

## Advanced Oxidation Processes in Water/Wastewater Treatment in removing environmental pollutants and study some of their application

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### Abstract

The biggest issue facing humanity today is environmental pollution, which is a long-standing phenomenon and one of the main environmental causes of disease and mortality. air, water, and soil pollution kinds, their sources and effects, and strategies for reducing pollution for a healthy and sustainable environment. AOPs reduce the amount of contaminants in the water by using strong chemical oxidants. Along with this purpose, these procedures can also eliminate odor, enhance the drinking water's flavor, and kill microorganisms (as a disinfectant). One of the non-photochemical AOPs techniques is the production of hydroxyl radicals without light via the Fenton reaction or ozonation. The photochemical AOPs methods produce reactive hydroxyl radicals by combining UV light with H<sub>2</sub>O<sub>2</sub>, O<sub>3</sub>, and/or Fe<sup>2+</sup>. When traditional O<sub>3</sub> and H<sub>2</sub>O<sub>2</sub> are unable to fully oxidize organic contaminants, the photochemical approach is employed; otherwise, the non-photochemical method is frequently employed. Nevertheless, the kind of contamination that needs to be eliminated determines which AOPs techniques are used.

**Keywords:** Environmental pollution, Advanced Oxidation Processes, Photochemical, non – Photochemical.

### Introduction

Environmental pollution is a widespread issue that has a negative impact on the environment and endangers human and ecological health [1]. Pollutants are a global problem because they disturb natural habitats, reduce biodiversity, and have detrimental effects on air, water, and soil[2]. They can also linger in the environment for long

periods of time, causing extensive environmental harm. Through air and water currents, these contaminants' detrimental effects can spread across great areas[3]. It consists of biological contaminants, chemicals, heavy metals, greenhouse gasses, and particle matter. Environmental pollution can take many different forms, such as noise pollution, soil contamination, water pollution, and air pollution. However, if they are present in sufficient amounts, even very little and undetectable pollutants can occasionally lead to pollution. Environmental pollution can also result from human activity introducing contaminants into the air, water, and land, or from natural occurrences like volcanic eruptions[4]. Ingestion, inhalation, and ingestion are the three primary ways that contaminants enter the body. Reducing the causes of pollution, particularly those that are human-caused, like industry, can help to lower pollution overall. By employing ecologically friendly production methods and procedures, as well as by establishing dedicated drainage channels for chemicals—whether gaseous, solid, or liquid—and, if feasible, recycling them, industries can lessen pollution. Anyone responsible for environmental contamination must face harsh punishment from the government[5]. The purpose of this study is to elucidate the many kinds of pollutants, their impacts on both the environment and people, and the function of sophisticated oxidation techniques in their removal.

### **Types of pollution:**

#### **❶ Water pollution**

Water is necessary for life, but it also serves as a popular hiding place for pollutants and filth. As everyone is aware, both natural and human factors contribute to water contamination. But as industrialization has accelerated, human activity has played a significant role in the decline of water quality, leading to more complicated and severe water contamination. Inorganic pollutants (such heavy metals, acid and base salts, and radionuclides), organic pollutants (like pesticides, medications, and materials, colors), and microbiological pollutants (like bacteria and viruses) are the three categories of pollutants that contaminate water[6]. Furthermore, paints and their byproducts have the potential to kill both people and the environment, which results in significant pollution of the environment[7].

### ❷Pollution of soil

Natural elements (geology/lithogenic inputs, geographic features, local climate) or human activity can cause metals to enter soil. Metal concentrations in soil are typically low by nature. Human activity, however, has the potential to change the fundamental characteristics of soils, which can result in the buildup of metals and elevated levels of contamination. One of the main anthropogenic pollutants is cadmium, which is particularly released by industrial effluents. Cadmium buildup in roots, stems, and leaves, notably in the edible portions of crops and especially in market garden goods, may result from its transmission in the soil–plant system[8].

### ❸Pollution in Medicines

Pharmaceuticals are one category of environmental contaminants that are becoming a serious problem for surface water and the environment (both residential and industrial). Because of the dangers involved, there are some concerns about the way pharmaceutical waste is released[9]. The most polluted locations were found in low- to middle-income nations and were linked to pharmaceutical manufacture, inadequate wastewater treatment facilities, and waste management infrastructure. Caffeine, metformin, and carbamazepine were the most commonly found substances, appearing at more than half of the sites under observation[10].

### ❹Pollution of Air

One of the biggest environmental hazards to human health is air pollution. Although natural events like wildfires and volcanic eruptions can create pollution and contamination of the environment, man-made activities like transportation, industry, and agriculture are mostly to blame[11]. Cancer, respiratory disorders, and other chronic ailments are just a few of the serious health effects that this pollution can have on people. Chemical pollutants are now significant pollutants that are raising the toxicity of the air, soil, and aquatic ecosystem. The cost of cleaning up contaminated places and reducing the negative impacts on human health are just two examples of the substantial economic repercussions that environmental pollution and contamination can have[12]. Figure 1 depicts a planet that is split according to its deeds and results. The gloomy haze of industrialization covers half of it, showing contaminated landscapes,

smoke-belching factories, and waste-filled rivers. The vibrant energy of renewable sources emanates from the opposing half.



**Figure 1. Addressing global environmental pollution using environmental control techniques: a focus on environmental policy and preventive environmental management[13].**

### **Effects of pollution on human and environment:**

The air is generally polluted by dangerous materials that come from both natural and artificial sources. The primary sources of pollutants include power plants, burning trash, vehicular emissions, chemical firms, and volcanic eruptions[14]. These sources include heavy metals, biological contaminants, ozone, carbon monoxide (CO), sulfur dioxide (SO<sub>2</sub>), and tobacco smoke are all released into the air that is inhaled. When these contaminants are consumed, they disrupt the body's natural processes, leading to illnesses like cancer, heart disease, reproductive disorders, problems with the fetal central nervous system, and respiratory disorders[15]. Health problems are caused by tobacco smoke, which contains dangerous substances like nicotine, formaldehyde, arsenic, benzene, and cadmium. Both smokers and passive smokers will develop cancer from it, and volatile chemical compounds can induce headaches, nausea, loss of coordination, and irritation of the eyes, nose, and throat[16]. Long-term exposure can harm several bodily parts, primarily the liver. Water pollution has a profound effect on ecosystems and

the environment, influencing not only the quality of the water but also the survival and well-being of plants and animals[17]. Populations of species that rely on healthy water ecosystems for existence may drop as a result of water pollution, which can also upset the food web. Aquatic environments may become eutrophic due to an overabundance of nutrients, especially nitrogen and phosphorus, which can lead to excessive growth of plants and algae. Aquatic life may suffer severe consequences as a result of this depletion of the water's oxygen content[18]. Additionally, because it can reduce the availability of drinkable water as well as water for agriculture and other uses, water pollution can have a substantial negative economic impact. This can hurt the economies of communities who depend on water for their livelihoods and raise the price of supplying clean water[19]. The environment is greatly impacted by air pollution because it releases a variety of man-made substances, including SO<sub>2</sub>. It is well recognized that these pollutants impact the radiative balance and composition of the atmosphere, which affects atmospheric stability and circulation patterns. The hydrological cycle may be impacted by the interaction of air pollutants with cloud formations, which can alter cloud albedo and precipitation patterns. Moreover, acid rain and ground-level ozone generation are facilitated by these pollutants. Contamination of the soil has the potential to alter the dynamics of nutrient cycle and greenhouse gas emissions, as well as disrupt the soil-microbial consortium. Polluted soil contains contaminants that can seep into groundwater, contaminating drinking water supplies widely and harming people's health[20] .

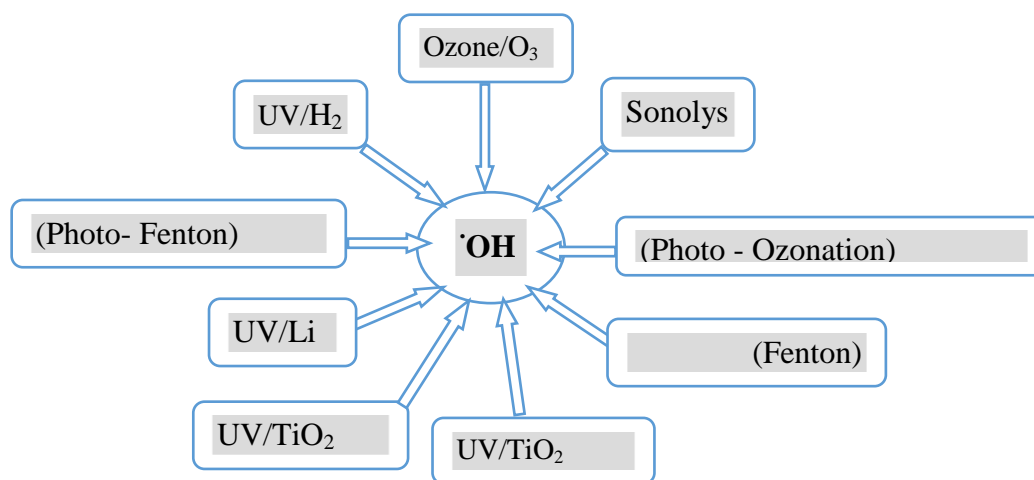
**Advanced Oxidation Processes:**

There are methods for removing organic contaminants from water that are generally acknowledged to be successful[21]. Because of their special physicochemical characteristics, transition-metal nanoparticle catalysts have demonstrated outstanding efficacy in recent years in inducing AOPs for the removal of organic pollutants. Advanced oxidation processes (AOPs) are frequently employed to clean up contaminated soils and purify water bodies[22]. They are also becoming more efficient and environmentally benign methods of treating persistently hazardous contaminants. AOPs encompass a range of methods, including electrochemical oxidation, photocatalytic oxidation, ozone oxidation, and Fenton oxidation. They were initially created in 1987 as a method of treating wastewater that produces potent oxidants, including hydroxyl radicals, to break down organic and non-biodegradable contaminants at room temperature and

pressure. Toxic organic molecules in industrial wastewater can be effectively broken down and totally oxidized by AOPs, which facilitates biological treatment. By oxidizing these contaminants, AOPs transform them into less dangerous compounds[23]. The classification of AOPs is shown in Table.1. The main sources for generation of  $\cdot\text{OH}$  are explained in Scheme 1[24].

**Table 1. The Classification of Advanced Oxidation Processes[25].**

Non-Photochemical	Photochemical
Ozonation	Photocatalytic oxidation,UV/Catalyst
Ozonation with hydrogen peroxide ( $\text{O}_3/\text{H}_2\text{O}_2$ )	$\text{UV}/\text{H}_2\text{O}_2$
Fenton and related processes ( $\text{Fe}^{2+}$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2$ )	$\text{UV}/\text{O}_3$
Wet air oxidation (WAO)	$\text{UV}/\text{O}_3/\text{H}_2\text{O}_2$
Electrochemical oxidation	Photo-Fenton and related processes processes ( $\text{Fe}^{2+}$ or $\text{Fe}^{3+}/\text{H}_2\text{O}_2/\text{UV}$ )
Catalytic wet air oxidation (CWAO)	Heterogeneous Photolytic Oxidation $\text{UV}/\text{ZnO}$ , $\text{UV}/\text{SnO}_2$ , $\text{UV}/\text{TiO}_2$ , $\text{UV}/\text{TiO}_2/\text{H}_2\text{O}_2$


**Scheme 1. Main Sources of  $\cdot\text{OH}$  in Advanced Oxidation Processes[26].**

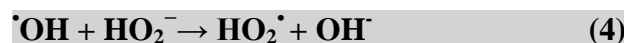


Therefore, partial breakdown produces some molecules that are smaller in molecular mass, have fewer electrons, and are more hydrophilic and biodegradable than the basic contaminants[27]. The subsequent stages of treatment technology can handle these chemicals more readily. Depending on the reactive phase (homogeneous and heterogeneous) or the mechanism of producing reactive radicals (chemical, electrochemical, and photochemical), the advanced oxidation processes can be categorized. Significant attempts have recently been made to lower reactor and operating expenses by using solar energy rather than UV or visible bulbs. The reality that significant actions still need to be made to attain high efficiency is highlighted by the fact that the findings were not always favorable[28]. Advanced oxidation processes that use solar energy are typically placed in ultrasonic or microwave fields to attain high efficiency, which raises the reactors' running expenses. Furthermore, it must be considered that the high reactivity of the radicals produced in the system is the foundation for the effectiveness of the advanced oxidation processes[29]. Nevertheless, because these radicals are non-selective, they will affect the system's natural organic material as well as the target chemicals, which are often present in little amounts. As a result, the target compounds' degradation efficiency can be substantially lower than the system's total organic material degradation efficiency. The process of decolorizing wastewater dye is a crucial step in removing any organic or inorganic materials that give water its color[30].

### **Classification of Photochemical Advanced Oxidation Processes:**

#### **●Photo-Peroxidation (H<sub>2</sub>O<sub>2</sub>/UV):**

UV radiation with wavelengths ranging from 200 to 300 nm can photolyze H<sub>2</sub>O<sub>2</sub>. The H<sub>2</sub>O<sub>2</sub> molecule's O–O link can undergo homolytic fission, which results in the creation of <sup>•</sup>OH radicals via a sequence of subsequent events[31]. as shown in the following equations:

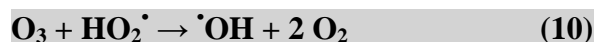
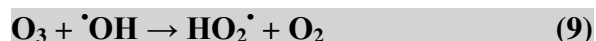




The free radicals  $\text{HO}_2^{\bullet}$  and  $^{\bullet}\text{OH}$  can be produced by UV light. Nonetheless,  $\text{H}_2\text{O}_2$  has a relatively low molar absorption coefficient in the UV region[32]. High concentrations of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ) must be utilized to remove the target pollutants (both traditional and emergent contaminants) from wastewater because the molar absorption of  $\text{H}_2\text{O}_2$  in the UV region is insufficient. In conclusion, the initial concentration of hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), the UV light's intensity, the wastewater's pH, and the components present all affect the photo-peroxidation (UV- $\text{H}_2\text{O}_2$ ) process[33].

### ❷ Photo-Ozonation ( $\text{O}_3/\text{UV}$ ):

Ozone has a molar absorption value of  $\epsilon_{\text{max}} = 3600 \text{ L mol}^{-1}\text{cm}^{-1}$ , meaning that it absorbs UV rays between 200 and 360 nm, with a maximum at 253.7 nm. Ozone photolysis is more efficient than  $\text{H}_2\text{O}_2$  photolysis because  $\text{O}_3$ 's  $\epsilon_{\text{max}}$  value ( $\epsilon_{\text{max}} = 18.6 \text{ L mol}^{-1}\text{cm}^{-1}$ ) is higher than  $\text{H}_2\text{O}_2$ 's at this wavelength.  $^{\bullet}\text{OH}$  radicals, which are more reactive and effective oxidizing species, are created when ozone photolyzes in water[34]. According to a series of competitive steps as shown in equations (8) to (11).



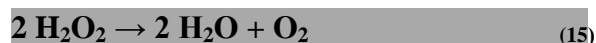
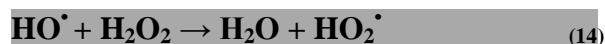
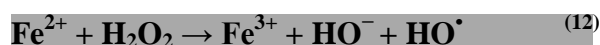
With intriguing outcomes,  $\text{ZnO}$  and  $\text{TiO}_2$  have recently been tested as heterogeneous catalysts for the photo-ozonation process. More research may be done on the application of heterogeneous catalysts in the photo ozonation process because these materials were proven to be effective catalysts in producing the oxidant species in the presence of photons[35]. Ozonation often produces oxidation intermediates such organic acids, aldehydes, and ketones but struggles to fully mineralize organic contaminants into  $\text{CO}_2$  and  $\text{H}_2\text{O}$ . UV will encourage the breakdown of



ozone, as was previously mentioned. Consequently, organic contaminants have been degraded more effectively by the O<sub>3</sub>/UV process than by the O<sub>3</sub> and UV processes alone[36].

### ☉Photo Fenton (Fe<sup>2+</sup>/H<sub>2</sub>O<sub>2</sub>/UV):

In addition to the initial organic dyes and the products of their breakdown, dye bath wastewater from textile dyeing and processing also contains high levels of inorganic salts, surfactants, and other auxiliary preparations[37]. Energy consumption, sorbent regeneration or disposal, membrane fouling and permeability issues, or waste sludge disposal are all constraints of the aforementioned systems. Consequently, there is a strong need for more advanced and highly effective technology to completely remove pollutants from the aquatic environment. Advanced oxidation processes (AOPs) are still being considered as a means of destroying organic molecules. AOPs were primarily based on the generation of hydroxyl radicals (radical dot OH), which are highly reactive and non-selective agents that are appropriate for the mineralization of organic materials, even in the first ten years of the twenty-first century. The issue is that in order to produce this oxidant, the majority of published efforts employ costly potassium peroxydisulfate (K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>) as a precursor. Additionally, either heat, UV light, or transition metal ions are required to activate both precursors. It should be mentioned for the sake of objectivity that transition metals and oxides, like Fe, Co, or Mn, have been employed as the most efficient activators, not just for peroxysulfate (PMS) and peroxydisulfate (PDS). Fenton highlights the reaction pathways of the production of radical dot OH in the application processes[38]. In addition, a lot of work has been focused on the photodegradation of organic dyes by various UV irradiation systems, such as combinations with H<sub>2</sub>O<sub>2</sub>[39].



Reactive (·OH) radicals are produced by the breakdown of H<sub>2</sub>O<sub>2</sub> in acidic conditions, which is started and catalyzed by the Fe<sup>2+</sup>. The Fenton reagent is a mixture of H<sub>2</sub>O<sub>2</sub> and ferrous iron salts (Fe<sup>2+</sup>), which results in the Fenton treatment process. This process involves a complex reaction sequence[40].

#### ④ photocatalysis:

It is a procedure where a catalyst that is activated by the absorption of photons with energy above its bandgap speeds up a chemical reaction[41]. The presence of contaminants in a fluid phase while the catalyst is in a solid phase is referred to as heterogeneous. After several attempts at this methodology, a novel advanced oxidation process (AOP) technology based on semiconductor photocatalysis was developed for energy and environmental applications[42]. A photogenerated hole ( $h^+$ ) is left in the valence band of a semiconductor when it is subjected to light with ultra-b-andgap energy, which excites a valence band electron to the conduction band. In the photocatalytic destruction of pollutants in moist conditions, the  $e^-/h^+$  couples can then move to the semiconductor's surface and take part in redox processes that produce hydroxyl radicals ( $\cdot OH$ ),  $h^+$ , and superoxide ion radicals ( $\cdot O_2$ ) as shown in (Figure.2). The catalyst and oxidation states influence how effective the photogenerated  $h^+$  is as an oxidant that directly breaks down organic pollutants[43].

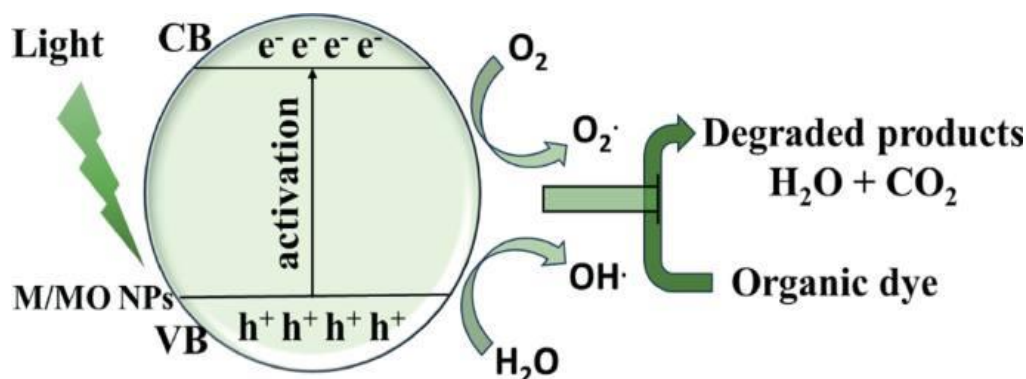


Figure 2. Schematic of photocatalytic reaction on photocatalyst surface[45][44].

In this process, valence band holes and conduction band electrons are produced when photoirradiation strikes the catalyst surfaces. Superoxide radical anions are produced when the valence band holes react with molecular oxygen absorbed on the catalyst surface, while  $\cdot OH$  radicals are produced when they mix with water. Degradation kinetics for pharmaceutical pollutants are affected by a number of operational factors, including the substrate's starting concentration, catalyst loading, type of  $TiO_2$  photocatalyst, wavelength/light intensity, solution

pH, and water matrix. Heterogeneous photocatalysis requires several items to be fulfilled, such as the following[35]:

- (a) A photon emitted at the suitable wavelength.
- (b) A semiconductor material as a catalyst.
- (c) A strong oxidizing agent.

The challenge obstacle is related to the development of novel catalyst types with higher quality.

There are some restrictions that need to be detailed, as follows[40]:

1. Bandgap regulation to obtain a type of catalyst that has activity in the visible range.
2. Delay or avoidance of recombination of electron holes.

### **Classification of non-photochemical Advanced Oxidation Processes:**

#### **❶ Ozonation:**

Ozone is incredibly efficient at degrading medications. Ozone is used as a disinfectant and to regulate taste and odor in drinking water[46]. Research on the treatment of pharmaceuticals in later stages has been carried out in drinking water facilities and WWTPs. Ozonation degrades wastewater's target compounds and yields readily biodegradable byproducts. It can greatly increase biodegradability, particularly in antibiotic-containing effluent[47]. Pharmaceutical wastewater, particularly those containing antibiotics, is much more biodegradable when ozonation is employed as a pre-treatment procedure. It can improve the breakdown of medications in wastewater either by itself or in conjunction with biological treatment. Utilize ozone-based methods with  $H_2O_2$  or UV radiation to increase the generation of hydroxyl radicals in order to promote the breakdown of pharmaceutical contaminants in water[48]. During these treatments, variables such as temperature, ozone dosage, and pH are critical to the conversion and mineralization of medications. It's crucial to remember, though, that ozone's short lifespan makes it a quite costly technique, and its high energy requirement might prevent it from being used in practical settings. Although ozonation efficiently eliminates APIs such as trimethoprim, sulfamethoxazole, and carbamazepine, it results in low mineralization rates because of lingering byproducts. Target APIs can be eliminated with low ozone dosages, however this frequently leads to insufficient mineralization rates[49]. Research indicates that the efficacy of ozonation on medications differs according on their molecular makeup. Compared to non-catalytic

[www.zjhms.alzahraa.edu.iq](http://www.zjhms.alzahraa.edu.iq) ozonation, which demonstrated a 79.2-fold increase in cephalexin degradation with the catalyst, catalytic ozonation with unanchored zeolite eliminated 97% of cephalexin in 2 minutes. Low solubility in water, increased energy consumption, and the creation of hazardous byproducts are some disadvantages of ozone-based water treatment. These problems can be resolved, though, by employing a catalyst in a procedure known as catalytic ozonation. A variety of catalysts, such as metals and carbon-based materials, are essential for facilitating the complete breakdown of organic compounds while reducing the production of toxic byproducts. By using catalysts, contaminants can be completely eliminated by favoring indirect oxidation over direct electrophilic ozone reactions. Micropollutants, microbiological count, color, odor, and foam are all successfully eliminated by ozonation. It might not, however, completely mineralize the target molecules, which could result in the creation of additional dangerous chemicals. Reactive oxidation products require further treatments, such as sand filtering. It's crucial to remember that although ozonation has several advantages, there are additional energy expenses involved[50].

### ❷Catalytic wet air oxidation (CWAO):

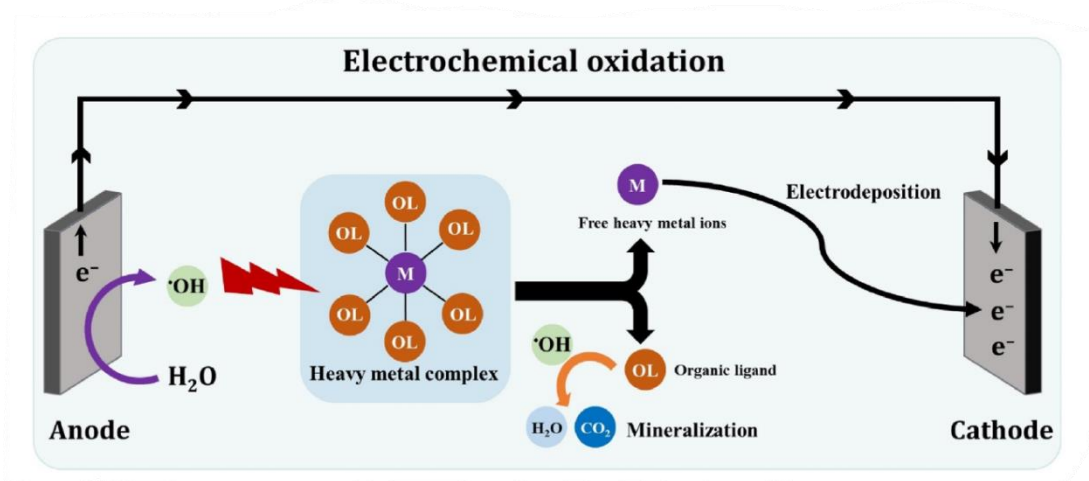
Conditions of the reaction In addition to lessening the severity, catalytic wet air oxidation (CWAO) breaks down even refractory pollutants more readily, which lowers operating and capital costs. Because of its shorter residence time and softer working conditions, CWAO has an operating cost that is around half that of non-catalytic WAO, however this varies depending on the kind of wastewater[51].Despite the effectiveness of homogeneous catalysts, such as dissolved copper salts, a further separation step is necessary to extract or recover the metal ions from the treated effluent because of their toxicity, which raises operating expenses. Because a separation phase is not required, the development of active heterogeneous catalysts has so drawn a lot of attention. Noble metals, metal oxides, and mixed oxides are among the solid catalysts that have been extensively researched for the CWAO of aqueous pollutants. With an emphasis on catalytic performances and reaction conditions, the current study examines the recently published literature (mostly within the last ten years) on the heterogeneous CWAO of refractory organic pollutants, such as phenolics, carboxylic acids, nitrogen-containing chemicals, and actual wastewaters. To make heterogeneous catalytic reactions easier to grasp, reaction mechanisms and kinetics that have been postulated for the heterogeneous CWAO of organic compounds—

primarily phenol—are addressed. The primary causes of catalyst deactivation in heterogeneous CWAO, namely metal leaching and carbonaceous deposits, are finally discussed[51].

### ❶Electrochemical oxidation:

Heavy metal ions are most commonly recovered from heavy metal complexes via electrochemical oxidation. The removal of Cu-EDTA complexes from wastewater via an electrolytic reduction technique was examined[52]. According to the study, ferrous ions might be produced using waste iron enclosed in a Ti mesh cage as a sacrificial anode. The elimination of Cu-EDTA complexes was significantly aided by these ferrous ions. By employing a Fe anode, the efficiency of Cu removal was greatly improved, and it rose as the current intensity increased[53]. This resulted in a considerable reduction in the amount of time needed to accomplish 100% Cu removal. examined the removal of Ni-EDTA complexes from wastewater using an electrocoagulation system (ECS). According to the study, applying current and preferred acidic conditions improved the elimination of Ni-EDTA complexes. Additionally, the air-purged mode greatly increased the Ni-EDTA complex removal efficiency. Furthermore, the iron scrap packed-bed anode outperformed the iron rod anode in terms of cost, energy consumption, and removal efficiency[54]. Organic materials with carboxylic and amino groups can be broken down by chlorine radicals, which are extremely reactive chemicals. This has been demonstrated in investigations into the breakdown of Ni-EDTA, where a boron-doped diamond (BDD) anode led to a noticeably higher rate of decomposition. Compared to when  $\text{Na}_2\text{SO}_4$  and  $\text{NaClO}_4$  were present, the measured reaction rate constant was 2.7 and 4 times greater, respectively. This implies that a promising catalyst for the electrochemical decomplexation of chlorine-containing wastewater is the BDD anode. This may result in water treatment techniques that are simpler, more affordable, and more efficient. A hybrid process that combines photocatalysis with electrocatalysis is called photoelectrocatalysis[55]. In order to direct photogenerated electrons towards the cathode, an external bias potential is applied to a photocatalyst that is placed on a conductive substrate as the anode. When water molecules react with photogenerated holes on the anode, hydroxyl radicals ( $\cdot\text{OH}$ ) are created. These radicals can react with a wide range of organic molecules since they are highly oxidizing and non-selective. Heavy metals can be released when OH radicals break down the molecule's bonds. The cathode is subsequently coated with the liberated heavy metals. These procedures involve the anode

directly destroying heavy metal complexes in the anodic region or producing hydroxyl radicals in situ, which result in the deposition of free heavy metal ions on the cathode (Figure 3).



**Figure 3. Electrochemical method for decontamination of HMC[56].**

Wastewater containing Cu-EDTA complexes was treated by combining electrocoagulation and electro-Fenton. This procedure eliminated copper metal and oxidized EDTA at the same time. Adsorption, coagulation, co-precipitation, and cathodic reduction were effective methods for removing the resultant copper ions. The Cu-EDTA complexes were destroyed by hydroxyl radicals[57].

#### ④ Wet air oxidation (WAO):

It is well known that the wet-air or thermal liquid-phase oxidation (WAO) process, which produces active oxygen species like hydroxyl radicals at high temperatures and pressures, has a lot of potential for treating effluents with a high concentration of organic matter (chemical oxygen demand, or COD), or toxic contaminants for which direct biological purification is not practical[51]. Before being released into the environment, physiologically refractory compounds can be broken down by the WAO process into simpler, more readily handled molecules. By using active oxygen species such hydroxyl radicals, this aqueous phase flameless combustion process typically occurs at high reaction temperatures (473–593 K) and pressures (20–200 bar). A three-phase reactor's liquid-phase residence periods can vary from 15 to 120 minutes, and the amount of COD removed can usually be between 75 and 90 %. One of the incredibly



technologically and economically feasible AOPs that Zimmermann created and recommended for wastewater treatment is wet air oxidation (WAO) (Zimmermann, 1958)[58]. WAO either mineralizes the organic contaminants with carbon dioxide, water, and innocuous byproducts, or partially oxidizes them to biodegradable intermediates. In contrast to previous AOPs that employ costly and hazardous oxidizing agents like hydrogen peroxide or ozone, WAO is both economically and environmentally feasible. Sludge is a major by-product of wastewater treatment facilities (WWTPs) that poses a serious risk to ecological and environmental safety. It contains water, different nutrients, mineral components, and complicated contaminants[59]. Numerous technologies, including as landfilling, incineration, composting, and anaerobic digestion (AD), have been used for the treatment and use of sludge[60]. AD is a significant renewable energy technology that helps achieve the UN's global sustainable development goals. However, there are still issues with the digested sludge that anaerobic digesters release[61]. After being stored or micro-aerated, digested sludge may become an organic fertilizer. Due to the requirement for agricultural land and the potential risk of soil contamination and human health issues, this method is still rarely utilized in urban areas. The digested sludge is frequently mechanically dewatered, the effluent is delivered to WWTPs, and the sludge cake is either expensively burnt or landfilled with greenhouse gas emissions. AD can be combined with certain technologies to handle digested sludge. Because it can hasten the decomposition of organic materials and the disintegration of sludge particles, thermal hydrolysis is a useful pretreatment technique for AD[62].

### **Advanced Oxidation process applications**

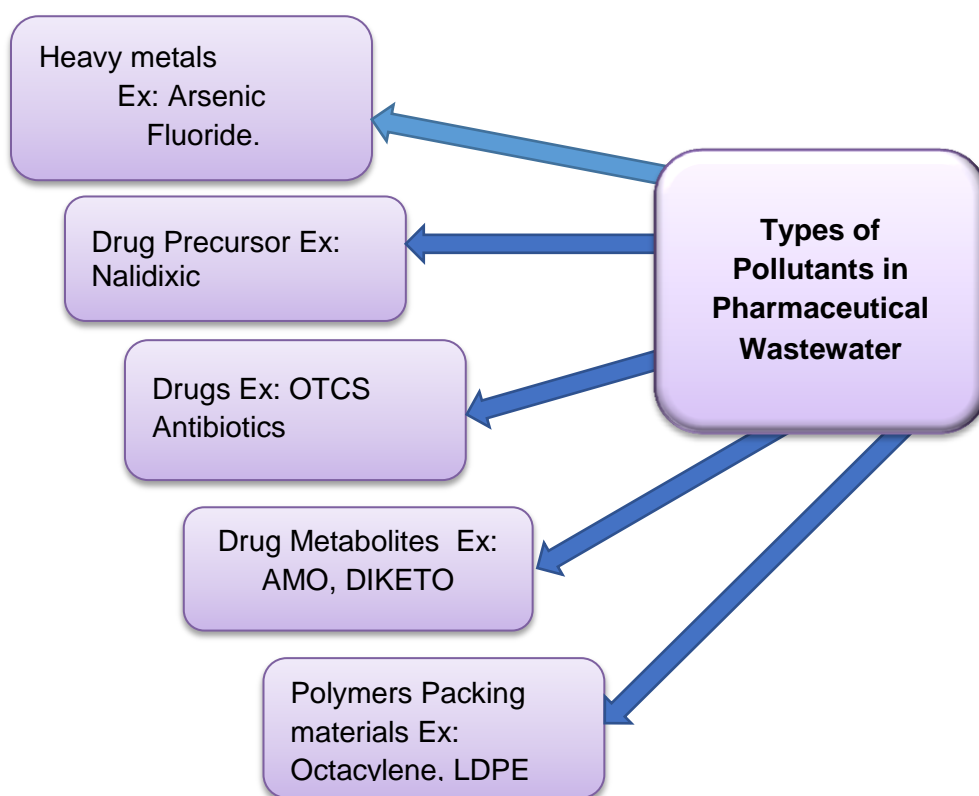
#### **❶ Heavy metal complexes decomplexation/removal in aqueous matrices.**

Heavy metal complexes in wastewater are becoming more widely acknowledged as dangerous substances because of their capacity to bioaccumulate and their enduring endurance in marine environments[63]. It is still difficult to remove harmful heavy metals from actual wastewater that have complexed with organic ligands. Both natural water and industrial wastewater frequently contain organic contaminants and heavy metals. Heavy metals can create stable organic complexes with organic groups like carboxyl, amino, and phenolic hydroxyl when these two interact. We refer to these compounds as heavy metal complexes. When released into the environment through a variety of pathways, heavy metals have the ability to build up and disturb

ecosystems, endangering human health by causing organ damage, problems of the nervous system, and even cancer[64].

## ❷ Sources of pharmaceutical wastewater.

Antibiotics are one example of a medication that can cause long-lasting genetic alterations in microbes, leading to resistance even in small amounts. Reliable data on contributing sources are essential to lowering pharmaceutical residue in water. References Hospitals, fish and cattle farms, STPs, and veterinarian body secretions are the sources of pharmaceuticals in catchment surface water[51]. They also contain industrial drug waste. Chemicals that are dangerous to aquatic life, carcinogenic, mutagenic, and teratogenic can be found in pharmaceutical company effluents. The components and their nature must be classified prior to treatment in order to uphold safety and quality standards. The physicochemical characteristics of effluents must be properly studied before the best treatment method is chosen. Types of possible pollutants in pharmaceutical wastewaters are shown in Figure.4[65].



**Figure. 4 Classification of various types of pollutants in pharmaceutical wastewater.**

### ③ Treatment of wastewater from dyes using oxidation processes.

Priority pollutants, dyes are frequently present in textile effluents at high concentrations. Humans and aquatic life may suffer greatly if wastewater contains dyes or other chemicals. Therefore, it's critical to remove dyes from wastewater to reduce their harmful environmental consequences. Manganese oxides (MnOs) at the nanoscale are one method of dye removal[66]. To date, there has been much work reported on the use of nanosized MnOs as sorbents for dyestuffs. Their amorphous nature, high specific surface areas (SSA), mesoporous structure, and low to moderate point of zero charge make them suitable sorbents for industrial usage. Dyestuffs can produce mutagens and cancer and are sensitive to heat and chemical reagents. Different aquatic life is impacted by the dyes found in water. As a result, there is a strong need to remove dyes from wastewater before it is released into the water. Due to the massive amounts of water needed in dyeing operations, textile companies generate large volumes of dye effluents[67]. Numerous treatment techniques have been studied for the removal of dyes from effluent water. These include photo-degradation, electrochemical oxidation, coagulation-flocculation, chemical reduction, adsorption, and chemical oxidation. Fenton oxidation, membrane separation, and biological techniques. Every one of these approaches has unique benefits and drawbacks. Due to its ease of use, low cost, and potential for efficient adsorbent material recycling, the adsorption process has drawn special interest. Manganese oxide (MnO), a metal oxide mineral, is frequently found in soil, sediment, and aquifers at the nanoscale. These naturally occur as mixed gels, colloidal/discrete particles, and in mixtures with other minerals, such as iron. Through abiotic oxidation, photochemical degradation, adsorption, and catalytic routes, they exhibit promise in controlling the environmental destiny and mobility of contaminants[68].

### ④ The role of oxidation processes in soil treatment.

One popular and eco-friendly method for concurrently breaking down TCP and CPF in soil is microbial remediation. Microbial degradation takes a long time, though, and it works best with little amounts of agriculturally contaminated soil. Advanced oxidation processes (AOPs) based on persulfate (PS) have been used to remediate soil contaminated by high concentrations of various pollutants, such as pesticides, polychlorinated biphenyls, and polycyclic aromatic hydrocarbons[69]. These processes have the potential to generate stronger reactive oxygen

species (ROS). For homogeneous PS activation, heat, ultrasonic, and alkali could be used; for heterogeneous PS activation, a range of materials could be used to create  $\text{SO}_4^{\bullet}$  ( $E_0 = 2.5\text{--}3.1\text{ V}$ ),  $\text{OH}^{\bullet}$  ( $E_0 = 1.9\text{--}2.7\text{ V}$ ). Because of its high degradation efficiency and short reaction time, MW-induced catalytic oxidation of PS has lately gained attention as a possible AOP for the degradation of pollutants. In contrast to traditional heating, MW causes a temperature increase because dipole rotation and molecular friction produce heat in alternating electromagnetic fields[70].

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