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# Transformation of Traditional Wastewater Treatment Methods into Advanced Oxidation Processes and the Role of Ozonation

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**ABSTRACT**

Technology advancement improves the quality of life, however, it might also introduce new pollutants to the ecosystem, which needs to deal with for the goal of a sustainable ecosystem. Municipal and industrial wastewater has always been important in improving the quality of life while maintaining the sustainability of our planet simultaneously. The diversity of pollutants in wastewater requires more advanced and demanding treatment processes. The ozonation, as a crucial part of the advanced oxidation processes, is a superior oxidation method compared to traditional oxidation methods. After the recognition of ozone as GRAS (generally recognized as safe), its applications have diversified and is used currently for microbial inactivation, degradation of recalcitrant organic compounds, removal of a diverse range of micropollutants, solubilization and reduction of sludge, and removal of color and odor components in wastewaters treatment processes. However, some considerable challenges still exist towards its universal application, such as high ozone generation costs, diversity of pollutants, and formation of ozonation by-products, which still require further studies. The main theme of this review paper is the transformation of traditional oxidation methods into advanced oxidation processes and the role of ozonation in this regard, including its applications, by-products, and its comparison with the traditional oxidation methods and advanced oxidation processes.

**Keywords:** wastewater treatment, traditional oxidation methods, ozonation, advanced oxidation processes, disinfection by-products, micropollutants.

## INTRODUCTION

Water reclamation and reuse can be significant steps forward toward global sustainability. Conventional wastewater treatment processes are not usually able to provide water with high standard quality, therefore, more effective treatments such as advanced oxidation processes (AOPs), including ozonation, are required for this purpose. Ozonation is commonly applied in wastewater reclamation facilities globally as an effective tertiary treatment procedure (Tang et al., 2014). At the present time, ozonation has been used for municipal wastewater quality enhancement for potable water reuse and environmental protection (Lim et al., 2022).

Firstly, what is ozone, and how has it found its way to wastewater treatment plants? The Dutch chemist, Van Muram, noticed an unusual odor during his laboratory experiments with his electrostatic machine in 1785. Later in 1839, it was discovered and made in a laboratory by German scientist Christian Friedrich Schönbein (McElroy & Fogal, 2008), and it was named ozone from the Greek word (ozein), which means to smell. Thomas Andrews showed in 1856 that only oxygen was involved in ozone formation, while a decade later (in 1865) Jacques-Louis Soret discovered the chemical formula of ozone.

German physician, Lender, published the first study regarding the practicality of ozone application for water disinfection and its biological effects in 1870, while for the very first time, it was Holland, where a water disinfection plant was built in 1893, which used ozone. Later in 1965, Ireland and the United Kingdom (including Scotland) reported using ozone for color removal of

surface waters. Meanwhile, ozone-related researches in Switzerland were more focused on its applications for the oxidation of micropollutants and pesticides (History of Ozone, 2021).

Ozone ($O_3$) is a bluish gas with a pungent fishy smell under ambient temperature and pressure. It is an unstable and extremely reactive allotrope of oxygen, not storable (Psaltou & Zouboulis, 2020), with powerful oxidizing properties, and capable of reacting with a large number of organic and inorganic compounds. Penetrability and its spontaneous decomposition to a non-toxic molecule, oxygen, are other features of ozone (Kim et al., 1999), which make it more desired. Some physical and chemical properties of ozone are presented in Table 1. Besides, the redox potentials of some common oxidizing agents are compared with ozone in the Table 2.

Ozone generation is based on creating oxygen atoms by adding energy and splitting oxygen molecules and further attachment of single oxygen atoms to other oxygen molecules. The first ozone generator was proposed by Werner von Siemens in 1857 (Kogelschatz, 2003), which was based on an electrical discharge system. Principles of ozone generation are described by Wei et al. (2017), among which corona discharge and ultraviolet light principles are widely applied:

- Gaseous discharge for ozone generation (corona discharge);
- Photochemical ozone generation (ultraviolet light);
- Phosphorus contact ozone generation;
- Electrochemical ozone generation.

Corona discharge ozone generator designed for lab scaling experiments was described by (Rubin, 1964). Three decades later, Sponholtz et al. (1999) developed a type of corona discharge ozone generator with simpler construction and with the possibility of assembling it from components commonly found in all laboratories of that time. In the early twentieth century, Park et al. (2006) designed an effective ozone generator by using a meshed-plate electrode in a dielectric-barrier discharge. Commercially available corona discharge ozone generators involve the utilization of high voltage discharge in an oxygen (or air) containing cooled (or dried) gaseous phase with the following reactions in discharged gas (Rekhate & Srivastava, 2020), as below:

$$O_2 + electric\ spark \rightarrow 2O^{\bullet} \quad (1)$$

$$O_2 + O^{\bullet} \rightarrow O_3 \quad (2)$$

In addition, ultraviolet light is also capable of exciting molecular oxygen and causing the production of atomic oxygen, which would accelerate ozone generation. Potassium ferrate reduction products also accelerate ozonation by hastening

**Table 1.** Some physical and chemical properties of ozone (Cuerda-correa et al., 2020; Varga & Szigeti, 2016; Wei et al., 2017)

| Properties | Value | Unit |
|---|---|---|
| Molecular weight | 48 | $g \cdot mol^{-1}$ |
| Density | 2.14 | $kg \cdot m^{-3}$ |
| Oxidation potential | -2.08 | V |
| Max. $O_3$ concentration in air or oxygen | 4–8 | % |
| Melting point (at 760 mm Hg) | -192.5 | °C |
| Boiling point (at 760 mm Hg) | -111.9 | °C |
| Critical temperature | -12.1 | °C |

**Note:** $kg \cdot m^{-3}$ – kilogram per cubic meters; $g \cdot mol^{-1}$ – gram per mol; *V* – volt; °C – degrees Celsius.

**Table 2.** Redox potential of some common oxidizing agents compared to ozone (Amor et al., 2019; Cuerda-correa et al., 2020; Wei et al., 2017)

| Oxidizing agents | $E°$ (V) | $E°/E°_{O_3}$ | Oxidizing agents | $E°$ (V) | $E°/E°_{O_3}$ |
|---|---|---|---|---|---|
| Fluorine ($F_2$) | 3.06 | 1.47 | Hydroperoxyl radical ($HO_2$) | 1.65 | 0.79 |
| Hydroxyl radical (OH) | 2.8 | 1.35 | Chlorine dioxide ($ClO_2$) | 1.57 | 0.75 |
| Sulfate radical ($SO_4$) | 2.6 | 1.25 | Hypochlorite (ClO) | 1.49 | 0.72 |
| Atomic oxygen (O) | 2.42 | 1.16 | Chlorine ($Cl_2$) | 1.36 | 0.65 |
| Ferrate ($FeO_4$) | 2.2 | 1.06 | Dichromate ($Cr_2O_7$) | 1.36 | 0.65 |
| Ozone ($O_3$) | 2.08 | 1 | Manganese dioxide ($MnO_2$) | 1.23 | 0.59 |
| Peroxodisulfate ($S_2O_8$) | 2.01 | 0.97 | Oxygen ($O_2$) | 1.23 | 0.59 |
| Hydrogen peroxide ($H_2O_2$) | 1.76 | 0.85 | Bromine ($Br_2$) | 1.07 | 0.51 |
| Permanganate ($MnO_4$) | 1.67 | 0.8 | | | |

**Note:** $E°$ – redox potential, V – volt, $O_3$ – ozone.

the breakdown of ozone into free oxygen radicals (Wang et al., 2022). Ozone generation from oxygen molecules under UV radiation is described by the reaction below (Fabbrocini et al., 2010):

$$3O_2 + h\nu \rightarrow 2O_3 \quad (3)$$

Ozonation is usually defined as the process of dissolving gaseous ozone into the water for the removal of contaminants or inactivation of pathogenic microorganisms in water and wastewater treatment processes (Zhou & Smith, 2000). The low solubility is a major challenge to the universal application of ozonation. The low solubility of ozone directly influences the utilization of ozone and is highly related to gas-liquid mass transfer in the reactor (Derco et al., 2015). Some researchers propose various mechanisms for overcoming the low solubility of ozone, such as using an ozone microbubble system (Chu et al., 2007). Ozone mass transfer rate is influenced more by gas flow rate than by ozone gas concentration (Manterola et al., 2008), besides other factors.

Optimization of ozonation parameters and application of catalysts can enhance the effectiveness of the ozonation process. Application of various catalysts have been reported in the catalytic ozonation process; such as electrochemically generated $Fe^{2+}$ (Heebner & Abbassi, 2022), Ce-MCM-48 (Li et al., 2015), nanocatalysts (Jin et al., 2023), CaO (Zhou et al., 2023), Mn-loaded C-SiO2 (Chen et al., 2023), and aluminum chloride and alum (Rizvi et al., 2022), among others. The most important influential parameters on the ozonation process and the schematic diagram of the ozonation are presented in Table 3 and Figure 1, respectively.

**Table 3.** Most influential parameters on the ozonation process (Remondino & Valdenassi, 2018; Sumegova et al., 2013; Ternes et al., 2003; Tripathi et al., 2011)

| Parameters | Influence |
|---|---|
| pH | The pH level influences the ozonation reaction pathway. Under acidic pH direct and alkaline pH indirect ozonation via hydroxyl (•OH) radicals dominate. |
| Ozone dosage | Up to a level of $O_3$ dosage, the efficiency of ozonation increases rapidly, while higher ozone dosages will result in lower ozone utilization and more by-product formation. |
| Contact time | Higher contact time results in a higher reaction rate & also more by-product formation. |
| Temperature | Temperature increase boosts the ozonation reaction rate and its decrease influence positively ozone solubility and its germicidal effect. |
| Catalyst presence | The presence of catalysts increases the ozonation reaction rate. |

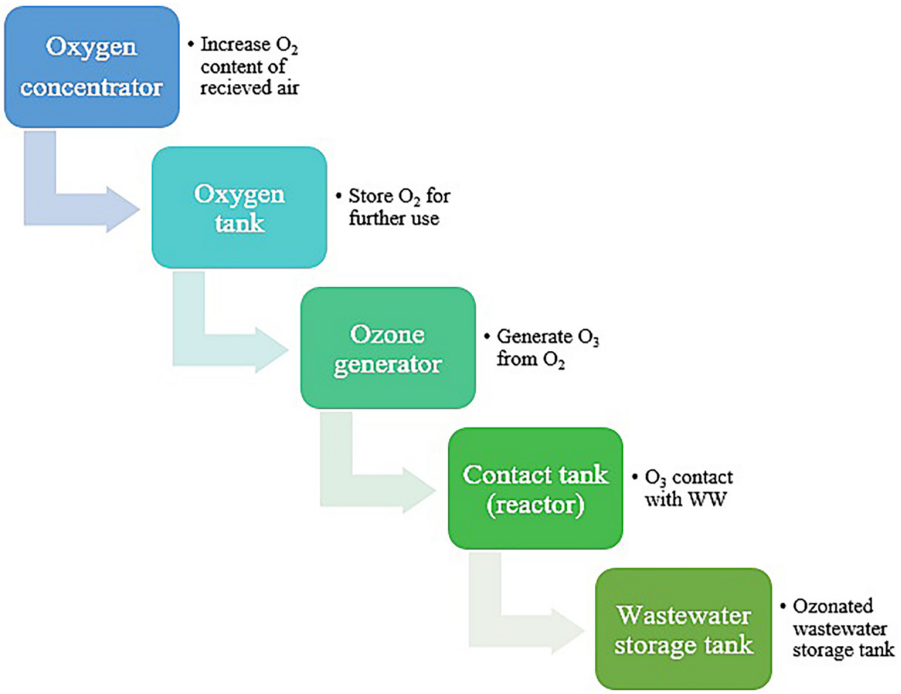


**Figure 1.** Simple schematic diagram of the ozonation process; $O_2$ – oxygen; $O_3$ – ozone; WW – wastewater

Two different mechanisms of ozone reaction exist; direct reaction and indirect reaction via hydroxyl radicals. Its direct reaction is selective to some organic functional groups, such as unsaturated and aromatic hydrocarbons containing substituents of hydroxyl, amine, and methyl groups (Andreozzi et al., 1998), while hydroxyl radicals are less selective compared to ozone (El-taliawy et al., 2017). A possible indirect formation of hydroxyl radical is shown below:

$$O_3 + H_2O \rightarrow O_2 + H_2O_2 \quad (4)$$

$$H_2O_2 \rightarrow 2OH^{\bullet} \quad (5)$$

Higher pH values (alkaline) favor the indirect mechanism of ozone reaction via hydroxyl radical, while at lower pH values (acidic), the direct (selective) ozonation mechanism is the dominant one (Derco et al., 2015).

On the other hand, the direct reaction of ozone occurs with pollutants according to the following categories (Rekhate & Srivastava, 2020):

- Electron transfer-based reactions between $O_3$ and $HO_2^-$ (or $O_2^{\bullet -}$);
- Cycloaddition reaction of ozone with pollutants;
- Reactions of electrophilic ozone with nucleophilic groups of aromatic compounds; such as $-OH^-$, $-NO^{2-}$ and $-Cl$;
- Reactions of ozone with compounds containing carbonyl or double and triple bonds of carbon-nitrogen. A recent study detected 178 carbonyl compounds in lake water and wastewater (Houska et al., 2023).

The main objective of this paper is to review the comparison of the ozonation process as a part of advanced oxidation processes with the traditional oxidation methods, describe applications of ozonation in wastewater treatment processes for microbial inactivation, elimination of micropollutants, solubilization and reduction of sludge, removal of color and odor compounds, and by-products of the process.

## COMPARISON OF OZONATION WITH TRADITIONAL AND ADVANCED OXIDATION PROCESSES

For a long time back, chlorination and other traditional methods have been extensively used for the disinfection of different waters. With the discovery of ozone and its application for disinfection and oxidation purposes and further development of advanced wastewater treatment processes, it replaced fully or partially conventional traditional methods in many areas. However, a single treatment is not able to fully achieve efficient removal of contaminants (Andreozzi et al., 1998), therefore, combined advanced oxidation processes have evolved.

### Traditional oxidation methods

Traditional oxidation methods are not as effective as ozonation for the inactivation of microorganisms, removal of odor and color, biodegradation of pollutants, and for removal of a broad range of micropollutants.

The most widely utilized traditional oxidation methods are based on the application of chlorine and some other oxidizing agents such as chlorine dioxide, hydrogen peroxide, and ultraviolet light.

A brief comparison of ozone and chlorine oxidation agents is presented in Table 4. Ozone is a faster oxidizing agent with higher redox potential and more inactivation power of microorganisms than chlorine. It produces more biodegradable effluents (Wang, 1990) and with better physicochemical properties.

The high toxicity of chlorination by-products led to the search for its alternatives. Of the methods experimented on, ozonation has proved to be a better disinfectant with less toxic by-products compared to ultraviolet light, hydrogen peroxide, and chlorine dioxide (Tyrrell et al., 1995). Its drawbacks compared to the traditional chlorination method are its low residual time in treated waters and the high costs of the process due to high energy consumption for ozone generation. However, by increasing the plant capacity, the costs of the process might decrease significantly.

Another traditional oxidation method is using chlorine dioxide, which is similar to ozone in terms of costs (Warriner et al., 1985). However, it has a higher mass transfer rate compared to ozone, but its toxic by-products such as quinones or chlorophenols, make it less popular compared to ozone. Sun et al. (2018) report that sodium hypochlorite (NaOCl) enhances the release of dissolved organic matter (DOM) from sludge better than ozone. However, the authors indicated ozone as a more eco-friendly and safer approach in terms of sustainability.

Hydrogen peroxide and activated carbon are other well-known oxidation agents, which are

**Table 4.** A brief comparison of ozonation and chlorination (Sources: Majumdar & Sprool, 1974; Tripathi et al., 2011; Tyrrell et al., 1995)

| Description | $O_3$ | Cl | Superiority |
|---|---|---|---|
| Redox potential (V) | 2.08 | 1.36 | $O_3$ |
| Toxic by-products | Less | More | $O_3$ |
| Process rate in water disinfection | 10x (/$Cl_2$) | 1/10x (/$O_3$) | $O_3$ |
| Physico-chemical properties of effluents | Higher | Lower | $O_3$ |
| Wastewater effluent biodegradability | More | Less | $O_3$ |
| Contact time (min) | 5 | 30 | $O_3$ |
| The relative ease of use | Higher | Lower | $O_3$ |
| Odor and taste removal | Yes | No | $O_3$ |
| Residual after treatment | No | Yes | $O_3$ |
| Costs (without dechlorination step) | Higher | Lower | Cl |
| Costs (with dechlorination step) | Lower | Higher | $O_3$ |

**Note:** $O_3$ – ozone; Cl – chlorine; V – volt; min – minute.

usually utilized for the decolorization of water and wastewater, however, they are also accounted as high-cost oxidation processes. Ultraviolet light was reported to be the most common wastewater disinfection alternative to chlorination in North America, sometimes back (Gehr et al., 2003).

### Advanced oxidation processes

Advanced oxidation processes are potential technology for partial or total mineralization of emerging pollutants by extremely reactive hydroxyl, hydroperoxyl, superoxide, and sulphate radicals (Priyadarshini et al., 2022). The AOPs are also defined as technologies that use (•OH) radicals for oxidation (Wang & Xu, 2012). Of AOPs, ozone-based AOPs, by having the advantages of simple operation procedures, are more likely to become key technologies for water and wastewater detoxification (Derco et al., 2015). Figure 2 illustrates some ozone-based advanced oxidation processes.

Optimization of AOPs is an important condition for their efficient utilization (Krishnan et al., 2017). If not optimized, AOPs might not have much higher efficiencies than single oxidation processes such as ozonation. Single ozonation process at lower pH values has a higher selectivity towards electron-rich compounds such as aromatics and unsaturated organic compounds, while ozone-based processes via hydroxyl radicals have lower selectivity in such cases. Microbial log reduction of ozonation is higher than $O_3/H_2O_2$ and lower than $O_3$/UV. Single ozonation is less costly than AOPs and also produces fewer by-products (Table 5).

## SOME APPLICATIONS OF OZONATION PROCESS

Application of ozonation can be dated back to the mid-nineteenth century, initially utilized as a water disinfectant. After being approved as

**Table 5.** Comparison of ozonation with some ozone-based AOPs, $O_3$/UV and $O_3/H_2O_2$ [Lee et al., 2014; Ternes et al., 2003; Wert et al., 2007]

| Description | $O_3$ | $O_3$/UV | $O_3/H_2O_2$ | Application |
|---|---|---|---|---|
| Microbial log reduction | 1.9 | 3.1 | 1.5 | Pharmaceutical |
| Coliform removal | More | - | Less | Tertiary |
| *E. coli* log reduction | 3.7 | 4.1 | 3.0 | Pharmaceutical |
| *Streptococci* log reduction | 2.4 | 3.4 | 2.1 | Pharmaceutical |
| *C. perfringens* log reduction | 0.8 | 1.1 | 0.2 | Pharmaceutical |
| Cost per $m^3$ treatment (€) | 0.04 | 0.05 | - | Pharmaceutical |
| By-products formation | Less | - | More | Tertiary |
| Micropollutants elimination: at pH=7 (/$O_3$) | 1.0 | - | 1.08 | Hospital |
| at pH=8.5 (/$O_3$) | 1.0 | - | 0.69 | Hospital |

**Note:** $O_3$ – ozone; UV – ultraviolet light; $H_2O_2$ – hydrogen peroxide; € – Euros; pH – potential hydrogen.

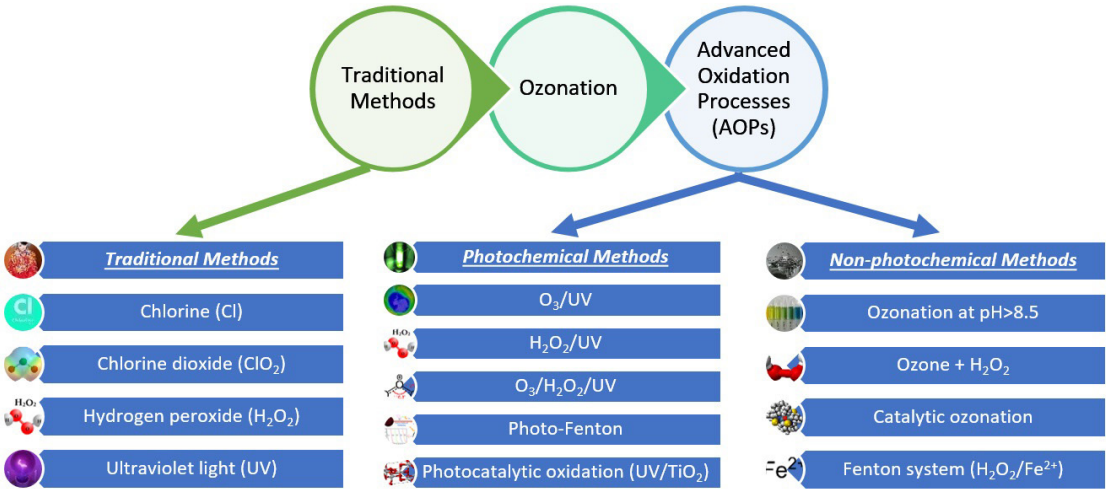


**Figure 2.** Some common traditional and advanced oxidation processes. $O_3$ – ozone; UV – ultraviolet light; $H_2O_2$ – hydrogen peroxide; $TiO_2$ – titanium dioxide; Fe – ferrum

generally recognized as safe (GRAS) in the United States (Kim et al., 1999), its applications have been diversified. The ability of ozone to oxidize complex organic molecules, pharmaceuticals, endocrine-disruptive chemicals (EDCs) and phenols has led to its extensive applications, especially in water and wastewater treatment processes, and more specifically for tertiary treatment purposes.

In water treatment processes, ozonation is used for color and odor compounds, pesticides, and organic material removal. It is also used in wastewater treatment processes for reducing the levels of COD (Chemical Oxygen Demand), DOC (Dissolved Organic Carbon) and absorbance of UV254 (ultraviolet light at a wavelength of 254 nm) and improving the biodegradability of effluents (Mecha et al., 2016). The main applications of ozonation in municipal and industrial wastewater treatment processes are microbial inactivation, color and odor removal, sludge reduction and solubilization, and elimination of micropollutants.

## Microbial inactivation

Ozone is well-known for its strong antimicrobial (Kim et al., 1999) and chemical oxidation power. Ozone is a powerful disinfectant with high potential as a viral (Katzenelson & Biedermann, 1976) and bacterial disinfectant, due to its ability to destroy the cell walls of microorganisms (Dytczak et al., 2007). However, recent research indicates Proteobacteria overgrowth stimulation by ozone-treated wastewater (Ribeirinho-Soares et al., 2022). On the other hand, another recent study even suggests that ozone can be a powerful oxidizing agent against SARS-CoV-2 (Bhattacharya, 2023).

Ozonation has been widely used for disinfection of secondary effluents to improve wastewater quality to meet the legislation standards for its reuse (Petala et al., 2008). It has been used since the 1970s to meet the discharge requirements for viral and coliforms inactivation. Coliforms show more

**Table 6.** Some research regarding the inactivation of viruses and bacteria by ozonation

| Microorganisms | $O_3$ dosage ($mgO_3.L^{-1}$) | Contact (min) | Efficiency (%) | References |
|---|---|---|---|---|
| *Bacteriophage f2* | 0.25-0.5 | 0.17 | >99.9 | Boyce et al., 1981 |
| *Bacillus cereus* | 0.12 | 5 | >99 | Broadwater et al., 1973 |
| *Escherichia coli* | 0.42 | 2 | >99 | Fetner & Ingols, 1956 |
| *Escherichia coli* | 0.36 | | 100 | Herbold et al., 1989 |
| Enteric viruses | 0.1-0.2 | 5 | >99.9 | Majumdar & Sprool, 1974 |
| *Hepatitis A* virus | 1.22 | | 100 | Herbold et al., 1989 |
| *Legionella pneumophila* | 0.32 | 20 | >99.9 | Edelstein et al., 1982 |
| *Poliovirus type 1* | 0.21 | 0.17 | >97 | Boyce et al., 1981 |
| *Poliovirus type 1* | 0.19 | | 100 | Herbold et al., 1989 |

**Note:** $mgO_3.L^{-1}$ – milligram of ozone per liter of water/wastewater; min – minute.

resistance to the ozonation process and therefore can be used as an indicator of the ozonation process's effectivity on microorganisms, while used as a disinfectant (Warriner et al., 1985). The efficiency of the inactivation of some viruses and bacteria by the ozonation process is presented in Table 6.

## Color and odor removal

Color and odor removal, along with microbial disinfection, are some of the first objectives of applications of the ozonation process. Ozonation has been a very effective process for the removal of color compounds derived from azo dyes (Sarasa et al., 1998), some of which are present in the European Economic Community (EEC) and United States Environmental Protection Agency (USEPA) priority pollutants list, colors caused by iron, manganese, or by peaty matter and taste and odor caused by the presence of phenolic compounds (Majumdar & Sprool, 1974). Ozonation is used globally as an effective tertiary treatment process dealing with odor and color removal from wastewater for their reclamation (Tang et al., 2014). Ozonation can decompose highly structured dye molecules. In addition, its combination with chemical coagulation and activated sludge processes increases the effectiveness of the process (Lin & Lin, 1993). Efficient color removal by combined ozonation and chemical coagulation was also reported (Sarasa et al., 1998).

Wu & Wang (2001) studied the ozonation of aqueous azo dyes in a semi-batch reactor. The authors reported that an increase in initial dye concentration increased the ozone transfer rate and decreased the rate constant. They also wrote that a rise in applied ozone dose and temperature improved the apparent rate constant. Soares et al. (2006) studied the influence of operational parameters on the ozonation of textile effluent. According to the authors, color removal efficiencies of the process for various ozone doses, pH values (5–9), and presence/absence of salt fluctuated between 76 and 100%. The presence of salt reduced the color removal efficiency. They added that color removal was enhanced at lower pH values, while TOC (total organic carbon) removal improved at higher pH values.

Wastewater color removal is primarily for its reuse purpose. Ciardelli & Ranieri (2001) studied treatment and reuse of textile industrial wastewater by ozonation. They reported high color removal rates of 95–99% and with possibility of reusing treated waters. Other researchers also documented high (91%) color removal rates after 15 min of ozonation (Meric et al., 2005).

The application of ozonation for wastewater decolorization hasn't been limited only to the textile industry, but its successful utilization in various other productions has also been reported. Battimelli et al. (2010) studied the application of combined ozonation and biological processes for the removal of colored and biorefractory compounds from industrial wastewater of the molasses fermentation industry. Wastewater from the molasses fermentation industry contains melanoidins, which can be problematic for aquatic life and wastewater treatment plants, as these molecules are biorefractory. Ozonation of this wastewater with ozone doses of 0.5 g $O_3$ $g^{-1}$ COD increased the biodegradable fraction from 0 to 33% without posing any noticeable toxicity on biomass. Ozonation also helped with the color removal with slight loss of carbon through mineralization. Refractory compounds convert to more biodegradable forms when ozone is applied (Narkis & Schneider-Rotel, 1980).

Beltran et al. (1998) studied the effects of ozonation as a single process and also combined with hydrogen peroxide and ultraviolet (UV) radiation on the wastewater of debittering table olive industry. The authors found that with an ozone dosage of 0.5 g, its color was almost entirely (>90%) removed.

Not only color, but also odor-causing compounds are of concern while treating wastewater. Most odour-generating compounds are originated from the anaerobic decomposition of sulfur-containing and nitrogen-containing compounds and during various processes. Some of these compounds are but are not limited to hydrogen sulfide, mercaptans, ammonia, amines, aldehydes, ketones, indole and skatole. Ozonation has proven rapid oxidation of these compounds (Hwang et al., 1994).

## Sludge solubilization and biodegradation

Biological wastewater treatment systems have been used for a long time, but it has a significant problem of excess sludge production. Treatment and disposal of excess sludge may account for up to 65% of the total operational costs (Yan et al., 2009), therefore, sludge ozonation for excess sludge reduction may be economical. Most research in this area is focused on sludge solubilization and excess sludge reduction. Excess

sludge reduction (Sui et al., 2011), biomass recycle system (Lee et al., 2005), and simultaneous use of several techniques (Sabet et al., 2023) have been proposed for decreasing excess sludge production. Ozonation has been proposed for sludge reduction for a long time now (Beltran, 2003). Ozonation coupled with an activated sludge system was also studied for minimization of excess sludge reduction (Chu et al., 2009).

Ozone dosage is a crucial factor in this case. Chu et al. (2009) proposed ozone dosages of 0.03 to 0.05 g $O_3$/g TSS (Total Suspended Solids) for keeping a balance between sludge reduction efficiency and the process costs, while Yan et al. (2009) reported that doses higher than 0.14 g $O_3$/g TSS failed in efficient sludge oxidation, because of the release of several microbial radical scavengers (such as $SO_4^{2-}$ and lactic acid) in sludge. On the other hand, ozonation (Dytczak et al., 2007) and recycling ozonated sludge to the anoxic zone (Manterola et al., 2008) could improve the denitrification rate, specifically in an anoxic/anaerobic reactor. Table 7 presents the main advantages and drawbacks of sludge ozonation.

Sludge solubilization results in the reduction of excess sludge production (Manterola et al., 2008). Ozonation has been proposed to be the most efficient means of sludge solubilization (Hwang et al., 2010). Besides, it also improves the biodegradability of the sludge (Lee et al., 2005). Organic matter solubility increases proportionally to ozone dosage, while an increase in inorganic element concentration slows down the solubilization of sludge (Sui et al., 2011). Ozonated sludge can have further applications in a biological nitrogen removal process as an external carbon source, which would significantly reduce the costs of the biological nitrogen removal process (Lee et al., 2005).

## Micropollutants elimination

Micropollutants are as anthropogenic chemicals which occur in the (aquatic) environments above their potential natural background in trace (up to microgram per liter range) levels (Chavoshani et al., 2020). Conventional wastewater treatment plants cannot effectively remove a broad range of micropollutants (Knopp et al., 2016), therefore, additional advanced treatment processes are needed to overcome this problem. If not removed, micropollutants can adversely affect aquatic life and ecosystems downstream of wastewater treatment plants (Thalmann et al., 2018). It can also pose serious risks to environment and human health (Rogowska et al., 2020).

Numerous organic micropollutants (OMPs) can be found in trace amounts in surface waters, groundwaters, and finished drinking water, including pharmaceuticals, personal care items, hormones, and their transformation products (Zoumpouli et al., 2020).

Ozonation is an emerging technology for the removal of micropollutants from wastewater (Misik et al., 2011) and for the reduction of loads of micropollutants released into the surface waters (Bundschuh & Schulz, 2011) via direct or indirect oxidation reactions. According to recent research removal of micropollutants by the ozonation process is mainly due to entrainment rather than their chemical degradation (Solis-Balbin, 2023).

The most crucial factor affecting the efficiency and effectivity of micropollutants (MPs) ozonation in wastewater effluents is the organic matter (Gijn et al., 2022). Trace organic compounds (TrOCs) with electron-rich functional groups are oxidized by ozone efficiently, while other TrOCs by hydroxyl (•OH) radical, through an indirect pathway (Zucker et al., 2016). Much attention has been drawn to the analysis of compounds such as endocrine-disrupting chemicals (EDCs) or pharmaceuticals in the past decades (Rogowska et al., 2020; Finckh et al., 2022; Stalter et al., 2011).

The diversity of micropollutants is a substantial challenge towards the ozonation of wastewater. Several hundred organic micropollutants are present in wastewater (Lee et al., 2014), such as

**Table 7.** Main advantages and drawbacks of sludge ozonation (Sources: Chu et al., 2009 & Wei et al., 2003)

| Advantages | Drawbacks |
|---|---|
| Successful in full-scale sludge reduction | High equipment and operational costs |
| High solids degradation and methane production efficiency during anaerobic digestion | Slight increase in TOC (total organic carbon) and phosphorus concentrations in effluent |
| No significant accumulation of inert solids in the aeration tank at optimal ozone dosages | Possible degradation of other organic matter by ozone |
| High improvement in sludge settleability | Transfer of metals to the liquid phase and the consequent need for further purification |

pharmaceuticals, hormones, personal care products, their transformation products (Zoumpouli et al., 2020), pesticides, fertilizers, heavy metals and others. The diversity of micropollutants has been a challenge towards its elimination by the ozonation process. Besides, technological progress diversifies the micropollutants range even more. The most effective actions for reducing micropollutants are as follows (Papa et al., 2013):

- Limiting their production by controlling the pollution sources;
- Reconfiguration of existing wastewater treatment plants;
- Applying an additional high energy-consuming process, such as ozonation.

Ozonation parameters are crucial for achieving a higher level of efficiency. Some research focused on this matter. Mecha et al. (2016) studied the effects of parameters on the ozonation of micropollutants in municipal wastewater treatment processes. They reported that the process efficiency for micropollutants' removal from primary and secondary municipal wastewaters depended on the pH and ozone dosage. El-taliawy et al. (2017) studied ozonation efficiency in removing micropollutants from various wastewater in Switzerland. They reported that for a lot of compounds removal rate of >90% can be reached, however, they didn't specify any exact ozone dosage and wrote that ozone dosage needs optimization based on the types of micropollutants present in the wastewaters. Zoumpouli et al. (2020) studied the simultaneous ozonation of 90 organic micropollutants. They reported high removal rates of micropollutants. The results showed that their 47 studied micropollutants reached >90% removal rates at neutral pH (7.0), while all their studied micropollutants achieved removal rates of >70% at an alkaline pH value (pH=11). Mostly high-performance liquid chromatography-mass spectrometry (HPLC-MS) and gas chromatography-mass spectrometry (GC-MS) are used for the quantification of micropollutants, besides other techniques.

The combination of ozonation with other processes can increase the efficiency of the process and result in better wastewater treatment processes. Combined ozonation and activated carbon is a treatment process applied in full-scale reclamation plants (Reungoat et al., 2012), which directly reduces most micropollutants (Eggen et al., 2014 & Zietzschmann et al., 2015). It acts as a barrier (Reungoat et al., 2012) to organic contaminants and is beneficial for removal of micropollutants (Zietzschmann et al., 2015) and ecosystem health (Stalter et al., 2010). Stalter et al. (2011) also reported that combined AC and $O_3$ effectively reduced endocrine activities (estrogenicity: up to 99%; androgenicity up to 96%; and arylhydrocarbon receptor (AhR) agonistic activity: up to 82%). Table 8 presents ozonation of some micropollutants.

Ozonation combined with biological post-treatment has also been studied in full-scale municipal wastewater treatment plants for trace organic compounds' (TrOCs) removal. This combination has been reported to be effective as ozonation enhances the biodegradability of the pollutants and decreases pH to a neutral level, with no need for further pH adjustment for biological post-treatment; whereas biological post-treatment removes (>95%) unknown and potentially toxic

**Table 8.** Ozonation specifications of some micropollutants

| Micropollutant | WW/Effluent | Ozone dosage | Contact (min) | Efficiency (%) | Reference |
|---|---|---|---|---|---|
| Diverse micropollutants | Hospital | 0.5[b] | | 93±9 | Lee et al., 2014 |
| Pharmaceuticals | Municipal | 10-15[a] | 18 | Non-detectable | Ternes et al., 2003 |
| Toxicity removal | Secondary | 1.4[c] | 15 | 100 | Meric et al., 2005 |
| Estrogen immunoreactivity | Tertiary | 0.6–1.1[b] | | 97.7±1.2 | Altmann et al., 2008 |
| Androgen immunoreactivity | Tertiary | 0.6–1.1[b] | | 56.3±16.5 | Altmann et al., 2008 |
| Anti-esterogenic activity | Secondary | 10[a] | | 65–87 | Tang et al., 20014 |
| Erythromycin | Municipal | 0.3[a] | 2 | Eliminated | Michael et al., 2017 |
| Ethylparaben | Municipal | 0.3[a] | 2 | Eliminated | Michael et al., 2017 |
| Carbamazepine (CBZ) | Secondary | 0.7[b] | | Efficient | Hubner et al., 2014 |
| Venlafaxine (VLX) | Pharmaceutical | 0.87[b] | | 98 | Lester et al., 2013 |
| Antiviral drugs | Municipal | | 20 | Immeasurable | Eryildiz et al., 2022 |

**Note:** (a) $mgO_3.L^{-1}$; (b) $gO_3.g^{-1}$; (c) $gO_3.L^{-1}$; DOC – dissolved organic carbon; min – minute; WW – wastewater.

transformation products (TPs) (Itzel et al., 2020). However, Itzel et al. (2020) reported that antagonistic effects were not reduced significantly during this process, and therefore, further studies of the effectivity of this combination are required.

A group of researchers studied the removal of 24 pharmaceutically active compounds (PhACs) during combined ozonation and sand filtration with activated sludge treatment (Nakada et al. 2007). The authors reported >80% removal rates of most target compounds with a C=C double bond or aromatic compounds with electron donors (i.e. phenol, alkyl, methoxy, or non-protonated amine) to be more susceptible. Other researchers also studied the efficiency of biological treatment followed by ozonation for various micropollutants' removal. Schepper et al. (2010) reported efficient removal of a large number of individual pollutants, mainly pharmaceuticals and personal care products refractory to biological treatment in a sewage treatment plant (STP). Biological treatment is also capable of detoxification of toxicity increased during ozonation (Lin et al., 2001).

Moerman et al. (1994) reported that activated sludge followed by ozonation for carbonization of wastewaters allows high-quality effluent. Biological treatment processes followed by ozonation have also been reported to be more efficient in the elimination of micropollutants from pharmaceutical wastewater (Lester et al., 2013). This research studied the treatment of pharmaceutical formulation facility wastewaters by biological processes and ozonation. The authors suggested treatment of such wastewater at the manufacturing site to limit further environmental contamination and also due to the financial costs. Another research also reported the efficient application of biological treatment processes followed by ozonation for COD (chemical oxygen demand), aromatics and total phenolic compounds removal from industrial wastewater (Beltran et al., 2000).

## OZONATION BY-PRODUCTS

Wastewaters differ in their composition and nature and have complex structures, therefore, ozonation cannot degrade all organic compounds and results in formation of by-products (Petala et al., 2008). Low-molecular-weight organic compounds such as aldehydes and carboxylic acids are major organic disinfection by-products (DBPs) of ozonation (Tripathi et al., 2011).

According to a study, reactions of aniline derivatives with ozone formed Azobenzenes, azoxybenzenes and benzidines, potent mutagens and carcinogens. However, the addition of mannitol, a hydroxyl scavenger, has been reported to reduce its formation significantly (Chan & Larson, 1991), while following chemical coagulation with $Ca(OH)_2$ has been described as a method for the total elimination of remaining compounds in the ozonation process (Sarasa et al., 1998). On the other hand, nitrosamine formation during the ozonation process has been identified as a challenge for municipalities toward avoiding reverse osmosis and ultraviolet (UV) irradiation with high doses (Gerrity et al., 2015).

The formation of halogenated by-products is another main challenge towards the ozonation process. Iodinated disinfection by-products (I-DBPs) are associated with genotoxicity and cytotoxicity. They are more toxic than their chlorinated and brominated counterparts (Allard et al., 2013). However, of more concern and widely studied ozonation by-products are brominated disinfection by-products (Br-DBPs) due to their dispersity. Bromide is the most dispersed ion in seawater. It is the principal precursor of bromate during ozonation and the end product of microbial bromate reduction (Falas et al., 2022). A recent study regarding newly-identified Br-DBPs found that bromophenylacetonitriles and 2,4,6-tribromophenol are cytotoxic, 2,4,6-tribromophenol and bromostyrenes are genotoxic, and bromophenylacetonitriles and bromostyrenes cause oxidative damage (Zhang et al., 2022).

European Union (EU) and the United States Environmental Protection Agency (USEPA) have already established the maximum level of bromate $(BrO_3)^-$ in drinking water to be 10 $\mu gL^{-1}$ (Michael et al., 2017). Reactions of bromate formation during ozonation are presented below (Grguric et al., 1994):

$$O_3 + Br^- \rightarrow O_2 + OBr^- \quad (6)$$

$$O_3 + OBr^- \rightarrow 2O_2 + Br^- \quad (7)$$

$$2O_3 + OBr^- \rightarrow 2O_2 + BrO_3^- \quad (8)$$

Many studies have been conducted regarding the prevention of bromate formation. Some of the most notable methods for the prevention of bromate formation are presented in Table 9.

Lester et al. (2013) studied treatment of a pharmaceutical formulation facility wastewater by ozonation and biological processes. As ozonation

**Table 9.** Some of the most notable practices for the prevention of bromate formation

| Method | Specification | Reference |
|---|---|---|
| Temperature | Br-DBPs formation and temperature are directly related. | Zhang et al., 2005 |
| pH | Hydroxylamine (HA) presence alters the pH dependency of bromate formation during the ozonation process. | Yang et al., 2017 |
| $O_3$ dosage | By decreasing ozone dosage, both bromate formation and micropollutants' removal rate decrease. | Soltermann et al., 2017 |
| $NH_3$ | Ammonia addition can inhibit bromate formation. | Hofmann & Andrews, 2001 |
| $NH_3$ | $ClO_2$ and $MnO_4^-$ with $NH_4^+$ can be promising pre-treatment for the inhibition of bromate formation. | Antoniou et al., 2017 |
| $CeO_2$ | $CeO_2$ Minimizes bromate formation potential (BFP). | Zhang et al., 2008 |
| Catalyst | Catalysts can inhibit bromate formation; i.e. Ce-MCM-48 catalyst at pH = 7.6 and T = 25 °C | Li et al., 2015 |
| $H_2O_2$ | $H_2O_2$ dosage of 0.35 mg $H_2O_2$/mg $O_3$ almost completely prevented the formation of Br-DBPs. | Zhang et al., 2005 |

**Note:** Br-DBPs – brominated disinfection by-products.

by-products are more biodegradable than their parent compounds, therefore, the authors recommended a post-ozonation biological treatment process for removal of ozonation by-products.

## CONCLUSIONS

Recognition of ozone as generally safe (GRAS) has authenticated its status, which resulted in the diversification of its applications and scale-up of water and wastewater ozonation systems. Ozonation has proven to be a superior alternative to long-applied traditional methods. Ozone not only reacts directly, but also indirectly via hydroxyl (•OH) radical and is effective for microbial inactivation, degradation of recalcitrant organic compounds, removal of a diverse range of micropollutants, solubilization and reduction of sludge, and removal of color and odor components.

Toxicity related to chlorination disinfection by-products led to the search for an alternative and ozonation filled the gap quite rapidly due to its superior properties. However, various toxicities have also been reported of ozonation by-products and researchers are targeting widely brominated disinfection by-products (Br-DBPs). More detailed toxicity tests are needed to ensure the toxicological safety of reclaimed waters on humans, animals, plants and overall, the ecosystem.

Ozone generation costs have been an obstacle to its universal application as a tertiary treatment process and as part of the advanced oxidation processes (AOPs). Besides the diversity of micropollutants and persistent addition of new pollutants into the municipal and industrial wastewaters, due to advancing technology and formulation of new products, become another main challenge towards its diverse application. Further research might be more focused on more efficient and cost-effective ozone generation, optimization of ozone process parameters, catalysts for the ozonation of the specific and wide range of micropollutants, and toxicities related to the ozonation disinfection by-products.

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