Worldwide Applications of AOP

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Advanced Water Treatment Technologies

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Importance of Water

- Majority of Earth is surrounded by water
- Humans are made up of 70% water
- Water used for:
  - Drinking
  - Cooking
  - Washing
  - Agriculture
  - Energy Production
  - Waste Disposal
  - …

Figure 1: Example of Clean Water [Pine Harbour Water, 2021]

Figure 2: Clean Drinking Water [Wired, 2021]

What Happens to the Water

- Creates wastewater(WW) in
  - ➢ Domestic
    - ✓ Greywater
      - – Bathroom
      - – Laundry
      - – Kitchen
    - ✓ Blackwater
      - – Urine
      - – Faeces
  - ➢ Industrial
  - ➢ Stormwater Runoff

Figure 3: Waste contaminating water [SolutionsTRAK, 2017]

Figure 4: Influent Wastewater [TheWastewaterBlog, 2020]

Figure 5: Pollutants in Water [Medium, 2016]

Cleaning water with AOPs

- AOPs produce hydroxyl radicals that breakdown organic compounds and pollutants.
  - By a few hundreds' PPM to less than 5 PPB

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

$$PPB = \frac{Mass\ of\ Solute\ (g)}{Mass\ of\ Solution\ (g)} \times 10^9 \qquad \text{(Eq. 2)}$$

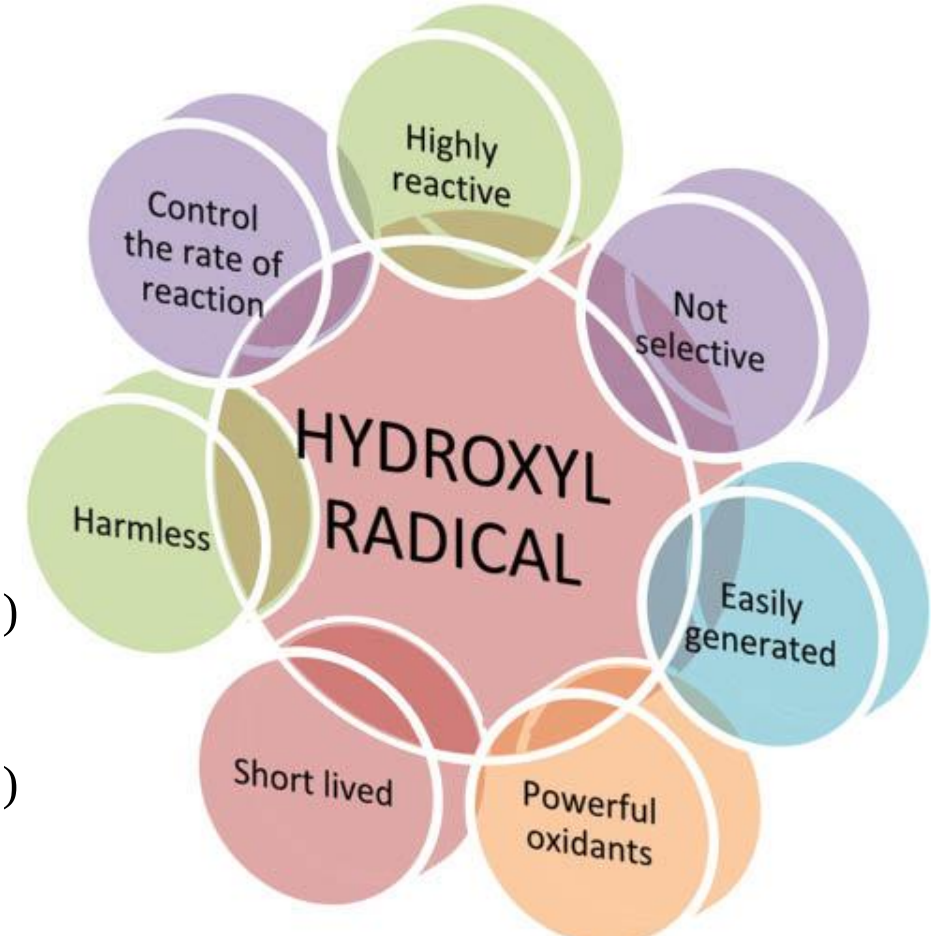


Figure 6: Properties of Hydroxyl Radicals [De Gruyter, 2015]

Advancements of AOP

- AOPs were first used in purifying drinking water in the 1980s
  - Was then used applied to treating municipal and industrial wastewater

- Discovered AOPs work more effectively when combined with a catalyst like ozone (O_3) or ultraviolet (UV) radiation in wastewater treatment

- AOPs in filtering water destroyed toxic synthetic organic matter (SOM)
  - Pesticides
  - Herbicides
  - Fuels
  - Solvents
  - Drugs

Figure 7: SOM in pesticides and waster pollution [SDWF, 2021]

Characteristics of AOPs

- Electrochemical Potential is in voltage (V) due to oxidation and reduction reactions
  - Change of electron

- Fluorine (F_2) has an oxidation potential of 3.0V [4]
  - Surplus amounts can be harmful to plants
  - 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.

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

Characteristics of AOPs

- Pairing AOPs with different catalysts allow for different harmful chemicals to be removed

- Different AOPs target different chemical waste to not form toxic by-products
  - ➢ Due to the change in physical and chemical properties of the pollutants and condition of wastewater
  - ➢ Different molecules will react differently when mixed with other types of molecules

- The strength of an AOP is based on how the chemicals in the AOP method react with the effluent [4].

The Process of Hydroxyl Radicals

- Hydroxyl radicals reaction rate range from 10^8 to 10^{10} $M^{-1}s^{-1}$
- Interact with organic pollutants/compounds to produce carbon centered radicals

R· or R· - OH

- Once oxygen (O_2) is presented in the solution, these radicals are changed to organic peroxyl radicals (ROO·).

- All radicals 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
  - Due to the short-lived radicals, they are paired with other oxidizing methods, on site, like UV radiation, ultrasound, hydrogen peroxide, ozone, and catalysts (like Fe^{2+}).

Worldwide Applications

Figure 7: General purpose water plant with high fluoride [Olmec Technical Services Ltd., 2018]

Figure 8: Largest metropolitan water treatment plant (WTP) [ABB, 2021]

Choosing the Right AOP System

- Common for industrial wastewater to have phenolic compounds
  - ➢ High toxicity
  - ➢ Displeasing smell and taste

- Factors to be considered are:
  - ➢ Water Composition
  - ➢ Purpose of Treatment
  - ➢ UV Dosage
  - ➢ Chemical Dosage
  - ➢ Cost and Design

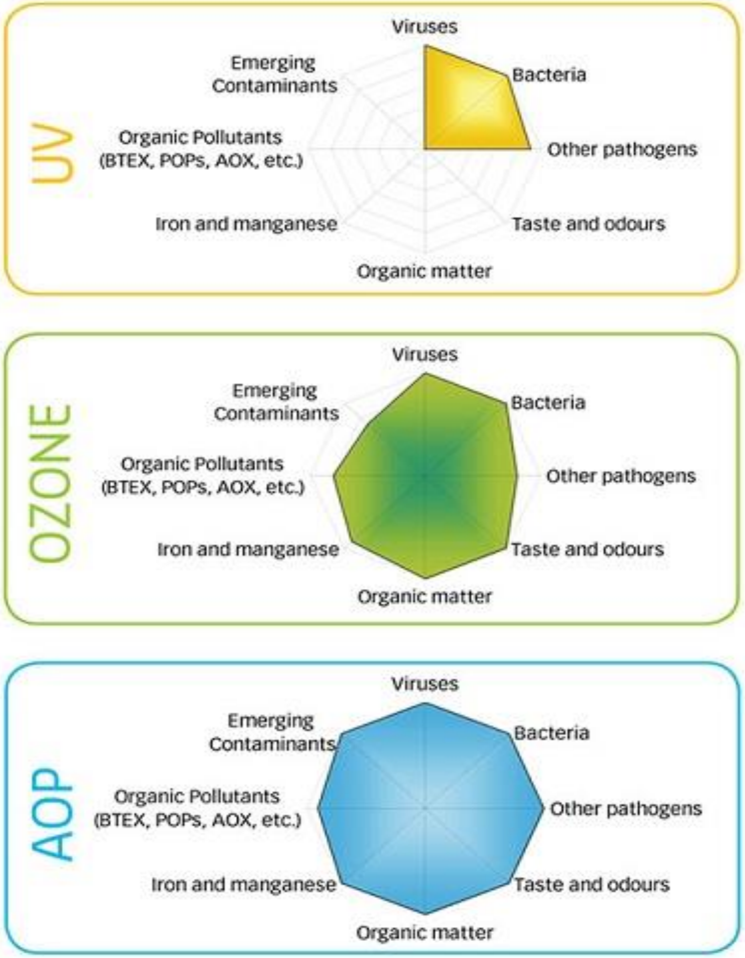


Figure 9: Using UV and ozone separately versus with AOPs [Suez, 2021]

Textile Wastewaters

- Textiles include
  - Clothing
  - Bags
  - Baskets
  - Accessories
  - …

Figure 10: Different colours of textile [GreenBiz, 2019]

- Leading Countries for producing and exporting textile goods are:
  - China
  - India
  - USA
  - European Union

- Unacceptable amounts of dye in effluent and hard to degrade

Solution

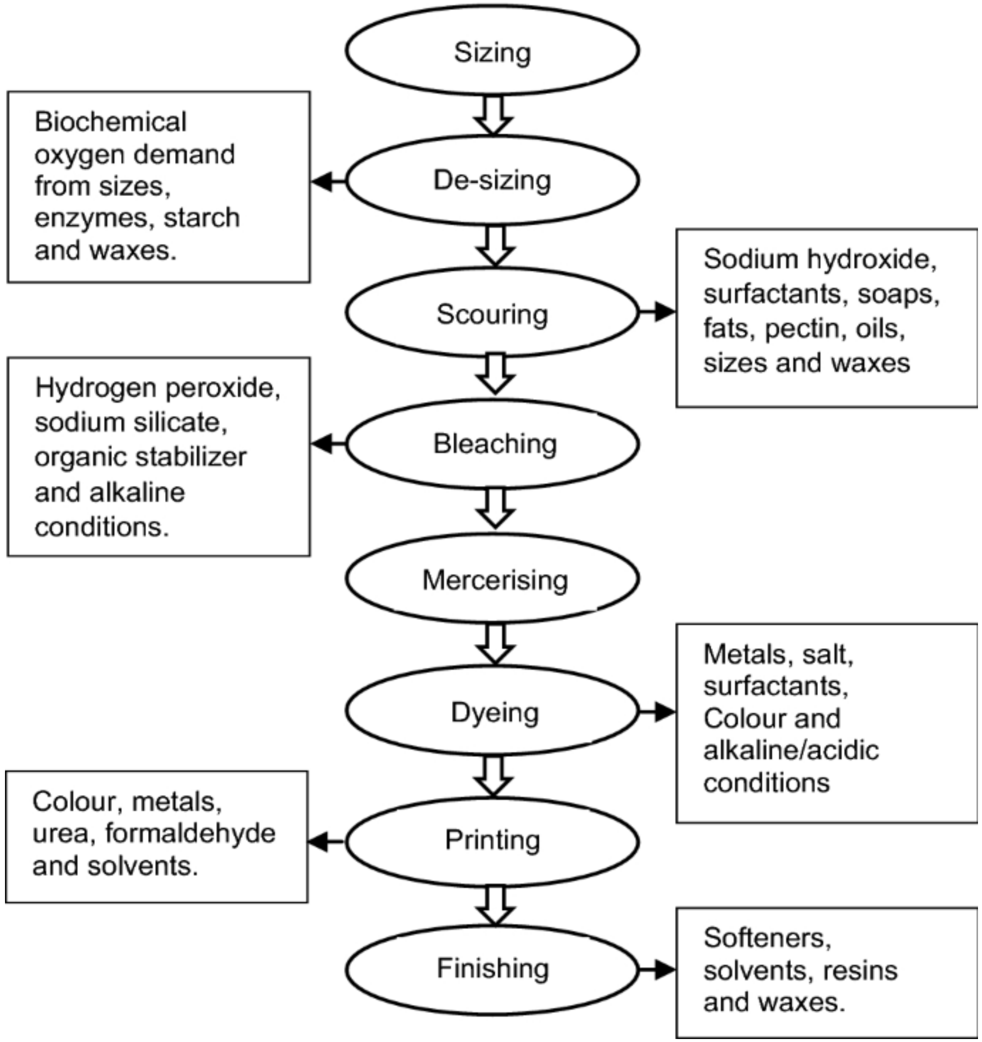


Figure 11: Steps that occur in a textile company and the waste discharged into the water [Yaseen et al., 2018]

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

Trial AOP System

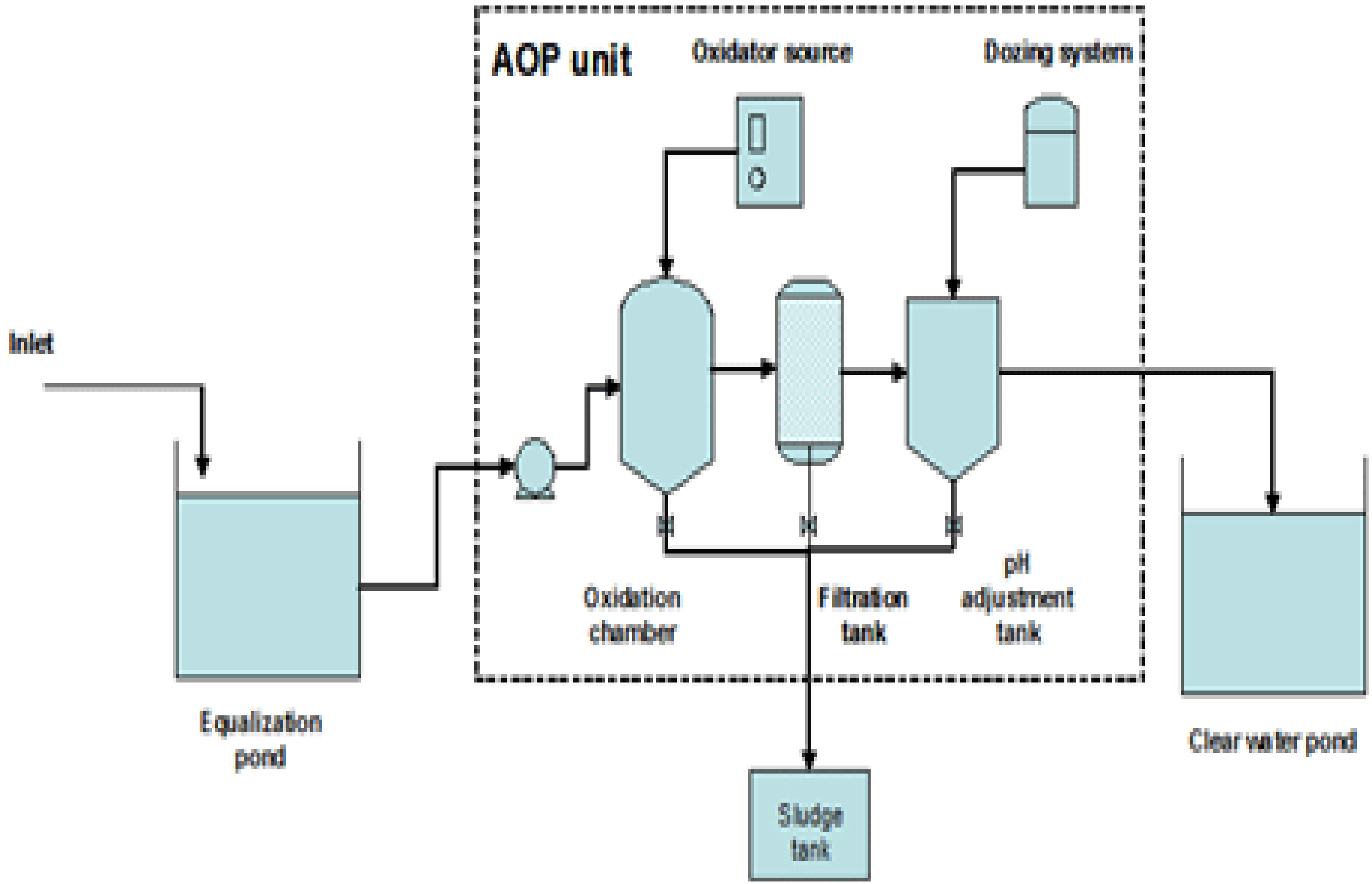
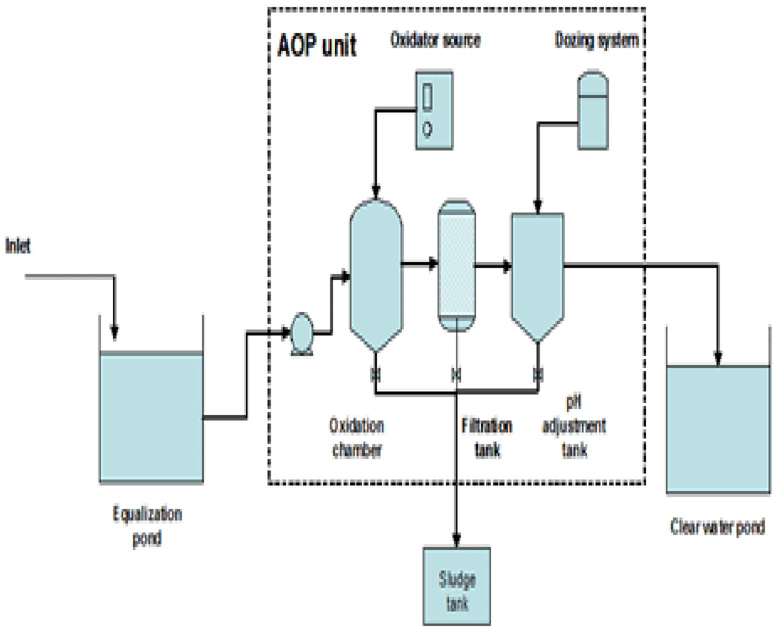


Figure 12: Schematic of an AOP trial system [Hutagalung et al., 2020]

Trial AOP System



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

Figure 13: Functions and specifications of the given trial AOP system [Hutagalung et al., 2020]

Ozone and UV

- Breaking the system down into several physical, chemical, and biological processes to treat contaminants.

- The process used in this test to treat textile wastewater was ozone and UV.

$$O_3 + \mathit{hv} + H_2O \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + hv \rightarrow 2(HO\cdot)$$

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

- Ozone used for it is a good oxidizer at high pH values.
  - Dyes in wastewater have a pH of 5-10

- Ozonation is also viable when discussing textile wastewater as it does not change the pH of the solution since no chemicals are being added

Disadvantage of using Ozone

- Ozone produced using corona discharge process

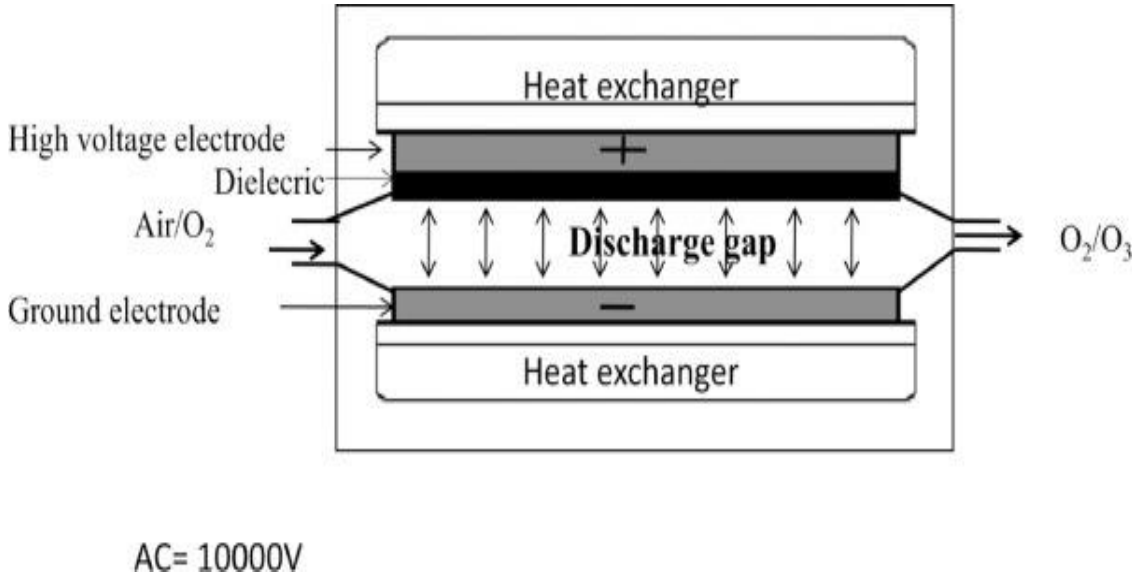


Figure 14: Visualization of the Corona Discharge Process [Rekhate et al., 2020]

- Becomes difficult to remove ozone particles from the water.
  - ➢ Minimize this by using an efficient electrochemical ozone generator where the appropriate amount of ozone is produced based on the water being treated

Results Found

- COD and SS decreased

- 51.73% decrease of COD from 16.167 mg/L to 8.364 mg/L after the process

Table 3: Findings of the trial AOP system [Hutagalung et al., 2020]

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

Results Found

a) *b)* *c)*

Figure 15: a) the decrease of SS in activated sludge, b) change in colour, and c) after processing the solution [Hutagalung et al., 2020]

Treating Swimming Pools

- Chlorine has been used for treating swimming pools for decades

- Adding chlorine to untreated water can form toxic disinfection by-products (DBP)
  - ➢ Trihalomethanes (THMs)
  - ➢ Chloramines (CAMs)
  - ➢ Haloacetic acids (HAAs)

- Chlorinated water mixed with photolysis of hypochlorous acid (HOCl) produced hydroxyl chlorine radicals to help remove waste

- Aikaterini et al. conducted a research that investigated how chlorine, nitrate, and hydrogen peroxide, as radical initiators, can be affected with UV irradiation.

Common Misconception

Table 4: 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

- 3 pools
  - 2 practice pools → average temperature of 26 °C
  - 1 therapy pool (hot tub) → temperature of 34 °C

- Tests conducted immediately after samples were collected for
  - pH
  - Free chlorine
  - Combined chlorine

- UV treatment used a quasi-collimated beam apparatus

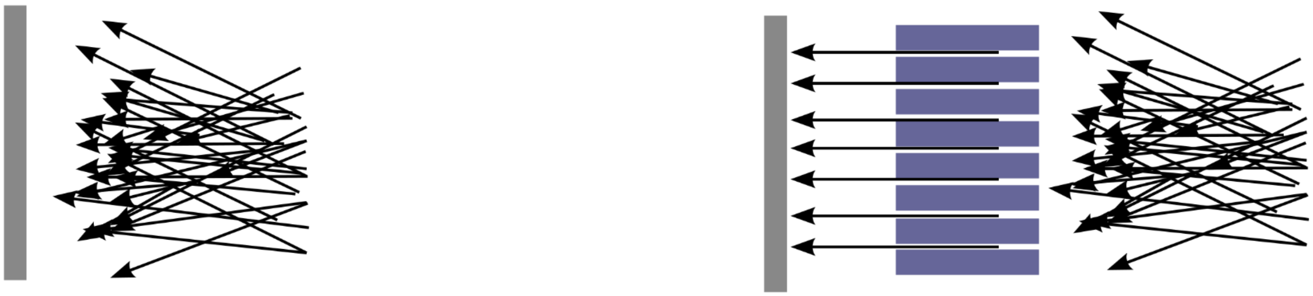


Figure 16: Using a collimated beam apparatus to minimize the light propagation [Wikipedia, 2016]

Results and Findings

- The results for the pools were
  - pH of 7.10 to 7.24
  - TOC of 1.58 to 2.14 mg/L
  - Free chlorine of 0.44 to 1.37 mg/L
  - Combined chlorine of 0.17 to 0.36 mg/L

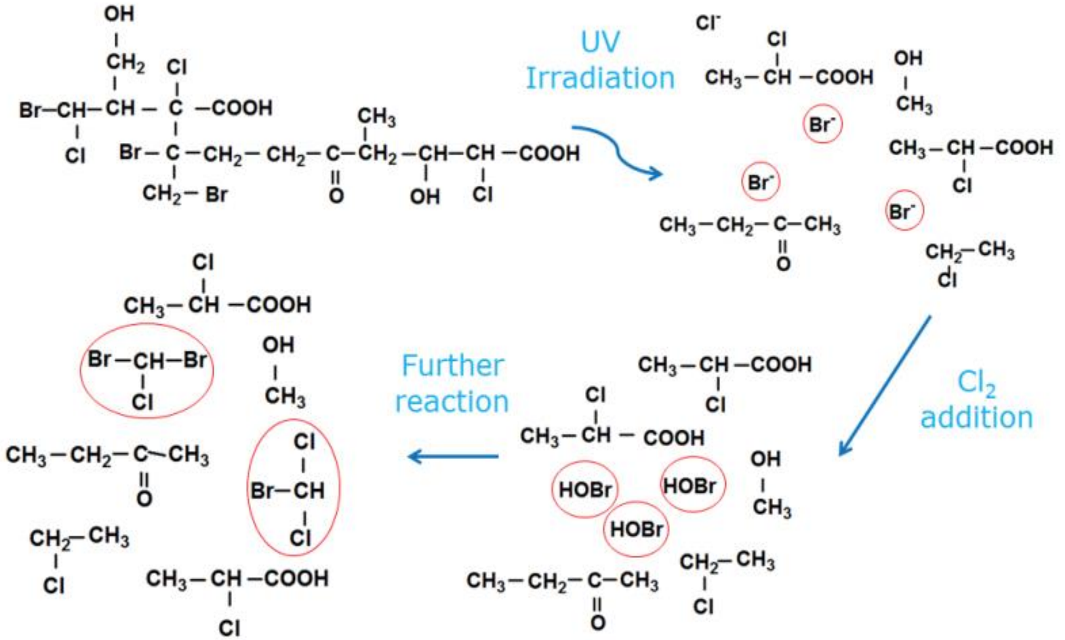


Figure 17: Chemical reactions of brominated species formation [Aikaterini et al., 2015]

Results and Findings

Table 5: 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

- Efficiency of AOP rely on:
  - Chemical properties of contaminants
  - Operation conditions
  - pH

- Composed of organic waste like:
  - Microorganisms
  - Metabolic products
  - Faeces
  - Results in: odour, colour, and taste change

- Composed of inorganic waste like:
  - Ammonium
  - Phosphorus
  - Sulphate
  - Metals
  - Results in: less transparency and thicker water

Managing Landfill Leachate

- Study showed approximately 25% of New Jersey was contaminated with landfill leachate
  - Costs $750K to $14M to manage
- AOPs first used on landfill leachate in 1990
  - Hydroxyl radical's ability to biodegrade organic waste and remove/breakdown organic constituents

Table 6: Advantages of using AOP with chlorine instead of just chlorine [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

Findings

- Fenton and hydrogen peroxide both scavenge for hydroxyl radicals
- Important to identify the molar ratio of Fe(II) and H_2O_2 to ensure enough radicals are present to treat the waste
- Pre-treatment of landfill leachate effluent using AOP was found to be useless as the BOD and COD was 0.50.
- Found that sulfate radicals may be more useful than hydroxyl radicals due to sulfate-based radicals having the ability to rapidly react with ammonia-containing molecules.
- Concluded that sulfate-based radicals yielded a 100% removal rate of ammonia and a reduction in COD by 91% in pH 3.0 to 4.0.

Future Work

- Purification using sulfate-based radicals should be used more often to determine if it is safe
  - Now knowing that it reacts with some compounds faster than the hydroxyl radical

- 2 of the 3 worldwide water treatment applications discussed used ozone. Thus, if more studies with ozone paired with other combinations of AOPs are conducted, it could deem to be useful.

Summary

- Textile wastewaters → COD lowered by 51.73% when using ozone and UV light
  - Colour, odour, and suspended solid in activated sludge was decreased

- Swimming pool waters and drinking waters cannot be treated the same way
  - UV light found to break bonds that contained bromine causing for toxic bromine by-products to form.

- Fenton and H_2O_2 processes were beneficial for removing organic and inorganic waste in landfill leachate
  - Sulfate-based radicals react with ammonia containing compounds faster than hydroxyl radicals as it has a 100% effective rate and has lowered the COD by 91%.

- Treating wastewater is crucial for maintaining a safe and healthy environment.

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