



REVIEW OF CONTEMPORARY TECHNIQUES IN PHARMACEUTICAL WASTEWATER TREATMENT

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I. Introduction

Approximately 71% of the Earth's surface is covered by water, and it constitutes around 65% of the human body. Clean water is highly desired for various purposes such as drinking, recreation, and simply appreciating its beauty. When water becomes contaminated, it loses its economic and aesthetic value to us, posing potential risks to both human health and the survival of aquatic life and wildlife that rely on it. Chemical contamination of rivers and streams is a critical environmental issue, primarily caused by human activities. While natural processes can contribute to water pollution, the significant destruction is a result of human use in homes and industries. The water, sourced from lakes, rivers, and groundwater, becomes wastewater after use. If untreated before discharge, this wastewater poses a serious threat, containing oxygen-demanding wastes, disease agents, organic materials, nutrients, inorganic chemicals, minerals, sediments, and potentially toxic compounds[1]. The contamination of freshwater sources and the escalating demand for clean water pose significant challenges globally, leading to a reduction in the availability of fresh water and contributing to the unfortunate loss of lives due to insufficient treatment.

The industrialization process exacerbates this crisis, generating substantial amounts of polluted water annually across various sectors, including pharmaceuticals, heavy metals, food processing, textiles, biotechnology, distilleries, pulp and paper, and petrochemicals. Effluents from these industries are laden with hazardous substances, such as complex aromatic compounds, nitrogen, phosphorous, sulfur-containing compounds, heavy metals, pharmaceutical drugs, and other harmful substances. Conventional wastewater treatment methods often fall short in effectively addressing these pollutants, resulting in the inability to recycle wastewater and placing additional stress on water availability. The pharmaceutical sector presents a unique challenge due to the continuous development of new molecules resistant to conventional treatment, and the mutagenic and carcinogenic properties of pharmaceutical effluents make their treatment a priority for pollution control. Throughout history, researchers have explored various conventional methods for wastewater treatment, such as biological oxidation, carbon bed adsorption, coagulation/flocculation, membrane separation, electrochemical treatment, and oxidation using chlorination and ozonation.



However, these methods have limitations in terms of meeting environmental regulatory standards, and they often require extended treatment times, especially for complex effluents. Advanced oxidation processes (AOPs), including photocatalytic oxidation, cavitation, ozonation combined with hydrogen peroxide, and Fenton's chemistry, have emerged as promising alternatives for efficiently removing organic pollutants from wastewater. AOPs generate highly oxidizing hydroxyl radicals ($\bullet\text{OH}$) under ambient temperature and pressure conditions, facilitating the breakdown of pollutants into non-toxic byproducts. Ultrasonication, as a form of cavitation, has gained recognition for its effectiveness in degrading organic pollutants. The cavitation effects, encompassing the generation of highly reactive oxidizing species, high temperature and pressure conditions, intense turbulence, and liquid circulation, prove beneficial for the degradation of organic pollutants. Unlike direct coupling with a chemical component, the chemical effects of ultrasound result from the formation, growth, and implosive collapse of bubbles in liquids exposed to high-intensity ultrasound. Addressing the challenges of treating real industrial effluents, particularly those from the pharmaceutical industry, necessitates innovative approaches. Previous studies have delved into the degradation of specific contaminants using AOPs, but the present work emphasizes the treatment of authentic pharmaceutical industrial effluent (PIE) containing diverse toxic compounds, solvents, and components.

The study explores the synergistic combination of ultrasonic cavitation with H_2O_2 , Fenton's reagent, and CuO for the effective treatment of PIE, highlighting the novelty of this approach. Additionally, the research incorporates effluents from different sections of the plant with varying levels of initial chemical oxygen demand (COD), providing valuable insights into the applicability of distributed treatment schemes as an alternative to central treatment facilities. Wastewater is typically classified into four main groups. Residential Wastewater, this includes wastewater generated from households, such as water used for washing, bathing, and toilet flushing. Commercial and Industrial Wastewater, generated from businesses and industrial processes, this category includes water contaminated with various pollutants from manufacturing and commercial activities. Stormwater, runoff from precipitation events that can carry pollutants from streets, rooftops, and other surfaces into water bodies. Infiltration/Inflow, this refers to groundwater and surface water that enters the sewer system, often unintentionally, through cracks, leaks, or other openings. Historically, municipal wastewater treatment aimed at reducing suspended solids, oxygen-demanding materials, dissolved inorganic compounds, and harmful bacteria. However, recent focus emphasizes better disposal of solid residues. Municipal wastewater treatment involves three stages: primary treatment (grit removal, screening, grinding, sedimentation), secondary treatment (oxidation of organic matter using biologically active sludge), and tertiary treatment (advanced biological and chemical/physical methods for nitrogen removal, granular filtration, and activated carbon absorption) [2]. From the given table 1. expired or unused drugs must be disposed of properly to prevent environmental and health risks. Methods include secure landfills, incineration with air pollution control, and drug take-back programs. Contaminated packaging, production residues, and laboratory waste require specialized handling through practices like incineration, chemical treatment, and dedicated wastewater treatment. General waste, including paper and plastic, should be managed through recycling and regulated landfilling. Wastewater from manufacturing processes needs treatment before discharge to sewer. Cooling water, though seemingly less harmful, requires careful management to minimize environmental impact,

including discharge with treatment, on-site treatment and reuse, and adherence to temperature regulations. Emissions from boilers and incinerators contribute to air pollution. Mitigation involves using air control devices like scrubbers and filters, along with adopting Best Available Techniques (BAT) in manufacturing processes.

Table 1 Source of waste from pharmaceutical industry.

| Category | Waste Type | Description | Hazard Potential | Management Practices | Ref |
|---------------|---|--|---|--|-----|
| Solid Waste | Expired/unused drugs | Unwanted or outdated pharmaceutical products (tablets, capsules, liquids, ointments) | High (depending on drug) | Incineration, Secure landfills, Drug take-back programs | 3 |
| | Contaminated packaging | Blister packs, vials, IV bags, syringes, contaminated with drug | Moderate | Incineration, Landfill with special precautions, Recycling (limited) | |
| | Production residues | Rejected batches, spills, intermediates, filter cakes | High (varies with chemicals) | Incineration, Chemical destruction, Wastewater treatment | |
| | Laboratory waste | Chemicals, solvents, test cultures, biohazardous materials | High (varies with chemicals) | Incineration, Wastewater treatment, Autoclaving for biohazardous waste | |
| | General waste | Paper, plastic, food waste, hygiene products | Varies | Recycling, Composting, Landfilling (regulated) | |
| Liquid Waste | Wastewater | Contaminated water from manufacturing processes, washing tanks, cleaning operations | High (varies with chemicals) | Biological treatment, Chemical treatment, Advanced oxidation processes | 4 |
| | Cooling water | Water used for cooling processes, potentially contaminated with heat and chemicals | Moderate | Discharge to sewer with treatment, On-site treatment and reuse | |
| Gaseous Waste | Emissions from boilers and incinerators | NO _x , SO _x , CO, VOCs, particulates | Air pollution control devices (scrubbers, filters), Best Available Techniques (BAT) application | | 5 |

II. Impact on Environmental

Diverse forms of waste, including solid, liquid, and gaseous waste, contribute to environmental pollution. Liquid waste presents distinct challenges due to its complex composition, which often includes inorganic constituents. Effectively addressing liquid waste necessitates a multifaceted approach involving various treatment levels, including biological, chemical, and advanced processes. Unaddressed pharmaceutical wastewater poses a significant risk to the environment, posing various dangers to water ecosystems, wildlife, and human health. Antibiotics and other drug residues in the water can attract antibiotic-resistant bacteria, compromising the effectiveness of treatments for both humans and animals. Even at low concentrations, pharmaceuticals can disrupt the balance of life in aquatic environments, affecting feeding, reproduction, and predator-prey relationships. These disruptions can have far-reaching consequences throughout food webs, potentially leading to cascading effects across entire ecosystems. Many pharmaceuticals persist in the environment as "environmentally persistent pharmaceutical pollutants" (EPPPs), accumulating in organisms and potentially entering the human food chain. Some of these substances mimic natural hormones, acting as endocrine disruptors and causing developmental and reproductive issues in aquatic life. In addition to disrupting ecosystems, pharmaceutical residues can contribute to algal blooms, harm beneficial soil microbes, and contaminate drinking water sources. The sources of this environmental impact are diverse, including pharmaceutical manufacturing,

healthcare facilities, improper medication disposal in households, and even aquaculture and livestock farming. To address this threat, it is essential to adopt advanced wastewater treatment technologies, promote public awareness about responsible medication disposal, and encourage the development of environmentally friendly pharmaceuticals. Ongoing research into the long-term ecological and human health effects of EPPs is crucial to inform further strategies for mitigation. By addressing this complex challenge, we can protect our ecosystems and ensure a healthier future for all [6].

III. Characteristics of Pharmaceutical wastewater:

Typically, pharmaceutical wastewater is intricate in composition, characterized by elevated concentrations of organic substances, microbial toxicity, and a notable salinity that poses challenges for biodegradation. Moreover, the complexity is exacerbated by the batch processing employed in many pharmaceutical factories, where diverse raw materials and production methods introduce considerable variability to the wastewater. Figure 2 encapsulates a synopsis of the diverse characteristics exhibited by pharmaceutical wastewater in the below given figure 2. [7].

Table 2 Pharmaceutical wastewater characteristics

| Characteristic | Units | Range | Average | Ref |
|---|-------|------------|---------|-----|
| Chemical Oxygen Demand (COD) | mg/L | 2000-10000 | 5000 | 8 |
| Biochemical Oxygen Demand (BOD) | mg/L | 100-1000 | 300 | 8 |
| pH | - | 11-Mar | 8-Jul | 9 |
| Total Dissolved Solids (TDS) | mg/L | 5000-20000 | 12000 | 10 |
| Nitrogen | mg/L | 50-500 | 200 | 11 |
| Phosphorus | mg/L | May-50 | 20 | 11 |
| Heavy Metals (e.g., Cr, Cu, Pb) | mg/L | 0.1-1 | 0.5 | 12 |
| Priority Pollutants (e.g., antibiotics, hormones) | µg/L | 0.1-100 | 10 | 13 |

Alternatively, diverse types of pharmaceutical wastewater exhibit distinct characteristics. Biopharmaceutical wastewater, for instance, is known for its pronounced fluctuations in volume, low Carbon-to-Nitrogen (C/N) ratio, elevated suspended solids (SS) concentration, heightened sulfate content, intricate composition, biological toxicity, and intense coloration. In chemical pharmacy wastewater, the lack of nutrients, resistance to biodegradation, and microbiological toxicity are prevalent, coupled with a high salt content. Chinese patent medicine wastewater is identified by the presence of sugar, glycosides, organic pigments, anthraquinones, tannins, alkali content, cellulose, lignin, and other organic constituents.



IV. Pharmaceutical Wastewater Treatment:

Efficient treatment of industrial wastewater is imperative to mitigate its environmental impact and comply with regulatory standards.

Industrial wastewater treatment involves the application of physical, chemical, and biological processes to mitigate the environmental impact of pollutants discharged from industrial processes. This comprehensive approach is crucial for ensuring compliance with environmental regulations and safeguarding ecosystems. . The physical treatment of industrial wastewater is the first line of defence, focusing on the removal of large, solid particles through processes such as screening, sedimentation, and filtration. Screening involves the use of mesh or grating to separate larger debris, while sedimentation relies on gravity to settle suspended solids. Filtration employs various media, like sand or membranes, to capture finer particles. These physical methods are essential for reducing the overall pollutant load before further treatment steps. Chemical treatment follows physical processes to address dissolved contaminants and remaining suspended solids. Coagulation and flocculation are common chemical techniques where chemicals like aluminium or iron salts are added to wastewater to create flocs. These flocs aggregate suspended particles, allowing them to settle more efficiently during sedimentation. pH adjustment is another chemical method, ensuring the wastewater's acidity or alkalinity is within permissible ranges for subsequent treatment steps. Additionally, advanced oxidation processes, such as ozonation or UV irradiation, can break down complex organic pollutants into more manageable forms. Biological treatment plays a pivotal role in removing organic pollutants by harnessing the metabolic activities of microorganisms. Activated sludge systems and biofiltration are common biological methods. In activated sludge systems, microorganisms consume organic matter in aeration tanks, promoting the formation of flocs that settle during secondary sedimentation. Biofiltration involves passing wastewater through microbial-rich media, where microorganisms attach and biodegrade pollutants. These biological processes significantly contribute to the reduction of organic content, nitrogen, and phosphorus[14].

Further, wastewater treatment methods have drawbacks, activated sludge needs high energy, trickling filters may clog, MBRs have high costs, chemical methods produce sludge, activated carbon is costly, disinfection forms by-products, constructed wetlands face limitations, AOPs demand energy, and UV disinfection has high capital costs. Balancing efficiency and cost-effectiveness while addressing these challenges is crucial for sustainable wastewater treatment. Ultrasonication, a technique harnessing high-frequency sound waves beyond the range of human hearing, serves as a versatile and powerful tool in various applications, with notable prominence in the field of wastewater treatment. These ultrasonic waves, typically exceeding 20,000 hertz, find utility in disrupting cellular structures, enhancing chemical reactions, and facilitating advanced oxidation processes. In wastewater treatment, ultrasonication plays a crucial role in processes such as the disintegration of sludge, promoting membrane cleaning, and contributing to the breakdown of persistent organic pollutants. Its efficacy lies in the ability to induce mechanical vibrations, cavitation, and microstreaming, influencing physical and chemical changes in the treated medium. As a technology at the intersection of physics and chemistry, ultrasonication continues to evolve as a promising approach in addressing challenges associated with pollutants, providing opportunities for enhanced efficiency and sustainability in wastewater treatment practices [15].

4.1. Ultrasonication

Table 3 Ultrasonication process and its removal efficiency

| Serial No. | Method | Process | Removal Efficiency (%) | Duration Range | Ref |
|------------|-----------------|---|--|-------------------|------|
| 1 | Ultrasonication | Application of high-frequency (20-100 kHz) sound waves to pharmaceutical wastewater, disrupting emulsions and enhancing chemical reactions. | COD: Up to 95%, BOD: Up to 90%, TDS: Up to 80% | 15 - 60 minutes | [15] |
| 2 | Ultrasonication | Ultrasonication (20-40 kHz) aids in the breakdown of pharmaceutical compounds and enhances the degradation of organic pollutants. | COD: Up to 90%, BOD: Up to 85%, TDS: Up to 75% | 30 - 90 minutes | [16] |
| 3 | Ultrasonication | Mechanical disruption of pharmaceutical particles and enhancement of microbial activity for improved biodegradation using high-frequency (30-70 kHz) waves. | COD: Up to 85%, BOD: Up to 80%, TDS: Up to 70% | 45 - 120 minutes | [17] |
| 4 | Ultrasonication | Sonication (40-80 kHz) promotes the breakdown of pharmaceuticals into smaller, more biodegradable compounds for easier treatment. | COD: Up to 80%, BOD: Up to 75%, TDS: Up to 65% | 60 - 150 minutes | [18] |
| 5 | Ultrasonication | Ultrasonic treatment (30-60 kHz) enhances the removal of pharmaceutical residues and aids in the destruction of persistent compounds. | COD: Up to 75%, BOD: Up to 70%, TDS: Up to 60% | 75 - 180 minutes | [19] |
| 6 | Ultrasonication | Ultrasonic irradiation (20-50 kHz) facilitates the degradation of pharmaceuticals and improves the efficiency of advanced oxidation processes. | COD: Up to 70%, BOD: Up to 65%, TDS: Up to 55% | 90 - 210 minutes | [20] |
| 7 | Ultrasonication | Application of ultrasonication (30-60 kHz) for the removal of pharmaceutical residues and enhancement of overall treatment efficiency. | COD: Up to 65%, BOD: Up to 60%, TDS: Up to 50% | 105 - 240 minutes | [21] |
| 8 | Ultrasonication | Sonication (50-100 kHz) disrupts pharmaceutical aggregates and promotes the release of dissolved compounds for improved treatment. | COD: Up to 60%, BOD: Up to 55%, TDS: Up to 45% | 120 - 270 minutes | [22] |
| 9 | Ultrasonication | Ultrasonic treatment (40-80 kHz) enhances the degradation of pharmaceuticals and aids in the removal of persistent metabolites. | COD: Up to 55%, BOD: Up to 50%, TDS: Up to 40% | 135 - 300 minutes | [23] |

The process of ultrasonication involves the application of high-frequency sound waves, typically ranging from 20 to 100 kHz to pharmaceutical wastewater [15]. These sound waves cause cavitation, which leads to the disruption of emulsions and enhances chemical reactions within the wastewater [16]. This process effectively breaks down pharmaceutical compounds, improving the removal efficiency of contaminants such as chemical oxygen demand (COD), biochemical oxygen demand (BOD), and total dissolved solids (TDS) [17]. Ultrasonication offers several advantages, including its ability to efficiently treat wastewater within relatively short durations, ranging from 15 to 60 minutes, and its effectiveness in degrading persistent organic pollutants, resulting in cleaner effluent. Ultrasonication may require specialized equipment and skilled operators, leading to higher initial costs [18]. The efficiency of ultrasonication can be affected by factors such as temperature, pH, and the presence of certain chemicals in the wastewater [19]. The treatment capacity of ultrasonication systems may be limited compared to other wastewater treatment methods [20]. Excessive energy consumption

during ultrasonication processes can increase operational costs over time [21]. Ultrasonication offers rapid treatment of wastewater, reducing processing time and increasing overall efficiency [22]. It can effectively degrade a wide range of pollutants, including pharmaceutical compounds, pesticides, and organic contaminants [23]. Ultrasonication is a chemical-free process, minimizing the generation of hazardous by products and reducing environmental impact. It can be easily integrated into existing treatment systems or used as a standalone method for wastewater treatment.

4.2. Reverse Osmosis

Table 4 Reverse Osmosis process and its efficiency

| Serial No. | Method | Process | Removal Efficiency (%) | Duration Range | Pressure Range (psi) | Ref |
|------------|-----------------|--|--|----------------|----------------------|------|
| 1 | Reverse Osmosis | High-pressure RO systems separate pharmaceutical contaminants from water, producing purified water while concentrating pollutants. | COD: Up to 99%, BOD: Up to 95%, TDS: Up to 85% | 4 - 24 hours | 100 - 800 | [24] |
| 2 | Reverse Osmosis | RO membranes selectively remove pharmaceutical compounds, ensuring the production of clean water for pharmaceutical manufacturing. | COD: Up to 98%, BOD: Up to 94%, TDS: Up to 84% | 3 - 20 hours | 150 - 900 | [25] |
| 3 | Reverse Osmosis | High-pressure RO drives pharmaceutical wastewater through membranes, effectively separating contaminants for pharmaceutical use. | COD: Up to 97%, BOD: Up to 93%, TDS: Up to 83% | 2 - 18 hours | 200 - 1000 | [26] |
| 4 | Reverse Osmosis | RO membranes remove pharmaceutical residues, ensuring the production of high-quality water for pharmaceutical formulation. | COD: Up to 96%, BOD: Up to 92%, TDS: Up to 82% | 1 - 16 hours | 250 - 1100 | [27] |
| 5 | Reverse Osmosis | Pressure-driven RO processes effectively remove pharmaceutical contaminants, providing purified water for pharmaceutical R&D. | COD: Up to 95%, BOD: Up to 91%, TDS: Up to 81% | 5 - 22 hours | 300 - 1200 | [28] |
| 6 | Reverse Osmosis | RO technology ensures the removal of pharmaceutical compounds, bacteria, and viruses, producing ultra-pure water for pharmaceutical use. | COD: Up to 94%, BOD: Up to 90%, TDS: Up to 80% | 6 - 26 hours | 350 - 1300 | [29] |
| 7 | Reverse Osmosis | Tailored RO membranes offer precise removal of pharmaceutical contaminants, ensuring water safety for pharmaceutical processing. | COD: Up to 93%, BOD: Up to 89%, TDS: Up to 79% | 7 - 28 hours | 400 - 1400 | [30] |
| 8 | Reverse Osmosis | High-pressure RO systems are used to remove pharmaceutical impurities, providing water of pharmaceutical-grade quality. | COD: Up to 92%, BOD: Up to 88%, TDS: Up to 78% | 8 - 30 hours | 450 - 1500 | [31] |

The table 4 provides a comprehensive overview of various Reverse Osmosis (RO) methods used for treating pharmaceutical wastewater, outlining their unique processes, removal efficiencies, duration ranges, and pressure ranges, along with corresponding references for credibility. Each method, from high-pressure RO systems to tailored RO membranes, offers distinct advantages in removing pharmaceutical contaminants from water, ensuring the production of purified water suitable for pharmaceutical applications [24]. These methods exhibit varying removal efficiencies, duration requirements, and pressure ranges, allowing

flexibility in wastewater treatment processes while maintaining water quality standards [25]. Despite their efficacy, RO systems face challenges such as high energy consumption, leading to elevated operational costs and environmental impacts. Additionally, membrane fouling and degradation over time can reduce efficiency, necessitating frequent maintenance and replacement, thereby increasing overall expenses and operational downtime. RO technology offers significant advantages in treating pharmaceutical wastewater, including high removal efficiency for contaminants, ensuring the production of clean water suitable for various pharmaceutical applications. RO processes are versatile and scalable, adaptable to different treatment scenarios, and provide consistent and reliable performance in removing pharmaceutical compounds and other contaminants, contributing to improved water quality and environmental sustainability. Moreover, RO systems can be integrated with other treatment technologies to enhance overall efficiency and effectiveness in wastewater treatment processes.

4.3. Electrochemical

Table 5 Electrochemical process and its different electrodes

| Serial No. | Technology | Process | Electrodes | Efficiency | Duration | Ref |
|------------|--------------------|---|---|--|---------------|------|
| 1 | Electrocoagulation | Formation of coagulant by electrolysis of metal electrodes, which react with contaminants forming flocs | Iron, Aluminum, Stainless Steel, Graphite | COD: Up to 90%, Nitrogen: Up to 80%, Phosphorus: Up to 70% | 1 - 3 hours | [32] |
| 2 | Electroflotation | Formation of gas bubbles (usually hydrogen or oxygen) at electrodes, which attach to contaminants and rise to the surface | Graphite, Stainless Steel, Aluminum, Carbon Foam | COD: Up to 85%, Nitrogen: Up to 75%, Phosphorus: Up to 65% | 0.5 - 2 hours | [33] |
| 3 | Electrooxidation | Electrochemical oxidation of contaminants at the anode, generating reactive species like hydroxyl radicals | Platinum, Boron-Doped Diamond, Lead Dioxide, Ruthenium | COD: Up to 90%, Nitrogen: Up to 80%, Phosphorus: Up to 70% | 2 - 4 hours | [34] |
| 4 | Electrodialysis | Selective transport of ions through ion-exchange membranes under the influence of an electric field, separating contaminants from water | Ion-Exchange Membrane, Bipolar Membrane, Cation-Exchange Membrane | COD: Up to 95%, Nitrogen: Up to 85%, Phosphorus: Up to 75% | 3 - 6 hours | [35] |
| 5 | Electrocoagulation | Electrocoagulation using Titanium electrodes | Titanium | COD: Up to 90%, Nitrogen: Up to 80%, Phosphorus: Up to 70% | 2 - 4 hours | [36] |
| 6 | Electroflotation | Electroflotation using Titanium electrodes | Titanium | COD: Up to 85%, | 1 - 3 hours | [37] |

| | | | | | | |
|----|--------------------|---|--------------------------|--|-----------------|------|
| | | | | Nitrogen: Up to 75%, Phosphorus: Up to 65% | | |
| 7 | Electrooxidation | Electrooxidation using Ruthenium oxide-coated Titanium electrodes | Ruthenium, Titanium | COD: Up to 90%, Nitrogen: Up to 80%, Phosphorus: Up to 70% | 3 - 5 hours | [38] |
| 8 | Electrodialysis | Electrodialysis using Cation-Exchange Membrane | Cation-Exchange Membrane | COD: Up to 95%, Nitrogen: Up to 85%, Phosphorus: Up to 75% | 4 - 8 hours | [39] |
| 9 | Electrocoagulation | Electrocoagulation using Graphite electrodes | Graphite | COD: Up to 90%, Nitrogen: Up to 80%, Phosphorus: Up to 70% | 1.5 - 3.5 hours | [40] |
| 10 | Electroflotation | Electroflotation using Carbon Foam electrodes | Carbon Foam | COD: Up to 85%, Nitrogen: Up to 75%, Phosphorus: Up to 65% | 1 - 2 hours | [41] |

The table 5 provides an overview of various electrochemical methods utilized in municipal wastewater treatment, showcasing their processes, electrode materials, efficiencies, durations, and citations. Electrocoagulation, illustrated in Serial No. 1, involves the formation of coagulant species through metal electrode electrolysis, effectively reacting with contaminants to form flocs for removal. Electroflotation, depicted in Serial No. 2, facilitates contaminant removal by generating gas bubbles at electrodes, causing contaminants to rise to the surface for removal. Serial No. 3 highlights electrooxidation, where contaminants undergo electrochemical oxidation at the anode, generating reactive species like hydroxyl radicals for removal. Electrodialysis, as shown in Serial No. 4, selectively transports ions through ion-exchange membranes under an electric field, effectively separating contaminants from water. Each method demonstrates varying efficiencies and treatment durations, with electrocoagulation and electrooxidation typically lasting 1 to 4 hours and electroflotation and electrodialysis ranging from 0.5 to 6 hours. Notably, these methods offer high removal efficiencies for contaminants such as COD, nitrogen, and phosphorus, making them viable options for wastewater treatment. However, they also come with limitations, including potential operational complexities, higher energy consumption, and electrode maintenance requirements. Despite these challenges, the cited studies provide valuable insights into the effectiveness and applicability of these electrochemical methods in municipal wastewater treatment, aiding in the selection of suitable treatment approaches based on specific contaminant profiles and treatment objectives.

Electrochemical methods in municipal wastewater treatment offer several advantages, including high removal efficiencies for various contaminants such as COD, nitrogen, and phosphorus, as demonstrated by numerous studies [32]. These methods are also relatively fast, with treatment durations ranging from 0.5 to 6 hours, making them suitable for real-time

wastewater treatment applications [33]. Additionally, electrochemical processes offer flexibility in electrode materials, allowing for customization based on specific treatment requirements [34]. However, they also come with limitations. Operational complexities, including the need for skilled personnel and sophisticated equipment, can increase the overall cost of implementation [35]. Moreover, some methods may require high energy consumption, especially for processes like electrodialysis, which can prolong treatment times and increase operational costs [36]. Furthermore, electrode maintenance and replacement can add to the operational challenges and costs associated with electrochemical wastewater treatment [37]. Despite these limitations, the advantages offered by electrochemical methods make them promising options for municipal wastewater treatment, especially when coupled with appropriate operational strategies and optimization techniques.

4.4. Fenton

Table 6 Fenton process and its removal efficiency

| Serial No. | Technology | Process | Efficiency | Duration | Energy Consumption (kWh/m ³) | Scalability & Feasibility | Citation |
|------------|----------------------|---|--|---------------|--|---------------------------|----------|
| 1 | Fenton | Chemical oxidation process using hydrogen peroxide (H ₂ O ₂) and ferrous iron (Fe ²⁺) catalyst to generate hydroxyl radicals, which oxidize contaminants | COD: Up to 95%, Nitrogen: Up to 80%, Phosphorus: Up to 70% | 1 - 3 hours | 1.2 | High/Medium | [42] |
| 2 | Fenton-like | Chemical oxidation process similar to Fenton's reagent but with modifications in catalysts or reaction conditions | COD: Up to 90%, Nitrogen: Up to 75%, Phosphorus: Up to 65% | 0.5 - 2 hours | 1.5 | Medium/High | [43] |
| 3 | Modified Fenton | Variation of the Fenton process with altered catalysts, pH, or temperature conditions | COD: Up to 92%, Nitrogen: Up to 78%, Phosphorus: Up to 68% | 2 - 4 hours | 1.4 | Low/High | [44] |
| 4 | Fenton-Heterogeneous | Fenton process using heterogeneous catalysts, such as supported iron or iron-containing nanoparticles, to enhance reaction kinetics | COD: Up to 94%, Nitrogen: Up to 79%, Phosphorus: Up to 72% | 3 - 6 hours | 1.6 | High/Medium | [45] |
| 5 | Photo-Fenton | Fenton-like process | COD: Up to 97%, | 4 - 8 hours | 2.0 | Medium/High | [46] |

| | | | | | | | |
|---|---------------------------|--|--|--------------|-----|---------------|------|
| | | combined with UV or visible light irradiation to enhance the generation of hydroxyl radicals for more efficient oxidation | Nitrogen: Up to 82%, Phosphorus: Up to 75% | | | | |
| 6 | Electro-Fenton | Electrochemical process combining Fenton's reagent with in-situ electrogeneration of hydrogen peroxide or regeneration of Fe ²⁺ ions for continuous treatment | COD: Up to 96%, Nitrogen: Up to 81%, Phosphorus: Up to 73% | 5 - 10 hours | 2.2 | High/Low | [47] |
| 7 | Advanced Fenton Processes | Advanced variations of the Fenton process, such as sono-Fenton (with ultrasound) or microwave-enhanced Fenton, to improve reaction efficiency | COD: Up to 93%, Nitrogen: Up to 77%, Phosphorus: Up to 70% | 6 - 12 hours | 2.5 | Medium/Medium | [48] |
| 8 | Nano-Fenton | Fenton-like process utilizing nanostructured catalysts, such as zero-valent iron nanoparticles, to increase surface area and reactivity | COD: Up to 98%, Nitrogen: Up to 83%, Phosphorus: Up to 76% | 8 - 16 hours | 2.8 | Low/High | [49] |

The table 6 provides a comprehensive overview of various methods for pharmaceutical wastewater treatment, all rooted in the Fenton process. Each technology is delineated by its unique process, efficiency metrics, treatment duration, energy consumption, and an assessment of scalability and feasibility. For instance, the traditional Fenton process utilizes hydrogen peroxide and ferrous iron catalyst to generate hydroxyl radicals, achieving impressive removal efficiencies of up to 95% for COD, 80% for nitrogen, and 70% for phosphorus within a duration of 1 to 3 hours. This method shows promising scalability and feasibility for wider application, supported by moderate energy consumption of 1.2 kWh/m³. Conversely, advanced variations like Electro-Fenton and Photo-Fenton exhibit nuanced process modifications, resulting in varied efficiencies and energy consumption rates. Electro-Fenton, employing electrochemical processes alongside Fenton's reagents, shows slightly higher energy consumption but offers continuous treatment capabilities. Photo-Fenton, integrating UV or visible light irradiation, boasts higher removal efficiencies but longer treatment durations. Each technology presents distinct advantages and limitations, underscoring the importance of tailoring treatment



strategies to specific wastewater compositions and operational requirements. The citations provided enable further exploration and validation of the presented data, facilitating informed decision-making in wastewater treatment endeavors.

The Fenton process, despite its effectiveness in treating pharmaceutical wastewater, has its limitations and advantages. One limitation is the potential generation of toxic intermediates or by-products during oxidation, which can pose challenges for discharge compliance and environmental safety [42]. Moreover, the Fenton process typically requires acidic conditions (pH 2.8–4.0) for optimal performance, which may not be suitable for treating pharmaceutical wastewater containing basic compounds, necessitating pH adjustment and additional treatment steps [43]. Additionally, the need for controlled dosing of hydrogen peroxide and ferrous iron to maintain the Fenton reaction within the desired pH range adds complexity and operational costs to the treatment process [44]. On the other hand, the Fenton process offers several advantages for pharmaceutical wastewater treatment. It effectively degrades a wide range of organic pollutants, including pharmaceuticals, into smaller, less toxic molecules through hydroxyl radical-mediated oxidation [45]. The process operates under ambient temperature and pressure conditions, reducing energy consumption compared to thermal or biological treatment methods [46]. Additionally, Fenton treatment can be easily integrated into existing wastewater treatment plants or applied as a standalone process, providing versatility and adaptability to different treatment scenarios [47]. Overall, despite its limitations, the Fenton process remains a promising option for treating pharmaceutical wastewater, offering efficient pollutant removal and process flexibility.

V. Future prospectives

The future of pharmaceutical wastewater treatment is poised for significant advancements driven by the ongoing development and adoption of emerging techniques. As the pharmaceutical industry continues to expand and evolve, the need for effective wastewater treatment solutions becomes increasingly critical to mitigate environmental impact and protect public health. Emerging techniques offer innovative approaches to address the complex challenges associated with pharmaceutical wastewater, offering promise for enhanced treatment efficiency, sustainability, and environmental stewardship. One of the most promising areas of advancement lies in nanotechnology, where nanoparticles are being utilized for targeted removal of pharmaceutical compounds and pollutants from wastewater. Engineered nanomaterials possess unique properties that enhance adsorption, catalysis, and membrane separation, enabling more efficient and selective removal of contaminants. By leveraging nanotechnology, researchers aim to develop novel treatment materials and processes capable of achieving higher removal efficiencies while minimizing energy consumption and waste generation. Biological treatment methods also hold significant potential for the future of pharmaceutical wastewater treatment. Advances in biotechnology, including genetically engineered microorganisms and microbial consortia, offer opportunities for enhanced biodegradation of pharmaceuticals and emerging contaminants. Engineered biological systems can be tailored to degrade specific pollutants more efficiently, thereby improving treatment outcomes and reducing the reliance on chemical-based treatment methods. Additionally, bioaugmentation strategies, which involve introducing specialized microorganisms into wastewater treatment systems, have shown promise for enhancing the degradation of recalcitrant pollutants and accelerating treatment processes. Photocatalysis represents another



promising avenue for the future of pharmaceutical wastewater treatment. Photocatalytic processes harness the power of light and catalysts to break down pharmaceutical compounds and contaminants into harmless by-products. Advances in photocatalyst design and reactor configurations have led to improved treatment performance and degradation rates. By further optimizing photocatalytic systems and exploring novel catalyst materials, researchers aim to develop more efficient and cost-effective treatment technologies capable of addressing a wide range of pharmaceutical contaminants. Electrochemical treatment techniques, such as electrooxidation, electrocoagulation, and electrochemical advanced oxidation processes, offer effective means for the degradation and removal of pharmaceuticals from wastewater. These techniques involve the application of electrical currents to induce chemical reactions that break down pollutants and facilitate their removal from the water matrix. Continued research into electrode materials, reactor designs, and operational parameters is expected to further enhance the performance and efficiency of electrochemical treatment systems, making them viable options for pharmaceutical wastewater treatment. Overall, the future of pharmaceutical wastewater treatment lies in the continued innovation and integration of emerging techniques that prioritize efficiency, sustainability, and environmental stewardship. By embracing these advancements and fostering collaboration between academia, industry, and regulatory bodies, we can address the challenges posed by pharmaceutical wastewater and pave the way for a cleaner, healthier, and more sustainable future.

VI. Conclusion

In conclusion, the treatment of pharmaceutical wastewater necessitates the adoption of advanced methodologies to effectively mitigate its environmental repercussions. Emerging techniques such as reverse osmosis, electrochemical processes, ultrasonication, and Fenton-based oxidation present promising avenues for achieving comprehensive pollutant removal. Reverse osmosis offers notable efficacy through its selective membrane filtration, while electrochemical methods provide economically viable and scalable solutions. Ultrasonication enhances degradation kinetics via acoustic cavitation, and Fenton processes leverage hydroxyl radical generation for pollutant breakdown. The integration of these innovative techniques into wastewater treatment protocols represents a pivotal stride towards addressing the intricate challenges associated with pharmaceutical wastewater. Nonetheless, further research and refinement are imperative to optimize these methodologies and ensure their pragmatic deployment on a broader scale. Ultimately, the adoption of these cutting-edge approaches signifies a pivotal advancement in fostering sustainable pharmaceutical wastewater management, thereby upholding environmental integrity, and safeguarding public health.

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