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Using Advanced Oxidation Processes To Solve Worldwide Issues and it's Limitations

Abstract

Advanced oxidation processes (AOPs) have been proven to help with removing organic and inorganic wastes with the use of hydroxyl radicals (HO ·). Constant advancements of technology, chemical use, and water consumption causes for pollutants, organic and inorganic waste, bacteria, pathogens, etc. to impurify the waster around the world. For this reason, AOPs have been found to be a faster and more reliable form of purifying water as hydroxyl radicals have a reaction rate of 10^8 to 10^{10} $M^{-1}s^{-1}$. Due to the characteristics and properties of AOPs, their strengths depend on the application they are being used in. Hence, in this paper, basic AOP methods have been thoroughly and visually explained along with other studies that have shown how different AOPs when treating textile wastewaters, swimming pools, and landfill leachate can prove to be beneficial. In textile wastewaters, effluents like dye and metal are mixed with other contaminates causing the water to be toxic and hazardous for humans and wildlife. It was found that when using ozone and UV AOPs, together, lowered the COD by 51.73% while also decreasing the colour, odour, and suspended solid in activated sludge. For swimming pools, humans excrete sweat, body oils, and other waste from their body and when mixed with water can cause harmful contaminants. The section also explores how swimming pools cannot be treated the same as drinking water and how UV light break bonds between organic compounds that result in bromine forming hazardous compounds like dibromochloromethane, bromodichloromethane, and bromoform. Lastly, it was found that Fenton and hydrogen peroxide (H_2O_2) processes are the best options for treating contaminants in landfill leachate however, the molar ratio for both Fe(II) and H_2O_2 should be carefully measured as excess amounts will cause for less hydroxyl radicals in the water treatment. In addition, due to hydroxyl radical's weak property of reacting with ammonia containing contaminants, sulfate radicals were used and measured to have a 100% removal rate of ammonia and a reduction of COD by 91% in acidic conditions, pH 3.0 to 4.0.

Keywords – textile, waste, AOP, treatment, COD, BOD, waste removal

Introduction

In today's world, water is not only used for drinking, bathing, and cooking, but now also used to produce paper from wood, steel for automobiles, and renewable energy. Since the human population is constantly growing and water-based technology is evolving, the water starts to become more polluted and dangerous for our health the more it is used and not cleaned. This is called wastewater, which is produced, simply, by doing regular day-to-day processes such as going for a shower, doing laundry, flushing a toilet, etc. Commutatively, any activities in the domestic, industrial, commercial, and/or agricultural realm can contribute greatly to wastewater. This causes for organic and inorganic waste to build up and toxify the water. To clean the waste and contamination in water, oxidation processes have been used to ensure that water is clean and livable for all water-dependent and air-breathing creatures.

Oxidation can be broken down into 3 categories – conventional chemical oxidation process, oxidation process at high temperatures, and advanced oxidation processes. In oxidation, it results in an element losing their electrons, therefore, in conventional oxidation processes, molecules like chlorine, chlorine dioxide, potassium permanganate are used which produce slower chemical kinetic reactions than oxidation processes that contain hydroxyl radicals. Furthermore, using higher temperatures for oxidation causes the diffusion rate to increase which causes the rate of oxidation to increase as well. From this it was found that the oxidation rate and temperature were proportional to each other. Moreover, in advanced oxidation, the goal is to generate hydroxyl radicals that speed up the rate of oxidation immensely. Some characteristics hydroxyl radicals possess, in terms of oxidation, include powerful oxidants, easily generated, not selective, highly reactive, harmless, and can control the rate of the reaction.

As mentioned earlier, chemical oxidation refers to an element losing their electrons whereas advanced oxidation refers to the same process but at a faster reaction rate – approximately billions of times faster than regular chemical oxidation in natural environments [1]. AOPs use radicals, specifically hydroxyl or sulfate, to remove a variety of wastes in water like organic and inorganic contaminants. This reaction occurs by using hydroxyl radicals ($HO\cdot$) to remove a hydrogen atom from an organic molecule ultimately producing an organic radical (R-). Advanced oxidation processes are now also utilizing sulfate radicals ($SO_4\cdot^-$). In Figure 1, a general reaction is shown to demonstrate how the hydroxyl group is used to separate an organic compound.

$R-H$	+	$HO\cdot$	$\rightarrow$	H_2O	+	$R\cdot$
Organic Compound		Hydroxyl Radical		Water		Organic Radical

Figure 1: General Overview of AOPs

Due to organic compounds nature of containing molecules like carbon and hydrogen, using a hydroxyl radical, which is a strong chemical oxidant, can react with majority of the organic compounds' hydrogen atom resulting in water and an organic radical. In AOPs, the hydroxyl radical also aids in the decomposition of organic compounds which reduces the pollutant in the water from a few hundreds' PPM (parts-per million) to less than 5 PPB (parts-per billion) [3]. It should be noted that PPM and PPB are both representing a concentration fraction, thus, PPM is a thousand times greater than the concentration in PPB [4]. The formula for PPM and PPB can be found in Equation 1.

$$\text{PPM} = \frac{Mass\ of\ Solute\ (g)}{Mass\ of\ Solution\ (g)} \text{ x } 10^6 \qquad \text{PPB} = \frac{Mass\ of\ Solute\ (g)}{Mass\ of\ Solution\ (g)} \text{ x } 10^9 \qquad \text{(Eq. 1)}$$

Back in the 1980's, advanced oxidation processes (AOPs) were presented and performed for treating municipal and industrial wastewaters [2]. Before advanced oxidation processes were applied to treat wastewater worldwide, it was first proposed for potable water treatment. This was a huge milestone for AOPs because using it to decontaminate the waste in drinking water proved that it could be utilized for bigger bodies of water. Using AOP in filtering water was found to help destroy toxic synthetic organic matter (SOM) like pesticides and herbicides, fuels, solvents, and drugs. Commonly used oxidants like chlorine and ozone are used for both decontaminating and disinfecting wastewater, however, AOPs sole purpose is to eliminate/remove organic and inorganic contaminants and make the water safe.

It was found that using AOPs with a catalyst like ozone (O_3) or ultraviolet (UV) radiation yielded to be the most effective way of treating wastewater [5]. AOPs have become one of the primary solutions for treating wastewater as it was found that industries are producing/releasing harmful chemicals in the effluent which is harmful to both human beings and the aquatic biota. Thus, these chemicals need to be treated rapidly and effectively to keep the air and water safe.

Water is being used everyday and is also being contaminated. Hence, to keep the water clean and safe for all beings and creatures who depend on water, it is important to treat wastewater, locally and worldwide. Therefore, AOPs are being applied to wastewater around the world, however, to understand how they are used thoroughly and correctly, an in-depth explanation of the various AOPs that currently exist will be discussed.

Types and Characteristics of Various AOPs

Pairing AOPs with different catalysts allow for different harmful chemicals to be removed in the wastewater. Depending on the type of AOP used, this can alter the chemicals being targeted. The reason for this is because when changing the type of AOP, the physical and chemical properties change the state of the pollutants and condition of the wastewater. Since various chemicals are being used, different molecules will react differently when mixed with other types of molecules. It should be noted that the chemicals in the wastewater being treated should be known so that harmful by-products are not produced. Therefore, the strength of an AOP is based on how the chemicals in the AOP method react with the effluent. The various common AOP types will now be discussed in greater detail.

i. <u>Hydroxyl Radical – Based AOPs</u>

In AOPs, the hydroxyl radical is used as it possesses a behaviour trait of non-selectivity. This means that it does not favour one molecule over another, and it can rapidly react with any/other species that may be present in water or wastewater. In water treatment, hydroxyl radicals were found to be the best oxidizing agent because of their oxidizing potential in acidic (pH 0) and basic (pH 14) solutions of 2.8 V and 1.95 V, respectively [2]. It should be noted that the unit for oxidizing potential is in voltage because electrons are being lost and gained in these reactions and they carry some electrical charge. These values were found using a saturated calomel electrode (SCE) which is a common reference electrode. In Table 1, a table of common oxidants are listed along with there electrochemical potential in volts (V) to better illustrate the strength hydroxyl radicals have over other oxidizing agents in an acidic solution.

Table 1: Oxidation Potential, in voltage, of common oxidizing agents in acidic solution [Yang et al., 2001]

Oxidants	Chemical Formula	Electrochemical Potential (V)
Free Radical	$\cdot OH$	2.8
Ozone atom	O	2.42
Ozone	O_3	2.07
Hydrogen Peroxide	H_2O_2	1.78
Potassium Permanganate	$KMnO_4$	1.7
Chlorine Dioxide	ClO_2	1.57
Chlorine gas	Cl_2	1.36
Oxygen	O_2	1.23
Bromine	Br	1.09
Hypochlorous Acid	HOCl	0.95
Sodium Hypochlorite	NaOCl	0.94
Iodine	I	0.54

Fluorine (F_2) has an oxidation potential of 3.0 however, it is not the best oxidant when dealing with wastewater as it was found that fluorine is harmful to plants, even at small doses, and harmful to humans in surplus amounts [6]. Since fluoride is already in the water and wastewater, limiting the consumption of fluoride is generally better [7]. Fluoride ions (F^-) have been used with calcium ions (Ca^{2+}) to form calcium fluoride (CaF_2) which precipitates and helps breakdown solid inorganic coagulants [8]. However, with hydroxyl radicals reacting with organic compounds to produce water and an organic, as seen in Figure 1, this is the best radical for water and wastewater treatment solution.

It was also measured that the reaction rate order of using hydroxyl radicals ranged from 10^8 to 10^{10} $M^{-1}s^{-1}$ [2]. When hydroxyl radicals interact with organic pollutants/compounds, they produce carbon centered radicals ($R\cdot$ or $R\cdot$ - OH). Once oxygen (O_2) is presented in the solution, these radicals are changed to organic peroxyl radicals ($ROO\cdot$). From here, all the radicals then start to react further and create other reactive molecules like hydrogen peroxide (H_2O_2) and super oxide ($O_2\ \cdot^-$). This aids in the decomposition of organic compounds to remove waste from water and wastewater. Since hydroxyl radicals cannot live long, they are paired with other oxidizing methods, on site, like UV radiation, ultrasound, hydrogen peroxide, ozone, and catalysts like Fe^{2+}.

ii. <u>Ozone-Based AOPs</u>

Ozone, O_3, has a strong electrochemical potential which was found to be 2.07 V using a SCE, as seen in Table 1. Although ozone has characteristics of a strong oxidizing agent, it is selective in terms of what molecules it reacts with. Ozone is produced through a series of chemical reactions that uses heat and sunlight between NO_x and a Volatile Organic Compound (VOC) [9]. With ozone's reaction rate of $1.0x10^3$ $M^{-1}s^{-1}$, ozone works best when it needs to react with ionized or decomposed organic compounds as it can produce hydroxyl radicals under certain conditions [2,10]. In Figure 2, when ozone is added into water, it displays how a hydroxyl radical, and 4 oxygen molecules are produced.

$3O_3$	+	$H_2 0$	$\rightarrow$	$HO\cdot$	+	$4O_2$
Ozone		Water		Hydroxyl Radical		Oxygen

Figure 2: Ozone-Based AOP producing a hydroxyl radical.

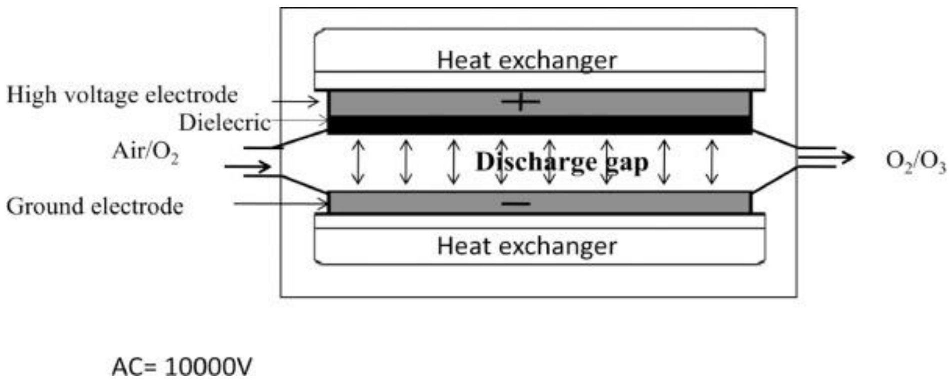
Due to hydroxyl radicals having a high order reaction rate, of 10^8 to 10^{10} $M^{-1}s^{-1}$, it is important to produce them for water and wastewater treatment. Therefore, ozone can also be paired with hydrogen peroxide, known as a peroxone (O_3/H_2O_2) system to produce hydroxyl radicals. In Figure 3, a breakdown of how the peroxone system produces the hydroxyl radicals are shown.

H_2O_2	$\rightarrow$	${HO_2}^-$	+	H^+
Hydrogen Peroxide		Hydroperoxyl Radical		Hydrogen Ion

${HO_2}^-$	+	O_3	$\rightarrow$	$HO\cdot$	+	${O_2}^-$	+	O_2
Hydroperoxyl Radical		Ozone		Hydroxyl Radical		Oxide Ion		Oxygen

Figure 3: Production of hydroxyl radicals using hydrogen peroxide and ozone.

The hydrogen peroxide is produced using ozone with an ultraviolet irradiation through a process of ozone photolysis. Through studies, it was found that the production of ozone was more environmentally friendly than chlorine and that ozone is a safer yet more reliable alternative for treating wastewater that has organic complexed metals [11]. Ozone production and water treatments involving ozone need to be done on site, in situ, as it is an unstable gas. This, ozone generation, can be done on site through using the corona discharge process [11]. In this process, a high voltage is applied to oxygen in the gaseous phase which creates oxide radicals (O·). From here, the oxide radicals are bonded with oxygen to create ozone. Figure 4 presents (a) the visualization of the corona discharge process, (b) the interaction between the high voltage discharge and oxygen, and (c) the generation of ozone.



(a) Visualization of the Corona Discharge Process [Rekhate et al., 2020]

O_2 Oxygen Gas	$+$	$high\ votage$ Electric Spark	$\rightarrow$	$2O\cdot$ O Radicals

(b) Interaction of Oxygen gas and high voltage discharge

O_2 Oxygen Gas	$+$	$O\cdot$ O Radical	$\rightarrow$	O_3 Ozone

(c) Ozone generation through the corona discharge process

Figure 4: (a) the visual of the corona discharge processes [Rekhate et al., 2020], (b) the interaction between the high voltage discharge and oxygen, and (c) the generation of ozone.

iii. UV-Based AOPs

When using UV AOP methods, titanium dioxide (TiO_2) is a catalyst that is often used. Other photocatalysts can be used such as ZnO, Fe_2O_3, WO_3, and other semiconductors.

However, TiO_2 is used more often due to its superior characteristics and chemical properties of toxicity, cost, availability, photo-corrosion resistance, and catalytic efficiency [12]. When TiO_2 is used with UV AOP methods, the particles become excited, thus creating positively charged holes in the valance band (hv^{+}_{vb}) and a negative charge, through electrons, at the conduction band (e^{-}_{cb}) [2].

TiO_2	+	hv	→	e^{-}_{cb}	+	hv^{+}_{vb}
Titanium Dioxide		Light (energy)		Conduction Band		Valence Band

Figure 5: The excitation formula of titanium dioxide

The excited valence is combined with hydroxide (OH^-) on the surface and absorbed water, to produce hydroxyl radicals.

$$hv^{+}_{vb} + OH^{-}_{(surface)} \rightarrow OH\cdot$$

$$hv^{+}_{vb} + H_2O_{(absorbed)} \rightarrow OH\cdot + H^{+}$$

UV light can used with hydrogen peroxide to help create more hydroxyl radicals.

$$H_2O_2 + hv \rightarrow 2OH\cdot$$

This can be very useful when trying to increase the number of hydroxyl radicals in water and wastewater to allow speed up in the purification treatment.

iv. Fenton-Related AOPs

Iron, Fe^{2+}, is commonly used when discussing Fenton-based AOPs, hence the name. This metal utilizes hydrogen peroxide to produce hydroxyl radicals that are used to treat water and wastewater. Ferryl ions are also produced in this process which then react with H_2O_2 to initiate a series of chemical reactions, Figure 6.

$$Fe^{2+} + H_20_2 \rightarrow Fe^{3+} + OH\cdot + OH^{-}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO^{\cdot}_2 + H^{+}$$

$$OH\cdot + H_2O_2 \rightarrow HO^{\cdot}_2 + H_2O$$

$$OH\cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}$$

$$Fe^{3+} + HO^{\cdot}_2 \rightarrow Fe^{2+} + O_2H^{+}$$

$$Fe^{2+} + HO^{\cdot}_2 + H^{+} \rightarrow Fe^{3+} + H_2O_2$$

$$2HO^{\cdot}_2 + H_2O_2 + O_2$$

Figure 6: Fenton-Based AOPs and the series of reactions that occur.

When Fe^{3+} is produced, it starts to form sludge in the water and wastewater which is unwanted and can be hard to treat. Thus, the complexity of the water and wastewater treatment increases as the sludge needs to be separated before it can be treated. The hydroxyl radicals that are produced in the Fenton AOP work best in acidic conditions; a pH level lower than 7 [2]. Furthermore, when Fenton processes are combined with UV irradiation or photo-Fenton reactions, UV-induced reduction can help address the sludge as it dissolves Fe^{3+} to Fe^{2+}.

Worldwide Application

As technology is constantly evolving, this means that systems and combinations of AOPs are too. They are being designed and vigorously tested to ensure the best results and the best systems exist to treat water and wastewater. In the section above, it was crucial to understand how different types of AOPs worked as there is not one specific AOP that is superior to another. It is all dependent on the application. It is no surprise that due to pollution and the release of organic pollutants from industrial discharges cause the water to become filthy and unclean ultimately effecting humans and the aquatic biota. Due to this, there are sensitive analytical tools and methods that take place to measure the concentration of organic pollutants, in the water, even in µg/L concentrations [5]. Organic pollutants are measured by quantifying the total amount of carbon (TOC), chemical oxygen demand (COD), and biological oxygen demand (BOD). The total amount of carbon (TOC) is used to determine the number of carbons that are present in the organic compound whereas COD is used for identifying the amount of oxygen that a reaction will consume in a definite solution. Common applications of COD are when determining the number of pollutants in surface waters, like lakes and rivers, that can be oxidized. Lastly, BOD is used for examining the amount of oxygen that will be consumed/used by bacteria and other microorganisms while decomposing organic waste [13]. All these analytical tools can be used for ensuring the quality of water and wastewater treatment. In industrial wastewater, many organic pollutants are present and exposed to the water daily. Through studies and multiple treatments of wastewater, it was found that industrial's wastewater contains phenolic compounds that are dangerous because of its high toxicity and displeasing smell and taste. Furthermore, some toxic effects phenolic compounds have on humans is that it becomes very reactive, if consumed, as the intermediate stages that occur once the compound is metabolized creates double bonds with proteins to spread toxic compounds to the entire body.

i. Choosing the Best AOP

AOPs are widely known to use hydroxyl radicals to help treat wastewater from dangerous organic contaminants and toxins. To ensure the best AOP method is chosen, it is vital to ensure that certain aspects like concentration of hydroxyl radical, target pollutant, and radical scavenger compounds are all identified. In addition, a wastewater's pH, pollutants present, and the ions that exist in the water should be known. At Genesis Water Technologies (GWT), a water company who strives to use AOPs to remove contaminants and waste, have identified categories of waste that their technology focuses on to remove. Some categories that were mentioned are: pharmaceuticals, pesticides, personal care products, and pathogens [14]. It was noted that drawbacks to AOPs such as potential by-product formation is a crucial step when choosing an appropriate AOP system.

ii. <u>Factors to be Considered</u>

As mentioned above, when choosing an AOP system for a specific wastewater, the compounds in the water must be identified and analyzed before treating it. Thus, the **water composition** should be carefully analyzed as it will be undergoing numerous chemical reactions that can produce harmful by-products if the pollutants in the waters are not determined correctly.

Secondly, the **purpose of treatment** should be known as there are different regulations based on what the water is being used for. A prime example of this is when comparing environmental water with drinking water. The regulations for environmental water may not need to be vigorously treated and is deemed to be safe and abides to the guidelines whereas drinking water would need to be treated numerous times to ensure that it is safe to drink for humans. This is important to identify because environmental regulated waters may only require a single/simpler process whereas stricter water regulations need to be treated with more than one type of process.

Next, the **UV dosage** should be taken into consideration as over exposure can cause harmful economical effects. The UV exposure should be correctly calculated to help manage energy and to avoid wasting money. This ties in with choosing the correct **chemical dose** as well because if too low or high of a dose can provide undesired results and safety standards.

Lastly, the **cost** of AOPs can be extremely high. In 2016, the AOP technologies averaged to be $4.4 billion whereas now, in 2021, the AOP technologies averaged $6.5 billion with a compound annual growth rate (CAGR) of 8% [15].

iii. <u>How Companies Select the Right AOP System</u>

In industrial wastewater, depending on what the company does, the company takes into consideration of all the factors mentioned above along with the types of chemicals they are constantly producing. For example, if a company is known for producing pharmaceutical wastes, they would choose an AOP system that helps mitigate those types of waste along with keeping the water composition, purpose of treatment, UV dosage, chemical dose, and cost factors in mind. Common questions asked are: Is the system effective? How hard is the system to install and operate? How much water is treated?

For system effectiveness, being able to measure the quantifiable amount of AOP being produced is key. For instance, when using ozone and UV, the exact number of hydroxyls can be determined. From this, using the corona discharge process, ozone can be generated to produce more hydroxyl radicals without the use of the UV bulb. This allows companies to save energy and cost money. There are third-party validation systems that help ensure all the organic wastes and harmful bacteria are treated and removed – NSF-50 certified.

When using any system, the company needs to ensure that it is easy to install, maintain, and operate. When using ozone and UV AOP systems, constant maintenance and servicing needs to be conducted for safety and efficiency purposes. Majority of the AOP systems today compliment an All-in-One design which incorporates all the mechanics in a casing. This allows for easy transportation, if needed, along with easy installation processes. Systems also have a display that shows the operator the system is working correctly or if servicing is required. It continuously checks the ozone, UV, and power source. Some current systems also have a one-line input and a one-line output to help with the installation process as it aids in reducing errors and increases servicing times.

The amount of water being treated is dependant on the system being installed, however, ideally, 100% of the water should be passing through the system to be treated. In addition, since hydroxyl radicals are short-lived, the radicals would need to be put in a full flow of water as soon as they are produced to achieve their objective. Therefore, AOP companies have designed AOP systems with a full-flow plumbing design that treats all the water and uses the hydroxyl radicals.

iv. <u>Results of Combined AOPs from a Water Treating Company</u>

A water technology and solutions company, SUEZ, heavily relies on using ozone, UV, and H_2O_2, for their water treatments and have provided a breakdown of why using them in combination with each other is so important [16]. In Figure 7, the effectiveness of when just UV or ozone is used for treating water and wastewater can be seen, as opposed to when they are used in combination.

Figure 7: Using UV and ozone separately versus with AOPs [Suez, 2021]

From the figure, it is evident that when UV is used on its own, contaminants like organic pollutants, iron, manganese, taste/odour, and organic matter are not effectively removed but viruses, bacteria, and other pathogens are. Like mentioned previously, it is very crucial to understand the application of the wastewater being treated before selecting an AOP method. SUEZ is a water technology company that aims to remove specified target pollutants like 1,4 Dioxane, hormones, atrazine, ibuprofen, etc.

v. <u>Examples</u>

Textile Wastewaters

In industrial wastewaters, it is common to see textile wastewaters. Textiles can include, but are not limited to, clothing, bags, baskets, and accessories. This means contaminants like dye and metal are mixed with other contaminants in the water to produce hazardous waste that needs to be treated. Although countries like China, India, USA, and the European Union are top leaders for producing and exporting their textile goods, the amount of effluent that contains dye is unacceptable and can become difficult to degrade. Thus, certain measures need to be taken. First, a research was conducted where a breakdown of how the textile productions is made [17]. Figure 8 displays the various steps that are required in a textile company and the various pollutants and waste that is created.

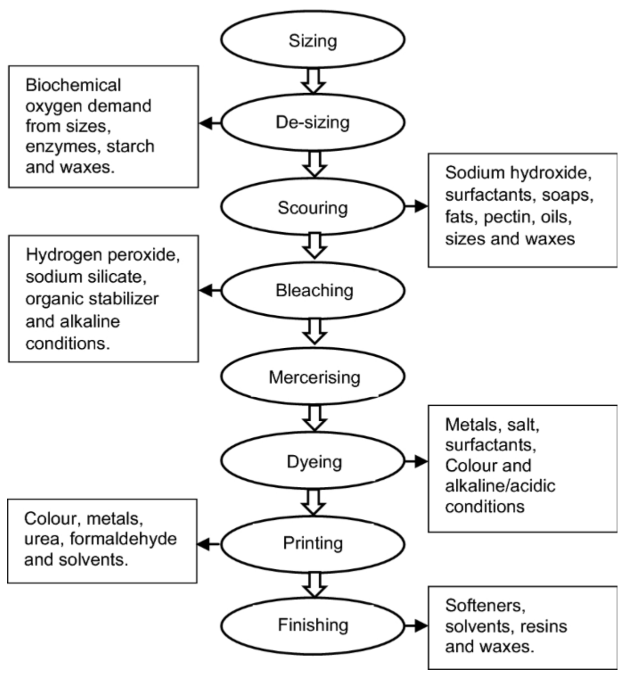


Figure 8: Steps that occur in a textile company and the waste discharged into the water [Yaseen et al., 2018]

Once the product has been dyed and finished, the amount of dye textile industry effluent becomes unacceptable due to its toxic-like characteristics and appearance. This unacceptable effluent then contaminates the soil and surface water causing wastewater challenges. Therefore, to protect humans, aquatic, and non-aquatic creatures it is vital to treat textile wastewater.

Dye effluents can be categorized by having strong colour, high pH, suspended solids (SS), COD, BOD, temperature, and salts [17]. Since it is important to identify what organic waste and contaminants are in the water, a table from Figure 8 was developed to determine the average value of the dye effluents being discharged into the water.

Table 2: Average dye effluent discharge in wastewater [Yaseen et al., 2018]

Process	pH (–)	Colour (ADMI)	TSS (mg/l)	TS (mg/l)	TDS (mg/l)	COD (mg/l)	BOD (mg/l)
Desizing				16,000–32,000		4600–5900	1700–5200
Scouring	10–13	694		7600–17,400		8000	100–2900
Bleaching	8.5–9.6	153		2300–14,400	4800–19,500	6700–13,500	100–1700
Mercerising	5.5–9.5			600–1900	4300–4600	1600	50–100
Dyeing	5–10	1450–4750		500–14,100	50	1100–4600	10–1800

ADMI
American Dye Manufactures Institute unit

TSS
Total suspended solids

TDS
Total dissolve solids

The reason due to high COD, BOD, TSS, TDS, and pH is due to the organic and inorganic contaminants/chemicals like equipment, carriers, surfactants, precipitates, rating agents, etc.

The purpose of the study is to ensure that the waste being discharged into the effluent is not harmful to anyone and is following regulation. Thus, a trial AOP system was used to determine if it was viable to mitigate the amount of dye effluent. In Figure 9, the trial AOP system being tested is shown along with Table 3, which explains the functions of parts in the system.

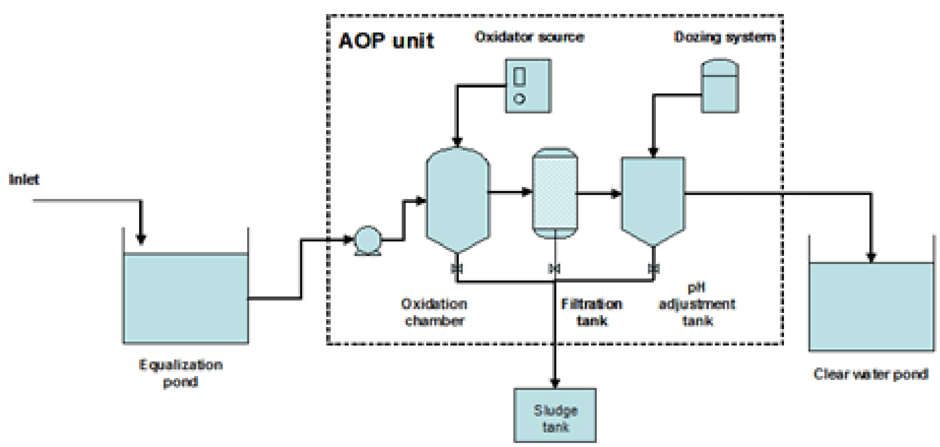


Figure 9: Schematic of an AOP trial system [Hutagalung et al., 2020]

Table 3: Functions and specifications of the given trial AOP system [Hutagalung et al., 2020]

No	Part	Specification	Function
1	Inlet pump set	Multi-stage/Centrifugal/Submersible 1 piece with a capacity of 40 L/minute, head 15 m, and power at 220V, 1 phase, 50Hz	drive the waste for the treatment process
2	oxidizing section	Fiberglass material, capacity of 8 SCFH	decompose chemical compounds and kill microorganisms in the waste
3	oxidation chamber	SS material, 1000 L capacity and atmospheric pressure	absorbing micropollutants which have not been deposited in the previous process
4	filtration tank room	SS material, 500 L capacity, and atmospheric pressure	absorbing micropollutants which have not been deposited in the previous process
5	pH adjusted tank	SS material, 500 L capacity	controlling pH

Due to different AOP techniques not being universally good for all types of wastewaters, it is important breakdown the system through several physical, chemical, and biological processes to treat the contaminants. The process used in this test to treat textile wastewater was ozone and UV. The production of hydroxyl radicals when ozone and UV, when used separately, is shown in Figure 4, however, when used together, the following chemical reactions occur:

$$O_3 + h\nu + H_2O \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + h\nu \rightarrow 2(HO\cdot)$$

$$2O_3 + H_2O \rightarrow 2(HO\cdot) + 3O_2$$

Ozone was used because it is a good oxidizer at high pH values, and from Table 2, it is seen that dyes in wastewater have a pH from 5.0-10.0 [17,18]. Ozone, at a pH greater than 11.0 can react with both organic and inorganic compounds [18].

Ozonation is also viable when discussing textile wastewater as it does not change the pH of the solution since no chemicals are being added. However, a disadvantage is that since ozone is being generated through the corona discharge process, discussed in Figure 4, it becomes difficult to extract or remove the excess remaining ozone particles in the water. Furthermore, the study mitigates this by using an efficient electrochemical ozone generator where the appropriate amount of ozone is produced based on the water being treated. The results of the findings can be seen below, Table 4.

Table 4: Findings of the trial AOP system [Hutagalung et al., 2021]

No	Sample	pH	COD	SS	Color
1	Activated sludge	7	15,693	9,225	heavy
	After process (homogenous)	7	15,504	5,100	
	After process (sediment)	7	7,956	687	
2	ex jet dyeing medium color T / R (ozone + UV)	7.9	2,346	162.5	heavy
	after the process of 10 minutes PAC was deposited	5.6	476	8	light
	After process (30 minutes)	6.9	5,916		
	After process (60 minutes)	7.2	5,022		
3	Ex Desizing non-color scouring (ozone)	7.1	28,254	162.5	moderate
	After process (60 minutes)	7	23,511		
4	Spunpolly (weight reduce) (Ozone + UV)	8.6	16,167	75	light
	After process	7	8,364	87.5	light
5	Mud from coagulation	5.9	7,089	9,075	heavy
	After process	5.7	7,293	8,850	heavy
6	C 26 (Resin finish) (Ozone + UV)	6.1	28,458	1,600	light
	After process	5.2	28,050	1,237	light
7	Concentrated color waste	7.9	1,224	62.5	heavy
	After process (homogenous)	7.2	1,648	46	decreased
	After process (sediment)	7.2	1,360	50	light

Once the experiment was conducted it was concluded that the AOP system worked as the COD and SS was seen to be decreasing, for the "After process" rows. Meaning it increases the dissolved oxygen concentration making the water less harmful to other life forms and the suspended solids/contaminants are being dissolved. It was calculated that there was a 51.73% decrease, in COD, from the original value of 16.167 mg/L to 8.364 mg/L after the process [18]. In Figure 10 a before and after picture of a) the decrease of SS in activated sludge, b) change in colour, and c) after processing the solution can be seen.

a) *b)* *c)*

Figure 10: A before and after picture of a) the decrease of SS in activated sludge, b) change in colour, and c) after processing the solution [Hutagalung et al., 2021]

From this study, it was concluded that textile industry waste can be reused using the trial AOP system that was designed as it lowered the COD by 51.73% while also decreasing the colour, odour, and suspended solid in activated sludge. Therefore, AOP for treating textile wastewaters serve to be more beneficial than traditional processing methods for textile industry waste.

Swimming Pools

For many decades, chlorine has been used to help remove and destroy contaminants in pool waters like viruses and bacteria, however, chlorine can react with organic matter which can potentially create toxic disinfection by-products (DBPs). Some of these DBPs include trihalomethanes (THMs), chloramines (CAMs), and haloacetic acids (HAAs) [19]. Once this was discovered, rapid advancements in the purification and treatment of swimming water were made. A study conducted 10 disinfection methods, to pool water, to observe how it would react and if any hazardous by-products would be produced. They discovered that when chlorinated water was mixed with a photolysis of hypochlorous acid (HOCl), hydroxyl chlorine radicals were produced which helped with removing contaminates, organic waste, and bacteria from the swimming water. In addition, due to nitrates ability to release hydroxyl radicals when exposed to UV light and its presence in natural water, this AOP method has also been used for disinfecting and cleaning pools [20]. This paper will indulge on how chlorine, nitrate, and hydrogen peroxide, as radical initiators, can be affected with UV irradiation. The study used sample concentrations of real swimming pools and measured the before and after concentrations of the DBPs. The experiments used a cell test-kit that measured the amount of free and total chlorine present in the solution. The 3 pool waters that were collected consisted of 2 main practice pools and one therapy pool (hot tub). The 2 practice pools had an average temperature of 26 °C and the therapy pool had a temperature of 34 °C [20]. The heat from the therapy pool is higher as it operates with a medium pressure UV lamp. The tests were conducted immediately after the samples were collected for the pH and free and combined chlorine. It should be noted that combine chlorine is referring to chlorine that has already been used to sanitize the pool waters whereas free chlorine refers to the chlorine that has not been used yet. The UV treatment of the pool water was conducted using a quasi-collimated beam apparatus. Figure 11 displays the goal the apparatus serves.

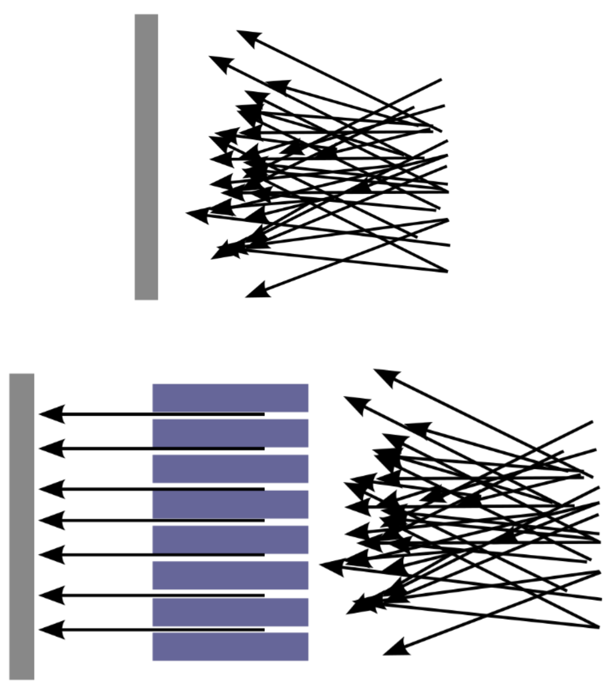


Figure 11: The purpose of using a collimated beam apparatus [Wikipedia, 2016]

Due to waters refractory property, when light is shined through water, the light starts to bounce and scatter randomly. Therefore, a collimated beam apparatus helps minimize the propagation of the rays to allow the light to travel in a straight line. Ideally, if no divergence occurred and perfect collimated beams were perfectly aligned, the light path would go in a straight line. However, since this is not an ideal world, the light rays minimally propagate which can cause discrepancies if repeated over trials. From the 3 indoor pools, the ranges for the pH were 7.10 to 7.24, TOC of 1.58 to 2.14 mg/L, free chlorine of 0.44 to 1.37 mg/L, and combine chlorine of 0.17 to 0.36 mg/L. From the experiments, it was found that longer exposure to UV light caused more chlorine consumption in pools. Moreover, the concentration of nitrite increased once the chlorine in the pool water was depleted, according to Weng et al. [20]. Although it was found that THMs were the highest DBP present in the pool, it was concluded that UV light broke down bonds between organic compounds and bromine forming hazardous compounds like bromoform, dibromochloromethane, and bromodichloromethane were produced. Figure 12 depicts how the organic compound bonds are broken with the use of UV light and how toxic by-products are produced.

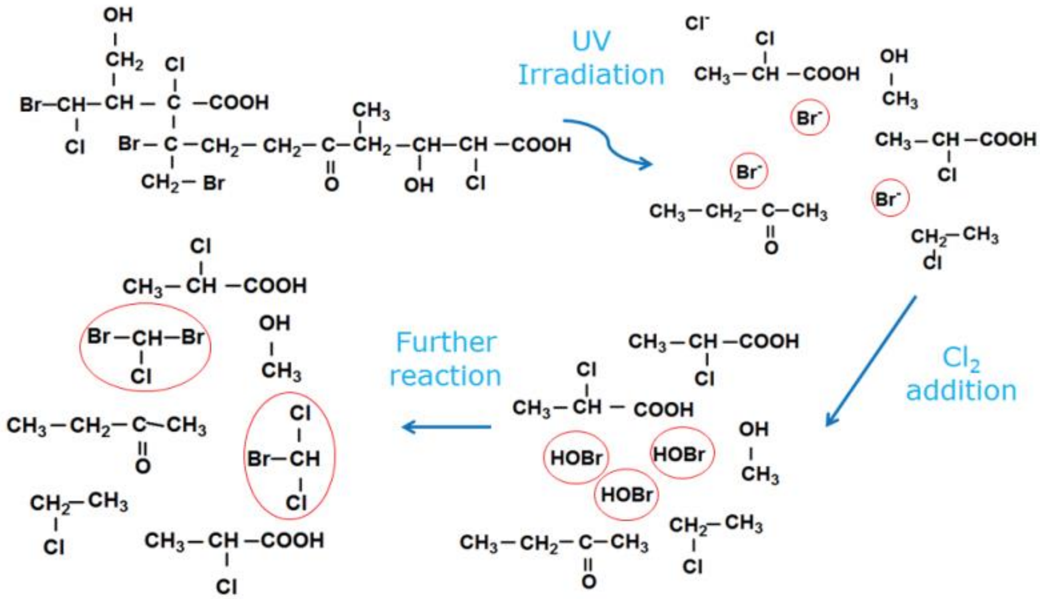


Figure 12: Chemical reactions of brominated species formation [Aikaterini et al., 2015]

An often misconception is that pool waters should be treated the same as drinking water. However, the DBP present in swimming water and drinking water differ as swimming water has a constant change in DOC and organic compounds which are released by swimmers. Table 5 will display the different reported values of drinking water and swimming water.

Table 5: Differences between drinking water and pool water [Ilyas et al., 2018]

Factors	Drinking Water	Pool Water
TOC	0.3-1.4 mg/L	0.5-7.0 mg/L
Nitrate-Nitrogen (NO_3^--N) Level	1.1-1.9 mg/L	6.6-23.8 mg/L
Total Nitrogen (TN)	0.1-0.3 mg/L	3.6-12.3 mg/L
Temperature	25-35 °C	1.0-23 °C
Free Residual Chlorine (FRC)	0.03-57 mg/L	0.24-1.4 mg/L
pH	6.8-7.8	7.6-8.2

The study concluded that the formation of THM is amplified when using UV treatment after chlorination and that the radicals formed do not cause the formation of THM. In addition, it was found that UV light can cause hazardous by-products such as brominated THM.

Moreover, CMP, a water treating company, developed a sanitizing machine that utilizes both ozone and UV light in swimming pools. They claim to destroy viruses, bacteria, organic, and inorganic pool contaminants with their AOP system. They also say that it removes odors and irritations one may feel when due to the formation of chloramines from sweat. Lastly, it reduces the chlorine chemical used while maintaining a safe residual in the pool for saving money and time [21]. Table 6 illustrates a list of advantages AOP methods have over chlorine in swimming pools.

Table 6: Advantages of using AOP with chlorine instead of just chlorine [Blue Haven Pools, 2019]

Number	Reason	Explanation
1	Unmatched Cleaning Power	AOP hydroxyl radicals destroy 99% of waste
2	Greater Water Clarity	AOP produces micro-flocculation which forms non-visible clumps, to humans, but is trapped by the pool filter
3	Comprehensive Disinfection	Known to remove different types of waste that is produced by humans such as sweat, body oils, bacteria, etc.
4	Safer, gentler sanitization	Dangerous to microorganism and toxic contaminates, but not to humans.
5	Faster Performance	Chlorine takes hours to kill, but AOPs are almost instantaneous with the hydroxyl radicals.
6	Lower Chemical Demand	Drastically reduce the level of chlorine
7	Environmentally Safe	Removes waste and does not for toxic by-products

Landfill Leachate

Due to AOPs discovery in 1980, until now, different AOP methods have been applied and recorded for treating municipal wastewater and landfill leachate. Since the efficiency of AOP treatments rely on chemical properties of contaminants, operating conditions, and pH, it becomes difficult to generalize wastewater and thus, in this report, landfill leachate will be further discussed. Landfills have been a common way for disposing municipal solid waste, but the concern arrives from the landfill's production of leachate [23]. In landfill wastewater, leachate is composed of organic waste like microorganisms, metabolic products, and leftovers from living organisms and inorganic waste like ammonium, phosphorus, sulphate, and metals [24]. Organic waste causes odour, colour, and taste to change whereas inorganic waste makes the water less transparent and thicker. Leachate occurs when the water passes through solid waste which is then is broken down in landfills and the water content of solid waste gathers causing the water to be toxic and polluted. It can affect the groundwater, soil, and surface water if not treated correctly [23,25]. A study showed that approximately 25% of New Jersey, in the USA, was contaminated with landfill leachate and has a cost that ranges from $750K to $14M, to manage. AOPs were first used on landfill leachate in the 1990s due to the hydroxyl radicals having the ability to biodegrade organic waste, remove organic constituents, and breakdown organic compounds [23]. Treatment efficiency for different AOP methods have been recorded which can be seen in Table 7.

Table 7: Treatment efficiency of AOPs in leachate removal [Deng et al., 2015]

AOP method	Average Leachate Removal (%) of COD	Standard Deviation (%)
Ozonation (O_3)	53	24
Ozone and hydrogen peroxide (O_3/H_2O_2)	43	23
Ozone and UV light (O_3/UV)	52	19
UV light and hydrogen peroxide (UV/H_2O_2)	77	11
Fenton Processes	71	13

Although ozone has an electrochemical potential of 2.07 V, it is fast to react with molecules like aromatics, phenols, and S-containing organics but slow to react with aldehydes, alcohols, and carboxylic acids in acidic solutions. However, hydroxyl radicals work best when the pH value is above 10 and reacts with most organic molecules. Furthermore, it was concluded that the Fenton process was the most cost efficient however it resulted in solid iron sludge. Since this sludge needs to be treated, the treatment cost for removing it increases. Knowing that Fenton works best in acidic environments, pH of 3.0-4.0, adjusting the pH would significantly increase the cost for water treatment.

Since Fenton and hydrogen peroxide both scavenge for hydroxyl radicals, it is important to identify the molar ratio of Fe(II) and H_2O_2 to reduce these effects. Some treatment issues that occur is that the BOD and COD of leachate effluent is 0.50 after AOP which indicates that AOP is not useful for pre-treatment [2]. In addition, some pollutants like ammonia nitrogen that are found in leachate cannot be rapidly broken down with hydroxyl radicals because of the slow reaction time between hydroxyl radicals and ammonia. For this reason, sulfate-based radicals were introduced, produced by heat-activated persulfate system, for leachate treatment to help remove and dissolve ammonia containing compounds. It was concluded that using sulfate-based radicals yielded a 100% removal rate of ammonia and a reduction in COD by 91% and was favourable under acidic conditions that had a pH range of 3.0 to 4.0 [2].

Future work

Seeing how water purification is a valuable aspect in today's world, it should be a common goal to find other radicals that can share the same safety properties as hydroxyl and sulfate radicals. For instance, it was discovered that hydroxyl radicals did not breakdown/react with ammonia-containing molecules quickly however, due to the properties and nature of sulfate radicals, this was not the case. In addition, from the 2 of 3 worldwide applications discussed in this paper, ozone AOP methods seemed to be used with other AOPs to achieve optimum water treatment. From this, if any other AOP methods were to be discovered, it should be tested with ozone to determine if the results of ozone based AOPs are amplified.

Summary

From the wastewaters discussed, it appeared that ozone was often paired with other AOPs to yield the best results. When treating textile wastewaters with ozone and UV, the COD found in the solution was lowered by 51.73%. The colour, odour, and suspended solid in activated sludge was also decreased. Moreover, due to different contaminants being released by the human body while swimming, pool water cannot be treated the same as drinking water. Hence, UV light was found to break bonds in organic compounds where if organic compounds had a bromine attached to it, toxic by-products were produced. Examples include dibromochloromethane, bromodichloromethane, and bromoform. To conclude, for landfill leachate wastewater treatment, Fenton and hydrogen peroxide (H_2O_2) processes were beneficial in removing organic and inorganic waste. However, due to their scavenger-like properties, the molar ratio of Fe(II) and H_2O_2 need to be measured accurately to ensure hydroxyl radicals remain in the solution. Sulfate radicals were then found to have a 100% effective rate against compounds that consisted of ammonia whereas hydroxyl radicals have slower reaction rates and are not often successful for dissolving this type of waste. Sulfate radicals worked best under acidic conditions that had a pH range of 3.0 to 4.0 and a reduction of COD by 91% for ammonia containing contaminants.

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