A comprehensive review on catalytic ozonation: emerging trends and future perspectives

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ABSTRACT

The push for advanced water treatment techniques has led to significant growth in research focusing on ozonation catalysis, aiming to enhance pollutant degradation efficiency and energy conservation. Conventional ozonation methods, although practical, face limitations in specific pollutant degradation and require excessive energy inputs. Introducing catalysis to ozonation can potentially overcome these challenges, driving the research frontier toward innovative catalyst materials and optimized procedures. This review delves deep into the fundamentals of catalytic ozonation, emphasizing its advantages and critical role in advanced water treatment solutions. To examine emerging trends, spotlighting state-of-the-art catalysts and their influence on improving ozonation outcomes. The future perspectives of catalytic ozonation are projected, highlighting its potential to revolutionize water treatment paradigms, harnessing the balance of energy efficiency and robust pollutant removal.

Keywords: Catalytic ozonation; Water treatment; Pollutant degradation; Catalyst materials; Advanced ozonation techniques; Energy efficiency

1. Introduction

The surge in global industrial activities and rapid urbanization are significant contributors to the deterioration of water quality, leaving many ecosystems in peril. A pivotal concern in the 21st century has been the presence of emerging pollutants in water systems, many of which are resistant to conventional treatment methods [1–3]. The advancements in environmental monitoring technology have revealed that trace amounts of numerous organic pollutants can persist in treated waters, leading to the presence of these contaminants in aquatic systems. The World Health Organization and several environmental agencies globally have expressed concern over the long-term health impacts of these pollutants, emphasizing the need for more efficient water treatment strategies [4–7].

Amidst the plethora of water treatment methodologies, ozonation stands out due to its potential to degrade a wide array of organic pollutants. However, standard ozonation processes have limitations regarding energy consumption and the complete mineralization of pollutants. Catalytic ozonation, where ozonation is paired with a catalyst, promises enhanced degradation rates and improved energy efficiencies [8–11]. Such processes involve generating potent oxidative species, making it possible to target even the most persistent contaminants. The effectiveness of this process
largely depends on the choice of catalyst and its interaction with ozone ($O_3$), emphasizing the need for extensive research in this domain.

Recent years have seen a substantial increase in the investigation of various materials as potential catalysts for ozonation, including metal oxides, carbon-based materials, and hybrid composites [12–15]. Notably, the efficiency of catalytic ozonation processes hinges on the catalyst's surface properties and ability to produce hydroxyl radicals (\(\cdot OH\)). As research advances, there is a growing trend towards designing catalytic ozonation for specific pollutant degradation, paving the way for targeted water treatment solutions. Fig. 1 showcases the escalating number of publications focused on catalytic ozonation and wastewater treatment, indicating the growing research interest and its potential for real-world applications.

While a substantial amount of literature discusses various aspects of catalytic ozonation, this work distinguishes itself by providing a holistic and up-to-date analysis of emerging trends and future perspectives. The meticulously collate and synthesize information from recent studies, offering readers a panoramic view of the latest advancements, innovative materials, and cutting-edge applications in catalytic ozonation.

The review stands out by critically evaluating the performance of different catalysts, shedding light on their mechanisms of action, and pinpointing the factors that influence their efficacy. This paves by weaving together threads of knowledge from diverse sources to present a narrative that encapsulates the current state of affairs and charts a course for future explorations in this vibrant and ever-evolving domain.

2. Basic principles of catalytic ozonation

The fundamental understanding of catalytic ozonation revolves around the combined effect of ozone decomposition and the catalytic reactions that facilitate the generation of reactive oxidative species.

2.1. Fundamental reactions involved in ozonation

At its core, catalytic ozonation enhances the traditional ozonation process by exploiting the surface of a catalyst to produce ozone decomposition and reactive oxidative species, most notably hydroxyl radicals [16–18]. Unlike conventional ozonation, where ozone ($O_3$) primarily acts as the oxidizing agent, the presence of a catalyst in catalytic ozonation promotes the quick decomposition of ozone into more potent oxidants [19,20].

When ozone comes into contact with water, it can undergo decomposition, resulting in the generation of hydroxyl radicals:

\[ O_3 + H_2O \rightarrow 2 \cdot OH + O_2 \] (1)

However, this reaction is considerably enhanced in the presence of a catalyst, which can provide active sites to promote ozone decomposition [17,21,22]. The following reaction can describe the formation of hydroxyl radicals on a catalyst's surface:

\[ O_3 + \text{Catalyst} \rightarrow \cdot OH + O_2 + \text{Catalyst} \] (2)

Hydroxyl radicals, due to their high oxidation potential, can indiscriminately oxidize a broad range of organic compounds present in water. The efficiency of the catalytic ozonation process, therefore, depends not only on the activity of the catalyst but also on the interactions between the catalyst and ozone, the catalyst and pollutants, and the availability of hydroxyl radicals [23–27].

Furthermore, the physicochemical properties of the catalyst play a pivotal role in the efficacy of the process [23,28–30]. Factors like the catalyst's surface area, pore size, and the presence of active metal sites significantly impact the production of hydroxyl radicals. It is essential to ensure the catalyst possesses optimized properties for effective ozone decomposition and subsequent pollutant degradation [31–33].

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![Fig. 1. Yearly rise in global wastewater treatment from 2000–2022 showcases the increasing need for efficient treatment methods. (Source: www.sciencedirect.com).](image-url)
The catalytic ozonation operates on the principle of enhanced ozone decomposition on a catalyst's surface, generating highly reactive species that can efficiently oxidize a wide range of pollutants in water.

2.2. Role and significance of catalysts in ozonation

The effective degradation of pollutants during the ozonation process requires the efficient generation and utilization of reactive oxidative species, particularly hydroxyl radicals. Catalysts play an instrumental role in catalytic ozonation by aiding in the decomposition of ozone to produce these reactive species, enhancing the overall oxidative strength of the process [31,34,35]. Different types of catalysts, depending on their mode of action and nature, have been employed to maximize the efficacy of the ozonation process.

2.2.1. Homogeneous catalysts

Homogeneous catalysts in catalytic ozonation are typically in the same phase as the pollutants and ozone. This group primarily consists of metal salt solutions such as ferrous or ferric salts, copper ions, and other transition metal ions [36,37]. Ferrous ions (Fe²⁺), in particular, have gained attention because they can react with ozone, forming hydroxyl radicals through the Fenton reaction:

\[
\text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot\text{OH}
\]

The main advantages of homogeneous catalysts include rapid reaction rates due to the molecular-level dispersion of the catalyst in the solution. However, one significant challenge associated with homogeneous catalysts is their separation and recovery after ozonation. This limitation often necessitates additional post-treatment steps, potentially escalating costs and complexity.

Moreover, the effectiveness of homogeneous catalysts can vary depending on the conditions, such as pH, temperature, and concentration of the catalyst. For instance, the Fenton reaction is highly pH-dependent, with optimal activity typically observed in slightly acidic conditions [38,39]. While using metal ions as homogeneous catalysts can lead to increased generation of hydroxyl radicals, there is also a risk of secondary pollution due to the residual metal ions left in the treated water.

Recently, research has been directed towards developing advanced homogeneous catalytic systems that are both efficient in ozone decomposition and easy to recover. Incorporating ligands, chelating agents, and other enhancers can maximize the benefits of homogeneous catalysts while minimizing their drawbacks [40,41].

While homogeneous catalysis offers an intriguing avenue for enhancing catalytic ozonation, future developments must ensure sustainable and eco-friendly practices considering this approach's challenges and potential risks.

2.2.2. Heterogeneous catalysts

2.2.2.1. Metal oxide-based catalysts

Metal oxides are an integral class of heterogeneous catalysts in catalytic ozonation processes, primarily due to their ability to generate hydroxyl radicals upon interaction with ozone. Their inherent characteristics, such as high surface area, thermal stability, and various oxidation states, make them viable candidates. The fundamental mechanism underlying metal oxide-based catalysts in ozonation is the transfer of electrons between the ozone molecules and the metal sites on the oxide surfaces. This interaction fosters ozone decomposition into more reactive species that can facilitate the degradation of various pollutants. However, while metal oxides like manganese dioxide (MnO₂), Fe₂O₃, and copper(II) oxide (CuO) show promising activity, challenges like leaching of metal ions into the treated water and deactivation over extended cycles can hamper their broader application. Recent advancements have explored developing mixed metal or doping oxides with other elements to enhance stability and improve their catalytic performance [42–47].

2.2.2.2. Carbon-based catalysts

Carbon materials mainly activated carbon (AC), carbon nanotubes (CNT), and graphene, have garnered significant interest as heterogeneous catalysts for catalytic ozonation. Given their expanded surface areas and modifiable functional groups, these materials can adsorb ozone and pollutants, positioning them close and accelerating the reaction rate. The primary mechanism here is the adsorption and subsequent decomposition of ozone on the carbon surface, leading to the generation of reactive oxygen species, particularly hydroxyl radicals. To further augment their catalytic activities, modifications such as doping carbon materials with other elements (e.g., boron, nitrogen) or metal nanoparticles have been explored [48–51]. While carbon-based catalysts are cost-effective and feature high stability, potential challenges include pore blockage due to the accumulation of intermediates and decreased activity over time. Recent research is directed towards designing hierarchical porous structures and surface functionalization to overcome these limitations [52–54].

3. Catalysts used in ozonation

Since the early days of research in environmental engineering and water treatment, the role of catalysts in ozonation has been recognized and studied. Catalysts, when used with ozone, amplify the degradation rate of pollutants and reduce the amount of ozone required. These catalysts can be broadly categorized based on their origin and characteristics, and they encompass a wide range of materials, including metal oxides, carbonaceous substances, and organic polymers [55–58].

Catalysts in ozonation serve primarily as platforms where ozone decomposes to generate highly reactive radicals, especially hydroxyl radicals, which are instrumental in the degradation of various organic and inorganic contaminants. These catalysts' physical and chemical properties, such as porosity, surface area, and active sites, are critical in determining their efficiency [59–61]. Additionally, these materials have found applications beyond water treatment, like air purification and industrial waste treatment, given their potential to accelerate reactions and improve the selectivity of specific processes [62].
Metal oxide-based catalysts, such as Fe₂O₃ and MnO₂, have emerged as a prominent choice due to their high activity and stability in ozonation processes. The structure and electronic properties of these metal oxides play a pivotal role in ozone decomposition and the subsequent generation of reactive species [25,63–65]. On the other hand, carbon-based catalysts, with their extensive surface areas and modifiable functional groups, offer an economical and robust solution, particularly in the treatment of water laden with pharmaceutical residues and dyes [13,49,66].

Furthermore, a recent study highlighted the capabilities of composite materials, which combine the beneficial properties of two or more materials, for catalytic ozonation [67–69]. Such composites often synergize the strengths of the individual components, thereby boosting the overall efficiency of the ozonation process.

Fig. 2 displays the removal efficiencies of different contaminants when treated using various catalysts. The catalysts are categorized into three types: oxide-based, carbon-based, and hybrid. Each bar represents the percentage of a specific contaminant successfully removed using a particular catalyst in catalytic ozonation processes. For instance, carbon-based catalysts seem particularly effective in removing atrazine, while oxide-based catalysts have high efficiency in removing semi-coke cooling wastewater. The hybrid catalysts, especially Fe/ozone-Ag, demonstrate versatility in treating multiple contaminants.

4. Emerging catalysts and materials for catalytic ozonation

4.1. Metal oxides

Metal oxides have recently emerged as one of the most promising materials for catalytic ozonation, primarily due to their stability, abundant nature, and significant reactive sites. Metal oxides like Fe₂O₃, MnO₂, and CuO have exhibited remarkable performance in accelerating the decomposition of ozone to produce reactive species, facilitating the degradation of contaminants [25,63,64,70–73].

The characteristics of popular metal oxides and their applications in catalytic ozonation. The synthesis of metal oxides typically involves calcination processes and sol–gel methods [74,75]. For instance, Fe₂O₃ can be produced by thermally treating iron-based precursors such as iron nitrate or chloride at elevated temperatures. The produced metal oxides possess varied morphologies, which can significantly impact their performance in catalytic ozonation. An example includes the synthesis of nano-structured TiO₂ using hydrothermal treatment, leading to higher surface areas and enhanced ozone degradation rates [76].

Table 1 provides a comprehensive overview of various catalyst types, the target contaminants they are designed to treat, and the key findings associated with their use. Spanning from metal-based catalysts to more complex compounds, the list reflects the versatility and potential of these substances in environmental remediation. The target contaminants vary from common pharmaceutical products to specific organic compounds, illustrating the broad spectrum of applications. Notably, many of these catalysts enhance the production of hydroxyl radicals, which play a crucial role in the breakdown of organic contaminants.

The performance of metal oxide catalysts in ozonation processes is closely related to their physico-chemical properties. For instance, MnO₂, with its inherent redox potential, is more active in ozone decomposition than some other metal oxides, leading to higher hydroxyl radical yields [64,97–100]. Recent advancement in this domain has been the doping or co-doping of metal oxides with other metals or non-metals to tailor their electronic and structural properties, thereby enhancing their catalytic performance [68,101,102]. For example, Fe-doped TiO₂ showcased a higher degradation rate for organic contaminants than pure TiO₂ due to increased reactive sites and better electron–hole pair separation.

Adding to the growing body of literature, researchers demonstrated that nano-MgO, when impregnated with CNT and graphite, forms a composite catalyst that exhibits enhanced catalytic performance, specifically in the...
degradation of micropollutants [103]. Furthermore, catalyst design and synthesis advancements have paved the way for creating hierarchical structures integrating micro and mesoporous domains, which enhance mass transfer and provide additional active sites for ozonation.

Moreover, insights from computational and simulation studies have shed light on the adsorption and reaction mechanisms of contaminants on metal oxide surfaces during ozonation [104]. For example, molecular simulations on the interaction of ozone with FeOx surfaces revealed the critical role of surface hydroxyl groups in promoting the formation of reactive species.

While the application of metal-based catalysts in catalytic ozonation has showcased promising results in the effective decomposition of pollutants, it is imperative to consider the broader environmental implications of these pollutants. The target pollutants, often from industrial discharges and agricultural runoff, threaten aquatic ecosystems and human health. They can disrupt hormonal balances, lead to the bioaccumulation of toxic substances, and degrade the quality of water resources.

In this scenario, the employment of heterogeneous catalysts represents a pivotal breakthrough. Recent advancements highlight the efficiency of heterogeneous catalysis in pollutant eradication, offering substantial benefits in catalyst stability, selectivity, and reusability [105]. Such innovations contribute to water treatment practices’ enhanced sustainability and cost-effectiveness, emphasizing the necessity for further research and implementation in this field.

Due to their versatility and adaptability, metal oxides continually evolve with research directed towards optimizing their structures, improving their performance, and integrating them with other materials to address water treatment and air purification challenges. Future directions should consider the sustainable synthesis of these materials, their scalability for real-world applications, and the exploration of novel metal oxides or hybrid systems that could offer superior performance in catalytic ozonation [55,106,107].

**Table 1**
Overview of catalyst types and their efficacy in contaminant treatment

| Catalyst type                                      | Target contaminants                  | Key findings                                                   | References |
|----------------------------------------------------|--------------------------------------|                                                               |           |
| Calcium-based carbon/alumina (Ca-C/Al2O3)          | High-salt organic wastewater         | Enhanced hydroxyl radical (‘OH), singlet oxygen (O2)          | [77]      |
| Sodium-doped titanium dioxide (Na-Pt/TiO2)         | Isopropanol                          | Ozone-assisted catalytic oxidation                             | [78]      |
| Two-dimensional iron(III) oxide-manganese(IV) oxide-hierarchical flower-like carbon microsphere (2D FeO3-MnO2-HFCM) | Tetracycline hydrochloride            | Enhanced hydroxyl radicals, superoxide radicals              | [79]      |
| Plasma-treated limonite                            | Sulfasalazine                        | Increased surface area and redox properties                    | [80]      |
| Activated carbon                                   | Dimethyl phthalate                   | Adsorption and catalytic                                      | [81]      |
| Ni-Co-zeolite                                       | Entrofloxacin, tylosin tartrate      | High catalytic activity and reusability                        | [82]      |
| Fe3O4@Ce-Uio-66                                     | Acetaminophen                         | Increased surface area and redox properties                    | [83]      |
| Metal-based catalyst                                | Paracetamol                           | Improved hybrid catalytic properties                           | [84]      |
| FeCeAC/O3-PAC                                      | Effluent organic matter              | Cascaded catalytic properties-enhanced coagulation            | [85]      |
| Ce-loaded sepiolite (Ce/SEP)                       | p-nitrophenol (PNP)                  | Enhanced hydroxyl radical (‘OH) reaction                      | [86]      |
| Cu-MnO2/γ-Al2O3                                     | Nitrobenzene                         | Enhanced adsorption and catalytic properties                   | [87]      |
| Fe3O4/Al2O3-SiC                                     | Hard COD in coking wastewater        | Hydroxyl radical production                                   | [88]      |
| Fe3O4/ZnO                                          | 1-Hexyl-3-methylimidazolium bromide  | High catalytic activity and reusability                        | [89]      |
| MnO2-CoO4                                          | Pharmaceuticals and personal care products | High catalytic activity and reusability                        | [90]      |
| Li-doped Mg(OH)2                                   | Metronidazole                        | Enhanced hydroxyl radical (‘OH) reaction                      | [91]      |
| Fe/Mn co-doped biochar (Fe-Mn-C)                   | Ibuprofen                            | Radical pathways (superoxide radicals and enhanced hydroxyl radicals) | [92]      |
| Nitrogen-doped CeO2                                 | Sulfamethoxazole                     | Improved stability and electron transfer                       | [93]      |
| CTAB-doped with Cu–CuFe2O4                         | Norfloxacin                          | Improved stability and electron transfer                       | [94]      |
| CaO                                                | Organophosphorus                     | Catalytic properties with reactive radicals                    | [95]      |
| MnCe4−xO2 nanorod catalysts                        | 1,2-Dichloroethane                   | Synergistic effect between surface acidity and oxygen vacancy | [96]      |
4.1.1. Practical challenges and considerations in catalytic ozonation

While catalytic ozonation has shown significant promise in laboratory and field demonstrations, it is imperative to consider the practical challenges associated with scaling up and real-world applications.

- **Energy consumption**: One of the primary concerns in catalytic ozonation is the energy demand. Efficient ozonation processes require optimized conditions to ensure that ozone generation and consumption are balanced. This optimization directly affects energy consumption. Studies such as those on the removal of 1,3-adamantanedicarboxylic acid using carbon xerogels [108] and atrazine with MnO\(_x\)/biochar and FeO\(_x\)/biochar [109] have shown that while catalytic ozonation can be more energy-efficient than conventional ozonation in specific settings, energy requirements can vary based on the nature of the wastewater, the type of catalyst used, and operational parameters.

- **Reactor design**: Robust reactor design is pivotal for the effectiveness of the catalytic ozonation process. The design must ensure effective contact between ozone, wastewater, and the catalyst while minimizing ozone off-gassing. Factors such as reactor geometry, mixing, and flow regime play a crucial role in determining the efficiency of ozone utilization and overall treatment performance. For example, biologically pretreated semi-coking wastewater using spinel-type MnFe\(_2\)O\(_4\) magnetic nanoparticles [110] or the treatment of nitrobenzene using Mn-Fe/ZSM-5 [111] both emphasize the importance of reactor design.

- **Nanoparticle recovery**: The use of nanoparticles as catalysts in ozonation brings forth challenges related to their recovery and reuse. Nanoparticles can be lost during the process or undergo agglomeration, affecting their catalytic efficiency. Technologies such as membrane filtration, magnetic separation, or flocculation can be employed for nanoparticle recovery, but each has advantages and limitations. Recent studies on dibutyl phthalate (DBP) degradation using the O\(_3\)/ZnO/ACs system [112] and sulfamethoxazole degradation with Fe\(_3\)O\(_4\)/Co\(_3\)O\(_4\) composites [113] highlight these challenges.

Understanding and addressing these challenges is crucial for successfully implementing and scaling up catalytic ozonation processes. As the field moves forward, ongoing research and development efforts aim to optimize these aspects, ensuring that catalytic ozonation remains an effective, efficient, and sustainable option for water and wastewater treatment (Table 2).

### 4.2. Carbon-based catalysts

The advent of carbon materials has consistently attracted researchers due to their distinct characteristics, including high surface area, tunable pore structures, excellent electrical conductivity, and remarkable stability, making them intriguing candidates for catalytic ozonation processes.

<table>
<thead>
<tr>
<th>Contaminant type</th>
<th>Catalyst material</th>
<th>Operational parameters</th>
<th>Removal efficiency</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1,3-Adamantanedicarboxylic acid</td>
<td>Carbon xerogels prepared at pH 5.5 (CX5.5)</td>
<td>O(_3) dosage: 30 mg/L; pH: 8; contact time: 15 min</td>
<td>65%</td>
<td>[108]</td>
</tr>
<tr>
<td>Atrazine</td>
<td>MnO(_x)/biochar (20 mg/L), FeO(_x)/biochar (20 mg/L)</td>
<td>O(_3) dosage: 2.5 mg/L; pH: 7; contact time: 30 min</td>
<td>83% (MnO(_x)/biochar), 100% (FeO(_x)/biochar)</td>
<td>[109]</td>
</tr>
<tr>
<td>Atrazine</td>
<td>MnCe oxide</td>
<td>O(_3) dosage: 0.8 mg/min; pH: 7; contact time: 40 min</td>
<td>99.99%</td>
<td>[110]</td>
</tr>
<tr>
<td>Biologically pretreated semi-coking wastewater</td>
<td>Spinel-type MnFe(_2)O(_4) magnetic nanoparticles</td>
<td>O(_3) dosage: 1.2 mg/min; pH: 7; contact time: 70 min</td>
<td>85.2% (COD), 94.1% (VP)</td>
<td>[111]</td>
</tr>
<tr>
<td>Dibutyl phthalate (DBP)</td>
<td>O(_3)/ZnO/ACs system</td>
<td>O(_3) dosage: 15 mg/L; pH: 4; contact time: 80 min</td>
<td>99.04% DBP degradation</td>
<td>[112]</td>
</tr>
<tr>
<td>Enrofloxacin (EFC), tylosin tartrate (TT), COD, BOD(_5), turbidity</td>
<td>Ni-Co-zeolite 5 Å catalyst, catalyst dose = 10 g/L</td>
<td>O(_3) dosage: 1.1 mg/min; pH: 7.1 ± 0.2; contact time: 30 min</td>
<td>EFC: 97%, TT: 98%, COD: 90%, BOD: 86%, turbidity: 93%</td>
<td>[82]</td>
</tr>
<tr>
<td>Fischer–Tropsch synthesis wastewater</td>
<td>Fe/Mn@CH (50 g/300 mL)</td>
<td>O(_3) dosage: 6 g/h; pH: 9; contact time: 60 min</td>
<td>64.37% (COD)</td>
<td>[113]</td>
</tr>
<tr>
<td>Nitrobenzene (NB)</td>
<td>Mn-Fe/ZSM-5</td>
<td>O(_3) dosage: 25 mg/L initial; pH: 6; contact time: 40 min</td>
<td>72% Removal rate of TOC, 33.5% higher than that in the bubbling reactor (BR)</td>
<td>[114]</td>
</tr>
<tr>
<td>p-CBA</td>
<td>Co(II), Fe(II); 1 mg/L</td>
<td>O(_3) dosage: 2 mg/L; pH: 7–8; contact time: 3 min</td>
<td>95.5% (O(_3)/Co(II)), 92.5% (O(_3)/Fe(II))</td>
<td>[115]</td>
</tr>
<tr>
<td>Sulfamethoxazole</td>
<td>Fe(_3)O(_4)/Co(_3)O(_4) composites, 0.10 g/L</td>
<td>O(_3) dosage: 6.0 mg/min; pH: 5.1; contact time: 60 min</td>
<td>60% TOC removal</td>
<td>[116]</td>
</tr>
</tbody>
</table>
Unlike traditional catalysts, carbon-based materials, specifically AC, graphene, and CNT, boast easy synthesis and offer unique physicochemical properties [117–124].

The sulfur-doped graphene catalyst enhance ozonation [121]. Its functionalized oxygenated groups and vast surface area were deployed to accelerate ozone decomposition and generate hydroxyl radicals. A systematic study suggested that oxygen functionalities facilitated the generation of active sites, which in turn showed superior ozonation rates compared to bare graphene.

Fig. 2 depicts a structural representation of sulfur-doped graphene, emphasizing its unique oxygen functionalities. The sulfur-doped graphene structure is illustrated on the left, with sulfur atoms represented in yellow. Interaction with O$_3$ generates HO•, which, in turn, contributes to the transformation of carbamazepine (CBZ) into its breakdown products.

Due to hollow cylindrical nanostructures and enhanced surface area, CNTs showcased a proclivity to activate ozone more effectively than other carbon materials. The study concluded that intrinsic metallic impurities in CNTs might act as active sites for ozone decomposition, thus accentuating the production of hydroxyl radicals [122].

Recent developments in the field of carbon-based heterogeneous catalysts for environmental remediation have highlighted the effectiveness of mesoporous graphitic carbon nitride (mpg-C$_3$N$_4$) and its composites. In particular, the sonocatalytic removal of methylene blue from water has been achieved using cobalt ferrite mesoporous graphitic carbon nitride (CoFe$_2$O$_4$/mpg-C$_3$N$_4$) nanocomposites, with the process parameters optimized through a response surface methodology approach [125]. A novel mpg-C$_3$N$_4$/Ag/ZnO nanowire/Zn photocatalyst plate was developed, demonstrating enhanced photocatalytic activity for dye pollutant degradation through a facile dip-coating process [126]. The potential of agricultural waste as a source for wastewater treatment is also gaining traction, with biochar and green nanoparticles derived from such waste showing promise in removing refractory pollutants from water and wastewater [127]. Together, these studies underscore the versatility and efficiency of carbon-based catalysts in wastewater treatment, presenting innovative approaches for pollutant degradation.

AC derived from sustainable resources was tailored for catalytic ozonation [128]. The tailored AC exhibited superior ozone adsorption due to its high porosity and vast surface area. The mechanism suggested the involvement of carbonyl and carboxyl groups present on the surface of AC in ozone activation. The results inferred that the tailored AC showed high ozonation rates and remarkable stability and reusability in successive cycles.

In conclusion, carbon-based catalysts offer a sustainable and efficient avenue for catalytic ozonation, with each type contributing unique attributes that facilitate the generation of reactive species crucial for enhanced water treatment. Future endeavors should focus on developing carbon-based composites that amalgamate the beneficial properties of each type, ensuring maximum efficiency and economic viability in real-world applications.

4.3. Zeolite-based catalysts

Zeolite catalysts, renowned for their structured micro- and mesoporous architectures, have recently seen an influx in research interest for their application in catalytic ozonation processes. These catalysts offer remarkable potential for pollutant degradation due to their defined porous structures, high surface areas, and inherent acidic sites, all contributing to enhanced ozone decomposition and the production of oxidative radicals.

Fig. 3 offers detailed microscopic images of two distinct zeolite-based catalysts. Image (a) captures the morphology of ZSM-5, characterized by elongated, prism-like structures. Conversely, image (b) presents the structure of hollow zeolite.

Fig. 3. Structural representation of sulfur-doped graphene with highlighted oxygen functionalities. Reproduced with permission by the study of Asghar et al. [121].
which, as the name suggests, displays numerous uniformly sized hollow spherical formations.

Zeolite Y, known for its supercage structure, to enhance the catalytic ozonation process for removing toluene pollutants [131]. The high aluminum content and unique structure enhanced the generation of hydroxyl radicals, leading to efficient pollutant degradation. Moreover, the stability of zeolite Y in ozone-rich environments was noteworthy, with minimal leaching of aluminum ions [132].

Another zeolite catalyst, ZSM-5, was demonstrated possess intriguing characteristics that favored ozone decomposition [129]. The spatial arrangement and concentration of aluminum sites played a pivotal role in determining the catalytic activity of ZSM-5. Intriguingly, ZSM-5 with higher silicon-to-aluminum ratios showed more excellent resistance to ozone degradation, rendering them more durable during the ozonation process.

Recent advancements have looked at integrating zeolite catalysts with other materials to capitalize on synergistic effects. For instance, the composite of ZSM-5 and nanometer cerium oxide (CeO₂) revealed an enhanced pollutant removal rate, where the zeolite provided active sites for ozone decomposition, and nanometer CeO₂ enhanced the degradation of sulfamethoxazole compounds [133].

Given their diverse structures and physicochemical properties, zeolites have emerged as potent catalysts in catalytic ozonation. Their capability to augment the generation of oxidative radicals while maintaining structural stability makes them promising candidates for sustainable water treatment technologies. Future endeavors may focus on optimizing the structural properties of zeolites and exploring novel composite materials to elevate their catalytic performances.

4.4. Metal–organic frameworks

Progressive research into the potential of metal–organic frameworks (MOF) as catalysts in ozonation processes has unveiled distinct advantages over traditional materials, especially in pollutant degradation [134–136]. MOFs' inherent porosity and tunability allow for the strategic placement of metal nodes to promote interaction with ozone molecules. The MOF, Ce-MOF enhancing the decomposition of ozone to form highly reactive radicals [134]. The presence of cerium nodes in Ce-MOF significantly boosted the generation of hydroxyl radicals, furthering the catalytic ozonation process.

Recent breakthroughs with the Fe-based MOF suggest intriguing revelations. The MOF showcases an admirable performance in the ozonation of water, mainly due to its iron clusters that enhance the formation of reactive radicals [137–139]. A comparative study observed that the ozonation rate with Fe-MOF exceeded that of other common catalysts, making it an optimal choice for water treatment applications.

To summarize, MOFs' diverse structural attributes and adjustable nature have propelled them to the forefront of catalytic ozonation research. With promising preliminary results, further research into the fine-tuning of MOF structures can undoubtedly lead to more efficient and sustainable ozonation processes in the future.

4.5. Nano-structured catalysts

The dynamic evolution of nanotechnology has ushered in a transformative era in the field of catalytic ozonation, with nano-structured catalysts demonstrating superior capabilities over traditional bulk catalysts. At the forefront of this innovation is the nanoparticulate realm, which optimizes catalytic performance through a significant increase in surface area and the potential for multifunctional synergism [124,140–143].

Nano-sized CeO₂ catalyst enhanced ozonation capabilities [144]. The nanostructure, attributed to the increased density of reactive sites and unique redox properties of Ce³⁺/Ce⁴⁺, facilitated faster ozone decomposition and generation of reactive oxygen species, thereby heightening pollutant degradation efficiency.

In another paradigm-shifting work developed iron oxide (Fe₂O₃) nanoparticles coated with AC for ozonation processes [145]. The hybrid nano-catalyst showcased efficient pollutant removal due to enhanced surface interactions and offered easy magnetic separation post ozonation, underlining the significance of nanotechnological integration.

Transitioning from metal oxides, noble metal-based nano-catalysts, particularly palladium (Pd), have come into focus. The synthesis of Pd nanoparticles supported on ceria, revealing a synergistic effect that magnified ozone decomposition rates, setting a new benchmark in the catalytic ozonation domain [146]. The nano-architecture was conducive to electron transfer, accelerating the formation of hydroxyl radicals.

Titanium dioxide (TiO₂) nanotubes surfaced as an excellent catalyst for ozonation processes [147]. The tubular structure, offering an increased surface area and enhanced light absorption, played a pivotal role in the rapid degradation of organic pollutants. The effectiveness of the tubular structure was further accentuated when doped with elements like ZnO or Ag and Pt, offering a more comprehensive range of photocatalytic activation [148,149].

Developing nano-structured MOF and covalent organic frameworks offers exciting avenues. Their porous structure and tunable functionality render them ideal candidates for ozonation catalysts, spotlighting the Ce-based nano-MOFs exhibiting rapid ozone decomposition and pollutant removal [150].

In essence, the infusion of nanotechnology in catalytic ozonation has precipitated a paradigm shift, with nano-structured catalysts signposting the future trajectory. Their superior capabilities, underpinned by the unique physicochemical properties and synergetic effects at the nanoscale, ensure they are at the vanguard of future research and applications in ozone-based water treatment systems.

4.6. Bio-based catalysts

Bio-based catalysts have begun to command attention in exploring sustainable solutions for catalytic ozonation, particularly for their eco-friendly nature, sustainability, and potential to tap into nature's inherent catalytic capabilities. These catalysts, primarily derived from organic biomasses, showcase a promising alternative to conventional catalysts in ozonation processes, making them critical candidates for advancing environmental remediation practices.
Biosynthesis protocol has the potential for bio-synthesized multi-metal oxides with varying Fe/Mn ratios as a catalyst for ozonation [151]. The porous nature of this bio-based catalyst, combined with the high presence of functional groups, manifested in an enhanced generation of hydroxyl radicals, making it a competent medium for pollutant degradation. Such a natural derivation, originating from abundant lignocellulosic biomass, places it as a front-runner in sustainability.

Biochar-supported catalysts, which complement bio-synthesized materials, have been spotlighted for their unique physicochemical properties in ozonation using piggyery bio-gas residue. Biochar significantly increased the ozonation rate of organic pollutants [152]. The bio-polymer matrix facilitates pollutant adsorption, while the metal sites act as active centers for ozone decomposition.

Furthermore, residues from agricultural by-products have been harnessed for catalytic applications [153,154]. When carbonized and activated, coconut shells, almond shells, olive pits, and rice husks exhibit a commendable capability for catalytic ozonation. Their high surface area and intrinsic functionalities support enhanced pollutant degradation rates, thus repurposing agricultural waste into a valuable environmental tool.

In summary, the infusion of bio-based materials in catalytic ozonation is emblematic of a broader shift towards eco-friendly and sustainable solutions. Bio-based catalysts promise enhanced ozonation efficiency and underscore the importance of harnessing nature’s resources judiciously. As research continues to evolve in this domain, these catalysts stand to redefine the standards of sustainable environmental remediation.

4.6.1. Utilization of biomass-derived adsorbents for pollutant removal

Degradation of pollutant include catalytic ozonation is adsorption catalytic. Using a catalyst with adsorption capacity will enhance pollutant removal and sustainability when using biomass-derived adsorbents. Recent advancements in the field have demonstrated the potential of mesoporous-activated carbons and composites derived from waste biomass for the adsorption of various pollutants [155–157].

Biomass-derived catalysts and adsorbents have attracted significant attention due to their sustainable and eco-friendly nature. The mesoporous zeolite-activated carbon composite prepared from oil palm ash [158] and the mesoporous-activated carbon prepared from chitosan flakes [159] are two exemplary biomass-derived adsorbents that have shown promising results for methylene blue removal. These materials are used for agricultural and industrial wastes and exhibit superior adsorption capacities compared to similar adsorbents. The composite outperforms many existing adsorbents and provides a low-cost alternative for dye removal [158].

When comparing these biomass-derived adsorbents with other studies, it is apparent that they have advantages in terms of cost-effectiveness and efficiency. The activated carbon prepared from rattan furniture wastes [160] and Karanja fruit hulls [161] via NaOH activation also exhibited impressive adsorption abilities towards methylene blue, showcasing the potential of biomass wastes as precursors for high-performance adsorbents [160,161]. However, it must be noted that the performance of these materials can be influenced by operational conditions, such as temperature, pH, and initial dye concentration, necessitating a comprehensive understanding of their adsorption mechanisms for optimization.

Despite the promising results, there are limitations and drawbacks associated with these materials. Preparing these adsorbents often involves chemical activation processes, which may pose environmental and safety concerns. These materials’ long-term stability and reusability need further investigation to ascertain their practical applicability. In this regard, the work on single-step pyrolysis of phosphoric acid-activated chitin for efficient adsorption of cephalexin antibiotic provides an alternative pathway, showcasing the feasibility of using less hazardous activating agents for the preparation of high-performance adsorbents [162].

Biomass-derived catalysts and adsorbents offer a sustainable and cost-effective solution for pollution remediation. Future research could address the limitations associated with their preparation processes, explore greener activation methods, and investigate their long-term stability and reusability to promote their practical implementation in environmental remediation further.

4.7. Transition metal catalysts

Transition metal catalysts, leveraging transition metals’ versatile and unique electronic configurations, have emerged as pivotal components in catalytic ozonation. These metals (e.g., Mn, Co, Cu, and Fe) stand out for their diverse oxidation states and the ability to mediate redox reactions efficiently, which are instrumental in promoting ozone decomposition and generating radical species [154,163–166]. The potential to modulate their electronic and structural properties offers myriad possibilities for tuning catalytic performance [167,168].

Prominent among these, the MnO$_x$-based catalysts have shown to possess an enhanced ozone decomposition capacity (Fig. 4). Studies revealed the efficacy of MnO$_x$-CeO$_2$ hybrid systems where the synergistic interplay enhanced ozone conversion, leading to an augmented generation of hydroxyl radicals [169]. Furthermore, the stability of these catalysts, even at varying pH levels, provides them an edge in real-world wastewater treatment scenarios.

A composite of Fe incorporated into AC [170] showcased an increased ozone decomposition rate and effective dye degradation. The surface chemistry of these catalysts, especially the availability of active Fe sites, facilitated efficient pollutant breakdown. The catalyst’s structure played a vital role, with more significant surface areas correlating with higher pollutant removal rates.

Exploring the potential of multi-metal systems, Ru-Cu bi-metallic catalyst exhibits a synergistic effect that enhances ozone decomposition and pollutant degradation [171]. This synergistic enhancement, as observed, arises from the spatial proximity of Ru and Cu active sites, promoting intra-catalyst electron transfer, thus speeding up radical generation.
Another groundbreaking development is the introduction of transition metal-doped porous structures. Synthesized Mn-Cu-doped porous zeolite has remarkable ozone decomposition capabilities [172]. The porous structure facilitated more extensive pollutant access, while the embedded Mn-Cu sites acted as hotspots for radical generation. Interestingly, these catalysts’ high surface area and intricate pore network could be modulated by adjusting the Mn-Cu content, resulting in varied performance characteristics.

Fig. 4 illustrates the sequential steps involved in ozone decomposition over MnO$_x$-CeO$_2$ catalyst surfaces. The process begins with ozone adsorption onto the catalyst, influenced by electrostatic forces and hydrogen bonding (Steps 1 and 2). This is followed by ozone decomposition, releasing hydroxyl radicals and oxygen molecules (Step 3). Surface reactions yield various products, including gaseous nitrogen oxides (Step 4). The latter stages (Steps 5 and 6) highlight the regeneration of the catalyst surface and the electron transfer process, preparing the catalyst for subsequent ozone decomposition cycles.

Conclusively, transition metal catalysts, backed by their distinct electronic properties and diverse redox capabilities, are emerging as indispensable tools in catalytic ozonation. By tailoring these catalysts at the atomic and macroscopic scales, advancements are pushing the envelope of what is achievable regarding pollutant degradation efficiency. As the quest for cleaner waterways persists, these catalysts hold the promise of reshaping the trajectory of sustainable wastewater treatment strategies.

4.8. Noble metal catalysts

Noble metal catalysts, predominantly consisting of metals such as gold (Au), platinum (Pt), palladium (Pd), and silver (Ag), have garnered significant attention in the domain of catalytic ozonation due to their unparalleled electronic and structural characteristics [173–177]. Their innate ability to function as excellent electron mediators promotes swift ozone decomposition, generating reactive oxygen species crucial for pollutant degradation.

Pd and bimetallic (Pd-Cu, Cu-Pd) zeolite catalysts [178] showcased the incredible characteristic. The electronic interactions between Pd-Cu nanoparticles and the zeolite support expedited ozone decomposition, producing hydroxyl radicals at an unprecedented rate, improved ozone conversion and increased the mineralization efficiency for complex organic contaminants. Similarly, Pt-based catalysts, with their distinctive electronic configurations, have set new benchmarks in ozonation [179]. A comparative study, leveraging Pt’s varied oxidation states, unraveled Pt’s potential (IV) in enhancing the lifetime of hydroxyl radicals, consequently magnifying pollutant degradation rates.

On another front, Pd-supported zeolites, through meticulous engineering, demonstrated promising outcomes [178]. Incorporating Ag into the zeolitic structure fortified ozone decomposition pathways and introduced a multifaceted mechanism, utilizing both molecular ozone and generated radicals, thereby optimizing contaminant removal efficiencies.

In retrospect, the inclusion of noble metals into catalytic ozonation platforms has paved the way for optimizing efficiency and broadening the applicability scope. As these metals offer diverse electronic and steric modulations, their calibrated integration into tailored catalyst systems sets the stage for revolutionary advances in water treatment strategies. Notably, while their exemplary performance is undisputed, challenges tied to their economic viability and sustainable sourcing remain. Future endeavors must balance performance prowess with economic and ecological considerations.

4.9. Polymer-supported catalysts

Polymer-supported catalysts have recently emerged as a potent arsenal in the toolbox of catalytic ozonation, paving the way for both versatility in application and enhanced pollutant degradation [180]. These catalysts, designed to leverage polymers’ innate flexibility and adaptability, have provided avenues to address challenges like leaching and recovery issues associated with traditional catalyst systems.

Due to their design flexibility, polymer-supported catalysts can potentially overcome catalyst separation and reuse issues. Moreover, the ability to tailor the polymer
characteristics—varying its porosity, chemical functionality, and mechanical properties—offers a multifaceted approach to optimizing catalyst performance. Future trajectories should be aimed at developing stimuli-responsive polymer supports, which can modulate the catalytic activity based on real-time pollutant concentrations, pH, or other environmental parameters. Such advancements will undoubtedly elevate the realm of catalytic ozonation to new pinnacles of efficiency and adaptability.

4.10. Magnetic catalysts

The incorporation of magnetic properties into catalysts for ozone decomposition stands as a progressive stride in the domain of catalytic ozonation. Magnetic catalysts, primarily composed of ferromagnetic materials or materials exhibiting paramagnetic properties, provide the dual advantages of effective ozone degradation and hassle-free catalyst recovery using external magnetic fields [181]. The latter proves paramount in ensuring the environmental sustainability of the ozonation process by facilitating catalyst recycling and reuse.

Notably, synthesized magnetically responsive MnFe₂O₄ nanoparticles and subsequently embedded them within a carbon microsphere matrix [182]. As elucidated in Fig. 5, this study introduces a comprehensive oxalic acid (OA) breakdown mechanism that includes OA adsorption. This mechanism offers valuable insights for further investigations into the catalytic degradation processes of small molecule acids and the quest for innovative, effective catalysts in wastewater management.

Fig. 5 showcases the proposed catalytic ozonation reaction mechanism on carbon microspheres (CMS) embedded with MnFe₂O₄. The process is delineated into two phases:

- **Early reaction phase:** In the initial stage, ozone adsorption (O₃) takes precedence, followed by nucleophilic addition and eventual O₃ decomposition. This results in forming various reactive species that partake in organic degradation processes.

![Fig. 5. Ozone decomposition pathways over MnOₓ-CeO₂. Reproduced with permission by the study of Meng et al. [130]](image-url)
酸（OA）分解。该反应的特征是处于一个高OA浓度的环境中。

• **Reaction's latter phase:** 作为反应的进展，条件的变化，映射一个较低的pH和更高的OA浓度。吸附图案被影响由的前在氧化物的孔隙。一系列复杂相互作用包括核捕获性连接，分解，电子转移，和有机酸分解占据这个阶段，释放二氧化碳（CO₂）和其他产物。

另一个值得注意的贡献在于其中钴铁（CoFe₂O₄）纳米粒子被用作一个磁性催化剂进行臭氧分解[183]。CoFe₂O₄催化剂展示了优越的催化臭氧分解效率，并证明了一个磁性响应，简化其回收后的过程。

磁性催化剂在催化臭氧化中推动了可持续和高效的途径。这些复合催化剂，具有协同性能和在反应条件方面的灵活性，能够为不同的环境设计复合催化剂结构来解决特定污染物。未来的研究可能探索未被探索的自然矿物品类。

### 4.12. Natural mineral-based catalysts

地球丰富的自然矿物质资源被证明为催化剂在臭氧化中的应用提供了可持续、高效、成本效益的水处理解决方案。这些自然矿物材料，独特的形态，以及内在的催化性能可以为增强臭氧分解的技术铺设道路。

在另一项创新方法中，浮石，一种多孔火山岩，被作为潜在的催化剂研究氧化[186]。他们的发现表明，浮石，显著地，当用金属离子修饰时，展示了非常好的臭氧分解和其它重要性能。浮石废物可能为未开发的自然资源，强调了它们在传感和氧化应用中的应用。

### 4.13. Layered double hydroxides

在以氧化钙为基础的催化氧化中，层状双氢氧化物（LDHs）被标记为它们的突出性能和它们的非水性、环保和可调的物理化学性质。这些层状化合物，也通过水合脱铝酸盐或含酸粘土，通常构成一种由不同金属氧化物和粘土的组合。

LDHs在污染过程中的应用[187]。这些层状LDH结构，具有特定金属组合，展示了增强的臭氧分解和羟基自由基生成，对于高效的污染物降解至关重要。}

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rates of contaminants when exposed to different concentrations of Ni-Fe LDH catalysts. As the catalyst concentration escalates, a noticeable increase in the degradation rate is observed, especially within the initial 30 min.

LDH modification by integrating metal nanoparticles will enhance the catalyst’s efficiency [188]. They observed that incorporating noble metals into the LDH structure facilitated electron transfer processes, thereby amplifying the production of reactive oxidative species.

LDHs’ ability to intercalate anionic species also plays a pivotal role in dictating their ozonation performance. Modulate the catalytic activity, allowing for tunable pollutant degradation profiles [189].

LDH are game-changers in catalytic ozonation, providing versatility and efficiency in pollutant remediation. Their structural flexibility and the potential for further modifications hint at a prosperous future for LDHs in water and wastewater treatment applications. Continued research in
this domain is pivotal for optimizing their performance and making them economically viable for large-scale applications.

5. Summary

In the context of ever-increasing environmental concerns, the treatment of pollutants using innovative methods, such as catalytic ozonation, has garnered significant attention. Ozonation is a robust and versatile treatment method capable of decomposing various pollutants. However, standalone ozonation can sometimes be energy-intensive and less efficient. Thus, integrating catalysts to expedite the process and increase its efficiency has led to the evolution of catalytic ozonation.

Among the myriad catalysts explored, materials like LDH, zeolites, and metal-based nanoparticles have shown immense potential in enhancing the ozonation process. These catalysts amplify the generation of reactive oxidative species, such as hydroxyl radicals, and ensure the complete breakdown of pollutants into harmless by-products.

While tremendous progress has been made in this domain, challenges persist. Some catalysts exhibit rapid deactivation over time, while others might leach harmful components into the treated water. Most catalysts' optimal operating temperature range remains below the typical wastewater temperature, necessitating either a cooling process or further catalyst modifications. Cooling, much like in the case of CO₂ capture, is energy-intensive and might offset the environmental benefits of the treatment process. Therefore, future research endeavors should focus on enhancing catalysts' stability and reusability, widening their effective temperature range, and exploring cost-effective catalyst synthesis methods.

Moreover, as we navigate through an era marked by rapid industrialization, the diversity of pollutants continues to increase. Such a trend necessitates continuous research to develop catalysts capable of addressing a broader spectrum of contaminants. In conclusion, catalytic ozonation emerges as a beacon of hope in wastewater treatment. As research deepens and technology advances, it is anticipated that this method will become an industry standard, ensuring cleaner water and a safer environment for all.

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