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Harnessing the power of heterogeneous photocatalytic process for sustainable pharmaceutical contaminant remediation in water environments

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ABSTRACT

Pharmaceutical pollutants in wastewater can be effectively degraded by heterogeneous photocatalytic processes (HPP); under light irradiation, these methods use semiconductor photocatalysts to produce reactive oxygen species (ROS), which can oxidize and mineralize organic pollutants (OPs) into innocuous byproducts. Reactant transport to the photocatalyst surface, reactant adsorption, charge carrier formation and separation, redox reactions, and product desorption are all part of the photocatalytic mechanisms. This review article analyzes and compares the various approaches used to prepare photocatalysts. The photocatalyst composition, morphology, crystallinity, and production scale, influence the synthesis technique selection. While hydrothermal, microwave-assisted, sonochemical, and mechanochemical processes provide greater variety in synthesising diverse photocatalysts with varying compositions, morphologies, and surface characteristics, flame hydrolysis is appropriate for large-scale production of TiO_2 photocatalysts. Because it regulates the photocatalyst's surface charge, the electrolytic solution's pH is significant in photocatalytic processes. Within a certain range, an increase in temperature generally results in a continuous increase in breakdown efficacy; beyond that, the rate of decomposition decreases. These findings besides giving researchers a broad overview of the current status of the HP process we believe will also inform its future applications and advancements.

1. Introduction

Toxic pollutants, including pharmaceutical contaminants, have created major environmental concerns [1]. Pharmaceutical pollutants in water are causing increasing concern due to their potential effects on aquatic ecosystems [2] and human health [3]. Human excretion, pharmaceutical production facilities [2], and the disposal of unwanted pharmaceuticals are the most common sources of pharmaceutical pollutants in water [4]. These compounds can reach aquatic bodies through municipal wastewater treatment systems that are not especially intended to remove pharmaceutical pollutants [5], as well as runoff from agricultural fields where pharmaceuticals have been utilized (for example, antibiotics in animal production) [6]. Pharmaceutical pollutants have been found in a variety of water settings, including surface water, groundwater, and drinking water supplies [7]. The amounts of pharmaceutical pollutants in the environment vary from ng/L to μg/L [8]. The fate of these pollutants in aquatic habitats is determined by variables such as their chemical characteristics, ambient circumstances, and the presence of other chemicals that may affect their degradation, sorption, or transformation [9].

Pharmaceutical pollutants can damage aquatic creatures including algae, crustaceans, and fish [10]. Some of the observed impacts include altered behaviour, growth inhibition, reproductive impairment [9], and the emergence of antibiotic-resistant microorganisms [11]. Furthermore, prolonged exposure to low quantities of pharmacological combinations may have synergistic or cumulative effects on aquatic creatures [10,11]. Although pharmaceutical pollutants in drinking water are typically negligible [7], there is worry about the long-term consequences [12], especially for vulnerable groups such as children, pregnant women, and the elderly [7,11,13]. Some medications can have negative impacts on human health, such as endocrine disruption [11], antibiotic resistance, and allergic responses [3,14].

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Although sorption [15] and membrane filtering [16] are efficient methods for eliminating organic and pharmaceutical contaminants from water, they are phase separation techniques that result in concentrated waste streams that need additional handling or disposal [15,17]. Advanced oxidation processes (AOPs) [18] such as heterogeneous photocatalytic process (HPP), on the other hand, may be able to break down and mineralize these contaminants, possibly preventing the production of concentrated waste streams [19]. The HPP is defined as photoreaction acceleration in the existence of a catalyst [20,21]. The utilization of semiconductor substances as catalysts to treat small levels of organic pollutants (OPs) and inorganic pollutants (IOPs) from fluid systems in environmental wastewater clean-up has been greatly exploited [22]. The application of semiconductors in cleaning water for domestic and industrial usage, and hospital applications has also gained attention [23]. This is due to the use of titanium dioxide's (TiO_2) capacity to degrade OPs and IOPs in fluids via redox reactions (RRs) [24]. TiO_2 has not only emerged as one of the most fascinating substances in photocatalytic techniques but has also piqued the interest of researchers and engineers seeking unusual materials with semiconducting and catalytic properties. [25]. Furthermore, in HPP, a solid phase (SP) is distributed, producing an electron-hole pair that decreases and oxidizes two matching species in the fluid. Besides, the SP is typically a semiconductor substance, specifically a photocatalyst [26].

Numerous research studies have carefully studied the use of HPP for wastewater treatment, as well as its advantages [27]. However, there is a limited holistic review of the current trends of HPP for pharmaceutical contaminants removal in wastewater; discussing mechanisms for the photocatalytic process and the various methods of catalyst preparation, comprehensively. This current manuscript seeks to bridge that gap. Additionally, high catalytic efficiency nitrogen-doped TiO_2 photocatalyst NPs are produced by green synthesis. HPP's employment in the breakdown of pharmaceutical pollutants in wastewater is attributed to its photocatalytic activities and the impact of different operational parameters on the reaction mechanism. This review is intended to provide researchers with an overview of the present state of research and technological development of the HP process, thus serving as a guide for the application of HPP in the degradation of pharmaceutical contaminants.

2. Mechanism for heterogeneous photocatalytic process (HPP)

To destroy OPs, heterogeneous photocatalysis transforms photon energy into chemical energy using semiconductor materials [23]. Semiconductors absorb photons with energies lesser/more than their band gap [28]. Also, electrons could move from the valence band (VB) to the conduction band (CB), parting with electron deficiencies in the VB. This aids in the electron-hole pairs being formed to transmit onto the surface of the particle, thereby initiating a reduction/oxidation sequence. The adsorbed substrates are left in the aqueous. The dissolved O_2 in the solution can degrade the surface electrons causing superoxide ion (O_2^-) or OH• to form HO_2^-. Electron-hole recombination is efficiently hindered in this manner, and the lifespan of positive holes is stretched. The spawned OH• in solution (primarily HO_2^- and O_2^-) are very effective non-selective oxidizers, resulting in the oxidation and ultimate oxidation of OPs [23].

2.1. Photocatalysts

TiO_2 and Ag_3PO_4 are commonly used in photocatalysts [29]. TiO_2 is the most widely and highly researched semiconductor material because of its elevated photoconductivity, chemical stability [29], limited toxic level, low cost and widespread availability [30]. Numerous attempts have also been made to project and manufacture nano-sized photocatalysts with higher photocatalytic activity [31]. TiO_2 has long been a mainstay in studies as the primary component. In the broad sense, three approaches have been developed for producing enhanced UV or visible-light photoactive titania. One approach is to control the size and morphology of exposed photo-reactive sites [32]. Many structures have been reported, including quantum dots (QDs), nanosheets, nanotubes, nanowires [33], and mesoporous hollow shells [34]. Other approaches include metal doping with charge transfer materials and nonmetals to improve charge separation and expand the range of pollutants that can be absorbed [35].

The noble, transition metals and nonmetals immobilized TiO_2 [36], TiO_2- CNT, and TiO_2-graphene composites are extensively studied [37]. Furthermore, creating an Anatase-Rutile (A-R), TiO_2 composite has received minimal attention but should not be overlooked [38]. According to Sewnet et al. [38], mixed-phase A-R samples add to charge carrier separation in photocatalytic reactions. The addition of A-R helps to outperform the single polymorph leading to a tremendous elevation of quantum yield and photocatalytic activity. Even though TiO_2 thin films typically have lesser photocatalytic activity than powder materials because of inherently lower specific surface area, their ease of separation for recycling is important in applications [38]. The referred paths are frequently used by researchers to modify titania films [37]. Visible-light photocatalysis is widely regarded as a greener AOP because it uses the sun's energy [39], making it both financially viable and eco-friendly. To achieve this objective, it is crucial to create an extremely visible nanocomposite with a narrow band gap. Semiconductor-based photocatalysts with great band gaps (like TiO_2) can absorb only UV light, which accounts for merely 4 % of the total solar spectrum [40]. Researchers typically utilize the above-mentioned techniques to construct extremely noticeable materials with narrowed band gaps to increase visible light absorption [41]. Nevertheless, several drawbacks regarding visible-light-stimulated photocatalysts need to be addressed. The main challenges are improving sunlight transformation and suppressing the recombination of photogenerated electron-hole conjugates. Essentially, investigations particularly focusing on the variable solar light in a photocatalyst reactor to construct a stable reaction system are imperative [41].

2.1.1. Photocatalysts preparation methods

2.1.1.1. Flame hydrolysis of $TiCl_4$ for photocatalysts synthesis. One popular technique for creating photocatalysts is flame hydrolysis, especially when creating TiO_2 from titanium tetrachloride ($TiCl_4$). TiO_2 nanoparticles are created during the procedure by the quick interaction of $TiCl_4$ vapour and water vapour in a high-temperature flame [42]. This procedure usually consists of five steps [42,43]: $TiCl_4$ is vaporized and combined with air, oxygen, or hydrogen to form a combustible mixture. The mixture is then ignited to produce a high-temperature flame, usually between 1500 °C and 2000 °C [44]. $TiCl_4$ reacts with the water vapour to hydrolyze $TiCl_4$ and form TiO_2 nanoparticles, which grow through coagulation and sintering in the flame. The nanoparticles are quickly cooled, and the resultant product is collected using filters or electrostatic precipitators [44,45].

In the majority of current reports, TiO_2 Degussa P25 is produced commercially from 80.0 % anatase and 20.0 % rutile. On average, particle size and the specific area are recorded as 30.0 nm and 50.0 m^2/g respectively. Flame hydrolysis of $TiCl_4$ at temperatures above 1200.0 °C in the existence of H_2 and O_2 is the main parameter for the fabrication [46]. In Ishigaki et al. [47]'s experiments, TiO_2 P25, and TiO_2 powder were thermal-treated in the air at temperatures ranging from 700.0 to 900.0 °C. An X-ray diffraction (XRD) study (for P25 powder) revealed 20.0 % and 80.0 % rutile and anatase phases respectively. Furthermore, the conversion from anatase to rutile stimulated by elevated-thermal treatment was almost complete at 750.0 °C, showing a minute level of anatase phase in the powder after the thermal treatment (at 900 °C). The conversion characteristics were coherent with the Raman scattering spectroscopy (RSS) results. Elevated heat transfer also caused the creation of oxide ion vacancies, according to Raman experiments. P25 powders were distributed in solvent methyl orange (MO) solution, and the bleach rate of MO was recorded to assess

photocatalytic activity under UV and visible light irradiation. The UV-light photocatalytic activity was significantly reduced after the heat treatment. Surprisingly, photocatalytic activity was elevated in visible light [47].

For the synthesis of TiO_2 photocatalysts, flame hydrolysis provides some benefits, such as quick reaction rates, excellent product purity, and control over particle shape and size. The resultant TiO_2 nanoparticles can be applied to solar cells, photocatalytic pollution degradation, and self-cleaning coatings, among other things.

2.1.1.2. Hydrothermal synthesis of photocatalysts. Since hydrothermal synthesis gives perfect control over the composition, morphology, and crystal structure of the final materials, it is a commonly utilized process for producing photocatalysts [48]. Using high-temperature, high-pressure water as a reaction media, this technique makes it easier for photocatalyst compounds to crystallize from their precursors [49]. Typically, there are four steps in this process [48]: selecting the right precursors for the required photocatalyst material. These could be metal oxides, metal salts, or other compounds containing metals. The precursors are mixed with a solvent, usually water, and any additional reagents, like mineralizers or pH adjusters, are added as needed [50]. The reaction mixture is then transferred to a sealed vessel and heated to the desired temperature and pressure for a predetermined amount of time. The precursors dissolve and recrystallize into the required photocatalyst material more readily at high temperatures and pressure, which also permits the vessel to cool naturally. After that, filter, wash, and dry the resultant photocatalyst material [48,50]. An essential step is characterizing the synthesized photocatalyst by employing several techniques such as electron microscopy, UV–visible spectroscopy, and X-ray diffraction to ascertain its structure, morphology, and optical characteristics [51]. Water splitting [33] or pollutant degradation is used to gauge how well photocatalytic processes are working [52,53]. Besides, Jin et al. [54] used cost-effective techniques to effectively synthesise a new nanocomposite using graphitic carbon nitride (g-C_3N_4) linked with TiO_2 and ornamented it with Ni. Melamine calcination was used to create immaculate g-C_3N_4 linked with TiO_2 and modified with nickel (Ni^+) by hydrothermal processing. Their strong crystallinity, increased by alteration, was observed during characterization. It was looked into how well these photocatalysts worked to break down the organic dye methylene blue (MB). The group also looked at the effects of pH, dye and photocatalyst doses, and contact time on the outcomes. The Ni-decorated composite g-C_3N_4-TiO_2 shown remarkable dye degradation performance [54].

Furthermore, a hydrothermal method was used to create TiO_2 with a crystallite size of 8.40 nm [55]. When likened to TiO_2 provided using the traditional sol-gel technique, it had a better anatase phase, a larger surface area, stronger UV absorption, and lesser agglomeration (sol-gel TiO_2). Its maximum photocatalytic activity in degrading dimethyl phthalate was 2.50 times that of sol-gel TiO_2 [56]. Tan et al. [40] created layered nanostructured TiO_2 (Fig. 1**a**). In the existence of tetramethylammonium hydroxide (TMAH), the group used a hydrothermal method at 125 C. TMAH intercalated into the layered nanostructured TiO_2 as a capping agent to Ti precursor. During the hydrothermal reaction time, the phase transition from layered nanostructure to the anatase phase happened (Fig. 1**b**). Nanostructured TiO_2 resulting was characterized using DLS size analysis, powder XRD diffraction (Fig. 1**c**), Fourier Transform Infrared (FT-IR) spectroscopy, thermogravimetric analysis, transmission electron microscopy (TEM), Raman spectroscopy, and luminescence spectroscopy. The embolism and decay of TMAH in TiO_2 were investigated. The demonstration of the formation of layered NSs was facilitated by the proposed growth mechanism. Layered NS-TiO_2 exhibited optical characteristics distinct from anatase-type TiO_2 NPs [40].

Fundamentally, hydrothermal synthesis provides high surface area and porosity materials, as well as control over composition, shape, and crystal structure which are beneficial for the preparation of photocatalysts. The technique is a flexible and effective tool for creating sophisticated photocatalytic systems since it may be used with a variety of photocatalyst materials.

2.1.1.3. Microwave-assisted synthesis of photocatalysts. Because microwave-assisted synthesis provides homogeneous energy distribution [57], increased reaction kinetics, and quick heating, it is a viable technique for producing photocatalysts [58]. Compared to traditional heating techniques, this approach produces a quicker and more efficient synthesis because it uses microwave radiation to heat the reaction mixture [58,59]. The green and eco-friendly microwave-assisted synthesis process was used to create nitrogen-doped TiO_2 photocatalyst NPs (N/TiO_2PNPs) by Sanchez Tobon et al. [60]. Experimented with temperature, period and precursor ratios. XRD, XPS, Raman spectroscopy (RS), FT-IR, diffuse reflectance spectroscopy (DRS), scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS), and nitrogen adsorption/desorption isotherms were employed to characterize the materials. Two optimization cycles were run to ascertain the optimal reaction temperature time and N content. Photoactive anatase was recognized as the phase composition of all N/TiO_2PNPs. The temperature of the reaction was discovered as an important parameter for the course of the samples' structural evolution. The nitrogen content was the least important for particle morphology development, but it was critical for photocatalytic activity. The breakdown of the antibiotic ciprofloxacin under dissimilar irradiation spectra: ultraviolet light (UVA), simulated sunlight, and visible light were used to assess the photocatalytic activity of N/TiO_2PNPs aqueous suspensions. Increased synthesis temperature and nitrogen content enhanced breakdown efficacies for all irradiation sources [60].

Falk et al. [61] created a simple, fast, and efficient synthesis procedure for elevated- -photocatalyst TiO_2 NPs and thin films via joining colloidal sol-gel and microwave-assisted hydrothermal method. The outcome showed that microwaving at 180.0 °C for 20.0 min was sufficient to fabricate crystalline TiO_2 NPs with anatase as a major phase and a specific surface area of 0.22 m^2/kg. Subsequent heating increased crystallinity and stimulated the A-R conversion. The photocatalytic activity of the as-synthesized powder was discovered to be the greatest without extra heat treatment. Finally, the thin films were fabricated by dip-coating, and their elevated photocatalytic activity revealed a kinetic curve similar to that of a thin film prepared from profitable TiO_2 powder under comparable settings [61]. Also, Andrade-Guel et al. [62] looked into the impact of the acid type employed as a catalyst on the phase transformation of TiO_2. SEM was utilized to characterize the samples obtained; the micrographs presented particles with irregular shapes. FT-IR (Fig. 2**a**) and XPS tests revealed the presence of oxygen and titanium. When hydrochloric acid was utilized as a catalyst, three titania polymorphs, anatase, rutile, and brookite, were detected by XRD, with crystallite sizes ranging from 9.0 to 16.0 nm (Fig. 2**b**). When acetic acid was added after only 15.0 mins of reaction time, a single anatase phase was formed. The average crystallite size of anatase was discovered to be between 11.0 and 22.0 nm [62].

For the preparation of photocatalysts, microwave-assisted synthesis provides several benefits, such as increased yields, quicker reaction times, and better control over particle shape and size. The technique is adaptable and effective for creating sophisticated photocatalytic systems since it may be used with a variety of photocatalyst materials.

2.1.1.4. Sonochemical synthesis of photocatalysts. A contemporary method for creating nanomaterials for effective photocatalysis while using the least amount of energy possible is sonochemical synthesis [63]. Using sonochemical methods, a wide variety of photocatalysts with high photocatalytic efficiencies have been created [63,64]; where sound waves provide the energy for the transformation of reactant materials into end products throughout this process. Because

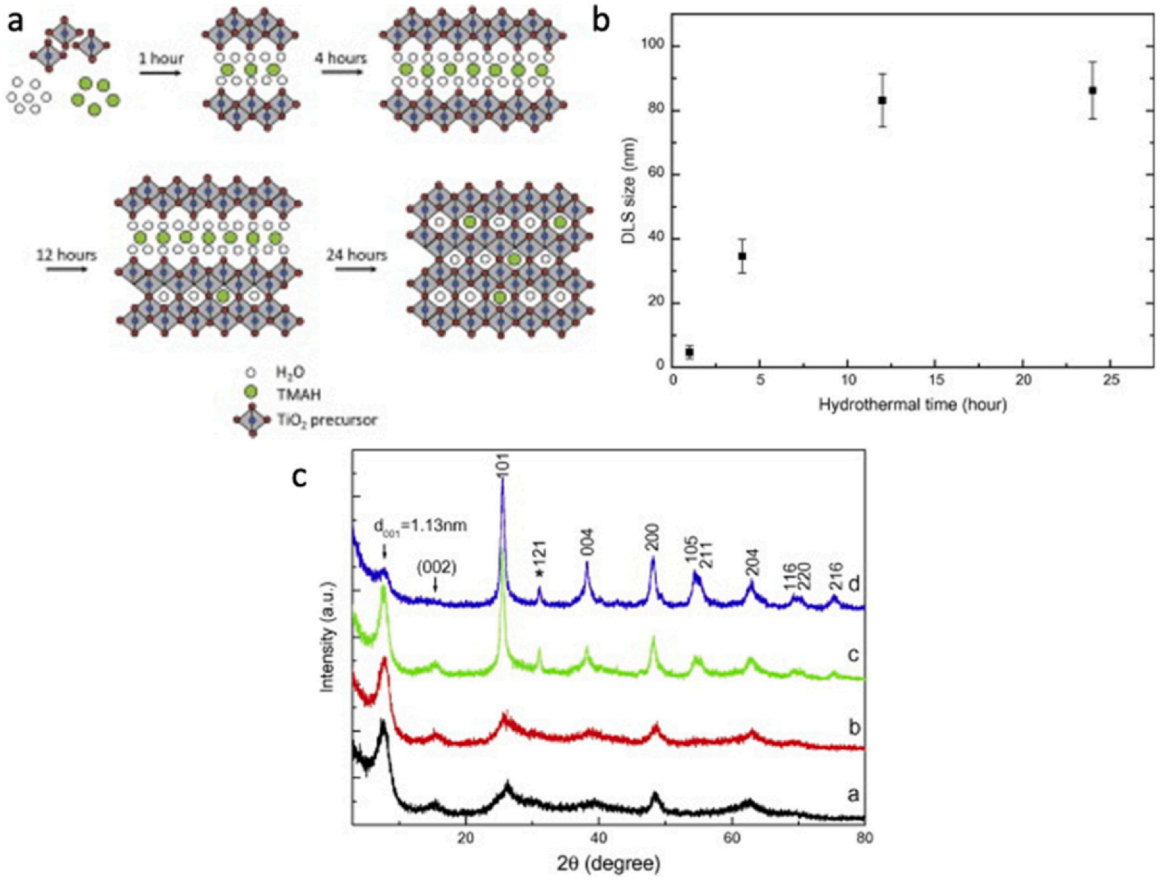

Fig. 1. Schematic illustration of layered nanostructured TiO_2 **(a)**; Time-dependent size distribution of TiO_2 nanoparticles made using the hydrothermal technique at low temperatures **(b)** TMAH was used as a capping molecule in the hydrothermal preparation of TiO_2 nanoparticles, as shown by the XRD patterns. One hour (a), four hours (b), twelve hours (c), and twenty-four hours (d) is the hydrothermal time.
(c) [40] Reproduced with permission; license number 5774060151369.

sonochemical synthesis is more affordable and can reduce the need for extra reagents during synthesis [63], it is becoming more and more popular in the field of green chemistry. It is a one-step process that spares the nanostructure from further heat treatment [63,65]. This method produces high-surface-area nanostructures with minimal agglomeration since heat treatment will reduce the surface area because of increased crystallinity. Besides, sound waves are employed in sonosynthetic chemistry to activate precursor materials during chemical processes [63]. It is a low-power process that produces materials with homogeneous and uniform morphology and significantly reduces the precipitation time for the creation of various semiconductors [66]. Besides, bubbles occur in the reaction mixture when sound waves collide with precursor materials because of the energy they release [67]. These bubbles have a relatively brief lifespan because acoustic cavitation causes them to expand and burst instantly. A zone of high tension is established near the bubbles during the development and dissolution of the bubbles, raising the local temperature and creating a high-pressure region of roughly 20 MPa [67,68]. The abrupt changes in temperature cause precursor materials to crystallise much more quickly, resulting in materials with extremely fast crystallization [63,69]. Under varying sound wave intensities, precursor materials' kinetic energy causes abrupt collisions between reacting molecules, resulting in the production of various morphologies with evenly dispersed nanostructures [63].

Hashim Khudhair et al. [70] created a unique $Mn^{2+}Mn_6^{3+}[SiO_4]O_8$ (braunite, MSO) nanostructure using an easy-to-use and reasonably priced sonochemical technique (Fig. 3). The product's homogeneity, structure, form, and size are influenced by the power and duration of sonication. The visible area employed $Mn^{2+}Mn_6^{3+}[SiO_4]O_8$ as a photocatalyst because of their appropriate bandgap. $Mn^{2+}Mn_6^{3+}[SiO_4]O_8$ nanostructures have been shown in photocatalytic studies to be able to destroy organic dyes, including high concentrations of Erythrosine (ER) and Eriochrome Black T (EBT). Therefore, at optimal conditions, with 70 mg of photocatalyst and 10 ppm EBT, the degradation rate is 94.8 %. The highest photocatalytic efficiency (94.8 %) is attained by the better rate constant, as per the kinetics investigation. The results of the recycling test demonstrate how stable $Mn^{2+}Mn_6^{3+}[SiO_4]O_8$ is. Following five cycles, the photocatalyst efficiency for ER and EBT fell by 14.2 % and 14.9 %, respectively. The scavenger test revealed that superoxide radicals were the most active radicals connected to the deterioration of erythrosine and EBT [70]. Also, The Sm_2CuO_4 nanophotocatalyst for the decolorization of various water-soluble organic pollutants was introduced by Yousefzadeh et al. [71] A quick and easy sonochemical process was used to create Sm_2CuO_4 nanostructures, which had an optical bandgap of 1.62 eV according to diffuse reflectance spectroscopy. To get the highest effectiveness, several variables were carefully examined, including the pH of the medium, Sm_2CuO_4 doses, organic contaminant concentrations, and various types of organic pollutants. The outcomes showed that Sm_2CuO_4 was quite successful in eliminating various organic pollutants from water. For instance, 91.4 % of the methyl orange was destroyed when 30 mg of Sm_2CuO_4 and 20 mg L^{-1} methyl orange were utilised under visible irradiation for 100 min. Further investigation revealed that holes were primarily responsible for pollutant photodegradation when using Sm_2CuO_4 as a photocatalyst. This finding suggests that Sm_2CuO_4 could be an excellent candidate for developing new materials to effectively remove water contaminants [71].

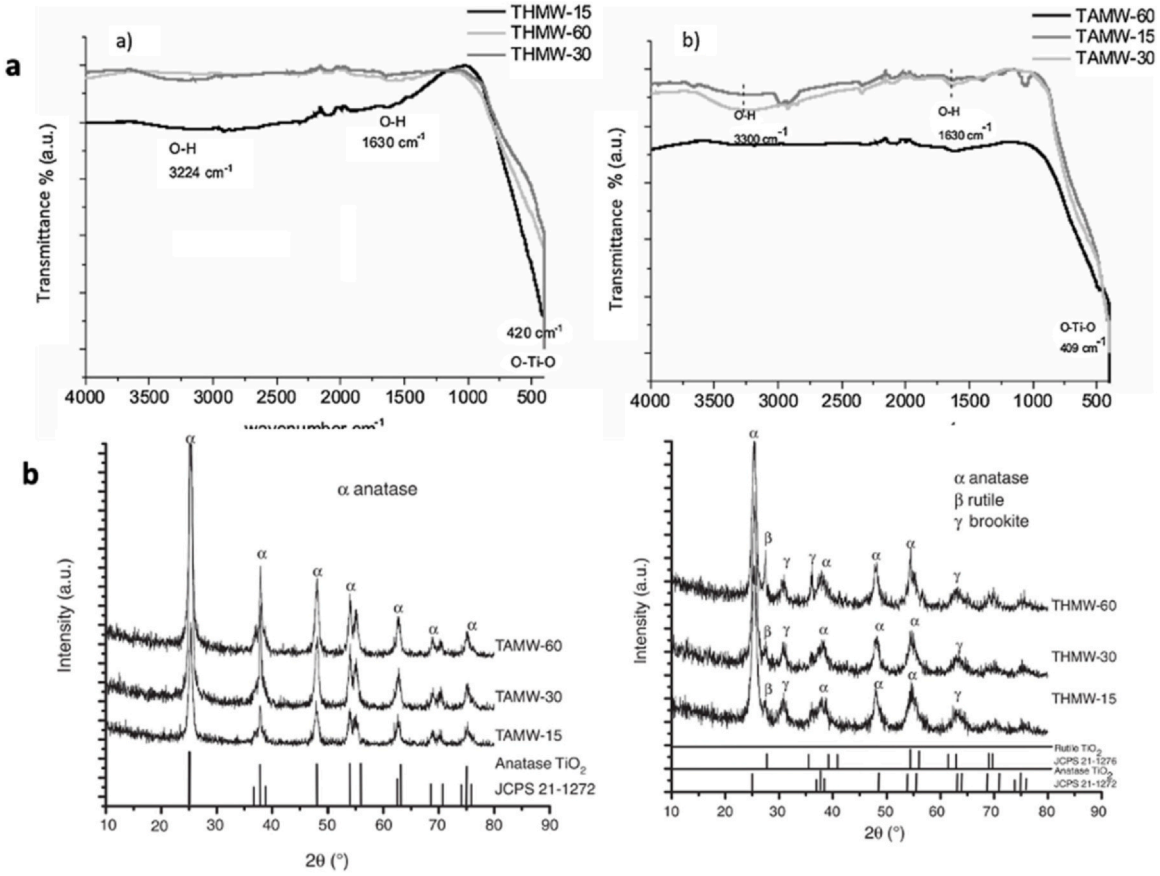

Fig. 2. FT-IR spectra of artificial materials: glacial acetic acid (TAMW) and hydrochloric acid (THMW) **(a)**; TAMW and THMW XRD patterns at various reaction times, respectively.
(b) [62]. Reproduced with permission under CC BY 4.0 license.

Considering its many benefits, sonochemical synthesis is a potential technique for producing photocatalysts for HPP. It enhances the photocatalyst's shape, surface area, and pore size, among other physical characteristics that have a beneficial effect on photocatalytic activity [71,72]. It also results in smaller particle sizes, which boost photocatalytic activity by increasing surface area. Because sonochemistry consumes less energy and generates less trash than conventional processes, it is regarded as a green technology [63]. Furthermore, it is an adaptable technique that can be used to create a variety of photocatalysts, such as heterostructures, metal oxides, and bio-based photocatalysts [68]. Because of these benefits, sonochemical synthesis provides a cost-effective and environmentally beneficial method for creating photocatalysts that may be used in energy generation and environmental cleanup.

2.1.1.5. Mechanochemical synthesis of photocatalysts. One approach that shows promise for producing photocatalysts for heterogeneous photocatalytic processes is mechanochemical synthesis [73]. This technique, which has been used to create CN, TiO_2, TiO_2-graphene nanocomposites [74], $Bi_2VO_{5.5}$, and other photocatalysts, uses mechanical energy to initiate chemical reactions [75]. Owing to the promise, Khosroshahi et al. [76] synthesised new metal-organic framework-808 (MOF-808) and $NiFe_2O_4$ nanocomposites with varying mass ratios for use in visible-light photocatalytic Cr(VI) reduction and meropenem degradation (Fig. 4). Characterization was done on the as-fabricated magnetic $NiFe_2O_4$/MOF-808 nanocomposites. The following comparison of the NiFe2O4/MOF-808 nanocomposites shows how the bandgap affects photocatalytic outcomes. The greatest photocatalytic activity was demonstrated by $NiFe_2O_4$/MOF-808 nanocomposites, which also had a smaller bandgap and an effective electron transport from photoexcited sources to the catalytic site. The highest and best efficiency was achieved by varying the catalyst quantity, pH, scavenger type, and drug dose. This led to the use of a 1:2 ferrite: MOF mass ratio of the nanocomposite, and under ideal circumstances, degradation happens in 60 min for each pollutant. The results showed how well chromium and meropenem were removed at ideal pH values of 2 and 6, respectively. Catalyst recovery experiments further demonstrate that even after eight consecutive cycles of this catalyst use, the deterioration rate has not decreased [76].

Furthermore, the layered double hydroxide (LDH)- precursor composites of cadmium sulphide (CdS)/magnesium (ZnS)CdS/Mg- aluminium (Al) was created by Li et al. [77] using a mechanochemical technique. An X-ray diffraction investigation verified that the CdS/Mg-Al LDH-precursor composites were formed. The homogeneous dispersion of CdS nanoparticles within the LDH-precursor matrix was revealed by SEM-EDS analysis. Under visible light irradiation, the produced nanocomposites demonstrated significantly enhanced photocatalytic activity on the breakdown of methylene blue (MB). One possible explanation for the strong photocatalytic activity is the unique structure of the widely distributed CdS nanoparticles within the LDH-precursor matrix. A thorough analysis of the photocatalytic process's mechanism and reaction kinetics was also carried out. The preparation of a series of photocatalysts based on LDH-precursor with well-dispersed transition metal sulphide within is made extremely easy and environmentally friendly by this work [77].

Because mechanochemical synthesis can yield photocatalysts with increased photocatalytic activity, crystalline structure, and regulated particle size, it is regarded as an environmentally friendly and effective method. It is a process that shows promise for creating photocatalysts that could be used in environmental remediation and energy production.

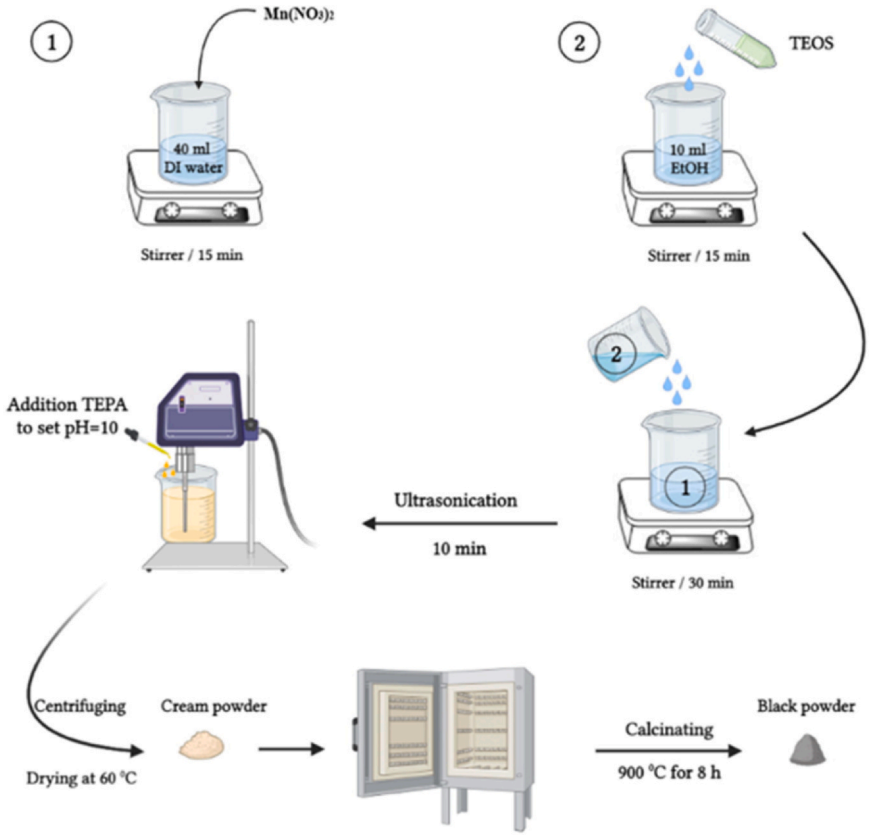

Fig. 3. Schematic of the fabrication process of $Mn^{2+}Mn_6^{3+}[SiO_4]O_8$ by sonochemical method [70]. Reproduced with permission under CC BY 4.0 license.

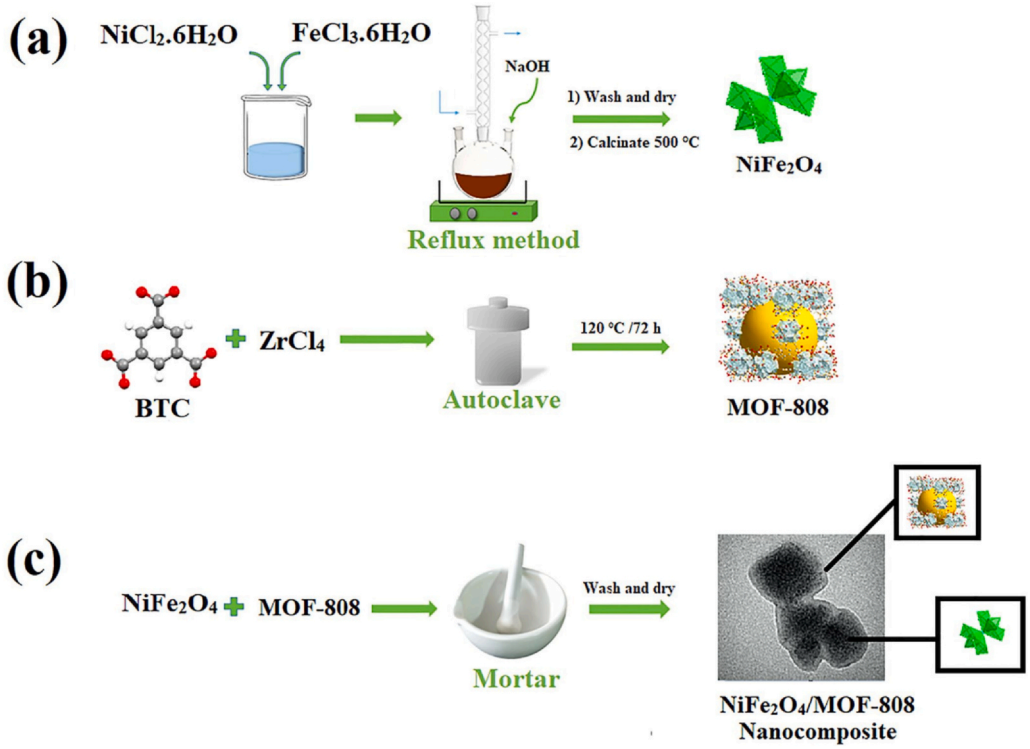

Fig. 4. Schematic illustration of the Synthesis method of (a) $NiFe_2O_4$, (b) MOF-808, and (c) $NiFe_2O_4$/MOF-808. Reproduced with permission under CC BY 4.0 license.

3. Parameters optimized for the effective heterogeneous photocatalytic process (HPP)

The pH of the electrolytic solution is important in the photocatalytic processes because it controls the surface charge of the photocatalyst, the size of the aggregates that occur, and the formation of oxidizing species. At pH 6.9 [78], the frequently used Degussa P25 was observed to have a point of zero charges [79]. Exploiting TiO_2, pH is connected to the ionization state of the photocatalyst surface and those of the reactant substrates and products [80]. The photocatalyst breakdown rate of weakly acidic pollutants rises with minor pH owing to an increase in adsorption [78,79]. Several OPs hydrolyze at higher pH, which contributes to better photocatalyst mineralization at alkaline pH [81]. Secondly, TiO_2 NPs incline to agglomerate in acidic solutions, resulting in decreased substrate and photon absorption. As a result, pH impacts substrate and photon adsorption on photocatalyst surfaces, a critical stage in the photocatalytic breakdown. Besides, the reaction of oxidizing species is impacted by the pH of the solution. Positive holes are thought to be the major oxidizing species at limited pH, while OH• is thought to be the main active species at neutral or alkaline pH. In general, low pH encouraged OP breakdown [41]. Other OPs like aureomycin, methanol, sevin, and methyl benzimidazol-2-ylcarbamate decayed extra easily in an essentially neutral solution [30,41,82]. Tayyebi et al. [78] observed that changing 7.0 to 3.0 pH significantly boosted the mineralization rate of methanol. Methanol is selected as the contaminant of choice for its lack of direct reactivity with ozone, it is an established scavenger of OH• and positive holes [78].

In most published studies, the tests happen at room temperature [37,78,83]. In general, an increase in temperature corresponds to a continual upsurge in breakdown efficacy within a specific range, beyond which the decomposition rate decreases. Temperature regulates photocatalytic ozonation in a variety of means, numerous of which have opposing impacts. Furthermore, increasing the temperature causes less adsorption of OPs and ROCs at constant pressure, resulting in less breakdown of adsorbed chemicals on the photocatalyst surface. When the temperature rises, the solubility of O_3 in water decreases, resulting in a lack of O_3 molecules to manage the photocatalytic ozonation procedure. Furthermore, increasing the solution temperature may improve charge carrier recombination while decreasing degradation efficiency. The increasing temperature could enhance all chemical reaction rates involved in the oxidizing system; such as O_3 decay and the creation of active species. As a result, it displays the ideal temperature for the combined system when the benefit outweighs the negative impacts [84].

The reaction rate in photocatalysis is mostly determined by the photocatalyst's absorbed photon flux, exhibiting a rise in remediation rate with increasing light intensity during photocatalyst processes. As a result, increased light intensity is a beneficial influence on the total efficacy of photocatalysts, allowing for more active species formation [85]. According to Xiao et al. [41], the total organic carbon (TOC) absorption in the O_3/UVA/TiO_2 procedure was half-order dependent on light intensity. Raising light intensity, on the other hand, would result in increased operating expenses. As a result, the ideal light intensity should take into account both oxidation efficacy and electrical input. It could be noted that the nature or shape of the light does not affect the reaction pathway, indicating that the band-gap sensitization mechanism is irrelevant in photocatalytic ozonation processes [41].

4. Applications of heterogeneous photocatalytic processes (HPP) in pharmaceutical pollutant removal

HPP uses renewable solar energy, produces little secondary pollution, and can be used on a variety of pollutants, it provides a sustainable and ecologically benign method for remediating pharmaceutical toxins. To increase its efficacy, affordability, and scalability for real-world uses, more study is necessary. Table 1 Summarizes numerous reported

Table 1
Applications of the heterogeneous photocatalytic process (HPP) for pharmaceutical wastewater treatment.

Operating parameters	Pharmaceutically active compound	Photocatalyst	Removal efficiency	Refs
Solar radiation, Time = 35 min; TiO_2 loads ranging = 0.1 to 0.5 g/L	Oxytetracycline (OTC)	TiO_2 P25 Degussa	95 %	[91]
UV irradiation, Time = 24 min; TiO_2 loads ranging = 0.1 to 0.5 g/L		Ag_3PO_4/TiO_2 @MoS_2	90 %	[92]
Visible light irradiation; Loading concentration = 10 mg./L	Tetracycline hydrochloride	AgNPs/$AgIn_5S_8$	95.3 %	[93]
Visible light irradiation; Loading concentration = 70 mg of photocatalyst and 10 ppm EBT	Eriochrome Black T (EBT) and Erythrosine (ER)	$Mn^{2+}Mn_6^{3+}[SiO_4IO_8$ (braunite, MSO) nanostructures	94.8 %	[70]
Visible light irradiation; Loading concentration = 30 mg of Sm_2CuO_4	Methyl orange	Sm_2CuO_4 nanophotocatalyst	91.4 %	[71]
Visible light irradiation	Ciprofloxacin and norfloxacin	Chitosan functionalized copper oxide (C-CuO) particles	71.07 % and 71.9 %	[72]
Visible light irradiation	Meropenem	$NiFe_2O_4$/MOF-808 nanocomposites	82.1 %	[76]
Solar radiation/ solar radiation.	Methyl orange dye	Cu-doped ZnO	95 %	[94]
	Rhodamine B	Ag-CMCH/CFP and Ag-Chi/CFP	95.31 % and 88.85 %	[95]
pH 3, and photocatalyst dosage = 0.5 g	Methyl orange dye	$Zn_{1-x}Cu_xO$ (x = 0 %, 1.5 %, 3.0 %, and 4.5 %) nanorods	98.28 % and 94.04 % > 81 %	[96]
UV light (wavelength: 320-400 nm), pH 1 (BBP), pH 14 (MB)	Bromophenol Blue (BBP) and Methylene Blue (MB)	Ag-ZnO/C_3N_4	98.6 % and 99.3 %	[97]
UV light (wavelength: 320–400 nm); Time = 24 min	Diclofenac	Sulfur-doped g-C3N4/ZnO	94 %	[89]
	Tetracycline		97 %	
Visible light irradiation; Time = 30 min	Acetaminophen	WO_3-AgCl	83.6 %	[90]
Ultraviolet light irradiation; Loading rate = 50- 500 mg./L	Carbamazepine (CBZ)	ZnO	Np	[98]
Visible light irradiation	Ibuprofen (IBP)	TiO_2	np	

*np = not provided.

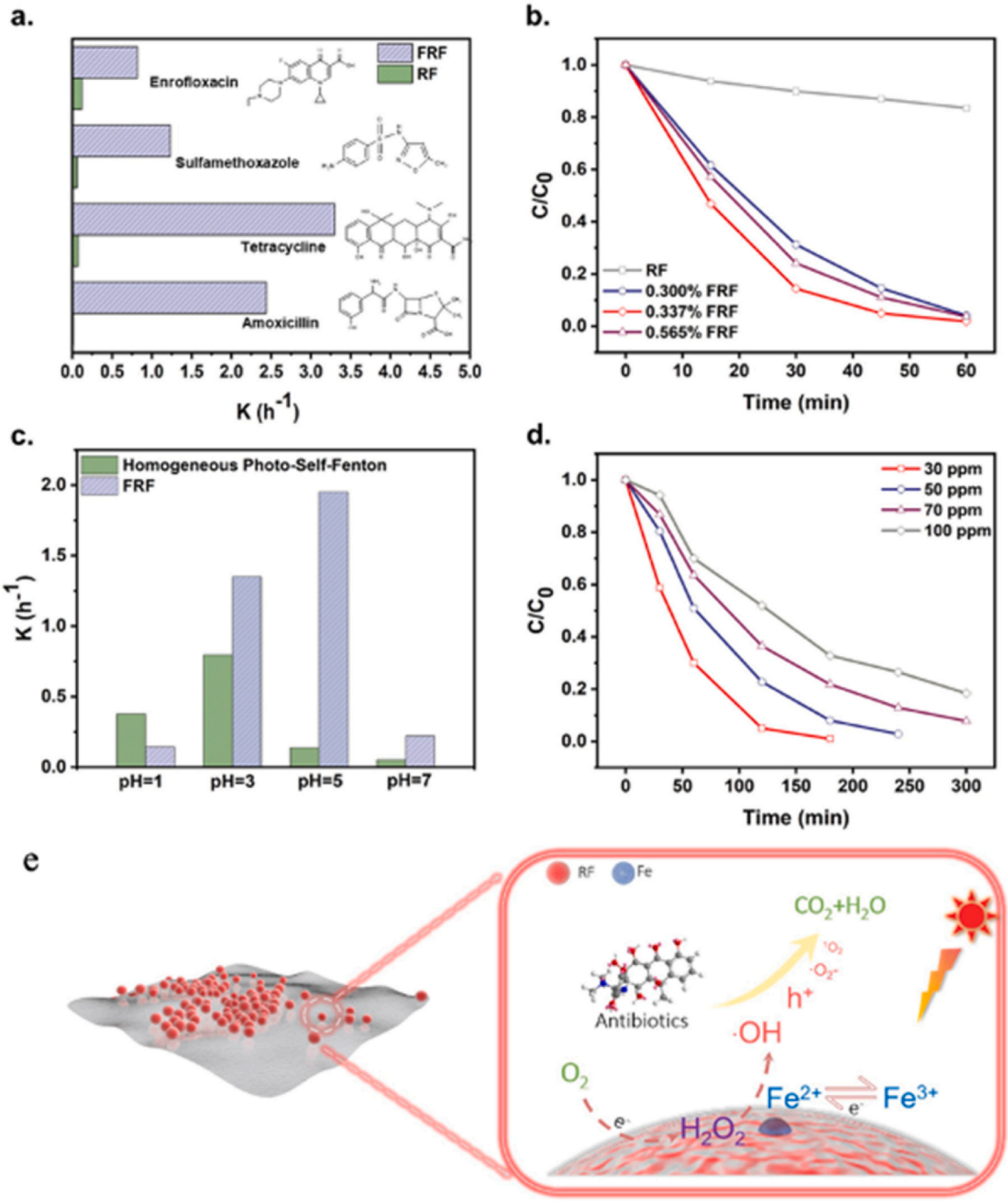

Fig. 5. (a) Photocatalytic rate constants for macrolides, sulfonamides, tetracyclines, and quinolones with resorcinol formaldehyde photocatalyst and heterogeneous photo-self-Fenton; (b) Oxytetracycline degradation curves of varied iron content catalysts at natural pH; (c) Comparison of sulfamethoxazole degradation rate constants in homogeneous photo-self-Fenton and iron-doped resorcinol formaldehyde heterogeneous photo-self-Fenton systems; (d) Effects of oxytetracycline starting concentrations on photocatalysis degradation; (e) iron-doped resorcinol formaldehyde [88].
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heterogeneous photocatalytic processes (HPP) for pharmaceutical wastewater treatment. This method uses photocatalysts, including TiO_2 [86], to produce reactive oxygen species (ROS) when exposed to light [86,87]. These ROS may efficiently break down pharmaceutical pollutants in wastewater. Zhang et al. [88] demonstrated a new heterogeneous photo-self-Fenton system based on iron-doped resorcinol formaldehyde resin (Fig. 5). Because this system can create and use H_2O_2 in situ, it is particularly effective at decomposing and mineralizing macrolides, sulfonamides, tetracyclines, and quinolones at neutral pH without the use of extra reagents. Surprisingly, the oxytetracycline degradation rate constant increased 34.2 times when compared with resorcinol formaldehyde photocatalysis. The improved deterioration performance of this system is due to (a) the iron-anchored resorcinol formaldehyde, which promotes the swift movement of photogenerated electrons, thus speeding up iron ion recycling and enhancing photogenerated carrier migration and separation efficiency. (b) The heterogeneous photo-self-Fenton reaction, which uses in situ produced H_2O_2 to generate a large number of OH•. Lastly, the mechanism of action and mineralization process of oxytetracycline were thoroughly investigated. The oxytetracycline is demethylated, hydroxylated, and ring-opened

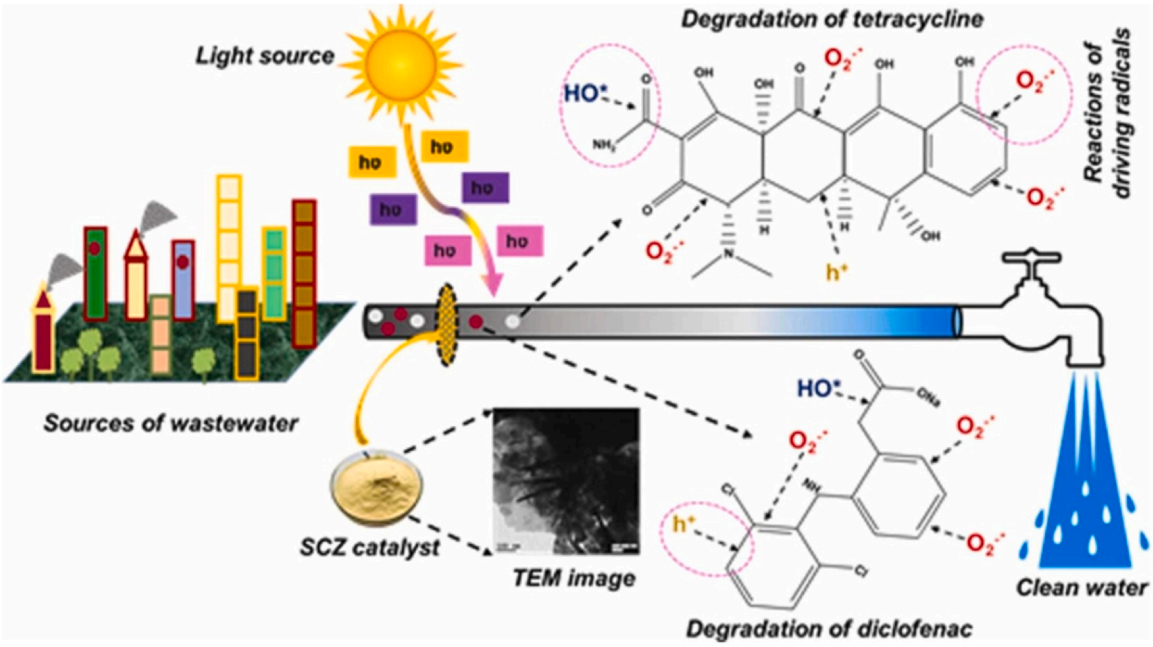

Fig. 6. Diagrammatic representation of a sulfur-doped g-C3N4/ZnO (SCZ) photocatalyst that uses UV light (wavelength: 320–400 nm) to remove diclofenac and degrade tetracycline in 240 min [89].
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before being fully mineralized to CO_2 and H_2O. The research paves the stage for the widespread construction of heterogeneous photo-self-Fenton systems [88].

The two pharmaceutically active substances that are commonly detected in water bodies are tetracycline and diclofenac. The employment of sophisticated treatment techniques has become necessary due to the limitations of conventional treatments. Using UV light, Bramha et al. [89] showed how to employ sulfur-doped g-C3N4/ZnO (SCZ) photocatalyst to remove tetracycline and diclofenac with 94 % and 97 % degradation efficiencies, respectively, in 240 min (Fig. 6). For the selected pollutants, the SCZ photocatalyst demonstrated improved mineralization efficiency (95 %) in 600 min and reusability (11 cycles). Similar to the pristine catalyst, the utilized catalyst's physicochemical analysis showed the existence of crystalline structures, flaws, and roughness. The diclofenac and tetracycline degradation routes outlined potential response mechanisms for the changed product forms. Pharmaceutical-spiked synthetic and actual wastewater was treated using the SCZ photocatalyst in a continuous photocatalytic reactor. Furthermore, the continuous photocatalytic reactor was connected to a fixed and moving bed bioreactor-sedimentation tank to eliminate suspended and biodegradable contaminants, increasing the organic removal efficiency from 70–94 %. When it came to the targeted pharmaceutical chemicals in the solution combination, the SCZ catalyst demonstrated an 85 % degradation efficiency. The study's findings point to the hybrid photocatalytic system and SCZ catalyst as potentially effective methods for treating drugs in actual wastewater [89].

Besides, Palharin et al. [90] employed a straightforward one-step hydrothermal process to create WO_3-AgCl photocatalysts using a variety of structure-directing chemicals, including urea, citric acid, oxalic acid, polyethene glycol, and Triton X-100. The materials' effective synthesis was shown using a variety of characterisation methods. The shape of the catalysts was significantly impacted by the guiding agent; the catalyst produced using citric acid had the highest photocatalytic activity and the most uniform dispersion of WO_3 and AgCl particles. After four cycle repetitions, stability testing showed a performance loss of only 18.8 %. Acetaminophen elimination was found to be 83.6 % in genuine effluent from a pharmaceutical manufacturing site. Furthermore, a continuous microstructured packed bed reactor experiment demonstrated 97.9 % steady-state [90].

HPP is a potential approach for the breakdown and mineralization of numerous pharmaceutical contaminants in water and wastewater, especially when utilising semiconductors like TiO_2. Because of its high photocatalytic activity, stability, and affordability, TiO_2 is a material that is extensively researched. To improve its performance and absorption of visible light, changes including doping, coupling, and immobilisation have been investigated. Numerous pharmacological pollutants, such as beta-blockers, anti-inflammatory medications, antibiotics, and antiepileptics, have demonstrated efficacy in this process. A few examples of the variables that affect HPP effectiveness include the features of the pollutant, the photocatalyst, the reaction conditions, and the presence or absence of other chemicals in the water matrix. Real pharmaceutical industry wastewaters have been treated with heterogeneous photocatalysis; to increase treatment efficiency, this technique is frequently used in conjunction with other AOPs including ozonation, Fenton, or UV/H_2O_2. HPP powered by the sun has also been investigated as a viable and affordable method of removing pharmaceutical pollutants. The goal of ongoing research is to employ HPP to remove pharmaceutical pollutants efficiently and sustainably. This involves enhancing photocatalyst design, process optimisation, and integration with existing treatment technologies.

5. Conclusion

The mechanism for the catalysis activity in heterogeneous photocatalytic processes (HPP) for the treatment of wastewater containing pharmaceuticals is covered in this review paper initially. then evaluates and contrasts the different methods for creating photocatalysts. On the other hand, microwave-assisted photocatalyst synthesis provides a faster and more efficient process since microwave radiation warms the reaction mixture. Furthermore, a green and ecologically safe synthesis yields nitrogen-doped TiO_2 photocatalyst NPs with good catalytic efficiency. HPP's photocatalytic activities and the effect of various operating parameters on the reaction process are what make it useful in the degradation of pharmaceutical contaminants in wastewater. In photocatalytic processes, the pH of the electrolytic solution is important because it controls the surface charge of the photocatalyst. Furthermore, degradation efficacy typically increases continuously with temperature

up to a certain point; after that, the rate of decomposition declines. HPP's photocatalytic activities and the effect of various operating settings on the reaction process are what make it useful in the degradation of pharmaceutical contaminants in wastewater.

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CRediT authorship contribution statement

Eric Danso-Boateng: Supervision, Writing – review & editing. **Josephine Baffoe:** Writing – review & editing. **Eliasu Issaka:** Writing – review & editing, Writing – original draft, Supervision, Resources, Methodology, Investigation, Data curation, Conceptualization.

Data Availability

Data will be made available on request.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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