrine disrupting chemicals

Endocrine disrupting chemicals, or EDCs, have been found to disrupt the endocrine systems of both humans and animals (Esplugas, et al., 2007). The endocrine system assists in the regulation of reproduction, growth, metabolism, and a variety of other functions. Therefore, interruptions to the endocrine system can have serious and dangerous consequences. For example, EDCs have been related to the feminization of male fish, complications to the reproductive system, and difficulties in egg shell breakage (Esplugas, et al., 2007). In humans, increases in certain types of cancers have occurred, as well as the presence of breasts in males and reductions in sperm (Esplugas, et al., 2007). EDCs have also been known to bio-accumulate in body fat, which means that concentrations can build considerably (Rahman, et. al., 2009). This is a particular concern for industries, such as fisheries, because humans or animals consuming fish with large concentrations of EDCs accumulated in their tissue will thus be exposed to a large dosage.

Known sources of EDCs include urban and agricultural runoff, landfill leachates, and concentrated animal feeding operations (Benotti et al., 2008). Furthermore, aquatic environments may be put at risk in the event that treated wastewater effluent is discharged, and EDCs are not adequately removed by traditional treatment methods. Consequently, this is also true of pollutants that may enter drinking water sources. Table

2.1 seen below lists a compilation of known EDCs, including a variety of pesticides, hormones, and heavy metals (Westerhoff, et al., 2005; Esplugas, et al., 2007; Belgiorno, et al., 2007).

Table 2.1 Examples of EDCs



Contaminant	Description
Bisphenol A	Preservative, Plastic Component
Butylated Hydroxyanisole	Food Preservative
DDT	Pesticide
Atrazine	Pesticide
17β-estradiol	Steroid Hormone
Estrone	Steroid Hormone
Testosterone	Steroid Hormone
Cadmium	Heavy Metal
Mercury	Heavy Metal
Lead	Heavy Metal
Arsenic	Heavy Metal
Musk Ketone	Fragrance
Hexabromocyclododecane	Flame Retardant
Caffeine	Stimulant

Many of these EDCs may not be familiar to most individuals, but some have become widely recognized. This is largely due to media coverage publicizing the potential negative side effects of various compounds. Among the most well-known EDCs are Bisphenol A (BPA), DDT, and estrogen (Rahman, et. al., 2009; U.S. EPA, 2015,). Bisphenol A has gained recognition due to its exploitation as a harmful preservative and component of many plastic products. This compound can leach or drain into drinking water from plastic supply pipes (Rahman, et. al., 2009). Furthermore, exposure to BPA can also occur through leaching from plastic food containers or baby bottles. This is a major concern, particularly considering that infants are put at risk; therefore, numerous plastic products now choose to advertise whether they are BPA-free. In addition, the use of BPA in products pertaining to infants (baby bottles, sippy cups, infant formula packaging, etc.) has been banned (U.S. FDA, 2015). The amount of BPA currently occurring in food containers is not considered harmful, but levels are continuing to be monitored. BPA is considered to be toxic to a variety of aquatic species if it reaches concentrations of 1-10 mg/L (Alexander, et al., 1988).

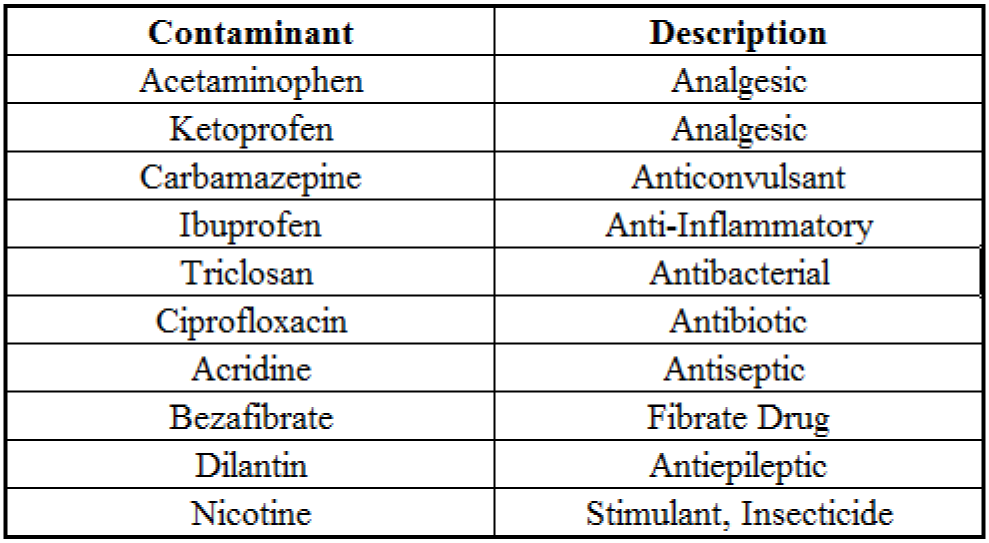
DDT (dichlorodiphenyltrichloroethane) is an organochloride that was once widely used as an insecticide and has become one of the most well-known and controversial EDCs in history. This compound was extremely successful in preventing vector-borne diseases, such as malaria. Ultimately, DDT was used extensively in agriculture. Notably, Paul Hermann Müller received a Nobel Prize for his synthesis of DDT. However, the compound did not prove to be as advantageous as it appeared. The adverse effects of DDT were publicized upon the release of Rachel Carson's book *Silent Spring* in 1962 (U.S. EPA, 2015). It was reported that cases of cancer caused by DDT were identified in both humans and wildlife. As mentioned previously, EDCs have the potential to cause thinning of egg shells in many birds; this was believed to be true of DDT. Many correlate the near extinction of the bald eagle and the peregrine falcon with the widespread use of DDT. The DDT controversy is also deemed as one of the driving factors of the environmental movement. As a result, the general use of DDT as a pesticide was banned in 1972 (U.S. EPA, 2015).

Estrogen, whether it occurs as a natural hormone or a synthetic chemical, is present in aquatic environments and drinking water sources. While estrogen is a known EDC, it can also occur in forms that can be considered as PPCPs, which are discussed in fuller detail in Section 2.1.3. Estrogen is a naturally occurring hormone that can be excreted from humans and animals. In addition, many forms of synthetic estrogen, such as contraceptive products, are widely used. Estrone and 17β-estradiol, as seen in Table 2.1, are common examples. Despite popular belief, the largest sources of estrogenic compounds are not contraceptives (Wise, et al., 2010). Much larger amounts are introduced through agriculture, industry, and livestock. Estrogen is a component in some industrial chemicals and fertilizers. Furthermore, livestock, such as cows, are fed a variety of hormones to increase the production of milk. Nonetheless, estrogen and related compounds are held under scrutiny due to endocrine disrupting consequences, such as early puberty and reproductive defects. There have also been indications that the immune system can be affected by hormones, as well as other EDCs (Rahman, et al., 2009).

2.1.3 Pharmaceutical and personal care products

Pharmaceutical and personal care products, or PPCPs, include pharmaceutical drugs, cosmetics, fragrances, and food supplements, as can be seen in Table 2.2 (Westerhoff, et al., 2005; Esplugas, et al., 2007; Belgiorno, et al., 2007).

Table 2.2 Examples of PPCPs



Contaminant	Description
Acetaminophen	Analgesic
Ketoprofen	Analgesic
Carbamazepine	Anticonvulsant
Ibuprofen	Anti-Inflammatory
Triclosan	Antibacterial
Ciprofloxacin	Antibiotic
Acridine	Antiseptic
Bezafibrate	Fibrate Drug
Dilantin	Antiepileptic
Nicotine	Stimulant, Insecticide

They are commonly sourced by sewage effluents and hospital and animal wastes (Esplugas, et al., 2007). In addition, it is not certain what the chronic effects of these contaminants may be (Benotti, et al., 2008).

These products are in widespread use, making this an imperative subject. PPCPs include products that are used by most populations on a daily basis and can later be inadvertently introduced into water sources. For example, an individual may use a lotion or cosmetic product every morning, only to wash it off later that same day. Ingredients or components of that lotion or cosmetic product can easily be distributed when the individual showers or washes his or her hands. Products such as these are not treated with vigilance, as they do not appear to be immediately threatening. Prescription medications, on the other hand, are often regarded very carefully. It is well known that medications can have undesirable side effects, causing many individuals to purposely avoid their use. However, these products are designed to be effective in small dosages;

therefore, even the small amounts that remain following water or wastewater treatment still warrant attention.

The effect on bacteria occurring naturally in water is another concern. The presence of increased amounts of antibiotics in water sources may increase the resistance of bacteria, which will reduce the effectiveness of existing medications. For example, the antiviral drug Oseltamivir, more commonly known as Tamiflu, has been reported to be extremely difficult to remove from wastewater. Traditional wastewater treatment processes were not successful in degrading Tamiflu, and even ultraviolet radiation had very limited success (Fick, et al., 2007). Tamiflu is used to treat various strains of the flu, including avian influenza. A resistance to diseases such as these could be very harmful and would cause widespread alarm.

2.1.4 Presence in waterbodies and drinking water

A large variety of reports can be located that provide estimates of concentrations of emerging contaminants found in an assortment of water sources. Generally, both EDCs and PPCPs can be found in concentrations in the ng/L to µg/L range (Rahman, et al., 2009). Several studies indicate that emerging contaminants can be found in treated wastewater, surface water, groundwater, and drinking water at concentrations ranging from 0.1µg/L to 20 µg/L (Miranda-Garcia, et al., 2010; Prieto-Rodriguez, et al., 2012). Another study targeted concentrations for treated wastewater effluents specifically and reported a range of concentrations of 1.0 ng/L to 1.0 µg/L (Esplugas, et al., 2007). A study regarding drinking water contamination details concentrations ranging from 2 ng/L to 150 ng/L (Yoon, et al., 2007).

Concentrations of emerging contaminants can vary for several reasons. This can depend on the type of pollutant, the water source, and the geographical location. Nicotine, which is highly toxic, can be found in wastewater, groundwater, surface water, and bottled water in concentrations in the range of ng/L to g/L (de Franco, et al., 2014). Clofibric acid was measured at a concentration of 270 ng/L in drinking water in Berlin (Heberer & Dumnbier, 2000). Carbamazepine was detected in wastewater effluents at concentrations of up to 2.3 μg/L and 6.3 μg/L in Canada and Germany respectively (Mohapatra, et al., 2014). A study completed in China presented concentrations of 4.4 ng/L to 6.6 μg/L in untreated wastewater and 2.2 ng/L to 320 ng/L in treated effluent, which is much lower than concentrations found in Europe and the United States (Sui, et al., 2010). In a study in Atlanta, 47 compounds were considered, including EDCs (Snyder, et al., 2003). Fifteen of these compounds were found in river water, while 14 were identified in drinking water.

2.2 Advanced Oxidation Processes

2.2.1 Introduction to advanced oxidation processes

As mentioned previously, emerging contaminants are not successfully removed by traditional water and wastewater treatment methods, requiring the introduction of new technologies that can complete the required task. Advanced oxidation processes (AOPs) have been proven as capable technologies regarding the degradation of emerging contaminants (Sichel, et al., 2011). In this process, organic compounds are fully oxidized into carbon dioxide (CO_2), water (H_2O), and mineral acids (Metcalf & Eddy, 2014). This is achieved through the production of oxidants known as free hydroxyl radicals (•OH).

These hydroxyl radicals react easily with organic compounds due to the unpaired electron.

The production of high amounts of hydroxyl radicals by AOPs is advantageous for the degradation of difficult organic compounds. Another distinct advantage of AOPs is the reality that pollutants are degraded, or broken down, not simply removed or altered. This indicates that there are theoretically no resulting products requiring removal following treatment. It follows that operational costs are reduced due to the lack of the secondary waste stream that would be present if other processes, such as adsorption, ion exchange, and stripping, were utilized (Metcalf & Eddy, 2014).

Oxidizing agents that are commonly used in AOPs include ozone (O_3), UV, and hydrogen peroxide (H_2O_2). These agents have portrayed some success individually when degrading emerging contaminants, but greater removal can be achieved through processes that combine multiple oxidizing agents (Metcalf & Eddy, 2014). AOPs investigated in this research include: H_2O_2/O_3, O_3/UV, and H_2O_2/UV. While these technologies are relatively well-known and developed, others are more novel. Titanium dioxide (TiO_2) photocatalysis and Fenton's reaction are also included in the analysis.

Table 2.3 provides relevant data for these processes. The source water for each process is described, as well as initial contaminant concentration in µg/L and energy consumption in kWh/m^3. The removal efficiencies of each process are not provided, as this data was not often available. It is the assumption of these studies that adequate removal was reached in order to be included in the original studies. All of the techniques discussed are considered capable technically of removing emerging contaminants; it is the remaining parameters that are of interest. Unless otherwise stated, the constituent matrix included a large variety of emerging contaminants. A more in-depth discussion of these processes follows.

Table 2.3 Advanced Oxidation Processes (Part a)

AOP	Source/Water	Initial Concentration (µg/L)		Specific Energy Consumption (kWh/m^3)		Reference
		Geosmin	MIB	Geosmin	MIB	
UV/O_3	Fish Farm (spiked)	0.0042-0.0067	0.0032-0.0087	19.00	8.00	Klausen & Gronborg
UV/H_2O_2	Fish Farm (spiked)	0.0042-0.0068	0.0032-0.0088	16.00	13.00	Klausen & Gronborg
		Oxalic Acid	Dichloroacetic Acid	Oxalic Acid	Dichloroacetic Acid	
TiO_2/O_3	Synthetic	126	129	17.0	50.0	Mehrjouei, et al.
TiO_2/UVA/O_2	Synthetic	126	129	63.0	350.0	Mehrjouei, et al.
TiO_2/UVA/O_3	Synthetic	126	129	7.0	24.0	Mehrjouei, et al.
O_3	Post MBR Wastewater	-	-	11.93		Chong, et al.
O_3/UV	Post MBR Wastewater	-	-	6.15		Chong, et al.
H_2O_2/UV	Post MBR Wastewater	-	-	0.23		Chong, et al.
Photocatalysis	Post MBR Wastewater	-	-	7.09		Chong, et al.
				80W Lamp	40W Lamp	
UV/HOCl	Tap Water	1.00		0.32	0.16	Sichel, et al.
UV/ClO_2	Tap Water	1.00		0.32	0.16	Sichel, et al.
UV/H_2O_2 (UV mp lamps)	Tap Water	1.00		0.5		Sichel, et al.
UV/H_2O_2 w/ RO	MF/RO Permeate	-	-	0.62		James, et al.
UV/H_2O_2 w/ MF	MF/RO Permeate	-	-	0.93		James, et al.

Table 2.4 Advanced Oxidation Processes (Part b)

AOP	Source/Water	Initial Concentration (μg/L)	Specific Energy Consumption (kWh/m^3)	Reference
UV/H_2O_2 w/ AC	MF/RO Permeate	- -		James, et al.
$O_{3\ (2\ mg/l)}$	WWTP Effluent	0.001-0.503	0.03	Kim & Tanaka
$O_{3\ (4\ mg/L)}$	WWTP Effluent	0.001-0.503	0.06	Kim & Tanaka
$O_{3\ (6\ mg/L)}$	WWTP Effluent	0.001-0.503	0.09	Kim & Tanaka
$O_{3\ (2\ mg/l)}$/$UV_{21.5W}$	WWTP Effluent	0.001-0.503	0.37	Kim & Tanaka
$O_{3\ (4\ mg/L)}$/$UV_{21.5W}$	WWTP Effluent	0.001-0.503	0.4	Kim & Tanaka
$O_{3\ (6\ mg/L)}$/$UV_{21.5W}$	WWTP Effluent	0.001-0.503	0.43	Kim & Tanaka
$O_{3\ (2\ mg/l)}$/UV_{65W}	WWTP Effluent	0.001-0.503	1.06	Kim & Tanaka
$O_{3\ (4\ mg/L)}$/UV_{65W}	WWTP Effluent	0.001-0.503	1.09	Kim & Tanaka
$O_{3\ (6\ mg/L)}$/UV_{65W}	WWTP Effluent	0.001-0.503	1.12	Kim & Tanaka
UV(10W)	Hospital WW	0.4	10.00	Kohler, et al.
UV(2.5W)	Hospital WW	0.4	6.00	Kohler, et al.
0.83 $gH_2O_2L^{-1}$	Hospital WW	0.4	2.00	Kohler, et al.
1.11 $gH_2O_2L^{-1}$	Hospital WW	0.4	2.00	Kohler, et al.
Conventional GAC	NF/GAC Plants	-	0.16	Bonton, et al.
Nanofiltration	NF/GAC Plants	-	0.55	Bonton, et al.

2.2.2 Ozonation

Ozone (O_3) is a strong oxidant that is also commonly used as a disinfectant due to its ability to cause cell lysis in bacteria. This compound can be created through electrolysis, photochemical reaction, or radiochemical reaction by electrical discharge (Metcalf & Eddy, 2014). It can also be produced in the atmosphere by ultraviolet light and lightening. Ozone must be produced on-site; however, because it cannot be stored, which has the potential to raise operational costs (Reynolds & Richards, 1996). Furthermore, concentrations of ozone that are greater than 23% are potentially explosive (Davis, 2010). Ozonation is the most commonly used dark oxidation method, which is supported by its ability to produce over 90% removal of emerging contaminants (Esplugas, et al., 2007).

Ozone presents physical hazards due to its classification as both a compressed gas and an oxidizer. In addition, health hazards are also present because it is a highly toxic material and may produce harmful or carcinogenic byproducts. Aldehydes, such as formaldehyde, acetaldehyde, glyoxal, methyl glyoxal, and bromate, are among the known byproducts. One positive effect is the rise in effluent dissolved oxygen (DO) concentrations, which may make it easier to reach DO standards (Metcalf & Eddy, 2014).

The following equations describe the decomposition reactions of ozone according to Metcalf and Eddy. It is this production of hydroxyl radicals that allows for degradation of emerging contaminants.

$$O_3 + H_2O \rightarrow HO_3^+ + OH^- \qquad \text{Eq. 2.1}$$

$$HO_3^+ + OH^- \rightarrow 2HO_2 \qquad \text{Eq. 2.2}$$

$$O_3 + HO_2 \rightarrow HO\bullet + 2O_2 \qquad \text{Eq. 2.3}$$

$$HO\bullet + HO_2 \rightarrow H_2O + O_2 \qquad \text{Eq. 2.4}$$

The use of an ozonation process requires the following units (Metcalf & Eddy, 2014):

- Feed gas conditioning facility
- Power supply
- Ozone generation facility
- Contact and reaction chambers
- Ozone destruction facility

2.2.3 Ultraviolet light (UV)

Ultraviolet light has had a successful history for use in disinfection for many years (Reynolds & Richards, 1996). However, its applications are extended to AOPs through the process of photolysis. Photolysis degrades contaminants through light exposure and absorption of photons (Metcalf & Eddy, 2014). The absorption of photons causes the outer electrons in compounds to become unstable, and thus they become reactive or split. UV lamps act as the light source for completion of photolysis in most units, but the sun is also a viable source. Experiments have been completed to determine the advantages and disadvantages of submerged versus overhead bulbs, resulting in the conclusion that submerged bulbs produce improved effects (Reynolds & Richards, 1996). In addition, either low-pressure or medium-pressure lamps can be used. Medium-pressure lamps require a smaller number of lamps because their intensity is greater than low-pressure lamps (Davis, 2010). Photolysis alone, however, is not always capable of degrading difficult emerging contaminants. Therefore, the use of UV light is often paired with the addition of O_3 or H_2O_2 in order to improve removal efficiencies.

The greatest shortcomings related to UV are associated with maintenance and cost. UV lamps are required to carry out photolysis, but these lamps demand periodic replacement, as well as maintenance due to fouling of the UV lamp sleeves (Metcalf & Eddy, 2014). In addition, UV lamps tend to be more energy intensive than other processes. The absorbance of UV light can also be affected by the influent water constituent matrix. Process efficiency is reduced if large amount of compounds, such as iron and nitrate, are present (NWRI, 2000).

2.2.4 Photocatalysis

Photocatalysis is an AOP that degrades contaminants by forming free hydroxyl radicals in the presence of a metal oxide semiconductor and has been reported to successfully degrade a wide variety of emerging contaminants (Haroune, et al., 2014). Titanium dioxide (TiO_2) is a common semiconductor and has been found to be among the most effective (Belgiorno, et al., 2007). The semiconductor can be utilized as either a slurry or an immobilized catalyst. Furthermore, photocatalysis has been found to not only degrade contaminants, but also the derivatives that are produced during most treatments (Haroune, et al., 2014). Removal efficiencies for emerging contaminants have been reported as greater than 98% in some studies (Esplugas, et al., 2007).

Figure 2.1 shown below outlines the mechanisms of photocatalytic degradation (Ibhadon & Fitzpatrick, 2013). A water sample is subjected to a UV light source. This can be either an artificial source, such as a lamp, or a natural source, such as the sun. The contaminants adsorb to the surface of the semi-conductor. Degradation of the contaminants occurs when free hydroxyl radicals are formed. The initial compounds are broken down from their original compositions, and water and carbon dioxide are released. The following equations describe the reactions that take place (Chong, et al., 2010). Equations 2.13-2.15 illustrate the production of degradation products.

$$\mathrm{TiO_2 + h\nu \rightarrow e^- + h^+} \qquad \text{Eq. 2.5}$$

$$\mathrm{e^-_{CB} + e^-_{TR}} \qquad \text{Eq. 2.6}$$

$$\mathrm{h^+_{VB} \rightarrow h^+_{TR}} \qquad \text{Eq. 2.7}$$

$$\mathrm{e^-_{TR} + h^+_{VB}\ (h^+_{TR}) \rightarrow e^-_{CB} + heat} \qquad \text{Eq. 2.8}$$

$$\mathrm{(O_2)_{ads} + e^- \rightarrow O_2 \bullet^-} \qquad \text{Eq. 2.9}$$

$$\mathrm{OH^- + h^+ \rightarrow OH \bullet} \qquad \text{Eq. 2.10}$$

$$\mathrm{R - H + OH \bullet \rightarrow R' + H_2O} \qquad \text{Eq. 2.11}$$

$$\mathrm{R + h^+ \rightarrow R^+ \rightarrow intermediates} \qquad \text{Eq. 2.12}$$

$$\mathrm{O_2 \bullet^- + OH \bullet \rightarrow HOO \bullet} \qquad \text{Eq. 2.13}$$

$$\mathrm{HOO \bullet + e^- \rightarrow HO_2^-} \qquad \text{Eq. 2.14}$$

$$\mathrm{HOO^- + H^+ \rightarrow H_2O_2} \qquad \text{Eq. 2.15}$$

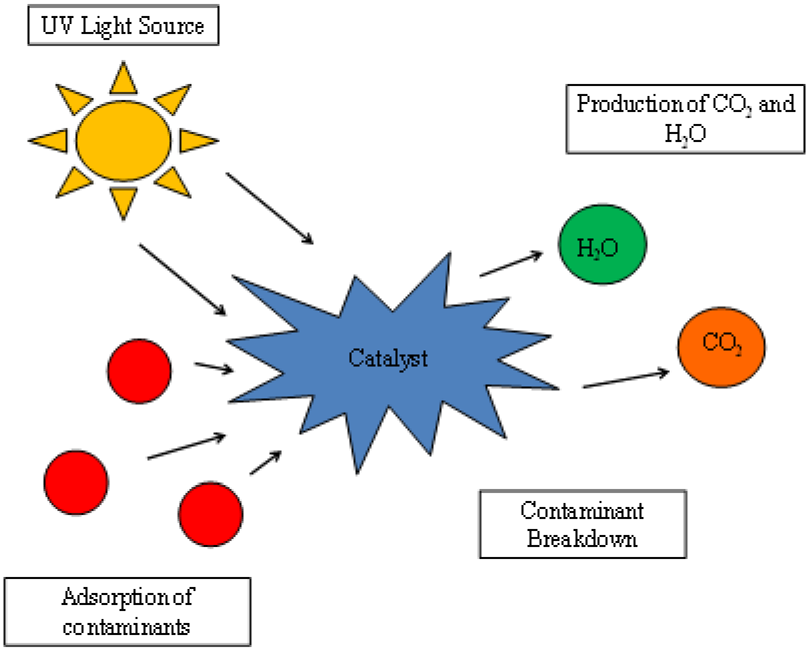


Figure 2.1 Mechanisms of Photocatalysis

Photocatalysis is a relatively new method; therefore, there are still related uncertainties regarding its unknown aspects. Over time and with additional research, these factors will expectantly be alleviated in pilot plant and full scale studies. Currently, there are disadvantages that have been identified. Fouling of the UV lamps sleeves is expected to occur, but fouling can also occur in the TiO_2 catalyst. Furthermore, maintenance involving the recovery of TiO_2 slurry is necessary (Metcalf & Eddy, 2014).

2.2.5 Fenton reaction

The Fenton reaction involves the production of hydroxyl radicals from the reaction between ferrous iron (Fe^{2+}) and H_2O_2 (Lloyd, et al., 1997). It has been reported that the Fenton reaction is capable of removing compounds, such as clofibric acid and X-ray contrast agents, which are not removed by more common methods, such as ozonation

(Esplugas, et al., 2007). The following equation describes the reaction that takes place during degradation through Fenton’s reaction (Andreozzi, et al., 1999):

$$\mathrm{Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH\bullet} \qquad \text{Eq. 2.16}$$

Disadvantages to Fenton treatment include the requirement of low pH conditions (Metcalf & Eddy, 2014). Optimal pH levels have been reported to be between 2 and 4 (Shemer, et al., 2006). If the pH is too low, the scavenging of hydroxyl radicals can increase, but if the pH is too high, the oxidation potential and degradation rates will decrease (Shemer, et al., 2006).

2.2.6 Integrated processes

The processes discussed in the previous sections, while capable of removing emerging contaminants, can be improved through the integration of individual methods. The processes of H_2O_2 /O_3, O_3/UV, and H_2O_2/UV are outlined in the subsequent sections.

2.2.6.1 H_2O_2/O_3

While the uses of H_2O_2 and O_3 have individually portrayed success when removing emerging contaminants, this accomplishment may be limited. The efficiency of these processes can be significantly increased if these compounds are merged into one technique (NWRI, 2000). Metcalf and Eddy report Eq. 2.17 as the reaction for the production of hydroxyl radicals when using both H_2O_2 and O_3.

$$\mathrm{H_2O_2 + 2O_3 \rightarrow HO\bullet + HO\bullet + 3O_2} \qquad \text{Eq. 2.17}$$

This combination of processes can be advantageous in some instances, such as during the degradation of compounds that do not absorb UV well (Metcalf & Eddy, 2014). Furthermore, H_2O_2/O_3 may be an improvement over UV processes because of the lack of related equipment and maintenance, such as those relating to UV lamps and energy requirements. The following units are necessary for the completion of the H_2O_2/O_3 process (NWRI, 2000; Metcalf & Eddy, 2014):

- H_2O_2 injection and storage system
- Ozone generation facility
- Contact and reaction chambers
- Ozone destruction facility

Disadvantages to this method involve the difficulties of maintaining the proper conditions, such as chemical dosages and pH level (Metcalf & Eddy, 2014). Ozone dosage is a particular concern because the actual required dosage is larger than estimated through stoichiometry; however, an excess of ozone or H_2O_2 will also cause difficulties. This can include unwanted byproducts, such as bromate, or quenching of hydroxyl radicals. Metcalf and Eddy provide Equation 2.18 for the quenching of hydroxyl radicals due to an excess dosage of ozone.

$$O_3 + HO\bullet \rightarrow HO_2\bullet + O_2 \qquad \text{Eq. 2.18}$$

Residual H_2O_2 can also disrupt the proper functioning and reaction of hydroxyl radicals. The removal of excess H_2O_2 may be necessary, but would introduce further operational and maintenance costs. Alternatively, multiple introduction points for O_3 and H_2O_2 in the reactor may resolve the problem, or several reactors could be used in series, as opposed to a single reactor (Metcalf & Eddy, 2014).

2.2.6.2 O_3/UV

Another viable integration of processes is O_3/UV. This process produces hydroxyl radicals by first producing H_2O_2 through the photolysis of ozone, which requires the use of UV light. This reaction, as explained by Metcalf and Eddy, is reported below.

$$O_3 + H_2O + UV\,(\lambda < 310\text{nm}) \rightarrow O_2 + HO\bullet + HO\bullet \rightarrow O_2 + H_2O_2 \qquad \text{Eq. 2.19}$$

The H_2O_2 created during this reaction can then react with the O_3 to produce hydroxyl radicals for use in the degradation of contaminants. The multiple mechanisms at work simultaneously contribute to the efficacy of this process. There are opportunities for degradation through not only the production and reaction with hydroxyl radicals, but also through ozonation and photolysis (Metcalf & Eddy, 2014). This process will typically require the use of the following key components:

- Ozone generation facility
- Contact and reaction chambers
- UV photolysis reactors

It has been reported that O_3/UV produces greater amounts hydroxyl radicals than H_2O_2/UV; however, this statement is contingent on the types of UV lamps used (NWRI, 2000). The O_3/UV process shares the same disadvantages discussed previously in the sections regarding ozonation and UV as individual processes. This includes the need for destruction of ozone following use, as well as the potential for UV lamp fouling. Furthermore, processes involving UV lamps tend to be more energy intensive (Metcalf & Eddy, 2014). In addition, the O_3/UV process creates H_2O_2, which may not be as feasible as simply introducing H_2O_2.

2.2.6.3 H_2O_2/UV

The photolysis of H_2O_2 can also be used to produce hydroxyl radicals. The reaction is shown below (Metcalf & Eddy, 2014).

$$H_2O_2 + \text{UV (or } h\nu, \lambda \approx 200 \text{ to } 280\text{nm}) \rightarrow HO\bullet + HO\bullet \qquad \text{Eq. 2.20}$$

High dosages of both UV and H_2O_2 may be necessary when completing this reaction effectively, however. This can subsequently lead to high amounts of H_2O_2 in the effluent, which can impede disinfection and must be removed. However, it has been found that these elevated H_2O_2 concentrations can be used to degrade pollutants that were are not able to be degraded by UV treatment alone (Linden, et al., 2004). The following units can be found in the H_2O_2/UV system (NWRI, 2000):

- UV lamps and accessories/cleaning equipment
- H_2O_2 injection and storage system
- Reactor chamber
- In-liner mixers

Once again, processes related to the use of UV lamps are subject to the associated fouling and energy consumption costs. H_2O_2/UV, in addition to TiO_2 photocatalysis, is the most commonly used light oxidation technique (Esplugas, et al., 2007). One advantage that H_2O_2/ UV has over processes utilizing O_3 is the lack of potential bromate production (NWRI, 2000).

CHAPTER III

ANALYTICAL METHODS AND TECHNIQUES

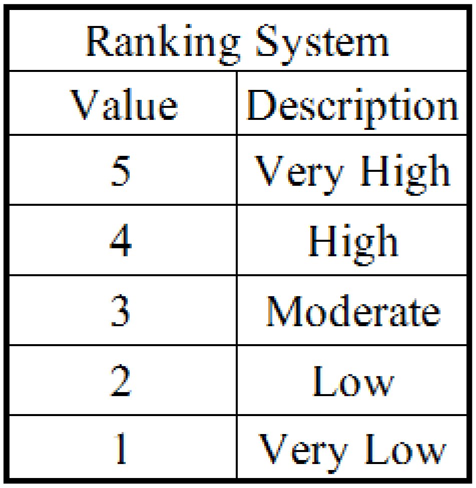
3.1 Holistic Analysis

With the intention of identifying the treatment process that is superior in a multi-faceted respect, a holistic analysis was completed. It is impossible to determine a single factor that can be used alone to establish the worth of a technology. Therefore, multiple parameters were chosen to achieve an in-depth and complex examination. These parameters reflect the process's success in a multitude of ways, so they were broken down into three categories: process engineering parameters, environmental parameters, and social and economic parameters. The process engineering parameters include: mechanical reliability, process reliability, flexibility, adaptability, and energy consumption. Among the environmental parameters are: contribution to climate change, eutrophication, terrestrial and aquatic toxicity, and degradation products. The selection of these parameters were influenced by the factors investigated during Life Cycle Analysis studies (SAIC, 2006). The social and economic parameters include: public acceptance, ease of use, and economic feasibility. A variety of AOPs were studied, including ozonation, H_2O_2, UV, TiO_2 photocatalysis, Fenton reaction, and combinations thereof.

3.2 Parameter Ranking Methodology

In order to effectively compare one process's performance in each category, the parameters were first quantified with an appropriate value. Each process received a ranking corresponding to each parameter. The introduction of a ranking system allows for all processes and parameters to be compared on a uniform, numerical basis. A similar approach was taken in another study where factors were noted as either "high", "medium", or "low" performance (NWRI, 2000). Table 3.1 below displays the methodology used when applying the rankings. A ranking of five indicates the highest positive value possible, while a value of one suggests the poorest performance. Subjective parameters are supported by tables illustrating a summary of the approach used, while the more objective parameters are supported by values and conclusions taken from previous studies.

Table 3.1 Parameter Ranking System



Ranking System	
Value	Description
5	Very High
4	High
3	Moderate
2	Low
1	Very Low

3.3 Comparison and Assessment

The overall performance of each technology could then be compared across the parameter. Furthermore, the individual parameter rankings were united into one average ranking for each category, meaning that each process also possesses a ranking for each of the three broad categories. This allows for the determination of the process that performs the best in each category. In addition, a final cumulative comparison was completed, revealing the technologies that function well in all three categories. An overall ranking could then be calculated based on the rankings in each of the three categories. The AOPs with the highest final rankings would presumably be the superior technologies.

Radar charts were produced to emphasize the discoveries of the analysis. This type of chart allows for comparisons of multivariate data, which is applicable to the various parameters and processes studied. The rankings of each process for each parameter could thus be compared and evaluated simultaneously in a simple, straightforward plot. As discussed previously, these rankings were treated in a collective manner, so plots were produced not only for comparisons across each category, but also for a final, cumulative assessment.

CHAPTER IV

RESULTS

4.1 Process Engineering Parameters

4.1.1 Mechanical reliability

The consistency and dependability of a process is reliant on the mechanical soundness. The maintenance and replacement costs will inevitably increase for processes that utilize more mechanical pieces. In addition, mechanical failure can be detrimental to the successful functioning of the overall process and may be costly or difficult to remedy. Therefore, a process that is mechanically simple will be more reliable, which is an important attribute when discussing the never-ending supply to wastewater treatment plants.

A variety of AOPs were given rankings based on their mechanical reliability. The results can be viewed in Table 4.1 below, as well as a summary of the approach in Table 4.2. O_3, H_2O_2, and H_2O_2/O_3 were given a ranking of four, indicating that their mechanical reliabilities are high. Ozone generators and ozone gas diffusers require inspection and cleaning routinely. The precipitation of carbonates can lead to sparger fouling, which decreases the efficiency of ozone transfer (NWRI, 2000). Both O_3/UV and H_2O_2/UV received rankings of three. This was based on the need for replacement of UV lamps, as well as periodic inspections (Metcalf & Eddy, 2014). The processes receiving the lowest rankings were TiO_2 photocatalysis and Fenton process, each ranked two, due to high maintenance requirements relating to condition parameters such as pH, mixing, and chemical (TiO_2 and iron) addition (NWRI, 2000).

Table 4.1 Mechanical Reliability Ranking

Mechanical Reliability	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	3
H_2O_2/UV	3
TiO_2	2
Fenton	2

Table 4.2 Mechanical Reliability Approach Summary

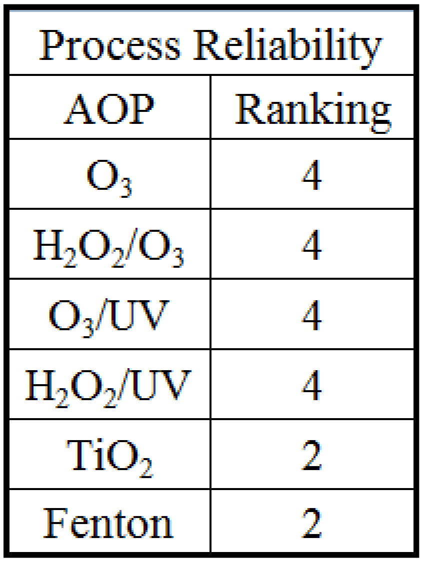
Mechanical Reliability					
AOP	Inspection	Cleaning	pH Sensitive	Mixing	UV Lamp
O_3	X	X			
H_2O_2/O_3	X	X			
O_3/UV	X	X			X
H_2O_2/UV	X	X			X
TiO_2	X	X	X	X	X
Fenton	X	X	X	X	

4.1.2 Process reliability

The process reliability of a system is its ability to consistently produce a satisfactory effluent that meets all required water quality standards. If a process is not able to be relied upon to complete the task that has been assigned to it, then the unit is essentially useless. An effective technology will not only produce the required effluent, but it will also do so steadily, despite variations is flow, influent quality, and environmental conditions.

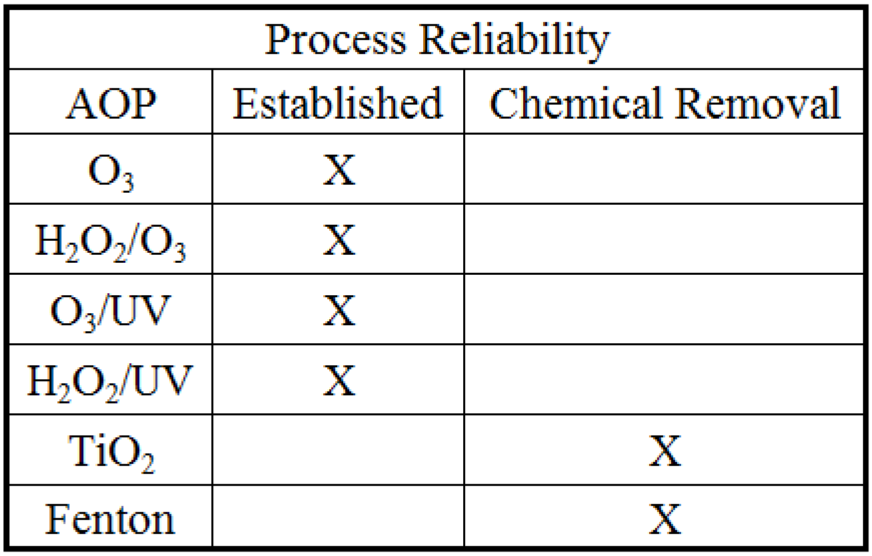
Treatment processes that have been in use for longer periods of time generally display greater process reliability (NWRI, 2000). They are capable of regularly producing an adequate effluent without complications. Therefore, O_3, H_2O_2/O_3, O_3/UV, and H_2O_2/UV each received rankings of four because of their history of being reliable systems. Conversely, newer technologies tend to be less reliable. These processes have not undergone the same level of testing and do not display equivalent confirmation of dependability. In addition, processes such as TiO_2 photocatalysis and the Fenton process also require removal of chemicals used, which will vary the quality of the effluent (NWRI, 2000). TiO_2 photocatalysis requires the removal of TiO_2 slurry, while the Fenton process will require the removal of precipitated iron. TiO_2 photocatalysis and the Fenton process thus received rankings of two.

Table 4.3 Process Reliability Ranking



Process Reliability	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	2
Fenton	2

Table 4.4 Process Reliability Approach Summary



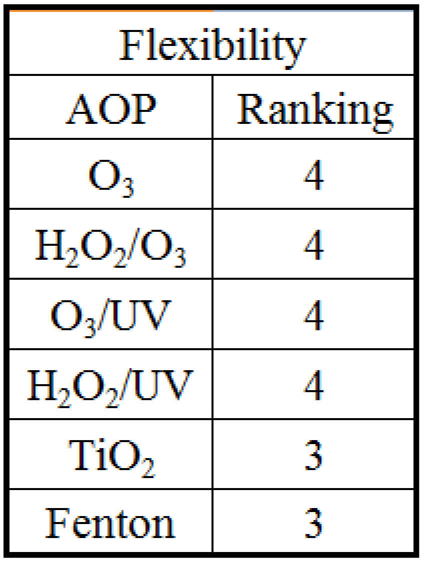
Process Reliability		
AOP	Established	Chemical Removal
O_3	X	
H_2O_2/O_3	X	
O_3/UV	X	
H_2O_2/UV	X	
TiO_2		X
Fenton		X

4.1.3 Flexibility

Another parameter related to process reliability is process flexibility. This refers to the process's capability of adjusting to changes in the influent flow rate. A successful technology can continue to operate properly despite variations both above and below the designed flow rate. Changes in flow rate can occur for multiple reasons, including storm events, seasonal variations, diurnal variations, and even seasonal population variations. Population, and thus flow rate, has been known to vary significantly in communities, such as college towns, when the number of citizens will change drastically according to events such as holidays or vacations.

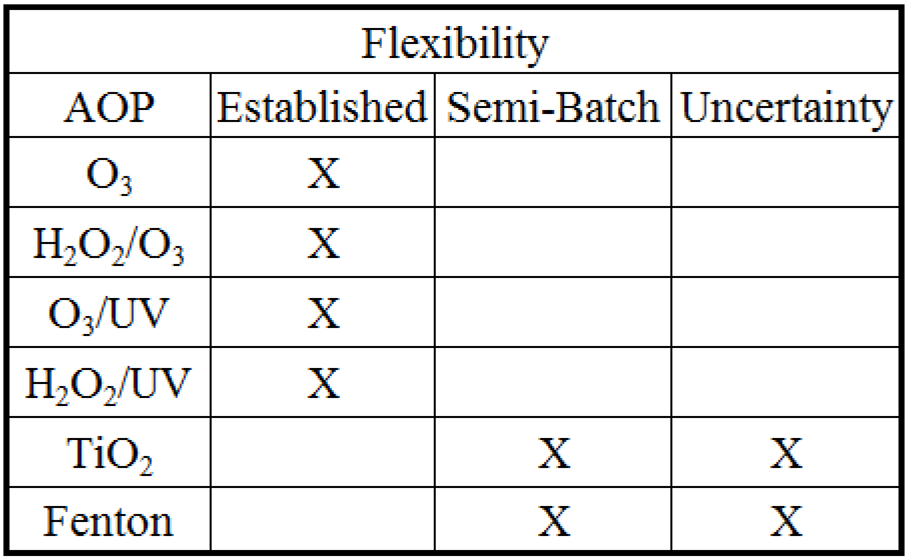
As discussed previously, older technologies have been given the opportunity to corroborate their flexibility, while more recent processes have not. The chemical dosages can easily be adjusted in response to fluctuations in flow rate. This implies that processes using ozone or UV can react to these situations with relative ease. Furthermore, more mature processes have also had the opportunity to implement an appropriate factor of safety, allowing for proper function following the introduction of flow rate variations. This earns O_3, H_2O_2/O_3, O_3/UV, and H_2O_2/UV a ranking of four. While TiO_2 photocatalysis and the Fenton reaction are newer technologies, they are also fairly flexible. These processes are often designed in semi-batch reactors, suggesting that they can manage flow rate fluctuations (NWRI, 2000). However, there is still a level of ambiguity associated with these more modern processes, so they are ranked as a three.

Table 4.5 Flexibility Ranking



Flexibility	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	3
Fenton	3

Table 4.6 Flexibility Approach Summary



Flexibility			
AOP	Established	Semi-Batch	Uncertainty
O_3	X		
H_2O_2/O_3	X		
O_3/UV	X		
H_2O_2/UV	X		
TiO_2		X	X
Fenton		X	X

4.1.4 Adaptability

Adaptability is similar in some aspects to the previous parameter, flexibility, but it concerns variations in water quality instead of quantity. The influent water quality can have a considerable impact on the efficacy of a process. The quality of a water source is not guaranteed, but an effective process must be able to respond to changes in the constituent matrix without negative impacts on the effluent.

The turbidity of the influent water can have a potentially negative effect on processes using a UV light source because penetration may become limited (NWRI, 2000). Consideration of submerged or overhead bulbs could be valid in this discussion. The particular constituents found in the influent are also important. As discussed previously in Section 2.2.3, the presence of nitrate and iron can reduce the degradation efficiency of processes that utilize UV. Furthermore, both O_3 diffusers and UV lamp sleeves are subject to scaling and fouling due to the influent matrix (NWRI, 2000). TiO_2 photocatalysis produces hydroxyl radicals quickly, and may be capable of responding well to changes in water quality; however, the UV component is still susceptible to the difficulties mentioned previously (NWRI, 2000). The Fenton reaction is expected to respond relatively well to variation in water quality, but it should be recalled that this process is sensitive to pH conditions. Overall, all AOPs are highly dependent on the quality of influent waters, and the rankings reflect this aspect. All processes, with the exception of O_3/UV and H_2O_2/UV (which received rankings of 2), were assigned rankings of 3.

Table 4.7 Adaptability Ranking

Adaptability	
AOP	Ranking
O_3	3
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	2
TiO_2	3
Fenton	3

Table 4.8 Adaptability Approach Summary

Adaptability			
AOP	Turbidity	Scaling	pH Sensitive
O_3		X	
H_2O_2/O_3		X	
O_3/UV	X	X	
H_2O_2/UV	X	X	
TiO_2	X		
Fenton			X

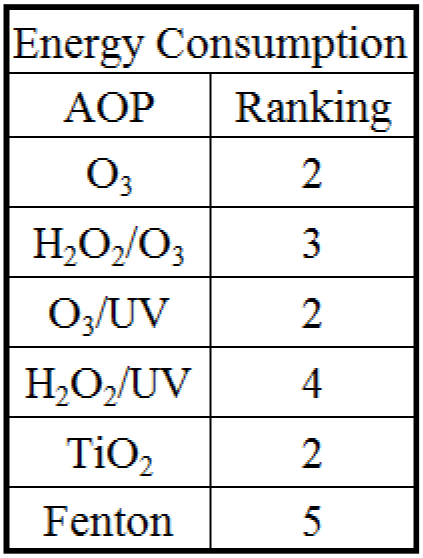
4.1.5 Energy consumption

While each of the parameters discussed have not been ranked or classified based on importance, energy consumption may be considered one of the most essential. It is currently a global goal to reduce the amounts of energy used in order to decrease depletion of fossil fuels and alleviate other negative impacts that energy production or use can have on the environment. In addition, energy consumption is one of the largest contributors to overall process costs. Tables 2.3 and 2.4 present energy consumption values in kWh/m^3.

The use of UV lamps is one of the greatest contributors to high energy consumption; however, an effective process has the potential to produce high quality removal with low energy if the other conditions are ideal. Most processes using UV lamps received low rankings, with the exception of H_2O_2/UV, which generally displays low energy consumption. Processes using O_3 were also assigned lower rankings, possibly due to the requirement for on-site O_3 generation. The Fenton process receives the highest ranking because its energy demands do not expand past simple pumping requirements (NWRI, 2000).

Energy consumption can also vary for one process based on the contaminant that is being removed, however (Mahamuni & Adewuyi, 2010). For example, when treating a post-membrane bioreactor wastewater sample, O_3, O_3/UV, H_2O_2/UV, and photocatalysis reported energy consumption values of 11.93, 6.15, 0.23, and 7.09 respectively, which indicates that O_3 requires more energy for this particular constituent matrix, while ozonation only reported 0.03-0.09 kWh/m^3 for a variety of ozone dosages (Chong, et al., 2012; Kim & Tanaka, 2011). These values also illustrate the significant influence of proper H_2O_2 dosage on lowering energy consumption. For comparison purposes, it can be noted that granular activated carbon (GAC) reported an energy consumption of 0.16 kWh/m^3, and nanofiltration was found to be 0.55 kWh/m^3 (Bonton, et al., 2006).

Table 4.9 Energy Consumption Ranking



Energy Consumption	
AOP	Ranking
O_3	2
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	4
TiO_2	2
Fenton	5

4.1.6 Overall process engineering results

The rankings assigned in the previous sections are summarized in the subsequent Table 4.10 and Figure 4.1. In addition, the average ranking for each process was determined so that a single process engineering ranking can be reported. Based on Figure 4.1, it can be observed that most processes performed on a similar level, with the exception of the Fenton process. However, while the Fenton process's performance was low across several parameters, its ranking for energy consumption was much higher. Ultimately, H_2O_2/O_3 received the highest average ranking, while TiO_2 photocatalysis received the lowest. Overall, however, most processes were relatively evenly ranked on average for process engineering parameters.

Table 4.10 Process Engineering Parametric Summary

	AOPs					
Process Engineering Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Mechanical Reliability	4	4	3	3	2	2
Process Reliability	4	4	4	4	2	2
Flexibility	4	4	4	4	3	3
Adaptability	3	3	2	2	3	3
Energy Consumption	2	3	2	4	2	5

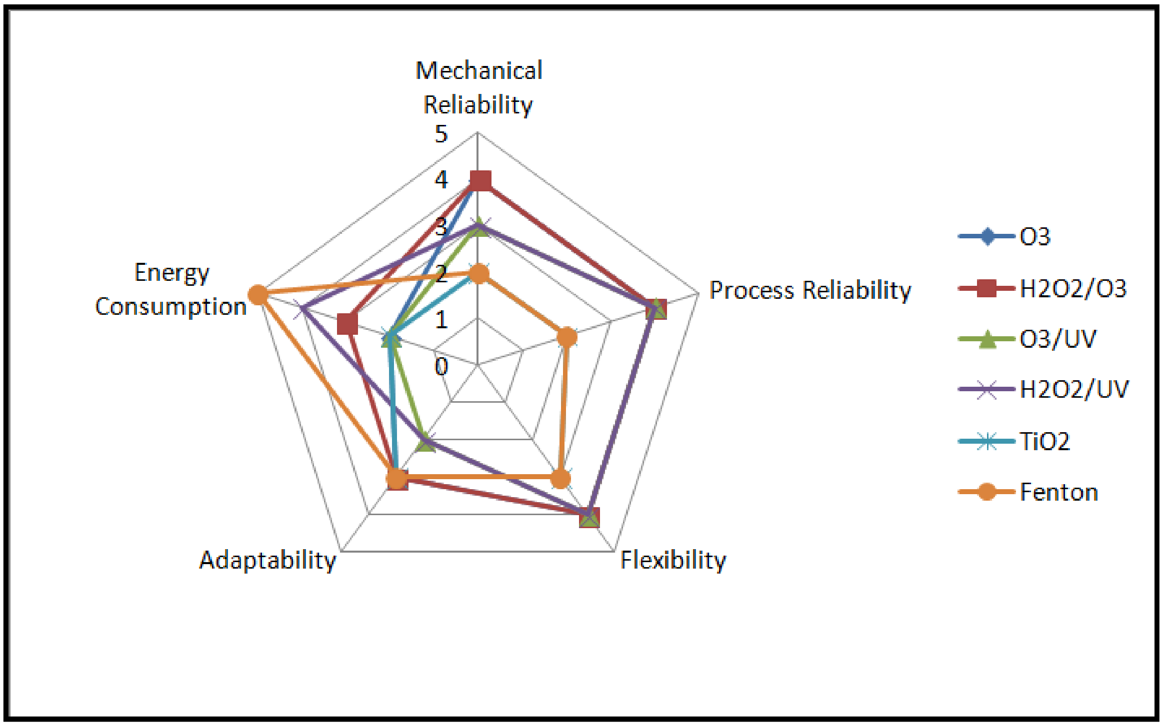


Figure 4.1 Process Engineering Parameters

Table 4.11 Average Process Engineering Rankings

AOP	Average Ranking
O_3	3.4
H_2O_2/O_3	3.6
O_3/UV	3
H_2O_2/UV	3.4
TiO_2	2.4
Fenton	3

4.2 Environmental Parameters

The total adverse effects on the environment are extremely sensitive subjects. This is particularly due to the potential negative effects of emerging contaminants. It is increasingly important that a treatment process is chosen that does not introduce additional environmental hazards. This includes the environmental-friendliness of the operation itself, as well as any chemicals or byproducts that are introduced.

4.2.1 Contribution to climate change

Global climate change is a constant concern, especially during the development of new technologies and methods. All efforts are made to decrease production of greenhouse gases in order to reduce effects such as polar melt, altered wind and ocean patterns, sea level rise, and change in seasons (SAIC, 2006). Contributors to climate change include: carbon dioxide (CO_2), nitrogen dioxide (NO_2), methane (CH_4), chlorofluorocarbons (CFCs), hydrochlorofluorocarbons (HCFCs), and methyl bromide

(CH_3Br) (SAIC, 2006). The greatest point of concern pertaining to AOPs is the production of CO_2. CO_2 emissions are directly related to the generation electricity; therefore, the rankings for this parameter are based on energy consumption. However, it should be noted that there are many other factors contributing to climate change. For example, additional resources and energy are utilized in the production of chemicals, equipment, etc. CO_2 is also released during the oxidation process, but these amounts would be incredibly small (comparable to the ng/L to µg/L scale of the original contaminant concentrations), and may never leave the aqueous solution.

The Fenton process and H_2O_2/UV received high rankings for their low energy consumptions, resulting in higher rankings for climate change. It should be noted that a high score indicates a positive reflection, or low contribution to climate change, while a low ranking signifies higher contributions. The other processes received lower rankings due to their larger energy consumption values.

Table 4.12 Contribution to Climate Change Ranking

Climate Change	
AOP	Ranking
O_3	2
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	4
TiO_2	2
Fenton	5

4.2.2 Eutrophication

Eutrophication due to excess nutrients, namely nitrogen and phosphorus, can potentially be incredibly harmful to aquatic wildlife. Operations that introduce additional nutrients into the environment are not considered viable. The following list includes nutrients of concern: phosphate (PO_4), nitrogen oxide (NO), nitrogen dioxide (NO_2), nitrates, and ammonia (NH_4) (SAIC, 2006). While AOPs are practical methods for removal of emerging contaminants, they are often preceded or proceeded with other technologies that target nutrients more specifically. Furthermore, the discussed nutrients are not created or released during operation, earning all processes high rankings of 5.

Table 4.13 Eutrophication Rankings

Eutrophication	
AOP	Ranking
O_3	5
H_2O_2/O_3	5
O_3/UV	5
H_2O_2/UV	5
TiO_2	5
Fenton	5

4.2.3 Terrestrial and aquatic toxicity/degradation products

While the intention of these treatment processes is to remove emerging contaminants to prevent harm to humans and wildlife, it is also possible that other toxic materials are introduced into the environment. This can result from chemicals used during the treatment methods, as well as from byproducts that are formed during the progression of the process. A technology that effectively removes emerging contaminants, but also releases other damaging or toxic materials is not a practical technology.

As mentioned in prior discussions regarding ozonation, bromate and other byproducts are produced when O_3 is utilized. These processes must be monitored carefully because bromate is carcinogenic, and thus raises considerable concern. The release of bromate can be minimized with proper care. For example, bromate production during H_2O_2/O_3 can be diminished with proper chemical doses (NWRI, 2000). Processes that employ UV lamps have the advantage of introducing no additional chemicals. TiO_2 photocatalysis requires recovery of the TiO_2 catalyst, and it poses potentially harmful effects. The Fenton process demands removal of iron. Although iron is an essential trace element, exposure should be limited (World Health Organization, 2003).

Another major aspect to consider is the production of degradation products from the contaminants themselves. It has been suggested that effluent from AOPs be treated subsequently by biofiltration, membranes, or other techniques to remove byproducts (Snyder, et al., 2003). Some studies question whether the degradation products of AOPs are actually more harmful than the original contaminant (Gomez, et al., 2008). This is a relatively new area of study that requires progress in analytical determination processes (Aguera, et al., 2013). Acetaminophen is one example of an emerging contaminant with known transformation products. One study noted the removal of acetaminophen, but the pollutant was instead degraded into 4-Aminophenol (del Mar Gomez-Ramos, et al., 2011). An in depth study of the degradation of the insecticide Thiamethoxam reported that a large number of byproducts were produced (Mir, et al., 2013).

Processes using O_3 received low rankings due to bromate formation; however, the ranking for H_2O_2/O_3 was slightly higher due to the potential for remedy as discussed previously. TiO_2 photocatalysis and the Fenton reaction also received lower scores because of introduction of catalyst and iron respectively. As UV processes do not directly introduce chemicals into the effluent, they received higher scores. The score for each process was also lowered due to the potential for transformation products. While particular degradation products have been identified during certain processes, those products are not necessarily explicitly related to that process.

Table 4.14 Terrestrial and Aquatic Toxicity Ranking

Toxicity	
AOP	Ranking
O_3	2
H_2O_2/O_3	3
O_3/UV	2
H_2O_2/UV	3
TiO_2	2
Fenton	2

Table 4.15 Terrestrial and Aquatic Toxicity Approach Summary

Terrestrial and Aquatic Toxicity			
AOP	Degradation Products	Bromate	Inorganic Compounds
O_3	X	X	
H_2O_2/O_3	X	X	
O_3/UV	X	X	
H_2O_2/UV	X		
TiO_2	X		X
Fenton	X		X

4.2.4 Overall environmental results

The subsequent Tables 4.11 and 4.12 and Figure 4.2 provide a comparison of the environmental parameters considered. The Fenton process and H_2O_2/UV earned the highest average rankings, while O_3, O_3/UV, and TiO_2 photocatalysis were given the lowest average. H_2O_2/O_3 received a score only slightly lower than the top ranking processes. It appears that the parameter supplying the most variation was contribution to climate change; therefore, processes with the lowest energy consumption earned the highest environmental rankings overall.

Table 4.16 Environmental Parametric Summary

	AOPs					
Environmental Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Climate Change	2	3	2	4	2	5
Eutrophication	5	5	5	5	5	5
Toxicity	2	3	2	3	2	2

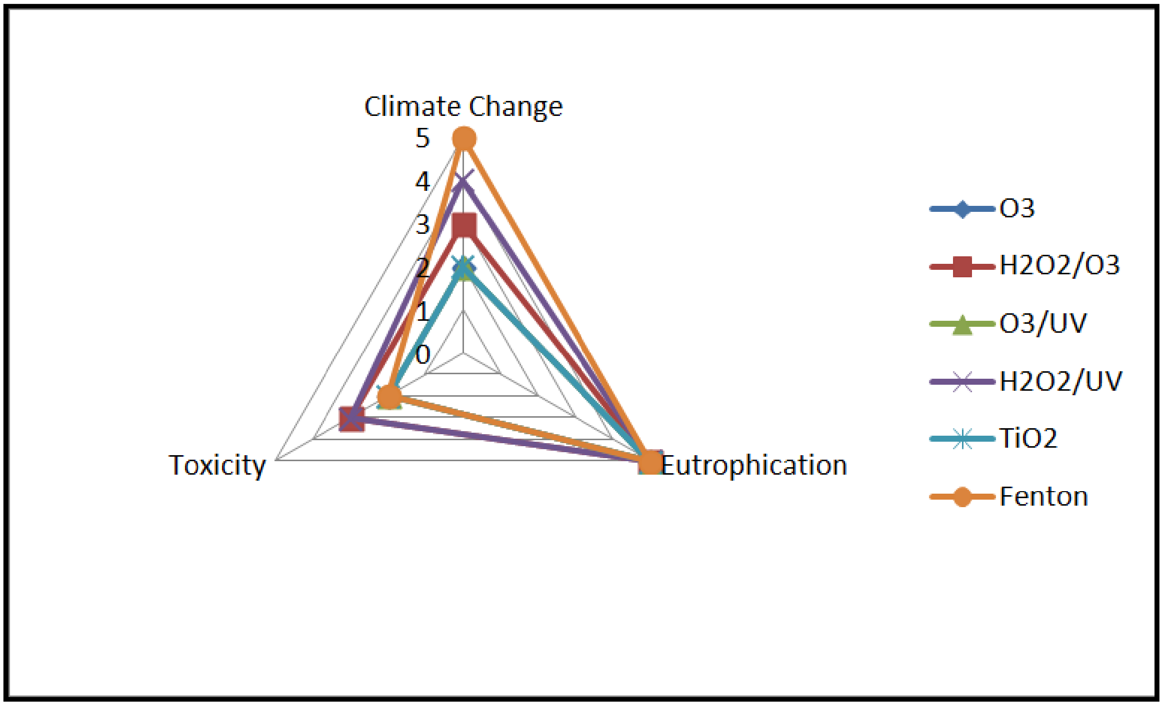


Figure 4.2 Environmental Parameters

Table 4.17 Average Environmental Rankings

Average	
AOP	Ranking
O_3	2.25
H_2O_2/O_3	2.75
O_3/UV	2.25
H_2O_2/UV	3
TiO_2	2.25
Fenton	3

4.3 Economic and Social Parameters

Economic and social factors are incredibly important. One of the largest issues when choosing an appropriate treatment technology is the cost. All industries strive to save money, but it can also be a critical factor. Quality treatment facilities cannot be afforded by all interested parties; therefore, the least expensive option is often chosen. Furthermore, the opinions of the individuals involved must also be considered. This includes not only the recipients of treated water, but also those men and women who are involved in the operation of the necessary facilities.

4.3.1 Public acceptance

The extent to which the general public accepts a treatment process is critical. The well-being of the public is given a very high priority, so the opinions of individuals outside of the design and implementation of processes must be considered. While the general population may not have an in-depth understanding of all water and wastewater treatment processes, they must be given the opportunity to be informed and give input.

Establishment of new processes can be difficult for many citizens to accept. Introduction of potentially harmful substances can be a very sensitive subject. Therefore, TiO_2 photocatalysis and the Fenton process receive low rankings. These processes are not only relatively contemporary ideas to the community who study them, but they are very new and unknown to the public. Furthermore, these processes require the addition of inorganic chemicals (TiO_2 and iron) that are viewed negatively (NWRI, 2000). The remaining processes are assigned higher scores because they are more well-known by the public. While these technologies also have their own advantages and disadvantages, they are more easily accepted because of the additional pilot scale and full scale demonstrations.

Table 4.18 Public Acceptance Ranking

Public Acceptance	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	2
Fenton	2

Table 4.19 Public Acceptance Approach Summary

Public Acceptance		
AOP	Established	Inorganic Compounds
O_3	X	
H_2O_2/O_3	X	
O_3/UV	X	
H_2O_2/UV	X	
TiO_2		X
Fenton		X

4.3.2 Ease of use

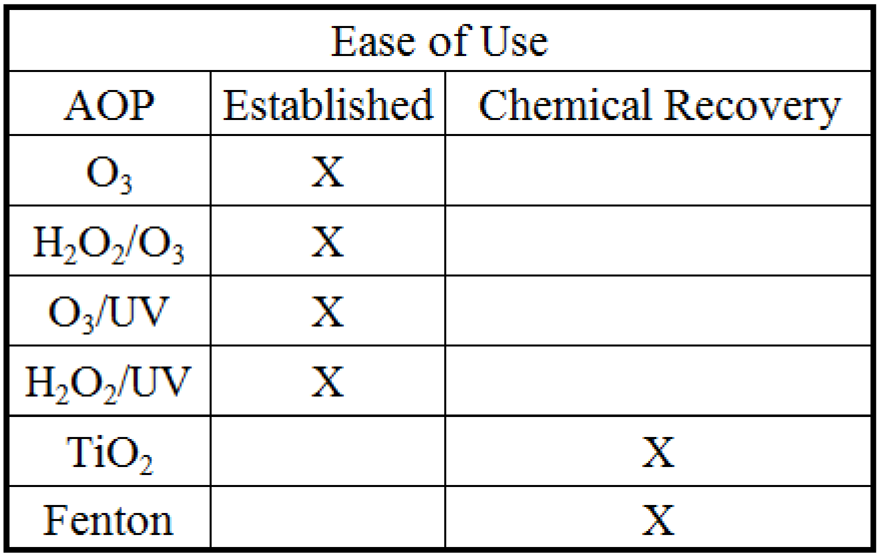
The simplicity of the utilization of each process plays a critical role in selection and implementation. A complicated process introduces the potential for a greater number of errors or mistakes to be made during execution. In addition, skilled personal may be necessary to manage a complex system, which can result in higher labor costs. It is also likely that a more intricate system will have higher operational and maintenance costs due to unusual chemicals or units.

Once again, the more novel techniques receive lower rankings, while the more senior processes reflect higher scores. Older techniques have been given the opportunity to be corrected and perfected, while TiO_2 photocatalysis and the Fenton process do not have the same background. These processes still require additional pilot scale or full scale use to give accurate representations of what daily use would involve. Furthermore, the required catalyst recovery involved with photocatalysis adds a level of difficultly.

Table 4.20 Ease of Use Ranking

Ease of Use	
AOP	Ranking
O_3	4
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	4
TiO_2	2
Fenton	2

Table 4.21 Ease of Use Approach Summary



Ease of Use		
AOP	Established	Chemical Recovery
O_3	X	
H_2O_2/O_3	X	
O_3/UV	X	
H_2O_2/UV	X	
TiO_2		X
Fenton		X

4.3.3 Economic feasibility

Perhaps one of the most critical features when choosing a treatment method is the economic practicality. Monetary resources are often the limiting factor in many situations. The lack of the ability to support a process financially immediately lessens a technology's appeal. While a process may exhibit many positive characteristics, high capital, maintenance, or operation costs reflect very negatively on the method.

Operation and maintenance costs include costs relating to part replacement, labor, analytical methods, chemical use, and electrical requirements (Mahamuni & Adewuyi, 2010). The general breakdown of capital costs for AOPs are as follows in Table 4.22 (NWRI, 2000).

Table 4.22 Capital Cost Breakdown

Factors	Percent (%)
Piping, Valves, Electrical	30
Site Work	10
Engineering	15
Contractor O & P	15
Contingency	30
Total	100

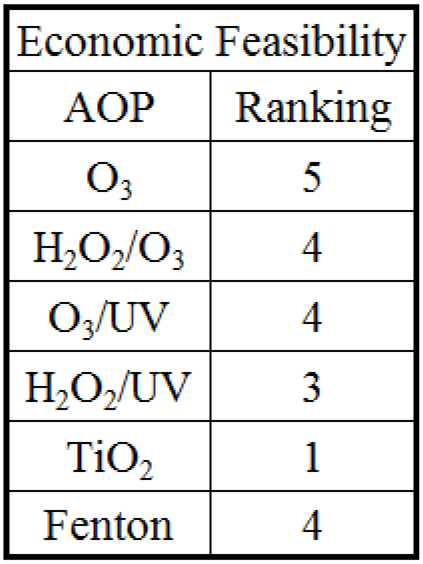
The following table presents various cost estimates for the degradation of phenol as reported by Mahamuni & Adewuyi (2010). Related assumptions include:

- Plant is working for the full year (52 weeks)
- Labor rate = \$80/hour
- Analytical labor rate = \$200/hour
- Electricity rate = \$0.08/kWh
- Amortization occurs over 30 years at a rate of 7%

Table 4.23 AOP Cost Estimations

AOP	Cost $/1000 gal	Amortized Annual Capital Cost	Annual O&M Costs
O_3	1.2023	7.55E+04	9.16E+04
O_3/UV	38.648	1.12E+06	4.25E+06
H_2O_2/UV	308.482	2.36E+06	4.05E+07
TiO_2	8648.79	2.51E+08	9.51E+08
Fenton	14.2829	-	1.99E+06

Table 4.24 Economic Feasibility Ranking



Economic Feasibility	
AOP	Ranking
O_3	5
H_2O_2/O_3	4
O_3/UV	4
H_2O_2/UV	3
TiO_2	1
Fenton	4

The rankings in Table 4.24 directly reflect the cost estimates in Table 4.23. Estimates were not found for H_2O_2/O_3, so a comparison between related technologies was used to assign ranking. Based on economic feasibility, ozonation performs incredibly well, particularly in comparison to the other processes. TiO_2 photocatalysis, however, shows little strength relating to economic feasibility as it reported a total cost of $8648.79/1000 gallons (Mahamuni & Adewuyi, 2010). The remaining methods portrayed average rankings. Ozonation received a very high score for is low cost of $1.023/1000 gallons (Mahamuni & Adewuyi, 2010).

4.3.4 Overall economic and social results

The tables and figure below summarize the results for economic and social parameters. It is obvious that overall, O_3, H_2O_2/O_3, O_3/UV, and H_2O_2/UV outperform TiO_2 photocatalysis and the Fenton process. However, the Fenton process received a high ranking for economic feasibility, raising its average ranking. TiO_2 photocatalysis received low scores for all parameters, which could partially be due to its relatively new introduction. Its poor score for economic feasibility is a significant concern.

Table 4.25 Economic and Social Parametric Summary

	AOPs					
Economic and Social Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Public Acceptance	4	4	4	4	2	2
Ease of Use	4	4	4	4	2	2
Economic Feasibility	5	4	4	3	1	4

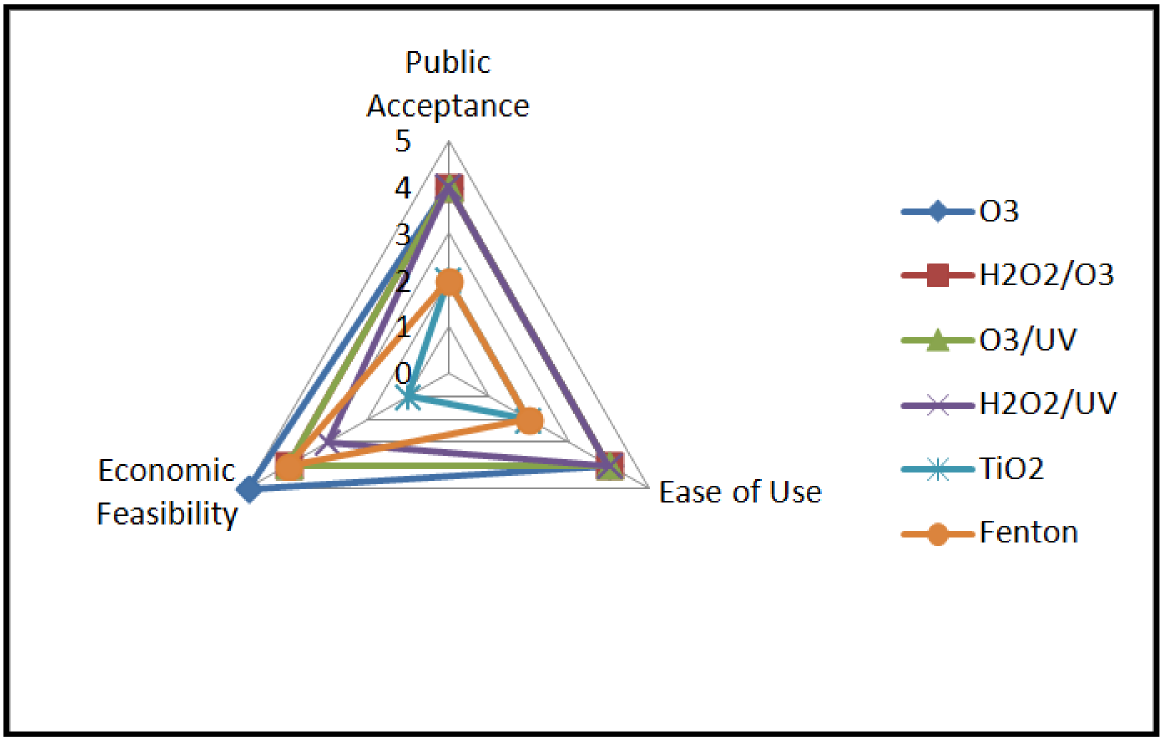
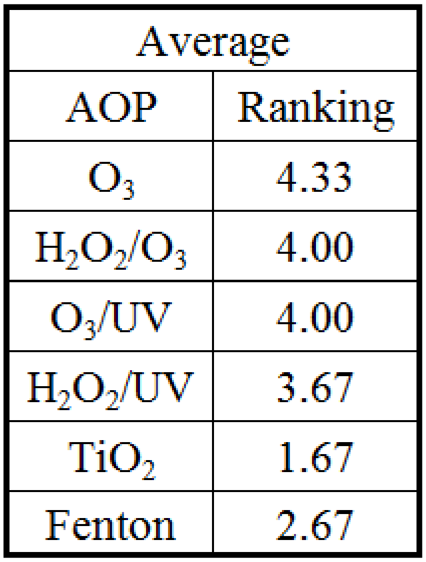


Figure 4.3 Economic and Social Parameters

Table 4.26 Average Economic and Social Rankings



Average	
AOP	Ranking
O_3	4.33
H_2O_2/O_3	4.00
O_3/UV	4.00
H_2O_2/UV	3.67
TiO_2	1.67
Fenton	2.67

4.4 Holistic Comparison

The average rankings for each category of parameters were averaged into a final ranking for each process, which can be viewed below in Table 4.27. Figure 4.4 provides additional comparison of the average performances of each category. With a holistic average of 3.45, H_2O_2/O_3 earned the highest score, while TiO_2 photocatalysis received the lowest score at 2.11. O_3, O_3/UV, H_2O_2/UV, and the Fenton process were assigned scores relatively near the highest scoring process. TiO_2 photocatalysis clearly presents the lowest performance. As can be noted in Figure 4.4 the economic and social parameters appear to have the greatest variation, while the remaining parameters exhibit more consistent results.

Table 4.27 Parameter Ranking Summary

	AOPs					
Parameters	O_3	H_2O_2/O_3	O_3/UV	H_2O_2/UV	TiO_2	Fenton
Mechanical Reliability	4	4	3	3	2	2
Process Reliability	4	4	4	4	2	2
Flexibility	4	4	4	4	3	3
Adaptability	3	3	2	2	3	3
Energy Consumption	2	3	2	4	2	5
Average Engineering	3.4	3.6	3	3.4	2.4	3
Climate Change	2	3	2	4	2	5
Eutrophication	5	5	5	5	5	5
Toxicity	2	3	2	3	2	2
Average Environmental	2.25	2.75	2.25	3	2.25	3
Public Acceptance	4	4	4	4	2	2
Ease of Use	4	4	4	4	2	2
Economic Feasibility	5	4	4	3	1	4
Average Economic and Social	4.33	4	4	3.67	1.67	2.67
Comprehensive Average	3.33	3.45	3.08	3.36	2.11	2.89

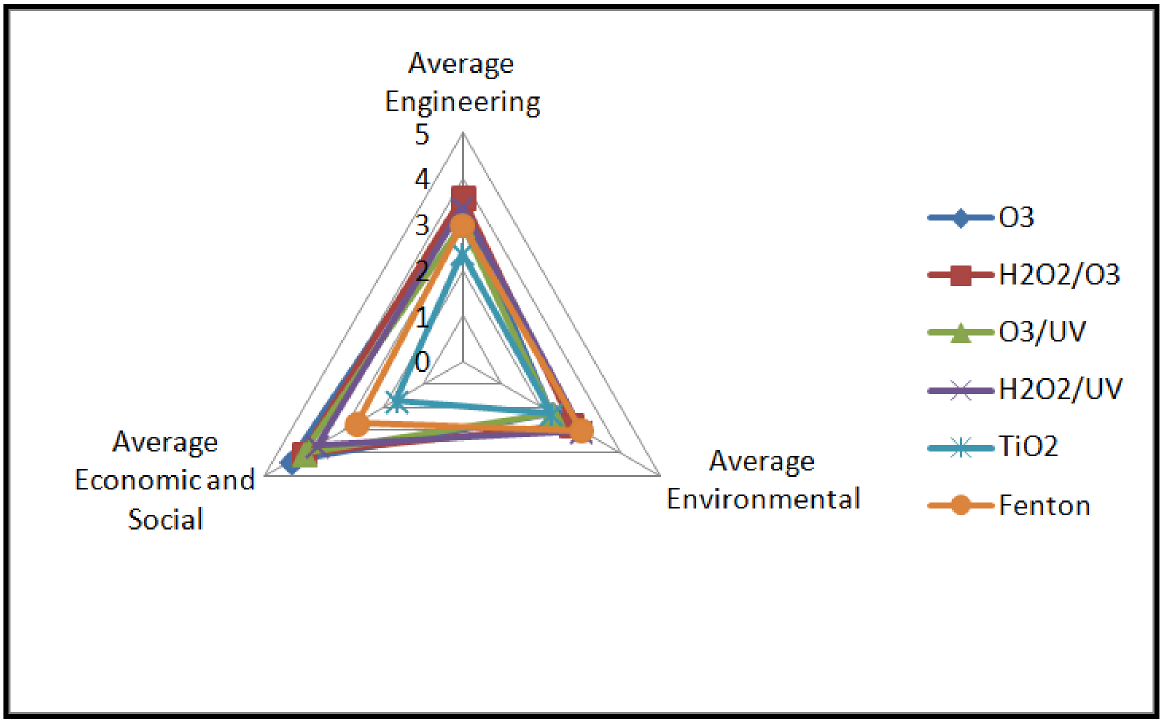


Figure 4.4 Comparison of Average Rankings

CHAPTER V

DISCUSSION

5.1 Potential for Disproportionate Comparison

A major issue to consider throughout this study is the reality that established processes and more modern processes are being compared on an equal level. Many of the parameters included in the examination were affected by characteristics representative of a novel technique. Newer processes, notably TiO_2 photocatalysis and the Fenton reaction, received lower rankings due to their more recent establishment. The other processes were supported by additional pilot scale and full scale studies, corroborating their worth. This is especially true amongst the economic and social parameters. It can be difficult to find endorsement or insight for processes that do not yet provide substantial verification of success and worth. It should be noted that a comparison based only on the most recent techniques could have produced a vastly different assessment. Furthermore, the same evaluation completed in the future could also present altered results following the addition of more extensive testing. Another point to make note of is the fact that the general population is becoming more open to new technology; therefore, the negative reflection on public acceptance to more modern processes may not be realistic.

It can be difficult to create an equal comparison between all of the processes discussed. A large variety of studies were considered, but the conditions of each investigation can vary easily. One key component is the constituent matrix of the influent to be treated. As mentioned in previous discussions, some pollutants are more readily degraded than others; therefore, processes operating in these conditions may be more likely to produce high rankings. Furthermore, some contaminants may be removed more easily by particular processes and conditions. A study completed upon a technique and a pollutant that it degrades well will obviously appear more adept than a technique being applied to a more recalcitrant compound. An examination of all processes across multiple source waters would be advantageous.

5.2 Additional Data Requirements

As the economic feasibility of the processes can be considered one of the most essential parameters and portrayed greater variation than many other parameters, a more in-depth analysis was deemed necessary. Additional data was acquired from Mahamuni & Adewuyi to create a comparison of the operational and maintenance costs, which is displayed in Table 5.1 and Figure 5.1 below. It quickly became clear that the poor performance seen previously by TiO_2 photocatalysis pertaining to economic feasibility is directly related to extremely high electrical costs. These costs are multitudes higher than that required by other processes. In order for TiO_2 photocatalysis to be considered a viable method, energy consumption and electrical costs must be reduced dramatically.

Table 5.1 Operational and Maintenance Costs

O&M Cost Breakdown						
AOP	Part Replacement	Labor	Analytical	Chemical	Electrical	Total
O_3	5.10E+02	4.54E+04	4.16E+04	0.00	4.09E+03	9.16E+04
O_3/UV	1.28E+06	5.94E+04	7.28E+04	0.00	2.84E+06	4.25E+06
H_2O_2/UV	2.78E+06	3.89E+04	3.12E+04	3.15E+07	6.17E+06	4.05E+07
TiO_2	2.95E+08	3.89E+04	3.12E+04	1.56E+04	6.56E+08	9.51E+08
Fenton	0.00	4.77E+04	3.12E+04	1.91E+06	0.00	1.99E+06

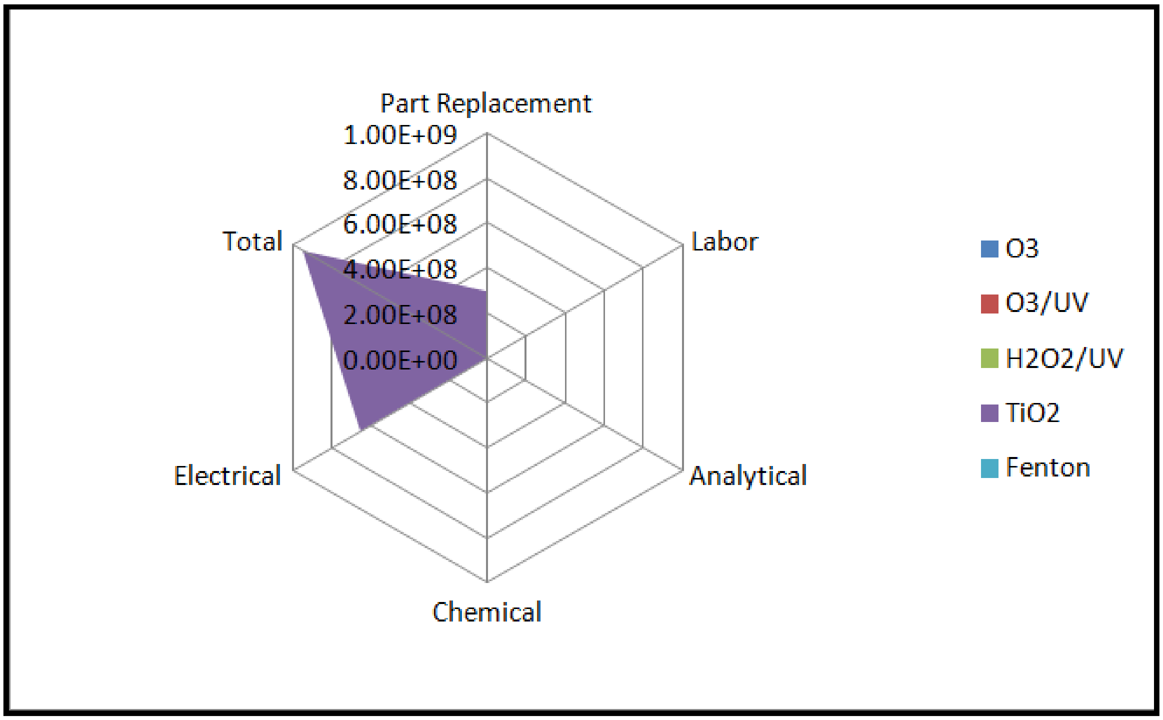


Figure 5.1 O&M Cost Comparison

The presence of degradation products is also a topic of concern. As these compounds are prospectively more harmful than their parent products, they must be treated with apprehension. Detection and identification of transformation byproducts is essential as these could have more detrimental effects on humans and the receiving environment (Gomez, et al., 2008). Improvements in this area can aid in the ultimate removal of these pollutants. Further research must be carried out to achieve a better understanding of these byproducts, as well as to determine the correct mechanisms of removal.

5.3 Proposed Ranking System Alterations

Another factor for consideration is the uniform significance of each parameter. All parameters included in this study were treated as if they had equal worth, which is not necessarily accurate. For example, economic feasibility is given the same merit as adaptability. While both parameters are essential, many would feel that monetary motives are the driving factor behind countless systems. Potentially, the parameters could be weighted according to their overall importance during calculation. However, the importance of parameters could potentially vary with the individual assigning their significance.

As discussed in Chapter Three, the ranking system employed used five levels of ranking. A more detailed study could be completed if, for example, ten levels of ranking were used. This would allow for a more in-depth comparison to be made. Many of the processes received similar scores in this examination, but this could potentially change if a larger number of ranking options were supplied. This would allow for the inclusion of more detailed information, making it probable that an enhanced, more robust study would result.

In addition, the ranking system includes a considerable amount of user bias. The personal opinions of the individual applying the rankings to each process may be affected by their personal experiences with certain processes or even the extent of his or her knowledge. Another individual could potentially assign vastly different rankings to processes based on his or her own influences. The bias found in this study was influenced by the biases of previous studies (NWRI, 2000). This is problematic when applying this ranking system for the use of others if it influences the overall accuracy of the approach. However, a straightforward solution to this problem may be difficult to identify. For example, surveys could be used to receive realistic opinions about the public's acceptance of each process, but this would also rely on the population surveyed. The input of several individuals knowledgeable in the area of concern could help to alleviate the issue.

CHAPTER VI

CONCLUSION

Upon examination of the various AOPs available for removal of emerging contaminants, a representative collection of technologies were chosen for further study. This includes: O_3, H_2O_2/O_3, O_3/UV, H_2O_2/UV, TiO_2 photocatalysis, and the Fenton reaction. As all of these processes have demonstrated successful degradation of emerging contaminants, and thus contribute to the reduction of the potentially harmful effects, additional parameters were chosen for an extended study. Engineering process parameters, environmental parameters, and economic and social parameters were selected for supplementary assessment. A constructed ranking system was then applied to classify the performance of each process.

Comparisons of individual parameter rankings, average category rankings, and holistic average rankings were used to determine the processes that function well not only technically, but also across a variety of other relevant parameters. Ultimately, H_2O_2/O_3 presented the highest ranking at 3.45. O_3, O_3/UV, H_2O_2/UV, and the Fenton process received similar average rankings (3.3, 3.08, 3.36, and 2.89 respectively), while TiO_2 photocatalysis achieved the lowest ranking at 2.11. These average rankings do not necessarily indicate superiority over other processes; however, as some parameters may be considered dominate. The influence of economic and social parameters was the greatest, because it showed the most significant variation in scores due to electrical costs.

This assessment effectively revealed not only the strengths of individual AOPs, but most importantly, their weaknesses. Newer technologies often received lower scores due to their relative lack of support or testing. This reinforces the fact that more detailed studies are required for these technologies. This research is also necessary to determine solutions for the other issues identified, such as high energy consumption and electrical costs. Faults in the ranking system were also recognized, including limited detail or accuracy and application of bias. Improvements could be installed if parameters were weighted according to their significance or if a wider range of ranks were available.

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