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RECENT DEVELOPMENTS IN CONVENCTIONAL AND NANOBASED TREATMENT OF PHARMACEUTICAL WASTEWATER: A REVIEW

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Abstract:

This review paper presents an extensive analysis of water and wastewater treatment methods targeted at mitigating pharmaceutical contamination. Chemical processes including Fenton reaction, ozonation, and electrochemical oxidation are evaluated for their efficacy in degrading pharmaceutical compounds. Biological treatments like sequencing batch reactors (SBR) and membrane bioreactors (MBR) are discussed as sustainable approaches leveraging microbial activity. Physiochemical methods such as membrane processes and adsorption are examined for their ability to physically separate and adsorb pharmaceutical pollutants. Additionally, the paper explores the emerging field of nanomaterial-based treatment, focusing on carbon-based, magnetic, and titanium dioxide nanoparticles. It discusses their applications and mechanisms in pharmaceutical wastewater treatment. By synthesizing existing knowledge, identifying research gaps, and proposing future directions, this review provides insights to advance water treatment strategies for pharmaceutical contaminant removal, addressing a critical environmental concern.

Keywords: Pharmaceutical, Ozonation, Fenton Oxidation,

I. Introduction

The Global Concerns about strict water treatment and reuse regulations are developing as a result of the world's increasing need for clean water, which is necessary for industrial, agricultural, drinking, and sanitation needs [1]. The pharmaceutical sector uses batch operations primarily for wastewater treatment in its high-value, low-volume multiproduct facilities. For the synthesis of bulk drugs, several factories use continuous, semi-continuous, or batch processes, employing specialised equipment to combine water, solvents, catalysts, and different reactants[2-4].

Processes for separation are essential because the kind of impurity rather than the purity of the medicine typically determines its price. Because of these intricate, multistep processes requiring significant volumes of solvents, the environmental effect factor (E-factor) in pharmaceutical manufacture generally ranges from 50 to 100 kg/(kg of intended output). Drug master file (DMF) guidelines state that strict laws forbid the reuse of ultrapure water, despite its critical use in pharmaceutical operations. Pharmaceutical residues in aquatic habitats continue to raise concerns about their toxicity, presence, and consequences. This emphasises the need to prioritise drug recovery and high-value active pharmaceutical ingredients (API) above therapeutic approaches[5].

Common medications like antibiotics and analgesics are used extensively, yet little is known about how they affect the environment. Pharmaceutical quantities that are detectable in a variety of environmental samples point to possible environmental dangers, underscoring the significance of rigorous monitoring and established analytical techniques for precisely determining the influence on the environment and reducing hazards[6].

The peculiarities of pharmaceutical wastewater—namely, high levels of organic pollutants, large variations, and a complex composition—present particular difficulties [7]. It also usually has higher than normal levels of chroma and ammonia nitrogen (NH_3-N), as well as higher than normal levels of Chemical and Biological Oxygen Demand (COD) and BOD, often with a significant difference between the two [8, 9]. Furthermore, salinity and suspended particles contents in pharmaceutical wastewater are often high [10]. Due of these intricate characteristics, conventional wastewater treatment facilities (WWTPs), which rely on physicochemical and biological processes, are ill-suited to handle wastewater effectively. In order to tackle this problem, this study conducts a thorough analysis of three different technologies—chemical, biological, and physicochemical treatments—offering a concise synopsis of methods to reduce this difficult industrial waste.

II. Pharmaceutical Waste Water Treatment Process

Water is a crucial ingredient in the production of chemicals and pharmaceuticals. A steady and consistent supply of high-quality water is essential for a variety of processes, including manufacturing, material processing, and refrigeration. Treating a variety of water types is part of an all-encompassing water management plan. These water types include potable water, process water, utility feedwater, wastewater, runoff from byproduct treatment, odour treatment water, desalination effluents, and irrigation water[11].

This review will exclusively examine pharmaceutical water, which plays a vital role in physicochemical, chemical, and biological processes. Ensuring the quality of process water holds considerable significance in pharmaceutical manufacturing and is a mandatory prerequisite for sterilizing containers or medical devices in various healthcare settings, such as water for injection. The term "process wastewaters" encompasses wastewater originating from any industry's processes. Hence, process wastewaters encompass water that interacts with raw materials, products, intermediates, byproducts, or waste products during manufacturing or processing, across various unit operations or processes.

Indeed, it is impossible to follow a single treatment technique due to the variability in the content and concentration of wastewater discharged by pharmaceutical companies. This problem results from the variety of products produced using shared equipment and the comparatively tiny amounts of wastewater produced. Putting water reuse techniques into practice can save money by reducing waste disposal costs and the requirement for fresh feedwater, which balances the operational costs of recycling wastewater.

III. Chemical Process Treatment

The chemical treatment of pharmaceutical wastewater is critical for environmental safety. Advanced oxidation processes (AOP), such as Fenton reaction and ozonation, offer effective

solutions. AOPs involve generating hydroxyl radicals to break down contaminants. Fenton reaction utilizes iron catalysts to produce hydroxyl radicals, while ozonation involves the use of ozone to degrade pollutants. These methods efficiently target diverse pharmaceutical compounds, ensuring water quality and mitigating ecological impact. This review examines the efficacy, mechanisms, and applications of AOPs, Fenton reaction, and ozonation in pharmaceutical wastewater treatment.

3.1 Fenton Oxidation

Another highly efficient advanced oxidation process (AOP) worth mentioning is Fenton oxidation. This method boasts a notably rapid reaction rate while avoiding the need for costly chemicals. The Fenton reaction entails the decomposition of hydrogen peroxide with ferrous ions serving as catalysts. It's worth noting that the optimal pH level for this process falls within the range of 2 to 4. The hydroxyl radicals produced play a pivotal role as active agents in breaking down pollutants within wastewater. The chemical reactions occurring during Fenton oxidation have been extensively studied and documented During Fenton oxidation, the following reactions occur eqn(1-3)[12-14]

$$Fe^{2+} + H_2O_2 = Fe^{3+} + OH^- + HO^{\bullet} \quad (1)$$

$$Fe^{3+} + H_2O_2 = Fe^{2+} + HOO\bullet + H^+ \quad (2)$$

$$Fe^{2+} + OH\bullet = Fe^{3+} + OH^- \quad (3)$$

Due to the Fenton reaction's optimal performance under acidic conditions, it becomes imperative to acidify wastewater. However, this process incurs additional expenses for the subsequent neutralization of effluents [13,14]. The effectiveness of the Fenton reaction hinges on the concentration of hydrogen peroxide utilized. It is observed that higher concentrations of H_2O_2 yield a greater abundance of active radicals OH• [15].

The homogeneous Fenton reaction suffers from two main drawbacks: a restricted pH operating range and the precipitation of insoluble iron oxy-hydroxides. These challenges can be alleviated by integrating Fenton oxidation with complementary pollutant removal techniques. Specifically, combining Fenton oxidation with ultraviolet (UV) radiation proves to be more effective in removing pharmaceutical contaminants, a method commonly known as photo-Fenton processes [16]. De la Cruz et al. conducted experiments to assess the removal of pharmaceuticals from wastewater using UV radiation at 254nm (UV254), Fenton oxidation in the absence of light (Fe^{2+} ,Fe^{3+} / H_2O_2), and photo-Fenton (Fe^{2+} ,Fe^{3+} / H_2O_2/light)[17]. The highest purification efficiency of effluent from municipal wastewater treatment plants was achieved when subjected to ultraviolet radiation combined with H_2O_2 (50mg/L) and Fe^{2+} (5mg/L).

Heterogeneous catalysts can also be used in the Fenton oxidation. The iron compounds seen in heterogeneous Fenton catalysts are typical. Tang and Wang (2018) present a notable advancement in Fenton catalyst development. Utilizing pyrolysis, they ingeniously integrated magnetic nanoparticles into a mesoporous carbon hybrid (Fe@MesoC)[18]. This innovative approach aimed to enhance catalytic performance within the Fenton process. To assess the efficacy of this catalyst, sulfamethoxazole, a common pharmaceutical pollutant, was selected

as the target compound for degradation experimentation. Remarkably, the Fe@MesoC catalyst facilitated complete degradation of sulfamethoxazole, underscoring its remarkable catalytic prowess in pollutant remediation applications.. The combination of the two chemicals' synergistic impact and high quantity of Fe-based nanoparticles account for this remarkable breakdown efficiency. The research also demonstrated the nearly total deterioration of medications. Under visible light exposure for a duration of two hours, the composite material consisting of $MnFe_2O_4$ /biochar exhibited significant performance. This was achieved at a hydrogen peroxide concentration of 100 mmol L^-1, resulting in the impressive degradation rate of 95% for tetracycline[19].

Electro-Fenton oxidation represents a distinctive variant of the Fenton reaction, distinguished by its electrochemical nature. Within this process, oxygen undergoes reduction at the cathode, leading to the generation of hydrogen peroxide (H_2O_2). The investigation delved into the pivotal role of the electro-Fenton reaction in the electrochemical degradation of carbamazepine (CBZ) [20,21]. Optimal operational conditions were identified at a pH of 3.0 and a current density of 0.2 A for the breakdown of carbamazepine. Following a duration of 120 minutes, a remarkable degree of disintegration reaching 73% was achieved, underscoring the efficacy of the electro-Fenton approach in pollutant removal.. Copper, chromium, and cobalt-containing catalysts can be used in place of iron catalysts. For instance, MnxCo3-xO4 was investigated as a possible stable electro-Fenton catalyst for the antibiotic ciprofloxacin (CIP) degradation process [22]. Within five hours, this substance eliminated 100% of the ciprofloxacin. The elevated level of pollutant elimination is linked to a rise in the rate of electron transfer, attributable to the combined influence of manganese and cobalt, working synergistically

3.2 Ozonation.

Ozone is renowned for its formidable oxidizing capabilities [23]. Its effectiveness in wastewater treatment is derived from two distinct mechanisms: direct oxidation facilitated by molecular ozone (O3) and indirect oxidation through the formation of hydroxyl radicals. These mechanisms collectively enhance ozone's efficacy in pollutant degradation, rendering it an indispensable component of modern wastewater treatment protocols. These reactions exhibit differing kinetics and yield varied byproducts [24,25]. Widely utilized across industries such as textile and paper processing, as well as air disinfection, ozone treatment can be enhanced through synergistic approaches like light irradiation or hydrogen peroxide addition [23]. However, careful consideration of H_2O_2 dosage is crucial, as excessive amounts can impede degradation efficiency. Furthermore, the efficacy of ozonation in pharmaceutical degradation exhibits a positive correlation with rising pH levels, underscoring the importance of ongoing monitoring of ozonated wastewater [25,26]. This necessitates a vigilant approach to ensure optimal treatment outcomes and mitigate potential environmental impacts associated with pharmaceutical residues.

The primary drawback associated with ozonation in water treatment lies in its considerable operating expenses. Firstly, this method demands substantial energy input, with approximately 85% of the energy generated being dissipated as heat, leading to reactor overheating. Secondly, ozone (O3) exhibits a short half-life of 15–20 minutes in water at temperatures ranging from 20 to 25°C. These limitations contribute to the elevated operational costs[27]. In terms of

electricity consumption for the breakdown of antibiotics such as ciprofloxacin and trimethoprim, as well as the pharmaceutical cyclophosphamide, the hierarchy of efficiency is as follows: UV > UV/O_3 > $UV/H_2O_2/O_3$ > O_3 > H_2O_2/O_3[28].

Numerous investigations have delved into the efficacy of ozonation in treating wastewater. Snyder et al. demonstrated that drugs such as acetaminophen, carbamazepine, diclofenac, naproxen, and sulfamethoxazole underwent decomposition rates of up to 80% through ozonation, while diazepam and ibuprofen exhibited removal rates of only 50%. Interestingly, the inclusion of H_2O_2 did not augment the degradation efficiency [29]. Assessments were undertaken to evaluate the efficacy of ozonation alone and in combination with hydrogen peroxide (H_2O_2) as pre-treatment measures for hospital wastewater prior to its introduction into wastewater treatment facilities [30]. Interestingly, it was observed that the combination of O3 and H_2O_2 proved to be less efficacious in drug degradation compared to conventional ozonation methods. Notably, common contaminants such as diclofenac and carbamazepine were substantially removed from wastewater by up to 95% through ozonation alone [31]. The concentrations of pharmaceuticals detected in wastewater exhibited a wide range, spanning from 2.2 to 320 ng/L and from 4.4 to 6.6 mg/L. Although subsequent treatment processes achieved nearly complete degradation, primary treatment demonstrated a comparatively modest degradation rate of 12%. Arslan Alaton and Caglayan conducted a study on the removal of Procaine Penicillin G (PPG) using ozonation in 2005[32]. They utilized a semibatch ozone reactor with pH levels of 3, 7, and 12 for their investigation. Within time intervals of 60 and 120 minutes, 37% and 82% of COD were respectively removed from PPG. It was observed that higher ozone dosages correlated with enhanced efficiency in wastewater treatment.

3.3 Electrochemical Oxidation

Electrochemical oxidation stands out as an exceptionally effective advanced oxidation technique applied for the degradation of pharmaceuticals within wastewater systems[33]. This approach operates through dual mechanisms. Initially, direct anodic oxidation occurs, entailing the removal of electrons at the anode. Additionally, there exists a potential for indirect anodic oxidation facilitated by highly reactive intermediates. Essential to the success of this process is the selection of electrode material possessing optimal traits such as elevated electrical conductivity, robust chemical resistance, and economic viability [33].

Electrochemical oxidation techniques were applied to degrade the antibiotics ofloxacin and lincomycin [34]. Various anode materials, such as titanium-platinum and graphite, were subjected to rigorous testing, alongside the utilization of Dimensionally Stable Anodes (DSA). Throughout the experimentation process, the degradation of Ofloxacin was consistently observed across all tested anodes. The electrochemical oxidation reaction displayed a discernible adherence to a first-order kinetic equation, underscoring the systematic and predictable nature of the degradation process. Additionally, a boron-doped diamond anode was utilized for the degradation of ciprofloxacin, sulfamethoxazole, and salbutamol [35]. The investigation delved into the effects of sulfates and chlorides on electrochemical oxidation. It found that the presence of sulfates increased degradation rates for both ciprofloxacin and sulfamethoxazole. While chloride ions showed effectiveness in degrading ciprofloxacin, higher current density led to the creation of notable halogenated organic compounds. [36]. Under the

specified conditions, electrochemical oxidation employing Sb-doped SnO2 electrodes at a current density of 20 mA/cm^2 accomplished complete degradation of ciprofloxacin within a span of 60 minutes.

The presence of aspirin, a prominent anti-inflammatory pharmaceutical, is routinely detected within hospital wastewater samples. In a meticulous investigation conducted by He et al. (2015), three distinct types of anodes were strategically employed for the anodic oxidation of aspirin: lead dioxide (PbO2), boron-doped diamond (BDD), and porous Ti/BDD. The degradation kinetics of aspirin adhere to a model of pseudo-first-order reaction. Notably, when employing a PbO2 anode, approximately 70% of the aspirin content was effectively removed. However, the most commendable efficiency in removal was discerned with the Ti/BDD anode configuration. It is hypothesized that the degradation mechanism involves a combination of direct and indirect anodic oxidation processes occurring on the surface of the BDD electrode. On the contrary, it is the PbO2 electrode that primarily facilitates the process of indirect electrochemical oxidation, distinguishing itself as the key contributor in this regard[37].

IV. Biological Process Treatment

The review paper explores pharmaceutical wastewater treatment through biological processes, focusing on Sequencing Batch Reactors (SBR) and Membrane Bioreactors (MBR). SBR offers flexible operation, enabling efficient removal of pharmaceutical compounds through sequential treatment phases. Meanwhile, MBR combines biological treatment with membrane filtration, enhancing pollutant removal and producing high-quality effluent. By elucidating the mechanisms and performance of these biological methods, the paper aims to provide insights into sustainable solutions for mitigating pharmaceutical pollution in wastewater streams.

4.1 Sequential Batch Reactor (SBR)

Pharmaceutical waste poses significant environmental and public health risks due to its complex chemical composition and potential for bioaccumulation in ecosystems. Conventional wastewater treatment methods often struggle to effectively remove or degrade the diverse array of pharmaceutical compounds present in industrial effluents. In response to this challenge, the Sequential Batch Reactor (SBR) emerges as a promising technology for the treatment of pharmaceutical waste[38].

Employing a fill-and-draw methodology for wastewater treatment (WW), Sequential Batch Reactor (SBR) technology emerges as a refined adaptation of the conventional Activated Sludge Process (ASP). Renowned for its variable reactor volumes and operational efficiency reminiscent of the Biological Nutrient Removal (BNR) process, the SBR treatment method offers notable advantages. Through enabling phase transitions, meticulous microbial kinetics management, and ensuring short retention durations, this method ensures unparalleled operational adaptability. The fundamental stages of the SBR process encompass fill, react, settle, decant, and idle phases [39].

Each stage within the Sequential Batch Reactor (SBR) process operates for a specific duration, thus effectively contributing to wastewater treatment. The SBR method is capable of accommodating a broad spectrum of hydraulic and organic loads, making it straightforward to

operate and cost-effective. Notably, utilizing the SBR process can result in over 60% savings in operating costs compared to the Activated Sludge Process (ASP). Furthermore, SBR systems necessitate minimal spatial requirements and a significantly reduced workforce for operation, making them a highly favored and widely adopted technology in Europe, as well as in densely inhabited areas like India [40].

Two reviews by Mace [41] and Singh and Srivastava [40] explored the use of Sequential Batch Reactor (SBR) technology for biological wastewater treatment. While these reviews focused mainly on the removal of nitrogen and phosphorus from domestic wastewater, this chapter will examine the performance of SBR processes in treating pharmaceutical wastewater. Emad et al. [42] evaluated the effectiveness of SBR in treating high-strength non-penicillin pharmaceutical wastewater and concluded that it was highly efficient, achieving a removal rate of 94% for BOD5 and 84% for COD.

In their comprehensive investigation, Muz et al. [44] meticulously explored the fate of six distinct Endocrine Disrupting Chemicals (EDCs), comprising carbamazepine (CBZ), acetaminophen (ATP), diltiazem (DTZ), butyl benzyl phthalate (BBP), estrone, and progesterone. This exhaustive study was conducted within the confines of a laboratory-scale anaerobic/aerobic Sequential Batch Reactor (SBR) system. The findings of their research unveiled a remarkable removal efficiency exceeding 80% for the targeted EDCs. Moreover, the study pinpointed biodegradation as the predominant mechanism driving the elimination of BBP, ATP, and progesterone from the complex wastewater matrix. These insightful revelations underscore the promising potential of SBR technology in effectively mitigating the environmental impact of EDC contamination.

In a groundbreaking application of environmental engineering, a sequential batch biofilter reactor was meticulously utilized for the remediation of pharmaceutical wastewater, characterized by its dauntingly high levels of phenols, O-nitroaniline, and a spectrum of other organic compounds, ranging from 28,400 to 72,200 mg/L. This innovative reactor configuration ingeniously integrated both anaerobic and aerobic stages, showcasing not only commendable efficiency in organic pollutant removal but also in toxicity mitigation. The anaerobic phase, serving as the initial line of defense, spearheaded the removal of a substantial 78.5% of the organic load, while the subsequent aerobic phase demonstrated unparalleled prowess in detoxification, a feat validated by comprehensive Microtox analysis. This pioneering approach, incorporating the synergistic actions of anaerobic and aerobic processes within the Sequential Batch Reactor (SBR) paradigm, heralds a promising advancement in the sustainable treatment of highly concentrated wastewater effluents, with COD levels reaching a staggering 28,400 mg/L, all achieved without resorting to dilution techniques [45]. Such innovative solutions underscore the continuous evolution of wastewater treatment strategies, driven by a commitment to environmental stewardship and technological ingenuity.

In a pioneering study, Stadler et al. delved into the intricate interplay of redox conditions within Sequential Batch Reactors (SBRs) and their impact on effluent laden with pharmaceutical residues. Intriguingly, the influent showcased the presence of conjugated derivatives of sulfamethoxazole and desvenlafaxine, which intriguingly reverted to their original compounds over the course of the reaction cycle. Notably, during the aerobic phase, atenolol and

trimethoprim underwent substantial degradation, highlighting the transformative potential of oxygen-rich environments. Conversely, sulfamethoxazole exhibited the most pronounced reduction in microaerobic SBRs, shedding light on the nuanced dynamics of oxygen availability in influencing degradation pathways. Surprisingly, phenytoin remained largely unaffected across all reactor conditions, underscoring its resilience to variations in redox environments [46]. This seminal investigation not only expands our understanding of pharmaceutical fate in wastewater treatment systems but also underscores the multifaceted role of redox conditions in shaping pollutant transformation pathways, offering valuable insights for the optimization of treatment processes.

In a pioneering endeavor, Wei et al. embarked on an extensive investigation into the efficacy of eliminating 26 organic micropollutants through the utilization of Sequential Batch Reactors (SBR) and SBR coupled with nanofiltration. This integrated treatment approach emerged as a standout solution, demonstrating remarkable superiority by achieving a substantial reduction of up to 70% in micropollutant levels. In a parallel endeavor, Chen et al. delved into the nuanced impact of varying salinity levels on the performance of SBR systems. Their insightful findings shed light on the adverse effects of elevated salinity concentrations, elucidating a notable decline in removal efficiencies concerning NH4-N, total phosphorus, and COD parameters [47]. Such multifaceted studies underscore the relentless pursuit of innovative methodologies in the realm of wastewater treatment, fueled by a collective commitment to advancing environmental sustainability and engineering excellence.

4.2 Membrane Bioreactor.

Membrane Bioreactors (MBRs) have emerged as a promising technology for pharmaceutical wastewater treatment. By integrating biological processes with membrane filtration, MBR systems effectively remove pharmaceutical compounds and other contaminants from wastewater streams. The biological treatment component utilizes microorganisms to degrade organic pollutants, while the membrane filtration stage physically separates suspended solids and microorganisms, producing high-quality effluent. MBRs offer several advantages, including compact footprint, consistent treatment performance, and the ability to produce reusable water.[48,49]

Radjenovic et al. [50] and Clara et al. [51] elucidated the superior efficacy of Membrane Bioreactors (MBRs) in removing various pharmaceutical compounds compared to Conventional Activated Sludge (CAS) systems, with removal rates surpassing 80% [52,53]. A parallel investigation highlighted the remarkable performance of MBR technology in pharmaceutical compound removal within Australian wastewater, achieving a staggering removal efficiency exceeding 90% for paracetamol, ketoprofen, ibuprofen, and triclosan [54]. Contrasted with the Activated Sludge Process (ASP), MBRs exhibit heightened effectiveness in eliminating hydrophobic and readily biodegradable compounds, as they readily migrate from the aqueous matrix and adhere to membrane surfaces, facilitating biodegradation [55,56]. Tadkaew et al. [57] delved into the intricate relationship between MBR-based removal efficiency and molecular attributes of trace organic contaminants, encompassing six classes of pharmaceuticals. Their analysis revealed that compounds characterized by high hydrophobicity (log D.3.2 at pH 8) and electron-donating functional groups boast removal efficiencies soaring

to 98% [58]. The processes of adsorption and biodegradation within MBRs hinge upon operational parameters such as Hydraulic Retention Time (HRT), Solid Retention Time (SRT), biomass concentration, temperature, and influent pH [59]. This body of research not only underscores the unparalleled performance of MBR technology in pharmaceutical compound removal but also underscores the multifaceted dependencies on operational variables, paving the way for optimized wastewater treatment strategies.

According to Dawas-Massalha et al. [60], heightened nitrifying activity plays a pivotal role in bolstering the degradation of pharmaceutical residues, a phenomenon further amplified by the implementation of Membrane Bioreactors (MBRs), which afford a prolonged Solid Retention Time (SRT). Tadkaew et al. [61] substantiated this notion by demonstrating that an escalation in nitrification rate precipitates a decline in the pH levels within the MBR system, resulting in a remarkable 90% degradation of ibuprofen at pH 6 and a 70% degradation of ketoprofen at pH levels below 5. Furthermore, De Gusseme et al. [62] documented a staggering 99% removal of 17β-EE2 within nitrifier-enriched biomass of MBRs.

Delving deeper into the multifaceted role of MBR technology in treating diverse effluent streams, comprehensive studies elucidated its efficacy across various stages of wastewater treatment. Notably, when applied to primary effluent treatment, MBRs showcased unparalleled effectiveness in reducing concentrations of caffeine, acetaminophen, sulfamethoxazole, carbamazepine, and gemfibrozil. Removal efficiencies ranged impressively from 99.1% for sulfamethoxazole to an astonishing 99.9% for acetaminophen, underscoring the transformative potential of MBRs in pharmaceutical residue management and wastewater treatment optimization [63,64].

V. Physcio Chemical Process

The introduction to physicochemical processes in pharmaceutical wastewater treatment encompasses various methodologies, including membrane processes and adsorption. Membrane processes, such as Microfiltration (MF), Ultrafiltration (UF), Nanofiltration (NF), and Reverse Osmosis (RO), play a pivotal role in separating contaminants based on size and molecular weight. These technologies offer efficient removal of suspended solids, organic compounds, and dissolved ions, ensuring high-quality effluent. Moreover, adsorption methods provide an additional layer of purification by capturing contaminants onto solid surfaces. Through this introduction, we delve into the efficacy and applications of these techniques in addressing the complex challenges of pharmaceutical wastewater treatment[65,66].

5.1 Membrane Process

The treated wastewater from conventional methods can potentially be repurposed for various operations or released into the environment. However, even after treatment, this water often retains a significant concentration of undesirable substances such as plasticizers, pharmaceuticals, pesticides, and detergent by-products. The effectiveness of filtration in most membrane systems relies heavily on the size of the pores.[67] The elimination process of visible components using polymeric membranes is influenced by several factors, including physicochemical properties, membrane type, and operational conditions.[68]

Membrane use for water treatment is increasing rapidly. Low-pressure membranes can remove microbial contaminants without additional disinfection. Reverse osmosis is commonly used for desalination or water reuse. Microfiltration or ultrafiltration is recommended for limited space or uncertain water quality. Nanofiltration and ultrafiltration are used for wastewater treatment and micropollutant removal. NF retains more EDC/PPCPs than UF, depending on pore size. RO and NF are effective in removing significant pharmaceutical compounds. Further analysis of the concentrate is needed to remove retained substances[58,63].

Membrane-based approaches for wastewater treatment encompass a diverse array of techniques, primarily categorized into four distinct types: microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), and reverse osmosis (RO). These classifications are predicated upon various factors including membrane architecture, composition, applied driving force, separation mechanism, and the size of targeted substances [69]. Notably, microfiltration (MF) and ultrafiltration (UF) membranes typically feature pore dimensions ranging from 100 to 1000 times larger than those of micropollutants, thereby making them less commonly utilized for the removal of organic contaminants. Table 1 illustrates the pharmaceutical effluent removal process, organized according to pore size classification. In contrast, membrane processes such as nanofiltration (NF) and reverse osmosis (RO), which operate under applied pressure differentials, have garnered substantial attention from researchers due to their remarkable efficacy in potable water treatment endeavors[70].

Research studies have highlighted the effectiveness of reverse osmosis (RO) and nanofiltration (NF) in the removal of pharmaceutical compounds, particularly in the context of tertiary water treatment. However, pioneering investigations by Deegan et al. (2011) have underscored the potential of ultrafiltration (UF), employing diverse membrane symmetries, to efficiently eliminate a broad spectrum of pharmaceutical personal care products (PPCPs), antibiotics, hormones, lipid regulators, and analogous substances[70]. These findings illuminate the multifaceted capabilities of membrane-based technologies in addressing the complex challenges associated with wastewater treatment, exemplifying the continual advancement and refinement of environmental engineering practices.

Shahtalebi et al. (2011) unearthed that the implementation of the NF technique exhibited remarkable efficacy, boasting an impressive removal rate of 97% for amoxicillin and concurrently slashing COD levels by a notable 40% within pharmaceutical wastewater streams. It is noteworthy that the intricate constituents, akin to organic matter, can be effectively eradicated through the utilization of either microfiltration or ultrafiltration (UF) methods [71]. As elucidated by Adams et al. (2002), reverse osmosis (RO) emerges as a pivotal player in the arsenal against pharmaceutical contaminants. RO membranes showcase exceptional prowess in segregating organic compounds characterized by heightened molecular weights. The adoption of RO membranes culminates in a staggering reduction of biochemical oxygen demand (BOD) and chemical oxygen demand (COD) by up to 98% and 96%, respectively, while simultaneously achieving a remarkable decline in total organic carbon (TOC) levels by as much as 96% [72].

The imperative removal of organic solutes, encompassing pharmaceuticals and personal care products (PhACs), stands as a pivotal measure in safeguarding the purity of water designated

for potable reuse. Nevertheless, the efficacy of this elimination process exhibits variability contingent upon the nature of the solutes at hand and the membrane technologies deployed. In an illuminating investigation spearheaded by Urtiaga et al. (2013), a pilot-scale endeavor was undertaken to scrutinize the exclusionary capabilities of reverse osmosis (RO) and ultrafiltration (UF) in treating wastewater effluents laden with 12 distinct pharmaceutical compounds. The findings unveiled a commendable elimination rate soaring to 99.3% for all scrutinized compounds, indicative of the formidable efficacy of the applied techniques [73].

Furthermore, the researchers delved deeper into the intricate realm of PhAC removal, exploring the multifaceted landscape through the lens of RO and nanofiltration (NF) methodologies within the ambit of a comprehensive potable water treatment regime. While RO emerged as a stalwart performer, achieving a remarkable elimination rate of up to 85% for the majority of compounds, it was observed that a select few eluded eradication to a lesser degree, with removal rates fluctuating within the range of 30% to 70% [74].

Table.1 Type of Pharmaceutical Process for removal of Effluent on the basis of pore size

Sr.No.	Membrane processes	Pore size	Particle size range
1	Reverse osmosis	2-7 Å	Atomic/ionic range
2	Electrodialysis	1 Å -1 nm	Atomic/ionic range
3	Forward osmosis	2 Å -6 nm	Atomic/ionic, low molecular range
4	Nanofiltration	8 Å -6 nm	Atomic/ionic, low molecular range
5	Ultrafiltration	6-100 nm	Low molecular, high molecular range
6	Membrane distillation	10 nm-1 µm	High molecular, microparticle range
7	Membrane bioreactor	14-400 nm	High molecular, microparticle range
8	Microfiltration	90 nm- 2 µm	Microfiltration

5.2 Adsorption

In the realm of environmental protection, tackling pharmaceutical waste poses a pressing challenge. These residues, pervasive in water systems due to human and veterinary use, threaten ecosystems and public health. Adsorption, the process of contaminants adhering to solid surfaces, offers a promising solution. Utilizing diverse adsorbents like activated carbon and zeolites, pharmaceutical compounds can be efficiently removed from wastewater. Optimizing adsorbent properties and operational parameters is crucial for effective waste management. This proactive approach not only safeguards water quality and ecosystem health but also promotes sustainable pharmaceutical practices, advancing the cause of environmental conservation[75-77].

The process of adsorption has garnered extensive attention in scientific inquiry due to its efficacy in the removal of organic substances like dyes and synthetic chemicals. This method is distinguished by its modest initial investment requirements, straightforward reactor/absorber layout, operational simplicity, and non-discriminatory nature [78]. A diverse array of economical adsorbents, ranging from natural resources to agricultural and industrial by-products, as well as municipal and animal husbandry residues, have been scrutinized for their capacity to extract organic compounds from water reservoirs. Initially, many of these materials

were proposed for water purification purposes, particularly targeting the removal of dyes and synthetic chemicals. However, in recent years, there has been a burgeoning interest in employing adsorption techniques for the elimination of pharmaceuticals from water sources, prompting a plethora of investigations to assess its efficacy in this particular domain [79,80].

In the realm of water purification, carbonaceous adsorbents emerge as a favored choice among researchers endeavoring to combat the pervasive contamination stemming from harmful chemicals and metals. These versatile adsorbents encompass a diverse array of materials, including activated carbon, charcoal, activated sludge, and graphite, each offering unique properties and applications. Among these, activated carbon stands out prominently, drawing considerable attention for its well-documented efficacy in pharmaceutical removal from water, attributed to its widespread availability and expansive surface area.

The adsorption capacity of activated carbon exhibits variability contingent upon the specific pharmaceutical solute targeted. For instance, a particular type of activated carbon boasting a Brunauer–Emmett–Teller (BET) surface area of 1,225 m^2/g showcased remarkable adsorption capabilities, capturing 338 mg/g of tinidazole, 328 mg/g of metronidazole, and 394 mg/g of ronidazole under identical conditions [81]. Similarly, another variant of activated carbon, with a slightly lower BET surface area of 885 m^2/g, absorbed 144.9 mg/g of metronidazole and 185 mg/g of sulfamethoxazole [82]. This insightful comparison underscores the profound influence of surface area, with the activated carbon boasting a higher surface area exhibiting nearly double the adsorption capacity for metronidazole compared to its counterpart with a lower surface area.Such meticulous investigations not only highlight the pivotal role of activated carbon in pharmaceutical removal from water but also underscore the intricate interplay between surface area and adsorption capacity, informing the ongoing refinement of water treatment methodologies.

Aluminosilicate compounds, which make up clay minerals, are essential elements present in rocks, sediments, and aquatic environments. These minerals create complex layered patterns in a variety of geological formations. They include quartz, metals, silicates, and carbonates. Clay minerals are rich in cations like H+ and K+ and anions like SO42-, NO3-, Ca2+, and Mg2+ on their surfaces[83]. These minerals demonstrate exceptional ion exchange characteristics. Because of their ability to interact with both basic and acidic medicines, they are used in a variety of pharmaceutical removal applications to target pollutants such as heavy metals[83], phenolic compounds[84], and methylene blue[78]. Clay minerals with particle sizes less than 2 μm are typically found in soil, rocks, sediments, and other materials, although they have not gotten much attention in studies on pharmaceutical elimination [83].

Utilizing sorbents based on silica has proven to be an effective method for the removal of pharmaceuticals. Silica boasts remarkable properties, including a high BET surface area, a porous structure, and mechanical durability, making it an ideal choice for such applications [85]. Moreover, silica components are naturally abundant in soil with a coarse clay proportion. The utilization of silica and its derivatives as adsorbents has become widespread across various adsorption scenarios due to their expansive surface area, resilience in harsh environments, uniform porous structure, rapid adsorption kinetics, and ease of regeneration.

A multitude of drugs, including carbamazepine, clofibric acid, diclofenac, ibuprofen, ketoprofen, cloprop, norfloxacin, ciprofloxacin, and TCH, are currently under scrutiny for their removal using silica-based adsorbents [86-89]. Mesoporous silica holds particular significance due to its ability to accommodate large medicinal molecules. Conversely, microporous silica, with its narrower pore diameters, exhibits reduced sorption capacity [90].

The integration of silica-based sorbents in pharmaceutical removal signifies a pivotal advancement in environmental remediation efforts. This innovative approach underscores the adaptability and efficacy of silica materials in addressing the challenges posed by pharmaceutical contaminants in water systems. As research in this field progresses, the potential applications of silica-based sorbents are poised to expand, contributing further to the arsenal of sustainable solutions for water treatment and environmental protection.

VI. Nanomaterial Innovation for Pharmaceutica wastewater treatment

Nanomaterials have emerged as promising tools for addressing the challenges associated with pharmaceutical wastewater treatment. Their unique properties at the nanoscale, including high surface area, reactivity, and tunable surface chemistry, make them well-suited for the removal and degradation of pharmaceutical compounds from wastewater. Here, we delve into the various types of nanomaterials and their applications in pharmaceutical wastewater treatment

6.1 Carbon-Based Nanomaterials

Carbon-based nanomaterials, including graphene, fullerenes (such as Buckminsterfullerene), multi-walled and single-walled carbon nanotubes (CNTs), and graphitic carbon nitride (g-C3N4), have become focal points of research across diverse fields. Their versatile applications range from powering Li-ion batteries and enhancing semiconductors to enabling sensors and molecular imaging, as well as catalyzing reactions and storing energy, all contributing to pollution control efforts. Notably, these materials are prized for their low or non-toxic nature, making them environmentally friendly choices. Their exceptional sorption capacities have garnered significant attention for their role in effectively extracting toxic metal ions from wastewater, underscoring their importance in water purification processes[91,92].

Carbon nanotubes (CNTs) have garnered considerable attention due to their remarkable capabilities in water and wastewater treatment, showcasing prowess against an extensive array of chemical and biological contaminants. Notably, CNTs have demonstrated efficacy in the removal of a diverse spectrum of pollutants, encompassing heavy metals like Cr3+[93], Pb2+[94], and Zn2+[95], along with metalloids such as various arsenic compounds[96]. Moreover, CNTs display notable effectiveness in adsorbing organic pollutants like polycyclic aromatic hydrocarbons (PAHs), as well as an assortment of biological contaminants, spanning bacteria, viruses, natural organic matter (NOM), and cyanobacterial toxins. The efficacy of CNTs as an adsorbent medium for biological contaminants, especially pathogens, can be ascribed to their distinctive physical properties, cytotoxicity, and the capabilities of surface functionalization[97].

Recent research has shown that adsorption techniques using carbon nanotube (CNT)-based adsorbents can effectively remove pharmaceuticals like diclofenac, amoxicillin, sulfamethoxazole, and endocrine-disrupting compounds (EDCs) like bisphenol A [98-100]. With changes increasing their adsorption effectiveness, CNTs are versatile enough to be used with a variety of antibiotics, such as tetracycline, sulfapyridine, and fluoroquinolone [101,102].

Moreover, metal-organic frameworks (MOFs) have become a promising class of adsorbents; in particular, PCDMs, or porous carbon generated from MOFs, have demonstrated exceptional efficiency in the removal of medications such as diclofenac and ibuprofen [103]. Notably, Bhadra and Jhung (2018) used Bio-MOF-derived carbons (BMDCs) to effectively remove a variety of pharmaceuticals and personal care products (PPCPs) throughout a wide pH range, from primary to acidic[104].

6.2 Magnetic Nanoparticles

An new oxidative precipitation-combined iono-thermal synthesis approach was used to synthesise Fe-MNPs with excellent stability and efficiency for the degradation of organic pollutants in the presence of H_2O_2 [105]. These MNPs have outstanding catalytic activity, great recyclability, and magnetic recoverability. PEI-coated iron oxide MNPs were created by Lakshmanan et al. (2014) via chemical co-precipitation stabilised with trisodium citrate. Within 60 minutes, these MNPs were able to remove 50% of the total organic carbon (TOC) from a 0.5 L wastewater sample. They also significantly reduced the amount of total nitrogen, turbidity, colour, and microbiological content. Through the reduction of processing time, complexity, sludge generation, and the requirement for additional chemicals, the introduction of PEI-MNPs expedited the treatment process[106]. Additionally, a sustainable method of producing copper-doped Fe_3O_4 MNPs was accomplished, improving their capacity to activate H_2O_2. Cu-doped MNPs in comparison to undoped ones showed quicker H_2O_2 breakdown in the research, demonstrating its environmental use in the removal of 'rhodamine B' (RhB) from textile effluent, with an impressive removal effectiveness of over 97%[107].

In a recent groundbreaking investigation, Fe_3O_4 magnetic nanoparticles (MNPs) were ingeniously combined with 2-D graphene oxide (GO) and graphite carbon nitride (g-C3N4) to engineer an innovative adsorbent tailored for advanced wastewater treatment applications [108]. The pioneering research conducted by scientists unveiled the pivotal role of π-π and hydrogen bonding interactions in effecting the successful removal of both the hazardous antibiotic tetracycline (TC) and the dye methylene blue (MB) from wastewater matrices. Notably, the adsorbed TC and MB could be efficiently reclaimed and recycled for up to five consecutive cycles, underscoring the sustainability of the adsorption process.

Furthermore, Mohammadi et al. (2018) reported on the remarkable efficacy of an amino-modified magnetic nano adsorbent Fe_3O_4@SiO2 NH2 in eliminating methylparaben (MeP) from wastewater samples [109]. Under optimal conditions, the removal efficiency for MeP reached an astounding 98%, with an impressive adsorption capacity of 75 mg/g. The application of a mere 1.1 g/L of adsorbent coupled with a response time of 120 minutes yielded remarkable results, emphasizing the potential of this novel approach in addressing MeP contamination challenges.

Moreover, Arabkhani et al. (2021) employed solid-state dispersion and solvothermal methodologies to fabricate a distinct magnetic nanocomposite (NC) [110]. This NC exhibited exceptional efficacy in eliminating the pharmaceutical compound diclofenac sodium from wastewater streams, maintaining consistent removal efficiency even after undergoing five successive regeneration cycles. These pioneering findings signify a significant leap forward in the realm of wastewater treatment, showcasing the transformative potential of advanced

nanomaterial-based adsorbents in mitigating the impact of emerging contaminants on environmental and human health.

6.3 Titanium dioxide nanoparticles

Titanium dioxide (TiO_2) is extensively studied as a photocatalyst due to its chemical and biological inertness, stability, and cost-effectiveness, coupled with its high photoactivity as a semiconductor material. Moreover, TiO_2 retains its catalytic activity even after multiple uses. The photocatalytic mechanism mediated by TiO_2 has been thoroughly documented in the scientific literature. Under irradiation with light energy exceeding the bandgap of the semiconductor, TiO_2 generates positive holes in the valence band. These positive holes effectively produce hydroxyl radicals in the aqueous phase, serving as potent oxidants capable of mineralizing organic contaminants through oxidation[111].

Carbamazepine (CBZ) stands as one of the most frequently prescribed antiepileptic medications, and its presence, along with its metabolites, is pervasive in aquatic ecosystems. Through TiO2 photocatalysis, CBZ can undergo partial elimination, resulting in the generation of various transformation products (TPs), which can vary depending on the specific irradiation sources employed[112]. Among the TPs produced during photocatalysis, two hydroxylated forms of CBZ have been identified in aquatic environments, resembling human metabolites of CBZ. Moreover, studies indicate that the TPs generated during photocatalytic treatment exhibit significant toxicity towards aquatic organisms such as Vibrio fischeri and Daphnia magna[113,114]. This underscores the potential of TiO_2 nanoparticle-based treatment for pharmaceutical wastewater in mitigating the environmental impact of CBZ contamination, while also highlighting the importance of further research into the identification and assessment of these transformation products.

One of the main ingredients in contraceptive tablets is 17α-Ethinylestradiol (EE2), a steroidal oestrogen that has earned a spot on the EU watch list of chemicals [116]. Because it has been connected to the feminization of male fish and changes in fish populations' ability to reproduce, this synthetic hormone raises serious ecological problems [117]. The removal of EE2 from pharmaceutical wastewater requires the synthesis of intermediates and/or end products that are both less hazardous and have no estrogenic activity than EE2. This strategy is essential for reducing the threats that EE2 pollution poses to the environment and public health. Given TiO_2 proven effectiveness in degrading a variety of pharmaceutical chemicals, using TiO_2 nanoparticle-based treatment approaches offers interesting pathways for reaching such aims.

It has been determined that EE2 is phytotoxic to Proteus vulgaris and Vigna radiata [118]. On the other hand, the reaction mixture's phytotoxicity decreased when EE2 underwent photocatalysis. Attacks by superoxide and hydroxyl radicals were suggested to be the main mechanisms for photocatalytic degradation. According to Sun et al. [119], the phenol moiety of EE2 is primarily responsible for its estrogenic action. They observed that the alteration of the phenol moiety resulted in a decrease in estrogenic activity when exposed to photocatalysis with TiO_2. Similar results of reduced or eliminated estrogenicity after photocatalytic TiO_2 treatment of EE2 were documented. Furthermore, EE2 might be photolytically treated with UVA to remove estrogenicity from the reaction mixture, although this would take 2.4 times longer compared to photocatalysis[116].

VII. Conclusion

In conclusion, the review paper extensively examines a range of physiochemical, chemical, and biological processes for water and wastewater treatment. Membrane separation and adsorption techniques stand out for their effectiveness in physically removing contaminants, providing adaptable and scalable solutions. On the chemical front, electrochemical oxidation, Fenton reaction, ozonation, and photocatalysis oxidation show promise in degrading organic pollutants, although their efficacy and suitability vary. Additionally, biological methods like sequencing batch reactors and membrane bioreactors demonstrate the potential of leveraging microbial activity for contaminant breakdown, offering sustainable and economical options. Incorporating multiple techniques is crucial for comprehensive water treatment strategies, given the distinct advantages and challenges associated with each process. Looking ahead, further research and technological advancements, particularly in utilizing titanium dioxide, Magnetic Nanoparticle Carbon-based nanoparticles, and other innovative materials, are essential for enhancing efficiency, affordability, and environmental sustainability in addressing global water quality challenges.

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