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Aops: Assessment Of Mechanisms, Applications And Innovations In Wastewater Treatment

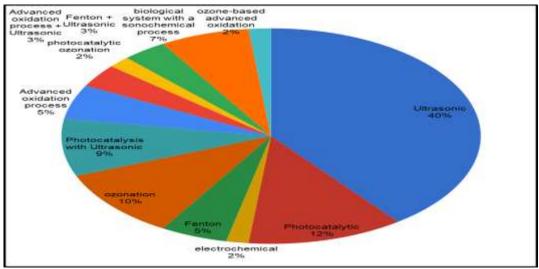
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Abstract

This study examines the distribution of various processes in a specific field, likely related to advanced oxidation or chemical treatment methods, based on their prevalence in a representative dataset. The analysis reveals that ultrasonic processes dominate, accounting for 40% of the total share, highlighting their extensive applicability and effectiveness. Photocatalytic (12%) and ozonation (10%) methods also play significant roles, reflecting their importance in pollutant degradation and treatment processes. Hybrid approaches, such as photocatalysis combined with ultrasonic (9%) and Fenton + Ultrasonic (3%), indicate a growing interest in synergistic effects to enhance efficiency. Moderate contributions from biological sonochemical systems (7%), Fenton processes (5%), and general AOPs (5%) further emphasize the diversity of methods explored in the field. Meanwhile, specialized techniques like electrochemical (2%), photocatalytic ozonation (2%), and ozone-based advanced oxidation (2%) represent emerging or niche applications. This paper discusses the principles, types, and applications of AOPs, along with their advantages and limitations. Schematic diagrams and tables provide a visual understanding of the processes. These findings suggest a trend toward integrating multiple methods for improved performance, reinforcing the significance of advanced oxidation and hybrid chemical treatment techniques in scientific and industrial applications.



Keywords: Wastewater; Pharmaceutical effluent; Advanced oxidation; Active pharmaceutical components

INTRODUCTION

Water pollution caused by industrial effluents, medicines, and emerging contaminants presents significant environmental challenges. AOPs are a group of water treatment technologies that utilize hydroxyl radicals (*OH) to degrade organic contaminants, pathogens, and other hazardous substances. These processes are highly effective in breaking down complex contaminants that do not respond to traditional treatment methods, which often struggle to remove recalcitrant compounds (Kim et al. 2024). AOPs provide a promising alternative by generating powerful oxidants capable of mineralizing organic compounds into "harmless" byproducts such as "water" and "carbon dioxide". This study investigates the degradation of seven medicines in both mineral and distilled water using ultrasound. The effects of chemical structure, pollutant concentration, and water matrix composition on degradation efficiency were evaluated. Results indicate that bicarbonate ions present in mineral water enhance the degradation of hydrophilic compounds by generating carbonate radicals, thereby improving the oxidation process (Perea et al. 2021).

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Potential Reasons for Fluctuations in Publications

Fig 1 illustrated the steady rise in publications from 2012 to 2018 suggests growing interest and development within the research area. This could be due to advancements in technology, increased funding, or greater awareness among researchers. The sharp increase in publications in 2019 and 2020 may be attributed to new discoveries or innovative methods often result in a surge of publications. More researchers may have entered the field, contributing to more publications. Special grants or funding initiatives might have driven higher output. The COVID-19 pandemic might have caused a spike in research output, especially if the publications were in health, epidemiology, or related fields. The drop in publications in 2021 could be due to research activities might have slowed due to lab closures or logistical challenges. Researchers might have pivoted to other urgent areas of study. The recovery in publication numbers in 2022 suggests that the field has stabilized. Research activities and funding likely resumed at a more consistent pace.

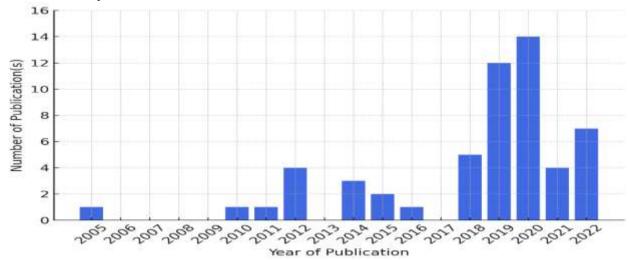


Figure 1: Number of publications per year

AOPs are defined by their ability to generate "hydroxyl radicals (\bullet OH)", which are highly reactive and capable of breaking down a broad spectrum of pollutants. These radicals can be produced through several methods, including: Ozone-based processes: Ozone (O_3) is introduced into water, where it decomposes to form (\bullet OH), facilitating pollutant degradation. Hydrogen peroxide-based processes: UV radiation activates hydrogen peroxide (H_2O_2), generating hydroxyl radicals that oxidize contaminants. Photocatalysis: A semiconductor, typically titanium dioxide (TiO_2), is exposed to UV light, producing hydroxyl radicals that decompose organic pollutants. Fenton and photo-Fenton reactions: These processes utilize hydrogen peroxide (H_2O_2) and ferrous iron (Fe^{2+}) to generate hydroxyl radicals. The photo-Fenton reaction is further enhanced under UV light, increasing its efficiency (Zhang et al. 2021 and Ameta et al. 2018).

The primary objective (Table 1) of AOPs is to transform organic contaminants into simple and harmless by-products such as carbon dioxide, water, and inorganic ions.

Table 1: Applications to reduce contaminations in the waste water

Application	Description	
Water and Wastewater Treatment	Removal of toxic chemicals, pesticides, and pharmaceuticals.	
Industrial Wastewater Treatment	Treating effluents from chemical, pharmaceutical, and textile industries.	
Drinking Water Purification	Removal of bacteria, viruses, and organic pollutants.	
Soil Remediation	Degradation of organic contaminants in soils.	
Air Purification	Removing volatile organic compounds (VOCs) from the air.	

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BACKGROUND

The research paper explores the ultrasound-assisted synthesis of BiFeO3 (BFO) as a catalyst for activating peroxymonosulfate (PMS) to degrade tetracycline (TCH) (Xing etal. 2021). A novel CeO₂–ZrO₂@MoS₂ hybrid nanoflower catalyst (CZ0.75M) was developed using hydrothermal and self-assembly methods. It exhibited optimized morphology and optical properties for effective sonophotocatalytic applications (Talukdar et al. 2021). The study investigates the scale-up of "vortex-based hydrodynamic cavitation (HC)" devices for degrading 2, 4-dichloroaniline (DCA), a complex organic pollutant, in water. The focus is on how HC device performance changes across scales (~200 times capacity increase) (Ranade et al. 2021). This research investigates the scale-up of vortex-based hydrodynamic cavitation (HC) systems for degrading organic pollutants like 2,4-dichloroaniline (DCA). The study examines how scaling impacts degradation efficiency and develops a model for predicting degradation performance (Perea et al. 2021).

Synthesis and Characteristics

The BFO catalyst was synthesized using a one-pot hydrothermal method with ultrasound assistance. The resulting BFO (BFO-u) exhibited a higher level of Fe²⁺ and OH⁻ groups than BFO synthesized without ultrasound (BFO-o) (**Xing et. al. 2021**). Pharmaceutical wastewater has a complex composition (Table 2), with a high content of organic matter, microbial contamination, high salt, and a difficult biodegradability (**Guo et.al. 2017**).

Table 2: Physicochemical Properties of Pharma Wastewater (Guo et. al; 2017)

Properties	Concentration Range
Chemical Oxygen Demand (COD)	1000 - 20000 mg/L
Biological Oxygen Demand (BOD)	500 - 2500 mg/L
Total Nitrogen (TN)	500 - 1500 mg/L
Total Phosphorus (TP)	50 - 250 mg/L
Suspended Solids (SS)	200 - 500 mg/L
рН	1 - 8
Temperature	25 - 80 °C

Occurrence of Medicines in wastewater effluents

Medicines have been identified in marine ecosystems globally, largely due to advancements in analytical detection methods (Hua et al., 2006 and Fatta et al., 2007). The recent research has extensively examined pharmaceutical contamination in different water sources. After being excreted by humans and animals, these substances enter sewage systems and wastewater treatment plants (WWTPs), ultimately spreading to soil, ground surface water, and drinking water supplies (Darlymple et al., 2007). Furthermore, improper disposal of medications from households, healthcare facilities, manufacturing sites, and agricultural activities contributes to environmental contamination. Veterinary drugs, in particular, enter the environment through direct application on land and subsequent runoff, affecting both surface and groundwater quality (Khetan and Collins, 2007).

Medicines reach the environment through various pathways, with major sources including pharmaceutical production sites; wastewater treatment plants (WWTPs), hospitals, landfills, and burial sites (Khetan and Collins, 2007 and Lillenberg et al., 2010). Active pharmaceutical ingredients (APIs) excreted by humans, often bound to polar molecules like glucuronides, enter WWTPs, where enzymatic processes can break them down, released the active pharmaceutical ingredients in the environment (Heberer, 2002). Research has also identified pharmaceutical residues in both drinking water (Webb et al., 2003) and hospital wastewater (Suarez et al., 2009). Additionally, wastewater from pharmaceutical manufacturing, which contains APIs, organic solvents, catalysts, and other chemicals, poses challenges for standard treatment processes (Sreekanth et al., 2009). Table 3 summarizes the most prevalent pharmaceutical compounds in wastewater along with their quantified concentrations.

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Table 3: Different medicines in wastewater with their concentration (Gomez et. al., 2007, Vieno et. al., 2007, Al-Rifai et al., 2007)

Sr. No.	Category	Drug Examples	Concentration Range (mg/L)
1	Central Nervous System Drugs	Caffeine	0.0032 - 0.01144
2	Antibiotics	Sulfamethoxazole	0.00002 - 0.00058
		Ofloxacin	0.000006 - 0.000052
		Ciprofloxacin	0.000006 - 0.00006
3	Cardiovascular Drugs	Metoprolol	0.00001 - 0.00039
		Propranolol	0.00005
		Clofibric Acid	0.00047 - 0.17
4	Absorbable Organic Halogen Compounds	Iomeprol	0.0016
		lopromide	0.000026 - 0.0075
5	Analgesics	Acetaminophen	0.01 - 0.02333
		Ibuprofen	0.00049 - 0.99
		Carbamazepine	0.0001 - 0.00168

Mechanism of AOPs

The core principle of AOPs is the generation of hydroxyl radicals, which possess a strong oxidation potential (2.8 V). These radicals non-selectively attack organic molecules, breaking them down through a series of oxidation reactions. Initiation: Activation of chemical, photochemical, or sonochemical reactions to produce radicals. Propagation: Radicals react with pollutants, forming intermediate species. Termination: Complete mineralization or transformation into biodegradable compounds.HC involves the generation, growth, and collapse of cavities (bubbles), producing high shear forces, local pressure, and hydroxyl radicals for pollutant degradation. Vortex-based HC devices were used due to their advantages: early cavitation inception, high cavitation yield, and reduced clogging or erosion compared to linear HC devices like venturi and orifice systems (Ranade et al. 2021). The primary active species identified were singlet oxygen (${}^{1}O_{2}$), hydroxyl radicals (${}^{\bullet}OH$), and superoxide radicals (${}^{\circ}O_{2}$). ESR spectroscopy and scavenger experiments confirmed their roles in the degradation of NPX (Talukdar et al. 2021). Hydrophobic medicines degrade faster due to proximity to cavitation bubbles. Hydrophilic medicines degrade better in "mineral water" due to the bicarbonate effect. The sono-Fenton process accelerates degradation in distilled water but has limited effects in mineral water (Perea et al. 2021).

AOPS - AN EFFECTIVE APPROACH FOR MEDICINE DEGRADATION

AOPs utilize hydroxyl radicals (OH), which are highly reactive and non-selective chemical oxidants (Table 4), to degrade organic pollutants that conventional oxidants like ozone, oxygen, and chlorine struggle to break down (Munter, 2001). These hydroxyl radicals act as potent electrophiles, reacting swiftly with electron-rich organic molecules and promoting their decomposition (Glaze et al., 1987). Once formed, these radicals facilitate the breakdown of organic compounds through mechanisms such as electron transfer, hydrogen abstraction and radical recombination (Kejia Wu et al., 2023).

Table 4: Oxidation Potential of different oxidants (Deng and Zhao; 2015, Carey; 1992)

Oxidant	Oxidation Potential (V)
Hydroxyl Radical	2.8
Oxygen (Atomic)	2.42
Molecular Oxygen	1.23
Hydrogen Peroxide	1.78
Chlorine	1.36
Fluorine	3.03
Ozone	2.08

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Vamsi and Anji Reddy (2015) outlined the key steps involved in AOPs. In oxidative reactions, either an electropositive molecule, radical, or electron is removed, or an electronegative atom is introduced. These reactions can be facilitated by factors such as oxygen, heavy metal ions, and light, leading to the generation of "strong oxidizing" agents like hydroxyl radicals (OH •). These radicals play a crucial role in breaking down toxic compounds into simpler organic intermediates. Eventually, these intermediates undergo further oxidation, resulting in harmless end products such as water, carbon dioxide, and inorganic salts. *Sonolysis*

In recent years, cavitation has gained recognition as an effective advanced oxidation process (AOP) due to its effectiveness in breaking down complex organic pollutants into simpler short-chain molecules (Gogate, 2008a). Its efficiency can be further improved by combining it with other AOPs (Gogate and Pandit, 2004). Cavitational reactors operate as multiphase systems, utilizing large-scale energy release and the formation of reactive species through the intense collapse of cavities (Gogate, 2008b).

Numerous wastewater treatment studies have demonstrated the benefits of cavitation, leveraging its physical and chemical effects, such as the generation of hot spots and highly reactive free radicals (Sivakumar and Pandit, 2002; Gogate and Pandit, 2004). High-intensity acoustic irradiation at specific frequencies, typically around 25 kHz, induces cavitation and triggers sonochemical reactions (Gadipelly et al., 2014). The efficiency of this treatment depends on multiple operational factors, including ultrasonic power, pH, frequency, irradiation time, temperature, initial substrate concentration, and the "water matrix" (such as the presence of additional oxidants and gas sparging) (Guo et al., 2017). Among these, ultrasonic power is particularly crucial, as higher power levels enhance degradation efficiency (Hapeshi et al., 2010). In the United States, sonolysis and other AOPs have been effectively used for the mineralization of various pharmaceutical compounds.

Ultrasonic-assisted AOPs have proven effective in degrading various pharmaceutical contaminants. Acetaminophen (ACP) degradation has been extensively studied using acoustic cavitation (AC) and hybrid methods, achieving significant removal rates. **Isariebel et al.** (2009) observed 95% removal of ACP under sonication at 574 kHz, while **Im et al.** (2013) reported 86.1% removal at 1000 kHz. Combining AC with catalysts such as TiO₂ or Fenton reagents has further enhanced degradation efficiency, with **Jagannathan et al.** (2013) finding that AC + UV + Fe³⁺ achieved a maximum degradation rate of 46.7%. Similarly, Wang et al. (2015) demonstrated that AC combined with Fenton oxidation resulted in over 80% ACP degradation, significantly outperforming AC alone.

For "nonsteroidal anti-inflammatory drugs (NSAIDs)" like diclofenac (DF) and ibuprofen (IBP), ultrasonic treatments have also yielded promising results. Hartmann et al. (2007) reported 90% DF degradation within 30 minutes using AC + TiO₂ (P25), while Madhavan et al. (2010) found that AC + UV + TiO₂ achieved the highest DF removal (73%) compared to other photocatalysts. For IBP, Guettaia et al. (2017) achieved 99.6% degradation and 70.2% COD removal through sonophotolysis (AC/UV), whereas Farhadi et al. (2020) demonstrated that an AC/UV/H₂O₂ system with a Zeolite-TiO₂ photocatalyst removed 98.9% IBP and 89% COD. Moreover, the use of single-walled nanotubes (SWNT) as a catalyst enhanced IBP degradation to 97% within 60 minutes (Al-Hamadani et al., 2017), highlighting the potential of nanomaterials in sonochemical AOPs.

Other pharmaceuticals, including carbamazepine (CBZ) and tetracycline (TC), have been effectively degraded using sonication-based treatments. Tran et al. (2013) reported a 90.1% CBZ removal efficiency at an initial concentration of 6 mg/L, while **Ghauch et al.** (2011) found that incorporating zero-valent iron (Fe₂) and H₂O₂ into an AC process resulted in 90% CBZ degradation. Tetracycline removal has also been optimized through the integration of AC with oxidation catalysts, achieving complete degradation when combined with goethite and ozone (**Wang et al., 2011**) or 93.6% removal with Fe₂O₂ and H₂O₂ (**Hou et al., 2016**). These findings emphasize the effectiveness of sonochemical AOPs in the degradation of persistent pharmaceutical pollutants.

Photocatalysis

Photocatalysis surpasses other advanced oxidation techniques, including ozonation, chemical oxidation, and biological processes, due to its various benefits. The photocatalysis method can degrade contaminants with extremely low concentrations in a very short amount of time (Omar and Puganeshwary, 2019). Photocatalytic degradation can be accomplished using a low-cost, highly active catalyst without the formation of any side or secondary contaminants (Kumar and Pandey, 2017). TiO₂, ZnO, sunlight, nano-composites materials such as Ag, Au, and Pt, as well as a combination of TiO₂ and nano-composites, can be used as a photocatalyst for pollutant oxidation (Nasr et. al., 2019). Photocatalysis in combination

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with ultraviolet irradiation appears to be a promising technology for the degradation of various pharmaceutical toxins (Bhuva and Bhatti, 2015).

Photocatalysis has emerged as an effective approach for the degradation of pharmaceutical compounds, with titanium dioxide (TiO₂) being the most widely used catalyst. Studies on "acetaminophen (ACP)" degradation have shown that TiO₂-assisted photocatalysis, combined with UV light, can achieve high degradation efficiencies. For instance, Aguilar et al. (2011) reported a 97% reduction in ACP within 60 minutes, while Zhang et al. (2008) achieved 95% degradation under slightly different conditions. Additionally, modified TiO₂ catalysts, such as platinum-loaded TiO₂ (Pt/TiO₂), have demonstrated even greater efficiency under solar light, highlighting the potential of doping strategies to enhance photocatalytic performance (Nasr et al., 2019).

"Diclofenac (DF)" and "carbamazepine (CBZ)" have also been effectively degraded using photocatalysis. A study by Mugunthan et al. (2019) found that ZnO-WO₂ catalysts under visible light optimized DF degradation at a pH of 6, with a catalyst dose of 800 mg/L. Similarly, TiO₂ photocatalysis has proven highly effective in removing CBZ from aqueous solutions, with Carabin et al. (2015) achieving 99% degradation within 90 minutes using a catalyst load of 1500 mg/L. Ibuprofen (IBP) degradation studies have also demonstrated promising results, with titania (P25) achieving an 85% removal rate at an optimal catalyst concentration of 10 mg/L under UV-Vis light exposure (Choina et al., 2013).

Advanced photocatalysts have further improved pharmaceutical degradation efficiency. Amoxicillin (AMX) has been effectively degraded using Co-doped TiO₂ nanocomposites, achieving over 90% degradation within 240 minutes under UV light (Caglar et al., 2019). Similarly, ketoprofen (KP) degradation has been enhanced using Bi₂S₂/TiO₂-Montmorillonite catalysts, leading to complete degradation within 120 minutes (Djouadi et al., 2018). These findings underscore the significance of catalyst modifications and doping techniques in enhancing the efficiency of photocatalytic degradation of pharmaceutical contaminants in wastewater treatment processes.

Fenton and Photo-Fenton Chemistry

The Fenton chemistry, a well-studied Advanced Oxidation Process (AOP), was first discovered by H. J. H. Fenton in 1894. Research suggested that Fenton chemistry involves more than 20 different reactions (Pliego et al., 2015). The efficiency of the Fenton process depends on factors such as contaminant concentration, pH, and concentration of Fenton's reagents like H_2O_2 and Fe^{2+} ions (Zhang et al., 2019). Due to the low output of iron sludge, the Photo-Fenton process has put a greater emphasis on the reduction of refractory organic contaminants. Integration of UV or visible light in combination with the conventional Fenton approach enhances catalyst catalytic activity, increases organic pollutant oxidation rate, and decreases iron sludge production. The photo-Fenton process accelerates the reduction. (Sun et al., 2011; Kalal et al., 2014; Lee et al., 2014). When Fe^{2+} interacts rapidly with H_2O_2 , Fe^{3+} (also known as [Fe(OH)]²⁺) is formed (Ahmed et al., 2011; Sirés and Brillas, 2012). As exposed to light, [Fe(OH)]²⁺ regenerates Fe²⁺, which accelerates the breakdown of H₂O₂ generating more *OH, which facilitate organic compound degradation (Avetta et al., 2015; Faust and Hoigné, 1990). In addition, the direct photolysis of H₂O₂ yields 'OH radicals, aiding in removal of organic pollutants (Wang et al., 2018, Li et al., 2013). The synergistic effects of Fe²⁺and light increase hydroxyl radical formation, leading to enhance the oxidation efficiency in the Photo-Fenton process. The mineralization of pharmaceutical compounds using Fenton chemistry and Photo-Fenton processes has been extensively studied under various operating conditions. For acetaminophen (ACP), researchers have investigated different combinations of Fe²⁺ and H₂O₂. Studies have demonstrated high degradation efficiency, with reductions ranging from 87.98% to complete degradation, depending on the Fe²⁺ and H₂O₂ concentrations, reaction time, and catalyst type. The inclusion of UV light in the process further improved degradation rates, achieving a maximum reduction of 91% and COD removal of 82% within 120 minutes (Manu & Mohamood, 2011). Similar trends have been observed for ibuprofen (IBP), where a combination of ZVI-Fenton and H_2O_2 led to complete degradation within one hour at pH 4, while other Fenton-based processes achieved partial degradation depending on catalyst loading and reaction conditions (Minella et al., 2019; Méndez et al.,

Carbamazepine (CBZ) has also been effectively treated using Fenton and Photo-Fenton processes, with UV-assisted Fenton oxidation achieving a 78% degradation rate within seven minutes (**Dai et al., 2012**). Similarly, studies on ketoprofen (KP) have reported degradation efficiencies of up to 100% when using Fe/ZSM5 as a catalyst, whereas conventional Fenton treatments showed slightly lower efficiencies ranging between 86% and 88%, depending on pH, reagent concentration, and UV exposure (**Mihaela et al.,**

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2018; Azusano et al., 2020). These results highlight the potential of combining iron-based catalysts with UV light to enhance oxidation efficiency and minimize treatment time.

For diclofenac (DF), Fenton and Photo-Fenton treatments have demonstrated rapid and effective degradation. Studies have reported nearly complete degradation within minutes, with UV-assisted Fenton processes achieving 96% degradation at an optimum H₂O₂ concentration (**Pérez-Estrada et al., 2005**). Furthermore, an alternative approach using pyrite as a catalyst achieved 100% diclofenac degradation within just 180 seconds, demonstrating the effectiveness of iron-based catalysts in accelerating pollutant removal (**Bae et al., 2013**). These results reinforce the significance of optimizing catalyst selection, reagent concentration, and reaction conditions to maximize pharmaceutical degradation efficiency in wastewater treatment.

Ozonation Process

As known for its strong oxidizing and disinfecting properties, ozone operates as an oxidant under acidic conditions. However, in acidic and basic environment, it largely relies on free radical reactions. It has been shown that ozone has a far higher oxidation potential than more commonly used oxidants. Ozone has the potential to oxidize and breakdown most organic substances in water quickly, allowing toxins to be easily removed. In the other side, direct mineralization is difficult. Instead, a biodegradable material can be made. Concurrently, it can safely remove turbidity and contaminants from runoff. The integration of ozone with other treatment techniques leads to evolution of advanced oxidation technology. It offers a higher oxidation potential but less selective for reactants such as O_3/H_2O_2 , O_3/UV , and so on (Guo et al. 2017).

Two reasons have contributed to the increasing performance of ozone applications in recent years: I ozone disposal costs have dropped dramatically over the past decade, and (ii) ozone has environmental benefits over chlorine. Ozonation is a low-cost method of treating wastewater containing organic complexed metals. Since ozone is a powerful oxidant, it can break down organic pollutants in two ways: (a) molecular ozone's direct electrophilic attack; (b) OH* radicals formed during the ozone decomposition process's indirect attack (Rekhate et. al., 2020). Ozonation in wastewater treatment systems has two advantages: sludge isolation and the elimination of recalcitrant organic contaminants from wastewater. It's been discovered that ozonation allows sludge to solubilise, resulting in a reduction in overall biomass production (Semblante et al., 2017).

Several AOPs have been investigated for the removal of pharmaceuticals from wastewater. Diclofenac (DCF) has shown significant degradation through different treatment methods. For instance, the combination of iron silicate-loaded pumice and ozone achieved 73.3% mineralization and 21.17% TOC removal (Gao et al., 2017). The O₂/TiO₂/UV-A process proved to be highly effective, reaching 100% DCF removal and 90% TOC removal (García-Araya et al., 2010). Additionally, using Fe-MCM-41 as a catalyst, 76.3% degradation and 70% TOC removal were observed (Chen et al., 2016b). Similarly, sulfamethoxazole (SMX) degradation varied across different processes, with O₂ + Fe₂O₂/CO₂O₂ achieving 60% TOC removal (Chen & Wang, 2019), while O₂ + UV resulted in 65.7% TOC removal (Chen & Wang, 2020). Ozone treatment alone led to only 14% TOC removal, whereas combining O₂ with H₂O₂ improved efficiency to 32% (Martini et al., 2015, 2019).

Amoxicillin (AMX) and acetaminophen (ACP) removal have also been widely studied. The UV/TiO₂/O₂ process was effective, achieving 68% TOC removal (Moreira et al., 2015). Ozone treatment alone removed 82.7% of amoxicillin at an initial concentration of 0.2 mg/lit (Mojiri et al., 2019), while iron-loaded zeolite A (Fe-Z) + O₂ reached 90% removal at pH 7 (Ikhlaq et al., 2020). For acetaminophen, the O₂ + Modified MgO process led to 94% mineralization of 50 mg/L ACP at pH ~5(Yaghmaeian et al., 2017). Ozone alone removed 84.8% ACP, and the solar light/Ag-g-C₂N₂/O₂ system resulted in 80% TOC removal (Mojiri et al., 2019; Ling et al., 2019). The O₂/Persulfate process proved to be the most effective, achieving 91.4% ACP degradation at pH 10(Khashij et al., 2020). These results emphasize the potential of different oxidation processes for effectively degrading pharmaceutical contaminants from wastewater.

Hydro-cavitation Process

Over the past decade, hydrodynamic cavitation (HC) has gained significant traction in the wastewater treatment industry. Its oxidative potential makes it highly effective in treating aqueous effluents contaminated with organic, hazardous, and bio-refractory pollutants. Additionally, HC's mechanical and chemical effects have been leveraged for microbial disintegration in biological applications. The HC mechanism operates through the rapid formation, expansion, implosion, and collapse of microscopic cavities, leading to the release of immense energy (Mancuso et al., 2020). This phenomenon occurs as

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liquid flows through a constriction, such as a throttling valve, orifice plate, or venturi tube (**Gogate and Pandit, 2005**).

As a novel and advanced technology, hydrodynamic cavitation presents an effective alternative to ultrasound-induced cavitation for decomposing complex molecules. In environmental engineering, HC enhances the efficiency of water and effluent treatment, offering a sustainable solution for pollutant degradation. Hydrodynamic cavitation systems are considered environmentally sustainable and waste-free technologies. Their primary benefits include: HC reduces the persistence of low-biodegradable, radioactive, and carcinogenic organic compounds, which are often resistant to conventional disposal methods. In cavitating liquid environments, pollutants such as pesticides, medicines, dyes, and other industrial chemicals undergo significant biodegradation (Dindar, 2016).

Hydrodynamic cavitation (HC) combined with other AOPs have been widely explored for the mineralization of pharmaceutical contaminants in wastewater. For instance, carbamazepine (CBZ) achieved 100% degradation when treated with HC + H₂O₂ + O₂, outperforming other HC-based processes (Thanekar et al., 2018). Similarly, HC + H₂O₂ alone resulted in 89% CBZ removal under optimized conditions (Zupnac et al., 2013). Diclofenac (DCF) degradation was significantly enhanced when HC was combined with UV and TiO₂, achieving 79.38% degradation compared to other treatments (Bagal & Gogate, 2014). The application of HC for ibuprofen (IBP) degradation showed promising results, with 60% degradation achieved at 3.5 bar pressure (Musmarra et al., 2016). Additionally, sulfadiazine (SDZ) degradation reached 81% efficiency using a HC + Hetero-Fenton + Persulfate system (Roy & Moholkar, 2019).

Other antibiotics also showed effective degradation under HC-based treatment processes. Tetracycline (TC) experienced 78.2% degradation through HC combined with TiO₂-based photocatalysis under optimized conditions (Wang et al., 2017). Ciprofloxacin (CIP) degradation varied across different processes, with HC + O₂ proving to be the most effective, achieving 91.4% removal (Mukherjee et al., 2021). Likewise, norfloxacin (NOR) removal was highly efficient, reaching 96.45% degradation and 71.57% TOC removal through a HC + H₂O₂ system (Yi et al., 2021). These observations showcase the potential of HC-based AOPs in effectively degrading pharmaceutical pollutants from wastewater, with combination treatments often proving more efficient than HC alone.

CONCLUSION

AOPs represent a critical advancement in water treatment technology, offering a robust solution for degrading complex pollutants. Ongoing research and technological innovations will further enhance their applicability and cost-effectiveness, contributing to global efforts in achieving sustainable water management. AOPs offer a promising solution for eliminating organic pollutants from water and wastewater. With their ability to generate hydroxyl radicals, AOPs can effectively degrade even the most persistent contaminants.

The bar chart visualizes the degradation efficiency (Fig 2) of pharmaceuticals, categorized by different AOP methods. This helps illustrate which treatments are most effective for various contaminants.

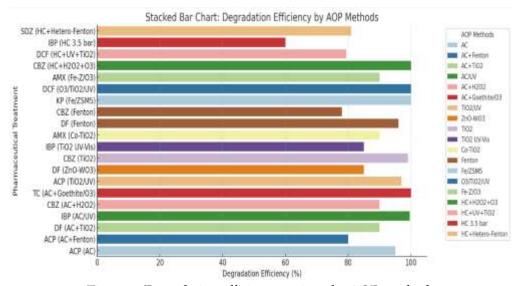


Figure 2: Degradation efficiency against the AOP methods

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However, challenges related to energy consumption, cost, and efficiency in treating all types of pollutants remain. Research is ongoing to optimize AOPs and make them more cost-effective for widespread use in environmental protection. The heat map (Fig 3) illustrating the degradation efficiency of pharmaceuticals across different AOP methods. The color intensity highlights which methods achieve higher removal rates, making it easier to identify the most effective treatments.

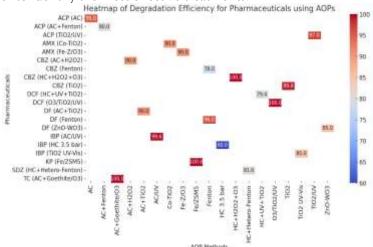


Figure 3: Heat map of Degradation efficiency against the AOP methods

The inclusion of hybrid methods suggests ongoing innovation in combining processes for better efficiency or effectiveness. The steady rise in publications from 2012 to 2018 suggests growing interest and development within the research area. This could be due to advancements in technology, increased funding, or greater awareness among researchers.

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