

Review

# Application of Nanocatalysts in Advanced Oxidation Processes for Wastewater Purification: Challenges and Future Prospects

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**Abstract:** The increase in population demands for industrialization and urbanization which led to the introduction of novel hazardous chemicals in our environment. The most significant parts of these harmful substances found in water bodies remain in the background, causing a health risk to humans and animals. It is critical to remove these toxic chemicals from the wastewater to keep a cleaner and greener environment. Hence, wastewater treatment is a challenging area these days to manage liquid wastes effectively. Therefore, scientists are in search of novel technologies to treat and recycle wastewater, and nanotechnology is one of them, thanks to the potential of nanoparticles to effectively clean wastewater while also being ecologically benign. However, there is relatively little information about nanocatalysts' applicability, efficacy, and challenges for future applications in wastewater purification. This review paper is designed to summarize the recent studies on applying various types of nanocatalysts for wastewater purification. This review paper highlights innovative work utilizing nanocatalysts for wastewater applications and identifies issues and challenges to overcome for the practical implementation of nanocatalysts for wastewater treatment.

**Keywords:** advanced oxidation processes; challenges; nanocatalysts; wastewater treatment

## 1. Introduction

The urbanization and new industrial age era are putting more severe challenges on the treatment and recycling of wastewater. The traditional contaminants such as polychlorinated biphenyls (PCBs), heavy metals, conventional dyes, pesticides, and many other pollutants released from industrial effluents may be manageable using established methods [1,2]. However, due to the introduction of hazardous contaminants such as polyfluoroalkyl substances, drugs, pharmaceuticals, hormones, antibiotics, disinfection by-products, Dioxane, Benzotriazoles, artificial sweeteners, and endocrine-disrupting chemicals, etc., [3–7] that are resistant to conventional biological treatment, toxic for aquatic environments, humans, mutagenic and carcinogenic, the treatment of wastewater becomes more challenging. More efforts are required from the scientific community to recycle the wastewater to introduce efficient and economical treatment options for wastewater purification.

Many conventional methods such as activated sludge processes, waste stabilization ponds, attached growth methods, sequencing batch reactors, membrane filtration methods, coagulation-flocculation, adsorption, etc., [8–15] have been studied to remove chemical oxygen demand (COD) and inorganic contaminants. Some of them were frequently applied on a larger scale and others on a small scale. Many extended forms of conventional methods were also tested and found effective for wastewater treatment [8–12]. However, hazardous contaminants were observed in the effluents of treated wastewater using conventional treatment processes [16–19]. This poses a severe threat to the environment and requires serious efforts to solve the problem [16–19]. The hazardous contaminants that were even observed in the effluents of treated wastewater using conventional treatment processes include organic pollutants, pathogens, heavy metals, pharmaceuticals, endocrine-disrupting chemicals, and many other persistent organics. Nada et al. [17] studied local wastewater treatment implying a conventional process for the removal of bacterial contaminants and antibiotic genes. In this conventional wastewater treatment process, the first screening of wastewater was carried, and then after screening, wastewater goes to a primary clarifier, aeration tank, secondary clarifier, and then to chlorination for the disinfection of bacteria. Even using the secondary treatment process and chlorination steps, antibiotic-resistant pathogens were identified in the effluent. This indicates that conventional treatment technologies were sufficient for the removal of pathogens and antibiotic genes. Another study accomplished by Du et al. [18] used various conventional treatment methods such as the advanced aerobic treatment system (ATS), septic treatment system (STS), or coupled with subsurface constructed wetland (STS+WET) and municipal treatment plant (MTP) for the removal of some conventional parameters such as total suspended solids (TSS), carbonaceous biochemical oxygen demand (CBOD), ammonia (NH<sub>3</sub>), and mainly contaminants of emerging concern (CECs). In this study, the effluent quality from ATS and (STS+WET) were compared with MTP. The study revealed that ATS and MTP processes were comparable for the removal of most of the CECs but the lowest removal efficiency was observed for the STS process which was enhanced by the coupling of STS with a WET process (STS+WET). Still, the overall outcomes of the study using various conventional processes showed that these processes were inefficient for the complete removal of the unwanted compounds. Khan et al. [19] conducted research on hospital wastewater treatment by using seven different conventional treatment technologies named as submerged aerated fixed films (SAFF) reactor, constructed wetland (CW), fluidized aerobic bed (FAB) reactor, eco-bio reactor (EBR), extended aeration (EA), membrane bioreactor (MBR), and sequencing batch reactor (SBR) for the removal of three types of pollutants; conventional wastewater pollutants (nitrate, alkalinity, TSS, phosphate COD, BOD), significant pharmaceuticals (ofloxacin simvastatin, furosemide, diclofenac, carbamazepine, erythromycin ibuprofen and diazepam), and micropollutants before discharge of the hospital wastewater into the sewage treatment plant. This study revealed that to conquer the deficiencies of conventional treatment technologies and for the reduction of significant pharmaceuticals, the coupling of AOPs must be established because these complex pollutants could not be removed completely by conventional treatment technologies. To conclude, this method is for efficient elimination of pharmaceuticals and safe discharge of hospital wastewater yet challenging. Therefore, AOPs such as ozonation and peroxone were applied. Moreover, MBR and CW are only two conventional treatments out of seven that reduced the conventional pollutants and pharmaceuticals from the secondary and tertiary levels of treatments. The above-mentioned conventional treatment technologies are summarized in Table 1.

**Table 1.** Application of conventional treatment technologies in contaminants' removal from wastewater.

Wastewater Type	Treatment Methods	Steps Involved	Target Contaminants	Effluent Quality	Reference
Industrial	Heavy metal adsorption using PAMAM/TiO <sub>2</sub> nanohybrid	Preparation, characterization, and adsorption	Heavy metals (Cd <sup>2+</sup> , Cu <sup>2+</sup> , and Pb <sup>2+</sup> )	Gradual process, Adsorption increased with the increase of nanohybrid dosage	[16]
Local Community	Local wastewater treatment plant	Screening, primary clarifier, aeration tank, secondary clarifier, and chlorination	Bacterial and antibiotic resistance genes	Insufficient; antibiotic-resistant pathogens were identified	[17]
Municipal	ATS, STS, MTP, and STS + WET	Permanent tank, aeration tank, return tank, and final clarifier	TSS, CBOD, NH <sub>3</sub> , and 19 CECs	Insufficient; TSS, CBOD, NH <sub>3</sub> , and various pharmaceuticals were identified	[18]
Hospital	SAFF, CW, FAB, EBR EA, MBR, and SBR	Single treatment, secondary and tertiary treatment, and coupled treatment	Pharmaceuticals, micropollutants, and conventional pollutants	Insufficient; pharmaceuticals were identified	[19]

Recently, it has been proposed that a combination of conventional and advanced treatment methods may be implied for the economical and efficient treatment of wastewater [20–22]. Since conventional wastewater treatment processes were found to be more economical than advanced treatment methods, a combination of them might be effective for the mineralization and recycling of wastewater [20–22].

Advanced treatment methods and advanced oxidation processes (AOPs) have been extensively studied in the last decade. Advanced oxidation processes can be defined as the processes and technologies which involve the generation of active species such as hydroxyl radicals (•OH) which act as efficient oxidants to decompose pollutants in wastewater treatment. Hydroxyl radicals are very reactive and non-selective species that are proficient in rapidly degrading a wide range of organic compounds. AOPs, including catalytic ozonation processes, radiation-based AOPs, ultrasound, electro-catalytic oxidation, Fenton, and Fenton-like processes, etc., were found to be highly efficient for the treatment of reclaimant organic contaminants [23–25]. Many materials such as zeolites [26–29], activated carbons [30,31], metal oxides, reduced graphene oxides (RGO) [32,33], and metal-organic frameworks (MOFs) [34,35] were implied as catalysts in such processes. Classification of AOPs based on the way the formation of hydroxyl radicals are explained are shown in Table 2. Table 3 summarizes the practical applications of various AOPs for the treatment of specific contaminants from wastewater.

**Table 2.** AOPs' classification based on formation of hydroxyl radicals.

Method	Hydroxyl Radical Production	Peroxone Based	Energy Transfer	Fenton Homogeneous and Heterogeneous Process	Catalytic Heterogeneous Process
Ultrasound	US-assisted cavitation	O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> -US Ultrasound peroxone	Sonolysis	H <sub>2</sub> O <sub>2</sub> -Fe(II)/Fe(III)-US Sono-Fenton method	Catalytic ultrasonic method
Chemical	OH <sup>-</sup> alkaline	O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> peroxone	-	H <sub>2</sub> O <sub>2</sub> -Fe(II)/Fe(III) Fenton method	Catalysts-O <sub>3</sub>
Electrochemical	Electrolytic generation	Electrolytic generation of O <sub>3</sub>	Anodic oxidation	Electro-Fenton method	Wet electrolytic oxidation
Photochemical	UV photolysis	O <sub>3</sub> -H <sub>2</sub> O <sub>2</sub> -UV Ultraviolet peroxone	Direct photolysis	H <sub>2</sub> O <sub>2</sub> -Fe(II)/Fe(III)-UV Photo-Fenton method	Catalysts-UV

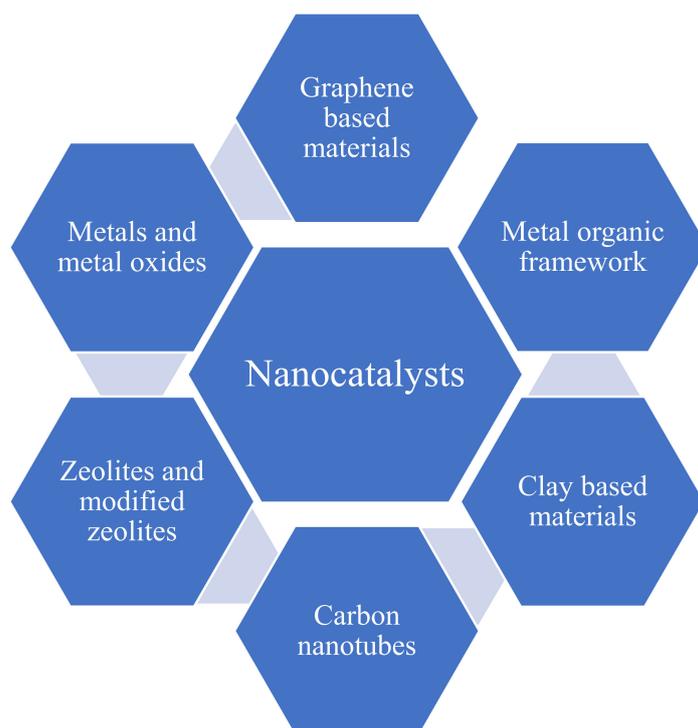
**Table 3.** Application of AOPs in contaminants' removal from wastewater.

Target Contaminants	Contaminant	Applied AOP	Wastewater Type	Evaluated Parameters	Mechanism	Reactor Type	Efficacy	Reference
Pharmaceuticals	Antibiotics (amoxicillin, ampicillin, cloxacillin)	Photo-Fenton	Aqueous solution	Effects of UV irradiation, antibiotics, initial concentration, irradiation time, and biodegradability	$\cdot\text{OH}$ reaction	Batch 600 mL Pyrex	Antibiotics' degradation in 2 min	[36]
Pharmaceuticals	Antibacterial compounds	Ozonation	Aqueous solution	Analysis, interpretation, microdilution, and deactivation	$\text{O}_3$ and $\cdot\text{OH}$ reactions	-	Deactivated	[37]
Pharmaceuticals	Ibuprofen	Solar photoelectro-Fenton, Electro-Fenton, UVA photoelectron Fenton	Acid aqueous solution	Process comparison, pH, kinetics, intermediates finding	$\cdot\text{OH}$ reaction	One compartment cell	Solar photoelectron-Fenton has 92% mineralization	[38]
Dyes	Levafix Blue CA, Levafix Red CA	Electro-Fenton	Industrial wastewater	Potential applied, pH, nature, electrolyte, kinetics	$\cdot\text{OH}$ -oxidative species	Undivided glass electrochemical cell	Complete decolorization and 90–95% mineralization	[39]
Dyes	Orange II	Heterogeneous Fenton process ( $\text{FeVO}_4 + \text{H}_2\text{O}_2$ )	Aqueous solution	Characterization, catalytic activity, pH, stability of $\text{FeVO}_4$	$\text{FeVO}_4$ produced $\cdot\text{OH}$ radicals	Cylindrical Pyrex vessel	94.2% after 60 min	[40]
Dyes	Rhodamine B	UV/ $\text{H}_2\text{O}_2$	Dye solution	Effects of dye concentration, pH, $\text{H}_2\text{O}_2$ dose, irradiation time, and kinetics	$\cdot\text{OH}$ reaction	Beaker	73% decolorization	[41]
Pesticides	Diazinon	$\gamma$ -irradiation	Aqueous solution	Effects of initial concentration, irradiation doses, intermediates' exposure	$\cdot\text{OH}$ attack	Airtight cap vials	Complete degradation	[42]
Aromatics	p-Nitrophenol	Sono-Fenton	Aqueous solution	Various operating conditions	$\cdot\text{OH}$ reaction	Sono-chemical reactor	66.4% degradation	[43]

In recent years, nanomaterials have been successfully implied as catalysts to treat wastewater [32,33]. In AOPs, surface reactions are essential for the effective degradation of pollutants because active surface sites interact with various oxidants ( $O_3$ ,  $H_2O_2$ ) leading to the production of hydroxyl radicals [44]. It is essential to mention that nanomaterials usually acquire high density at active sites due to larger specific surface area [45]; this prosperity is important in AOPs to effectively remove pollutants. Moreover, some nanomaterials have super-paramagnetism [45], which helps separate these materials from bulk. Nanomaterials also have a high density of active sites and larger surface area [45], leading to the adsorption of pollutants that helps to promote their degradation on the surface of catalysts in catalytic advanced oxidation processes.

Most studies using AOPs, both homogeneous and heterogeneous processes, were conducted on a lab scale. For this purpose, aqueous solutions of various pollutants were prepared to investigate the removal efficiency of nanocatalysts. However, the presence of hydroxyl radical scavengers (such as carbonate, bicarbonate, sulfates, phosphates, etc.) in real wastewater may affect the overall efficiency of nanocatalysts [46]. Furthermore, heavy metals, ammonia, nitrogen, and suspended particles may also affect the ability of a catalyst in real conditions [47,48]. Some recent studies reported the efficiencies of the nanocatalysts for real wastewaters. However, only a few studies were conducted on a larger scale to study the application of nanocatalysts in AOPs.

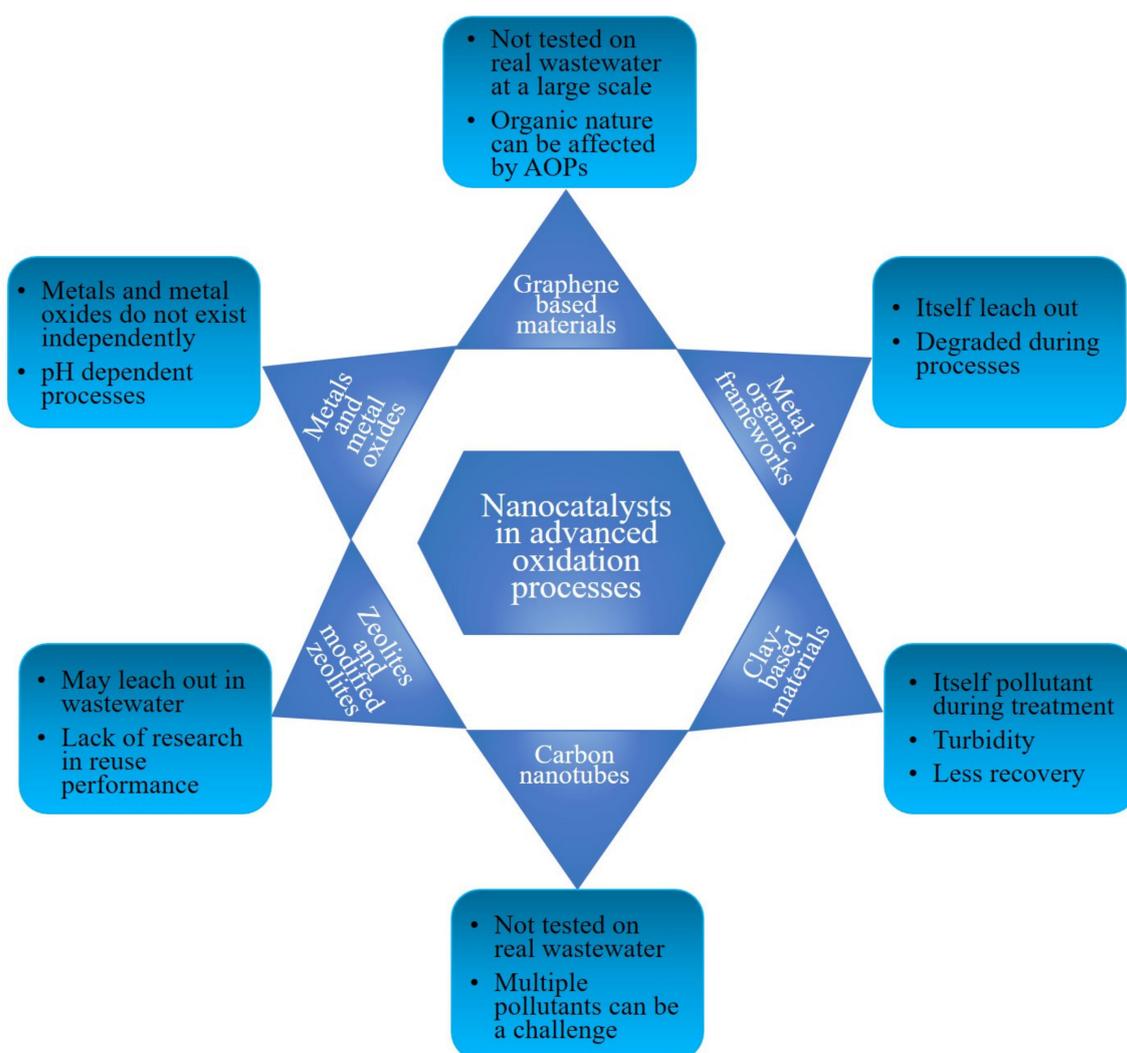
The current review focuses on studies using nanocatalysts as advanced oxidation catalysts in the treatment of actual wastewater samples. Most of the research reported in the literature used aqueous solutions of contaminants to examine the uses of nanocatalysts, but actual wastewater purification is more challenging [45,49]. Furthermore, other factors such as pH change caused by the catalyst, recycling of catalysts, leaching of metals and metal oxides deposited on the support, the reactivity of reactive oxygen species (ROS) with organic-based nanocatalysts, and adsorption of wastewater constituents should also be considered before applying nanocatalysts for large-scale applications. Therefore, it is of pivotal importance to study AOPs that imply nanomaterials as catalysts for real wastewater treatment. Moreover, this paper highlights the future challenges to applying nanocatalysts for AOPs in real industrial wastewaters. Multiple types of nanocatalysts used in AOPs are described in Figure 1.



**Figure 1.** Various types of nanocatalysts used in AOPs.

## 2. Nanocatalysts Used in AOPs for Wastewater Treatment

The nanoparticles possess a high surface area and high density of active site mainly due to their unique size ranging between 1–100 nm [45]. These unique characteristics enable nanomaterials for a variety of applications in wastewater treatment. Various nanomaterials as catalysts were used in the past for such applications; these include metals and their oxides, metal-organic frameworks (MOFs), carbon nanotubes (CNTs), and zeolites, etc. [45]. Nanocatalysts in AOPs and their challenges for practical application are shown in Figure 2.

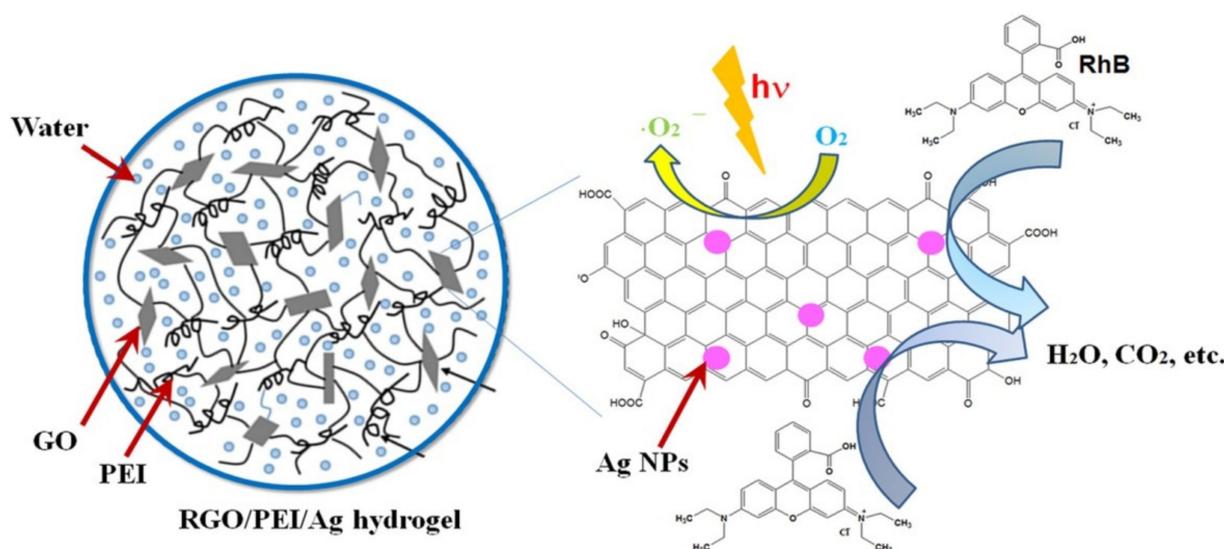


**Figure 2.** Nanocatalysts in AOPs and challenges for practical applications.

### 2.1. Graphene-Based Materials

Graphene is an allotropic form of graphite having a systematic honeycomb network. The reduced graphene and its modified forms were used as advanced oxidation catalysts in water and wastewater treatment since reduced graphene oxide (RGO) is less conductive than the parent form [45], and it has been observed that surface hydroxyl groups, Lewis acid sites, and  $\pi$ -electrons play an important role in generating hydroxyl radicals in various AOPs. Moreover, it has a reasonably high surface area and different functional groups (epoxy, carbonyl, hydroxyl) that enable graphene-based catalysts to adsorb pollutants on their surface [45] and efficiently degrade via adsorbed reactive oxygen species (ROS). The multiple pollutants may be a challenge for graphene-based catalysts, as per previous findings, the nature of the pollutant may affect the catalytic ability in AOPs. For example, pollutants may adsorb on the surface of the catalyst and block active sites. Each catalyst

type may behave differently for a particular pollutant [50–53]. RGO-based nanocatalysts were studied in various AOPs to degrade a variety of pollutants. Figure 3 illustrates the photocatalytic oxidation of dyes such as methylene blue and rhodamine B by using RGO. During the photocatalysis reaction, the charge transfer mechanism in the RGO/PEI/Ag nanocatalyst occurred, and the dye molecules moved from the aqueous solution to the composite surface and adsorbed with offset direct orientation via  $\pi$ - $\pi$  coupling between MB (and RhB) and graphene aromatic sections. When UV was applied on the surface of RGO/PEI/Ag nanocatalyst, the electrons which were photoexcited had a tendency of being rapidly injected into graphene sheets and then reacted with adsorbed oxygen molecules on the surface of graphene to produce  $O_2^-$  or/and  $O_2^{-2}$  radicals. In such a way, more electrons and holes could be generated by the prepared composite, and more superoxide anions and/or peroxide species produced, which disintegrated the dyes into the water, carbon dioxide, and other mineralization. As the result of the electron transfer process, recombination of charge was repressed in RGO/PEI/Ag nanocatalyst and consequently, it enhanced the efficacy of the photocatalytic properties [54].



**Figure 3.** Mechanism of photocatalytic degradation of dyes using RGO/PEI/Ag nanocatalyst. Reprinted with permission from Ref. [39].

It has been observed that graphene-based catalysts were mostly tested for the treatment of drinking water or synthetic wastewaters by AOPs. However, for large-scale applications, it is crucial to test these catalysts using real wastewater since constituents of real wastewater may affect the overall performance of these catalysts.

Another challenge to applying graphene-based nanocatalysts for water treatment is their organic nature [55]. Since AOPs involve ROS generation that may react with organic-based catalysts to denature them. It is pertinent to mention here that in most of the studies which involve the application of RGO or its modified forms, the loss of catalyst and its reactions with ROS were ignored. On the other hand, some findings indicate that the presence of hydroxyl radical scavengers (such as chlorides) may enhance the activity of RGO [55], which suggested that the catalyst reactivity may reduce in the presence of radical scavengers, and hence its performance may increase. Therefore, it is essential to apply these nanocatalysts using a real wastewater matrix. Table 4 shows examples of research conducted on applying graphene and its modified forms for wastewater treatment by AOPs. In this Table 4, the type of nanocatalysts, wastewater type, and removal efficiencies are addressed. For example, for the removal of methylene blue (MB) dye from the aqueous solution, ZnFe<sub>2</sub>O<sub>4</sub>-reduced graphene oxide was applied as a nanocatalyst in the photocatalytic process using H<sub>2</sub>O<sub>2</sub> resulting in 70% MB removal at optimum conditions [56].

**Table 4.** Graphene and its modified forms as a catalyst used in AOPs for wastewater treatment.

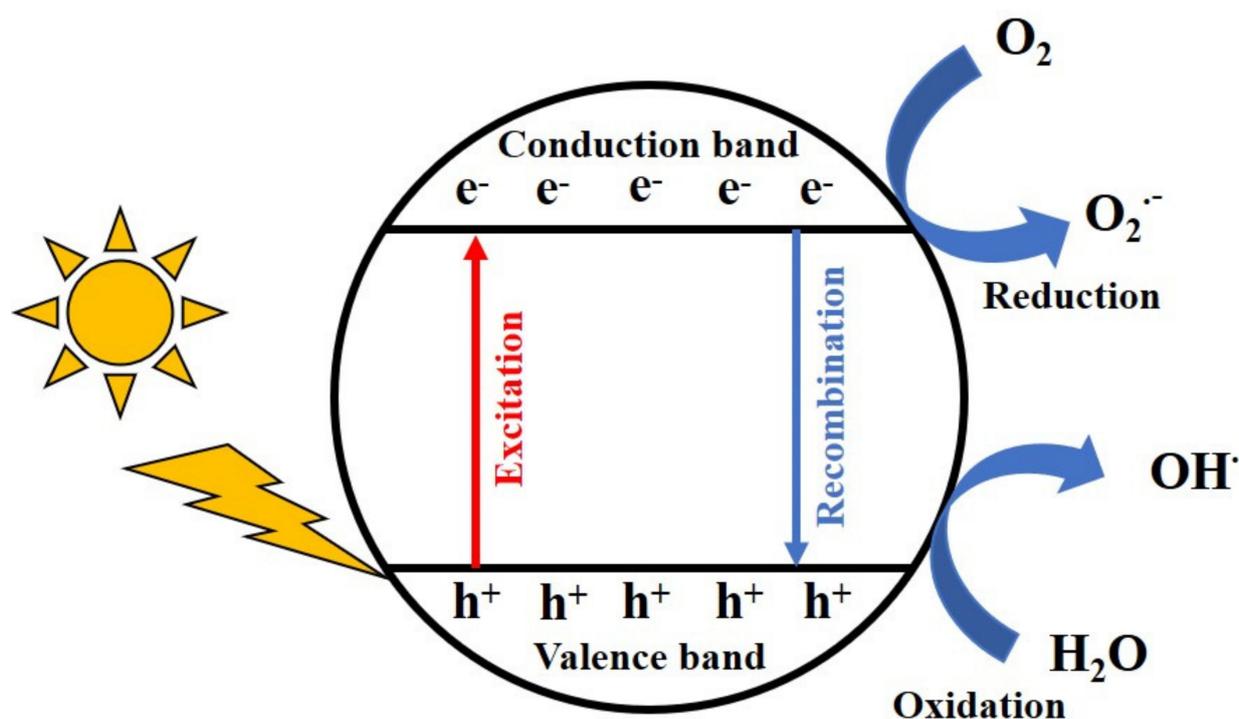
Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	Reference
RGO	Aqueous solution	<i>p</i> -hydroxylbenzoic acid (PHBA)	TOC removal about 100% in 60 min, at pH 3, PHBA = 20 mg/L	Catalytic ozonation	[57]
RGO-based silver nanoparticle	Aqueous dye solution	Methylene blue (MB), rhodamine B (RhB)	100% in 70 min for RhB and 30 min for MB	Photocatalytic oxidation	[54]
ZnFe <sub>2</sub> O <sub>4</sub> -reduced graphene oxide	Aqueous dye solution	Methylene blue (MB)	70% MB removal	Photocatalytic process using H <sub>2</sub> O <sub>2</sub>	[56]
N/S-doped graphene derivatives	Aqueous solution	Oxalic acid	96% in 15 min for photocatalytic ozonation and 20% for catalytic ozonation	Catalytic ozonation, photocatalytic ozonation	[58]
Hybrid nanocomposites, N-TiO <sub>2</sub> /graphene/Au, N-TiO <sub>2</sub> /graphene/Ag	Aqueous solution	Diazinon	76.7% for N-TiO <sub>2</sub> /G/Au and 81.1% for N-TiO <sub>2</sub> /G/Ag were observed at pH = 6 in 60 min	Photo-electro catalysis and photo-electro catalytic	[59]
ZnO/TiO <sub>2</sub> decorated on reduced graphene oxide nanocomposite	Real petro-chemical wastewater	Phenol	Complete degradation of phenol (pH =4), catalyst = 0.6 g/L, Phenol = 60 ppm in 160 min	Photocatalytic oxidation	[60]

**Challenges:**

1. Lack of application on real wastewater.
2. Only limited to aqueous solution.
3. Not tested on real wastewater at a large scale.
4. Organic nature can be affected by AOPs.
5. Cost of treatment neither estimated nor compared with other treatment methods.

**2.2. Metals and Metal Oxides**

Metals and their oxides were extensively implied as catalysts in both homogeneous and heterogeneous AOPs. It was reported that their surface hydroxyl groups and Lewis acid sites were the main active sites in AOPs [19,61]. Recently various modified forms of metal oxides were tested successfully as nanocatalysts for wastewater treatment. Metal oxide nanoparticles such as ZnO, TiO<sub>2</sub>, and CeO<sub>2</sub> have been widely studied to degrade contaminants in aqueous solutions [62–64]. The mechanism of the photocatalytic oxidation process is presented in Figure 4 [65].

**Figure 4.** Mechanism for photocatalytic degradation. Reprinted with permission from Ref. [50].

Ye et al. [65] carried out photocatalytic degradation of pharmaceuticals using TiO<sub>2</sub> nanotube arrays (TNAs) for the removal of  $\beta$ -blocker metoprolol (MTP) from aqueous solution through free hydroxyl radicals. In order to elaborate on the degradation mechanism, experiments with the addition of specific scavengers were performed. In this study, the maximum contribution of reactive species to MTP degradation was estimated at 88% by free hydroxyl radicals ( $\cdot\text{OH}$ ) in bulk solution, and around 9% by hydroxyl radicals ( $\cdot\text{OH}$ ) and photo-generated holes ( $h^+$ ). Tert-butanol and formic acid were added as a scavenger for  $\cdot\text{OH}$  and  $h^+$ , respectively. A major part of MTP degradation happened due to free hydroxyl radicals whereas minor degradation occurred on the catalysis surface through the reaction of  $h^+$  and  $\cdot\text{OH}$  adsorbed on the surface of catalysts. Other reactive species such as superoxide radical anions and photo-generated electrons participated in minor degradation of MTP over TNAs of about 3%. Due to their better photocatalytic performance and high surface area, metal oxide nanoparticles are considered better photocatalysts for water purification. Among the metal oxides, iron-based catalysts were extensively studied and were highly effective catalysts for the degradation of various environmental contaminants [62,66]. Iron oxides have advantages of recycling, reusability, and relatively lower usage cost and environmental risks. For example, higher efficiencies were obtained for the degradation of salicylic acid (20 g) using  $\alpha\text{-Fe}_2\text{O}_3$  in photocatalyst advanced oxidation process using batch mode [66].

The metals, metal oxides, and their various forms may not exist independently in aqueous environments. In the presence of water molecules, they may hydrate and form different complexes; this process may be pH-dependent [53]. Moreover, the addition of metal oxides and the contaminants present on them may alter the pH of water. Since the AOPs are pH-dependent processes, their mechanism and effectiveness (of various AOPs) depend on water pH [53]. Catalytic ozonation, Fenton-like processes, and UV-based processes are all pH-sensitive processes. For example, the ozonation process requires alkaline pH. Whereas the catalytic hydrogen peroxide decomposition using Fe-based catalysts (Fenton-like process) requires acidic pH to efficiently generate hydroxyl radicals which are necessary for the decomposition of pollutants. For this process, a pH 3 is considered as the optimum and most suitable pH regardless of the target pollutant [67]. At higher pH,  $\text{Fe}^{3+}$  forms  $\text{Fe}(\text{OH})_3$  which decreases the efficiency of the Fenton process, as less  $\text{Fe}^{3+}$  is present to react with hydrogen peroxide to generate hydroxyl radicals [67]. On the other hand, a lower pH than 3 causes the formation of Fe complex ( $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$ ), which reacts with hydrogen peroxide in the solution, hence lesser hydrogen peroxide is available as an oxidant. In addition, at very low pH, hydrogen peroxide forms stable oxonium ions  $[\text{H}_3\text{O}_2]^+$ , which are stable and less reactive compared to hydroxyl radicals, reducing its efficiency in oxidizing the pollutants [67]. The pH of the water may also affect the nature of active sites and the effectiveness of the catalysts. For example, the point of zero charge is an important property of a material that may determine the surface charges on a material at a particular pH and the nature of active sites (involvement of Lewis and Bronsted acid sites). Therefore, various materials have a characteristic point of zero charge [68–70]. Hence, it is indeed important to study the effect of pH on various materials in order to understand their ability to act as a catalyst for wastewater treatment. However, in many published works, the pH changes during the process, and due to contaminants on catalysts, were ignored. Therefore, the mentioned factor should be considered for further application of metals and metal oxides as nanocatalysts in wastewater treatment. Table 5 summarizes various studies applying metal oxides for wastewater treatment by AOPs. For example, Soltani et al. [71] applied sonocatalysis for the removal of COD in textile wastewater by using the ZnO nanoparticles (catalyst dosage of 6 mg/L) at 9 pH for 150 min of reaction time resulting in 44% COD removal.

**Table 5.** Metal oxides in AOPs for wastewater treatment.

Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	Reference
TiO <sub>2</sub> nanotube arrays (TNAs)	Aqueous solution	$\beta$ -blocker metoprolol (MTP)	87.09 $\pm$ 0.09% in 120 min, pH range = 3–11, nanotube diameter = 53 nm	Photocatalytic degradation	[65]
Fe <sub>2</sub> O <sub>3</sub> nanoparticles	Aqueous solution	Salicylic acid (SA)	53% of SA	Photo-electrocatalytic process	[66]
TiO <sub>2</sub> nanoparticles	Petroleum refinery wastewater	COD	83% in 120 min, pH = 4, COD = 100 mg/L	Photocatalyticoxidation	[72]
ZnO nanoparticles	Textile wastewater	COD	44% in 150 min, pH = 9, catalyst = 6 mg/L	Sonocatalysis	[71]
CeO <sub>2</sub> nanoparticles	Aqueous dye solution	Eriochrome black-T (EBT), Alizarin red S (ARS)	100% in 120 min, dye = 100 mg/L, catalyst = 0.6 g/L	Photocatalytic oxidation	[73]

**Challenges:**

1. Metals and metal oxides cannot exist independently.
2. This process is pH dependent.
3. Not tested on real wastewater at a large scale.
4. Cost of treatment neither estimated nor compared with other treatment methods.

### 2.3. Zeolites and Modified Zeolites

Zeolites are referred to as a family of aluminosilicate materials that consist of microporous structures [74]. Zeolites were extensively investigated for the removal of contaminants in water and wastewater. Their excellent stability, adsorption, and ion exchange capabilities make them unique from other nanomaterials [75]. Most of the zeolites-based AOPs were used to remove pollutants from aqueous synthetic solutions. However, in many recent investigations, real wastewater samples were used to study the effectiveness of these materials. Ikhlaq et al. [76] used iron-loaded zeolites-A to treat municipal wastewater in catalytic ozonation-based AOP. The results revealed that about 90% reduction in COD values was achieved in 1 h ozonation ( $O_3 = 0.9$  mg/min) [29]. Another recent study showed a successful application of zeolite A to treat veterinary pharmaceutical wastewater in a synergic electro-flocculation and catalytic ozonation process [77]. In this study, the COD and turbidity removal efficiencies were compared. Moreover, the removal efficiency of identified pharmaceuticals was also investigated [77]. The mechanism of the synergic process is presented in Figure 5.

In most studies, zeolites were employed as support, and the metal nanoparticles were deposited on their surfaces. Most of the published work lacks the investigation of the reuse performance of zeolite-based nanocatalysts [78]. Deposited, doped, or impregnated nanoparticles may leach out in wastewater. Therefore, it is essential to consider their reuse performance and leach out the tendency of metals or metal oxides deposited on various types of zeolites. Table 6 summarizes multiple research applications utilizing zeolites for wastewater treatment. For the removal of pollutant COD from veterinary pharmaceutical wastewater Fe-zeolite A utilized as a catalyst in the synergic electro-flocculation–catalytic ozonation process. When an ozone dose of 0.4 mg/min was provided in a reactor at neutral pH and the Fe-zeolite A dosage was 1.5 g/L, maximum COD removal of 85.12% was achieved [77].

**Table 6.** Zeolites used as nanocatalysts in AOPs for wastewater treatment.

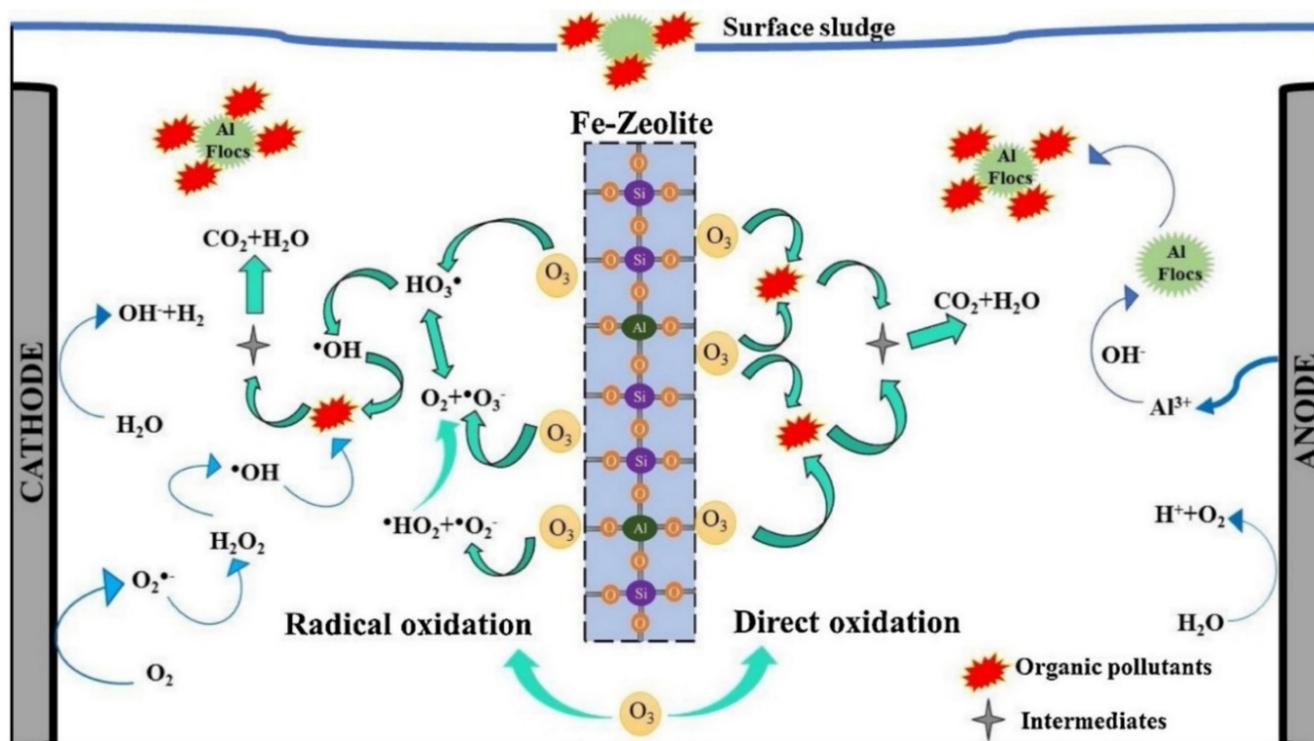
Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	Reference
Fe-zeolite A	Veterinary pharmaceutical wastewater	COD	85.12%, pH = 7, $O_3 = 0.4$ mg/min, catalyst = 1.5 g/L	Synergic electro-flocculation–catalytic ozonation	[77]
Fe <sub>2</sub> O <sub>3</sub> nanoparticles-zeolites Y	Aqueous solution	Phenol	90% at neutral pH in 2 h, catalyst = 0.0375 g/mL, $H_2O_2 = 0.14$ mol/L, phenol = 1.0 g/L	Fenton-like process	[79]
MgO-zeolite nano-structure	Textile wastewater	COD	61.5%, COD = 2650 mg/L, pH = 6.4, catalyst = 0.7 g/L	Sono-photocatalytic degradation	[80]

Table 6. Cont.

Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	Reference
ZnO-HY zeolites	Aqueous solution	MB	80% in 6 h, catalyst 10 mg/L, pH = 3	Electrochemical	[81]

**Challenges:**

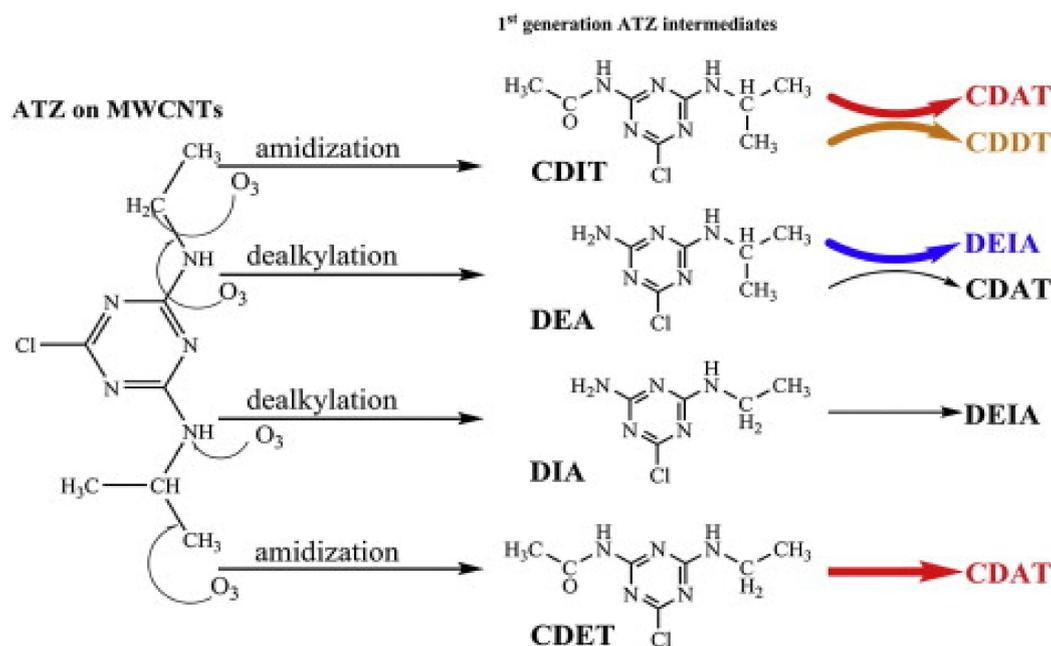
1. May leach out in wastewater.
2. Lack of research in reuse performance.
3. Not tested on real wastewater at a large scale.
4. Cost of treatment neither estimated nor compared with other treatment methods.



**Figure 5.** Mechanism for the synergistic electro-flocculation–catalytic ozonation process for pharmaceutical wastewater treatment. Reprinted with permission from Ref. [63].

#### 2.4. Carbon Nanotubes

Carbon is a unique and valuable element due to its many allotropes and catenation characteristics. Carbon nanotubes (CNTs) have a large surface area, which allows them to have strong chemical activity and good adsorption properties. CNTs have brought a revolution in the field of water and wastewater treatment. Therefore, these materials should be extensively applied to investigate their effectiveness and utility. CNTs have been studied under various categories such as single-walled or one-dimensional CNTs, multi-walled, and composite CNTs [45]. CNTs have been studied for their ability to remove a variety of contaminants. Figure 6 depicts the mechanism for removal of atrazine using multi-walled carbon nanotubes (CNTs). During the catalytic ozonation process of atrazine, various intermediates' formation was reported, and it was found that TOC removal was higher than adsorption and ozonation alone when treated with  $O_3$ /CNTs [82]. Many other modified CNTs used to treat various pollutants have been presented in Table 7. CNTs are highly recommended materials in AOPs due to their high removal efficiencies to treat highly resistant pollutants.



**Figure 6.** Degradation pathways of ATZ on MWCNTs. Reprinted with permission from Ref. [67].

**Table 7.** Carbon nanomaterials and nanotubes as nanocatalysts in AOPs for wastewater treatment.

Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	References
Multi-walled carbon nanotubes	Aqueous solution	Atrazine (TOC removal)	80% in 180 min, $C_0 = 10$ ppm, $m$ MWCNTs = 100 mg, ozone = 50 g/L	Catalytic ozonation	[82]
CeO <sub>2</sub> -carbon nanotubes	Aqueous solution	Phenol (TOC removal)	96% in 60 min, Phenol = 20 mg/L, catalyst = 0.10 g/L, ozone = 12 mg/L, pH = 6.2	Catalytic ozonation	[84]
Fe-CNTs	Real wastewater contaminated with dyes	TOC removal	40% TOC removal, 5% Fe, catalyst = 200 mg, H <sub>2</sub> O <sub>2</sub> = 0.4 M	Fenton-like and photo-Fenton process	[83]
CNTs	Aqueous solution	Nitrobenzene, benzoquinone, phenol	45% benzoquinone and 60% nitrobenzene, in 180 min, 100% phenol in 60 min, $C_0 = 20$ mg/L, temperature = 25 °C, catalyst = 0.2 g	Peroxy-monosulfate activation	[85]
Nitrogen-doped bamboo-like CNTs	Aqueous solution	Sulfachloro-pyridazine	90% oxidation in 180 min, catalyst = 0.2 g/L, SCP = 20 mg/L, pH = 7	Persulfate activation	[86]

**Challenges:**

1. Not tested on real wastewater at a large scale.
2. Multiple pollutants can be a challenge.
3. Cost of treatment neither estimated nor compared with other treatment methods.

However, most of the studies found in the literature revealed that CNTs were tested in an aqueous environment by using single or multiple pollutants. Only a few studies were conducted using real wastewater to scale up the process using CNTs. Since actual conditions may be more challenging, having multiple contaminants, pollutants, interfering chemicals, and scavengers may affect a catalyst's performance. Therefore, it is highly required to apply CNTs in real wastewater treatment. Since the real wastewater matrix may affect the ability and effectiveness of a catalyst, the real wastewater is a complex matrix that contained a variety of chemicals that can compete with the reactions of pollutants and oxidants (hydroxyl radicals). For example, carbonates, bicarbonates, phosphates, sulfates, etc., are hydroxyl scavengers. Moreover, the heavy metals and organic acids present in wastewater, if any, may adsorb on the catalyst and may block their active sites. Table 7 summarizes the practical applications of carbon nanomaterials and nanotubes as nanocatalysts in AOPs for wastewater treatment. A study conducted for the removal of

TOC from real wastewater contaminated with dyes using Fe-CNTs in the Fenton-like and photo-Fenton process showed a maximum of 40% TOC removal [83].

### 2.5. Metal-Organic Frameworks

Metal-organic frameworks (MOFs) are widely utilized as fillers in water purification membranes. These materials are referred to as adsorbents to remove contaminants from the environment [87]. The current paper focuses on their applications as a catalyst in AOPs. Due to their unique properties, such as three-dimensional structures, surface areas, and metal-containing active sites, MOFs have been recently studied in various types of AOP processes (Table 8). Table 8 presents the details of MOFs that have been recently studied in various types of AOP processes. Sun et al. [88] applied catalyzed Fenton process utilizing the Fe(BDC) (DMF,F) as MOFs for the removal of an aromatic compound such as phenol from the solution. It was found that higher removal efficiency of more than 99% was achieved by this treatment process. Although this process is efficient in terms of pollutant removal on a lab scale, there is a need to evaluate the application of this process on real textile wastewater.

**Table 8.** Metal organic frameworks in AOPs for wastewater treatment.

Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	References
NF/ZIF-67	Solution	Rhodamine B	99% in 30 min	Sulfur radical -AOPs	[89]
MIL-53(Fe)	Matrix solution	Methylene blue (MB)	87% in 240 min, MB = 10 mg/L, catalyst = 0.4 g/L	Photocatalytic process	[90]
Magnetic ( $\gamma$ -Fe <sub>3</sub> O <sub>4</sub> )	Matrix solution	Methylene blue (MB)	72% in 240 min	Photocatalytic process	[90]
Fe(BDC) (DMF,F)	Solution	Phenol	High removal efficiency (>99%)	Catalyzed Fenton process	[88]
STA-12 (Fe, Mn)	Aqueous solution	Rhodamine B and methylene blue (MB)	93% in natural sunlight in 40 min	Photo-Fenton oxidation	[91]
ZIF-67	Solution	Rhodamine B	80% in 60 min RhB = 50 mg/L, catalyst = 50 mg/L, PMS = 150 mg/L, T = 20 °C	Sulfate radical (SO <sub>4</sub> <sup>•-</sup> ) based AOP	[92]

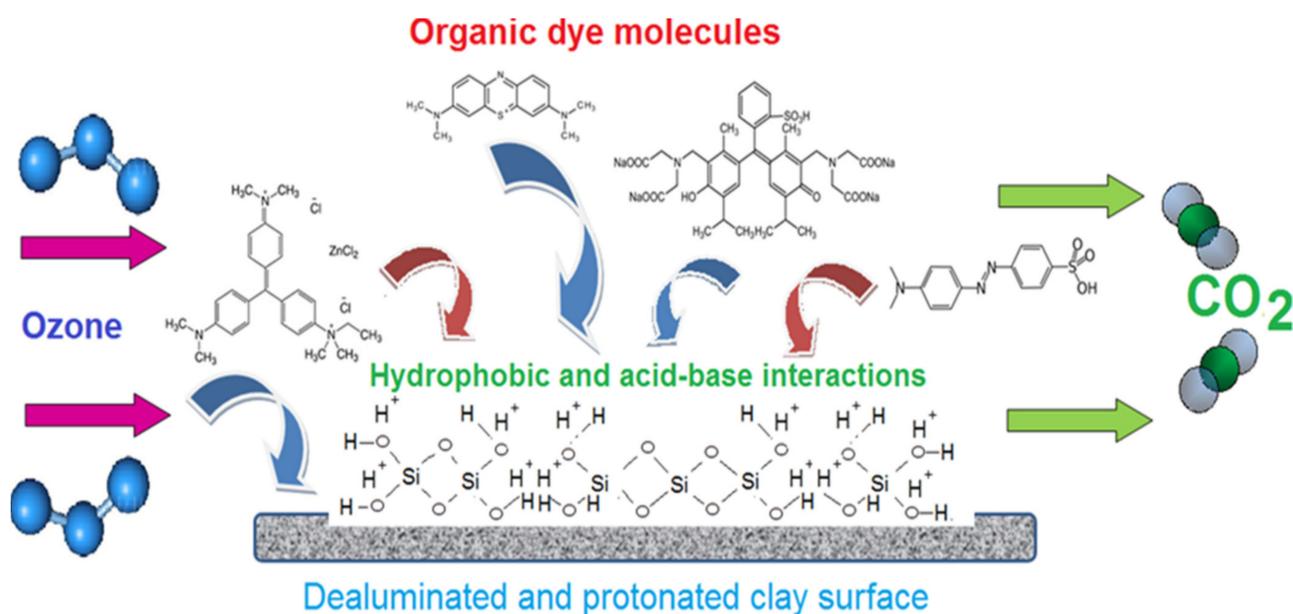
#### Challenges:

1. They themselves leach out.
2. Degraded during processes.
3. Cost of treatment neither estimated nor compared with other treatment methods.

However, the studies on the practical applications of MOFs are limited, and there is a need to test these materials using real wastewater samples. Moreover, it is also essential to investigate the self-degradation of MOFs in the presence of reactive oxygen species (ROS) as MOFs are organic-based materials that might react with radicals produced in AOP systems.

### 2.6. Clay-Based Materials

Various researchers investigated the clays due to their availability and economic considerations to promote the production of reactive oxygen species (ROS) to remove multiple pollutants. Among the various AOPs, wet catalytic oxidation and ozone-based catalytic processes were successfully studied to remove pollutants such as phenols and dyes [93,94]. Clays modified with various metals were widely applied to treat wastewater (Table 6). Boudissa et al. [94] suggested that protonated silanol groups (Bronsted acid sites) on clays may play an important role in the production of reactive oxygen species (ROS) while interacting with the dye molecules (Figure 7). Moreover, it was suggested that the charge on the dyes and surface charge on the catalyst might play an important role in the adsorption of various pollutants on the surface of the catalyst that might affect the overall efficiency [94].



**Figure 7.** Mechanism of catalytic ozonation on the dealuminated and protonated clay surface. Reprinted with permission from Ref. [79].

Despite several successful published applications of clay-based catalysts in AOPs as summarized in Table 6, they have not been implied on a larger scale for commercial applications. This might be due to the materials' limitations (recovery of clay waste catalyst and addition of turbidity to wastewater) and a lack of investigations with real wastewaters. The materials' limitations include a lack of maintaining high porosity and stability, resulting in turbidity to water [95]. Moreover, the leaching of metal nanoparticles deposited to these clay-based supports is very frequently observed during AOPs which also limits their applications in wastewater treatment. These above-stated limitations affect the catalysts' life and cause the deactivation of the catalysts. Such catalysts are not suitable for long duration processes and cannot be reused [96]. Table 9 summarizes the application of clays as nanocatalysts in AOPs for wastewater treatment. Kalmakhanova et al. [82] applied catalytic ozonation to the degradation of methylene blue, methyl green, methyl orange, and methyl-thymol blue in their aqueous solutions by using an acid-treated clay catalyst. The results showed removal of 49–96% dyes achieved in 20 min of reaction time.

**Table 9.** Application of clays as nanocatalysts in AOPs for wastewater treatment.

Catalyst	Wastewater Type	Target Contaminants	Removal Efficiency	AOPs	Reference
Pillared interlayered clay	Aqueous solutions/ wastewater	Phenols	>80%	Catalytic wet air oxidation, Fenton-like process, photocatalytic treatment	[93]
Zr and Fe/Cu/Zr polycations-pillared clay	Aqueous solutions	4-nitrophenol	78% TOC removal, C4-NP = 5 g/L, CH <sub>2</sub> O <sub>2</sub> CH <sub>2</sub> O <sub>2</sub> = 17.8 g/L, catalyst = 2.5 g/L, pH = 3.0, T = 50 °C	Catalytic wet peroxide oxidation	[97]
Al/Fe pillared clay	Aqueous solutions	<i>p</i> -chlorophenol	60% TOC removal	Catalytic wet hydrogen peroxide oxidation	[98]
Acid-treated clay catalyst	Aqueous solutions	Methylene blue, methyl green, methyl orange, methyl-thymol blue	49–96% removal in 20 min	Catalytic ozonation	[94]
Zn-clays catalyst	Dye wastewater	Dyes	>50% COD removal	Catalytic ozonation	[99]

**Challenges:**

1. Not tested on real wastewater at large scale.
2. Multiple pollutants can be a challenge.
3. Cost of treatment neither estimated nor compared with other treatment methods.

### 3. Conclusions

Nanoparticles are highly effective catalysts for wastewater treatment. AOPs based on nanocatalysis should be combined with conventional treatment processes to remove various biological-resistant contaminants from wastewaters. The foundation of AOPs is the efficient production of ROS and the benign removal of hazardous pollutants. AOPs offer the advantages of minimal secondary contamination and high mineralization efficiency as an innovative and efficient wastewater treatment technology. In terms of actual applicability, each AOP has its limits. The severe response conditions and expensive treatment costs are two considerations that limit its widespread adoption. Nanocatalysts-based AOPs such as photo-catalytic processes, catalytic ozonation, electro-flocculation, and modern Fenton-like processes are all highly important in today's environmental remediation.

### 4. Challenges and Possible Solutions

Unfortunately, there are several challenges that must be addressed before these techniques can be scaled up to their full potential and prove to be more effective and successful, which could be as follows.

#### 4.1. Reuse Performance

The reuse performance of catalysts is an important characteristic that helps to apply a catalyst effectively on a larger scale for practical application, since the application of a catalyst in real conditions (unlike lab-based conditions) required a stable and economical catalyst. In order to apply a nanocatalyst for practical application, the catalyst should be stable when applied in water and wastewater matrix. Unfortunately, most of the research work produced while applying nanocatalysts in AOPs is based on the applications of studied catalysts in deionized water. However, the wastewaters have different types such as municipal, pharmaceutical, textile, and chemical industrial wastewater, etc. Each type of wastewater has variable composition and constituents that may affect the catalyst performance. Hence, it is indeed important for the catalyst reuse performance that it should be tested in more challenging conditions (real water and wastewater), since in the case of AOPs, the hydroxyl radicals produced via different mechanisms react non-selectively with various species present in water and wastewater [67]. Therefore, the real water and wastewater constituents compete with the removal of pollutants. Hence, it is important to study the reuse performance of a catalyst in real conditions.

Ikhlaiq et al. [100] studied the removal of ibuprofen by using alumina as a catalyst in both the tap water and deionized water under a similar condition in the catalytic ozonation process. The results revealed that the reuse performance of the studied catalyst was highly efficient in deionized water, and the catalyst activity remains constant even after 12 successive runs for 300 minutes of ozonation time. However, the catalytic activity of the same catalyst was significantly reduced when tap water was used, and it was hypothesized that this may be due to the presence of natural constituents (chlorides, sulfates and phosphates, etc.) in tap water that leads to the poisoning of active sites on the catalyst [100].

Mecha et al. [101] investigated the reuse performance of TiO<sub>2</sub>-based photocatalytic AOP for the removal efficiency of phenol in aqueous solutions as well as in the effluent (treated wastewater) of secondary treatment. The results suggested that a significant decrease in the removal efficiency was observed when the photocatalytic process was performed in real wastewater. For example, the removal efficiency was reduced from 33% to 24% in the third successive run when TiO<sub>2</sub> used a catalyst. It was suggested that this could be due to the fouling of wastewater constituents that the catalyst may be adsorbed on its surface hence they compete with the adsorbed photons on the catalyst surface.

The removal efficiency of p-hydroxybenzoic acid was investigated in synthetic wastewater by Yuxian wang et al. [55], implying reduced graphene oxide as a catalyst in the catalytic ozonation process. The reuse performance of the studied catalyst was tested, and it was observed that total organic carbon (TOC) reduced from 90% to 60% even after two

successive runs. It was found that this may be due to the weight loss of the catalyst and adsorption of reaction intermediates.

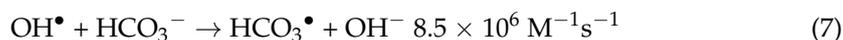
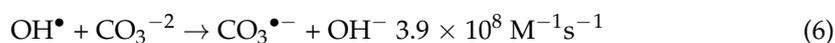
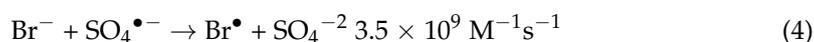
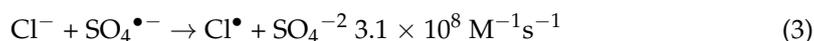
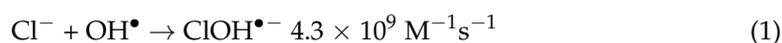
Keeping in view the above findings, and many other examples presented in the literature, it is indeed important to investigate the reuse performance of the catalyst in AOPs' processes. Moreover, the activity should be tested in real water and wastewater matrixes, since the catalyst reuse performance depends on various factors and conditions such as the type of catalyst, its mechanism, nature of active sites on the catalyst, the types of wastewaters, etc. Therefore, a catalyst should be tested in various conditions.

It is proposed that in order to enhance the reuse performance of a catalyst, the appropriate methods for catalyst recovery should be selected for a particular catalyst [55,102]. Moreover, catalyst stability tests should be conducted at various pH, temperature, agitation speed, and time intervals.

#### 4.2. Adsorption of Constituents

The adsorption of other wastewater constituents such as sulfates, phosphates, nitrates, carbonates, etc., should be investigated as they might lead to the poisoning of active sites of catalysts [103,104]. Hence, more studies are required to examine the effectiveness of nanocatalyst-based AOPs on a pilot scale in combination with conventional methods.

The following equations indicate the reactivity of oxygen species with inorganic ions that may compete with the degradation of pollutants in wastewater [103].



Previous findings indicate that inorganic ions significantly affect the performance of AOPs' catalysts. The inorganic ions may influence in the following ways [103]:

- The degradation by-products of the targeted contaminants may be altered.
- The stability of AOPs' oxidants may be affected.
- Change in the type of reactive oxygen species that may produce in AOPs.
- The activity of a particular catalyst may be affected.

Ikhtlaq et al. [105] studied the removal of coumarin by implying  $\text{Al}_2\text{O}_3$  and ZSM-5 zeolites in the catalytic ozonation process. Moreover, the removal of the targeted pollutant was investigated in the presence of phosphates. It was found that the presence of phosphates significantly reduced the catalytic activity of  $\text{Al}_2\text{O}_3$ ; on the other hand, in ZSM-5 zeolites, there was no significant effect on catalyst activity. It was found that the adsorption of phosphates on the catalyst ( $\text{Al}_2\text{O}_3$ ) may be responsible for the lack of catalytic activity.

The above-mentioned literature studies indicate that it is important to investigate the adsorption of various constituents' effect on the catalyst in water and wastewater matrixes, to identify a catalyst that may or may not be suitable for specific constituents. This may help to find the catalyst that may effectively operate under various conditions for inorganic constituents. Thus, the lack of adsorption of inorganic constituents on the surface of a catalyst may help to promote the surface reactions that may enhance the degradation of pollutants.

#### 4.3. Reaction Conditions

It is necessary to conduct extensive research on reaction conditions and active sites. An accurate understanding of the optimal reaction conditions makes it easier for the appropriate use of catalysts and keeps AOPs in practical use in the laboratory. The investigation of reactive sites in catalysts can assist researchers in better conceptualizing catalytic degradation of contaminants and optimizing the catalytic efficacy.

Previous findings suggested that the pH of the catalyst played a vital role in determining the reactivity of a catalyst, its stability, and the mechanisms of AOPs [70,104]. The initial pH of water and wastewater may change the charge on the surface of a catalyst. Moreover, it also depends on the nature of the catalyst which may lead to the variable of point of zero charges ( $\text{pH}_{\text{pzc}}$ ) of different catalysts. Hence the  $\text{pH}_{\text{pzc}}$  and initial pH are important to determine the charge on the catalyst surface and the types of active sites available at a particular pH, since Fenton-like heterogeneous catalytic processes operate better under acidic conditions and many findings reported efficient catalytic activity of various Fenton-like catalysts in aqueous solutions. However, the composition of real water and wastewater and its pH were different for different types of water and wastewater. Therefore, it is important to apply various catalysts in real water and wastewater matrixes to test their ability as a catalyst.

Sable et al. [106] studied the removal efficiency of chlorofibric acid (CFA) in a Fenton-like heterogeneous catalytic ozonation process implying the Pd/FeOOH catalyst; the effect of temperature was investigated and it was found that the removal efficiency of CFA was enhanced at 60 °C when compared with 40 °C and room temperatures. It was suggested that a temperature may increase the pollutant mineralization degree. In addition to the above study, various AOPs' catalysts were calcined at various temperatures, and it was found that calcination temperature may affect the performance of a particular catalyst as well as its stability and leaching of metals from its surface.

It may be suggested from the above findings that an AOP catalyst may be tested at various reaction conditions to know about its effectiveness. Moreover, differential thermal analysis (DTA) and thermogravimetric analysis may be implied to investigate the material stability at various temperatures.

#### 4.4. Cost of Treatment

The development of low-cost, high-performance nanocatalysts is essential. However, most research does not include the costs associated with such catalytic reactions (nanocatalyst-based AOPs). Moreover, in many findings, electrical energy demands, chemical costs, and the operational cost were presented, however, catalyst cost was excluded from such estimations [107]. In addition to the above issues, most of the studies presented in literature where cost estimation was conducted, were based on analysis in aqueous solutions using particular pollutants as representatives of wastewater. However, the composition and dynamics of real wastewater are variables depending on the type of wastewater (e.g., textile, municipal, pharmaceutical, chemical and biochemical, etc.). So, due to the variable compositions and COD loadings in real wastewater, the cost estimation in synthetic solutions may not be scaled up as being representative of real conditions.

It may be suggested from the above findings that estimating the costs of real-world wastewater treatment should be carried out and compared to the costs of traditional wastewater treatment methods. The development of highly easy and affordable catalysts will continue to be a research priority for the foreseeable future.

#### 4.5. Metal Leach-Out

It is important to extend the time spent studying the toxicology of catalysts in the environment. Due to the possibility that certain catalysts contain components that have a detrimental influence on the environment, it is essential to investigate the leaching of toxic materials into the environment and the environmental impact. Future challenges include the application of MOFs for the treatment of complicated wastewater from industries such

as textile and pharmaceutical. MOFs are being utilized for aqueous solutions; however, they have not been used on a laboratory-scale unit for actual wastewater treatment in the past. A logical consequence of the advanced oxidation process is the production of hydroxyl radicals, which induce the leaching of metal ions from MOFs and the degradation of the catalyst. Mahdiah et al. [108] studied the removal of COD and color from melanoidin wastewater by implying nano zero-valent iron (nZVI), activated carbons-coated nZVI (acc-nZVI), and chitosan-coated activated carbon (acc-CH-nZVI) as Fenton-like catalysts. The metal leach-out studies suggested that in the case of nZVI, 77% Fe leach-out was observed as compared with 3.76% and 1.98% for acc-nZVI and acc-CH-nZVI, respectively. The findings reveal that the more the leach-out, the lesser will be the performance of the catalyst in wastewater. The chitosan coating enhanced the binding strength of iron on acc-nZVI catalyst resulting in negligible leach-out of metal. The removal of tetracycline (TC) was investigated by implying nZVI and nZVI/ $\gamma\text{Co}_3\text{O}_4$  by Huang et al. [109], implying peroxydisulfate activated based on AOP. The iron leach-out in the reusability study revealed that over the four recycles (in 15 min), the TC removal efficiency was decreased from 93.7% to 70.6% in the case of the nZVI/ $\gamma\text{Co}_3\text{O}_4$  catalyst. While in the case of single nZVI, the TC removal efficiency was greatly reduced from 67.5% to 33.7%. It was further suggested that the significant reduction in the removal efficiency of TC was due to the iron leaching out from the catalyst. The study indicates that nZVI/ $\gamma\text{Co}_3\text{O}_4$  showed less leach-out as compared to a single nZVI.

Therefore, from the above-mentioned studies, it may be suggested that catalyst supports having a strong association with metal ions should be implied as nanocatalysts in AOPs. The metal loading on catalyst supports associated with physical adsorption may be quite reversible due to the weak forces on interactions that may lead to the metal leaching out in complex real water and wastewater matrixes. The chemisorbed association of metals with supports may be useful and more stable under extreme conditions.

#### 4.6. Clay-Based Catalyst

In addition, clay-based particles themselves contribute to turbidity by adding a pollutant to the water during the treatment process. The removal of phenol was investigated in water with laponite-based materials (nano clay) by Iurascu et al. [110] implying a heterogeneous photo-Fenton process. The results revealed that there was an increase of turbidity in water, which might further significantly lead to the incident radiation lost through scattering, and the reduction of absorbance. Therefore, the process is fully ruinous due to this deleterious effect of the contribution of the turbidity, which is itself a pollutant.

Many researchers [111–114] indicated that the UV-based AOPs were significantly affected by the reduction of UV light penetration by implying catalysts have small particle sizes since these catalysts were attributed to the solution turbidity.

Therefore, from the above-mentioned studies, it may be suggested that clay-based particles can be placed in pallet form for treatment to gain access to stability; for that, more composite materials with strong binding ability should be used for palletization, in order to avoid the leaching of clay particles from the pallets. The pallet form of clay-based materials may help in the recovery of the catalysts from the bulk solution and may be reused again, which may reduce the overall cost of the processes. However, implying the pallet forms may compromise the surface area of the nanoparticles may reduce their effectiveness.

Interpretation and optimization of the oxidation technology can help promote the better functioning of AOPs in the future. The minimization of the budget of the treatment method as well as the resolution of the corrosion challenge of the reaction infrastructure are two critical considerations for considering the industrial use of AOPs (Advanced Organic Processes). It is expected that this review article will support the practical process of AOPs by explaining the concepts and advancements in the use of nanocatalysts. We presume that this work will assist more individuals in understanding the application of nanocatalysts for AOPs for wastewater purification and will show the way forward for future research directions in this area.

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