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REVIEW

Role of Nanomaterials in Degradation of Cosmetics and Pharmaceutical Wastewater

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Biodiversity progress impacts the quality and availability of renewable natural resources. Ecological concerns about air and water pollution have been raised on communal and commercial levels. The continuous release and accumulation of cosmetics and pharmaceutical items in the environment pose significant threats to both ecosystems and human health. The presence of these emerging pollutants from pharmaceutical and cosmetic products has been reported in wastewater streams coming from industrial as well as wastewater treatment plants. This need has driven the development of technologies like advanced oxidation processes such as ozonation, Fenton's oxidation, photocatalysis, *etc.* for conventional wastewater treatments. Among these, the photocatalytic processes are presently being efficient since they not only utilize UV light but also visible light. This article mainly focuses on the review of preparation and comparative activity of photocatalysts on cosmetic as well as pharmaceutical wastes degradation. Photocatalysts, in their different forms like nanoparticles, nanorods and nanocomposites, hold great promise due to their stability, non-toxicity and reusability.

Keywords: Pollution, Cosmetics, Pharmaceuticals, Advanced oxidation processes, Photocatalyst, Reusable, n-type semiconductors.

INTRODUCTION

The significance of addressing the scarcity of natural resources like water needed for biological necessities and supporting various sorts of economic and developmental initiatives must be highlighted [1]. Water contamination is presently a major environmental issue resulting from the introduction of diverse persistent organic pollutants as well as cosmetic and pharmaceutical waste, from several sources into the natural water resources [2,3]. Currently, the water bodies are being affected by emerging contaminants [4,5] that are not regularly monitored in the environment. These contaminants have the ability to enter the environment and cause known or suspected negative effects on the ecosystem and human health. Due to the ineffective handling of urban, industrial and agricultural wastewater leads to the hazardous contamination or chemical pollution of drinking water ingested by millions of people. Thus, absence of regulatory frameworks, especially in developing nations, there is a continuous leakage of personal care products, pharmaceuticals and endocrine disruptors into the water sources, either by intentionally or unintentionally [6].

Sources and effects of cosmetic pollutants: Pollution escalation can result in the adverse consequences for both the environment and human well-being. In order to prevent the spread of infectious diseases, it is essential to practice good personal hygiene. Engaging in the daily activities such as showering, brushing teeth and washing the face and hair necessitates the utilization of suitable cosmetics to enhance physical appearance and beauty. These cosmetics contribute to the application of makeup and aesthetic enhancements [7], resulting in the emission of the additional non-biodegradable organic pollutants. The presence of preservatives in cosmetics is a major problem due to the inclusion of many substances such as contrast agents, hormones, preservatives, β-blockers, sunscreen UV filters, anti-inflammatory medications, soaps, disinfectants and detergents. Researchers have identified several contaminants in water habitats [8]. These substances may exhibit aqueous solubility, be insoluble in water and pose significant challenges for removal, even through water treatment processes. According to the reports, the water effluent from the water treatment plant comprises a variety of cosmetic organic wastes. Emerging contaminants persist in the environment since they are resistant to degradation. Emerging pollutants from cosmetic products and industries include preservatives such as parabens (methyl paraben, ethyl paraben, propyl paraben and butyl paraben), with methyl paraben and propyl paraben being detected at the highest concentrations (mean concentrations of 0.21 ng/mL and 0.22 ng/mL) [9]. Other pollutants include triclosan (concentration ranging between 20 and 100 ng/L in Spain) [10], 1,4-dioxane, benzalkonium chloride, plastic microbeads, formaldehyde, diazolidinyl urea, imidazolidinyl urea, sunscreen elements (organic and inorganic UV filters) and trace metals. The significant levels of benzophenone-3 present in the sunscreen lotions at the wastewater samples were detected in both the U.K. and U.S.A. [11,12]. The authors have also documented the biological hazardeness of these compounds on human health and aquatic ecosystems, such as genotoxicity, cytotoxicity, neurotoxicity, mutagenicity and estrogenicity [13].

Sources and effects of pharmaceutical pollutants: The pharmaceutical contaminants are a significant group of environmentally concern chemicals that originate from the pharmaceutical business [14]. Such compounds have the potential to treat, cure or prevent diseases due to their biological activity. Several reports are published about the detection of medicines in surface water and ground water ranging from micrograms per litre (µg/L) to milligrams per litre (mg/L) [15]. The presence of pharmaceuticals in aquatic environments has become a significant concern for community health in recent years [16]. Micropollutants in the aquatic environment are often linked to many adverse effects, such as acute and chronic toxicity, disruption of the endocrine system and development of antibiotic resistance in bacteria. A significant number of drugs exhibit low bioavailability and are eliminated from the human body without being effectively absorbed, either in their original form, as chemical compounds or as metabolites. Furthermore, numerous medications exhibit a lack of affinity for chromophores and possess high resistance to degradation by water, adsorption, organisms and inanimate objects. Consequently, sewage treatment works (STWs) are not effectively eliminating pharmaceutical compounds due to their focus on classical pollutants such heavy metals, chemical oxygen demand (COD) and 5-day biochemical oxygen demand (BOD5). Moreover, the sewage effluents and hospital effluents play a significant role in introducing pharmaceutical residues into both surface water and groundwater. The potential impact of pharmaceutical residues on aquatic organisms and potentially people, due to endocrine-disrupting effects or the development of antibiotic resistance in harmful bacteria, is a significant worldwide concern. Pharmaceuticals are the medicinal substances employed for the purpose of diagnosing, treating and mitigating animal and human ailments. Pharmaceutical production and utilization result in the discharge of these substances into waste streams [17].

Hospital effluents and pharmaceutical industrial waste are the major sources of the pharmaceutical pollutants that contaminate the environment and adversely affect the ecosystem [18]. Hazardous substances including toxic chemicals, by products, solvents, potent medications, disinfectants and heavy metals, released by hospitals during discharges, can persist in the environment for extended periods of time, posing significant risks to the ecosystem. Additionally, they exhibit significant mobility while present in the liquid state [4]. Prior to release these effluents into water bodies, it is crucial to employ efficient methods for their treatment. Pharmaceutically active compounds commonly detected in hospital effluents, wastewater treatment facilities, surface water, drinking water and ground water [19], which include antibiotics such as penicillin and tetracycline, analgesics, β-blockers like propranolol and atenolol, lipid regulators, anticoagulants, antihistamines like famotidine and ranitidine, anti-inflammatory, non-steroidal anti-inflammatory drugs such as ibuprofen, acetaminophen, diclofenac and naproxen, benzodiazepines (antidepressants), X-ray contrast media, lipid-lowering drugs and oestrogens. Approximately 30% to 90% of such compounds are non-biodegradable in human and animal bodies after ingestion, subsequently entering the aquatic ecosystems as active molecules.

Techniques for the elimination of contaminants from aqueous solutions: It is widely accepted that the conventional treatment techniques are not designed to eliminate polar pollutants. The utilization of activated carbon in the adsorption process enables the effective elimination of numerous pharmaceutical drugs and cosmetics from wastewaters. The utilization of adsorbents for eliminating impurities indicates that hydrophobic pollutants exhibit a greater attraction to the adsorbent surface compared to their hydrophilic counterparts [20]. Adsorption can decrease the quantity of organic matter in wastewater, enhance the biochemical process, despite the prevailing high cost of the adsorbent. By integrating this process with another treatment technique, the issue of separating the adsorbent from the treated water when utilizing activated carbon is partially resolved [21]. Research has indicated that wastewater treatment plants are inadequately insufficient to completely eliminate pharmaceutical drugs and cosmetics, leading to only partial elimination.

The biological treatment process is a contemporary method of treating wastewater using microorganisms, rather than relying on chemicals. Biological wastewater treatment involves the utilization of both aerobic and anaerobic microorganisms to effectively mitigate diverse contaminants found in water. Several methods of biological wastewater treatment can be employed to eliminate a wide range of contaminants from wastewater, including standard activated sludge processes, membrane bioreactors and trickling filter processes. The biological treatment of wastewater effectively removes organic pollutants, but it does not eliminate all types of pollutants, including detergents, cosmetic wastes, pharmaceutical contaminants, *etc*. Thus, the biological methods are not enough efficient in the process of mineralizing pharmaceutical and cosmetic chemicals [22]. The conventional sewage treatment plants are specifically designed to treat substances that can decompose. As a result, the non-biodegradable contaminants cannot be effectively eliminated using these conventional sewage treatment plants. Consequently, it is essential to develop effective treatment strategies for mitigating persistent pollutants that are difficult to eliminate and demand considerable energy in conventional treatment systems. There is an imperative to develop sophisticated treatment methods for wastewater. Furthermore, in order to enhance the effectiveness of sophisticated wastewater treatment process, it is crucial to prioritize the development of robust raw materials that have the ability to eliminate different types of aqueous pollutants from wastewater.

The prevention of these pollutants from reaching surface water has been difficult due to their low levels of concentration and the difficulties involved in analyzing them [23,24]. The utilization of technology for the eradication of pollutants is contingent upon various factors such as desired level of purity, properties of the pollutants and their concentration [25,26]. Over the past few decades, nanomaterials have been demonstrated to be a highly effective method for the disintegration and breaking apart the organic compounds [27]. These particles are intriguing due to their small number of atoms and a substantial proportion of them being located at or near surfaces. This arrangement significantly alters the atomic, electronic and magnetic structures, as well as the physical and chemical properties and reactivity of the particles compared to bulk material. The surfaces of nanoparticles themselves can possess unique characteristics, which are significantly different from their larger scale and molecular counterparts [28-33]. The purposely generated nanoparticles can be classified into four basic categories *viz*. (i) carbon based nanomaterials (size range of 1-100 nm), metal based nanomaterials (size range of 10-1000 nm), dendrimers (size ranging between 1-15 nm) and nanocomposites (size < 100 nm). Due to their cost effectiveness and strong chemical stability, nanomaterials have been extensively and effectively employed as photocatalysts in various fields (Fig. 1). Activation of the nanoparticles as photocatalysts necessitates a comparatively elevated level of photon energy. Consequently, numerous techniques have been suggested to reduce the band gap of photocatalysts with the specific goal of utilizing sunlight directly [27]. This review aims to investigate the ability of pollution removal by photocatalysts, synthesis and comparing various methodologies. The potential benefits and drawbacks associated with these approaches are also discussed.

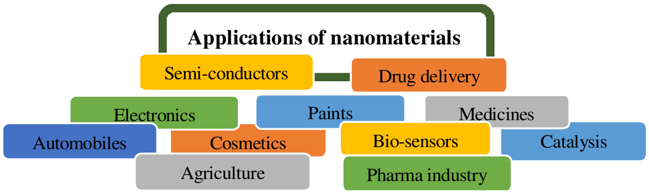

Fig. 1. Applications of nanomaterials

Advanced oxidation processes (AOPs) have become more widely used in recent years for the removal of organic contaminants, particularly pharmaceuticals [34]. This technique is a highly significant, effective and environment friendly technique which has been developed to eliminate persistent organic pollutants (POPs) from wastewaters due to their chemical stability. Typically, AOPs function by generating a potent oxidizing agent, such as hydroxyl radicals ($^{\bullet}OH$), precisely and in the appropriate quantity for water purification [35]. There are several advanced oxidation techniques available, including ozonation (O_3), ozonation combined with hydrogen peroxide (O_3/H_2O_2), UV irradiation (O_3/UV), a combination of ozonation, hydrogen peroxide and UV irradiation (O_3/H_2O_2/UV), ozonation combined with catalysts (O_3/catalysts), UV/H_2O_2, Fenton, photo-Fenton processes (Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2/UV), the ultrasonic cavitation process and photocatalysis [36,37].

Among the above mentioned process, photocatalysis is a very sophisticated oxidation process that has emerged as a viable solution for treating wastewater. It exhibits significant capability for breaking down organic contaminants (such as colours, medicinal chemicals, insecticides and phenols) and harmful metal ions under normal temperature and pressure conditions. Various catalysts, such as titanium dioxide (TiO_2), zinc oxide (ZnO), tungsten trioxide (WO_3), cadmium sulfide (CdS), zinc sulfide (ZnS), tin dioxide (SnO_2), molybdenum trioxide (MoO_3), magnetite (Fe_3O_4), gallium phosphide (GaP) and graphitic carbon nitride (g-C_3N_4), are utilized to convert harmful organic pollutants in wastewater into less toxic and non-toxic inorganic compounds, such as CO_2 and H_2O [38,39].

Photocatalytic activity: In this process, a semiconductor as a catalyst is empolyed to decompose pollutants activated by ultraviolet (UV) radiation [40]. TiO_2 is a type of nanomaterial that acts as a heterogeneous photocatalyst and is classified as a semiconductor material that has a wide energy band gap of 3.2 electron volts (eV). The valence band of TiO_2 consists of hybridized 2*p* orbitals of oxygen and the 3*d*-orbitals of titanium, whereas the conduction band is solely constituted of the 3*d*-orbitals of titanium. When TiO_2 is subjected to near-ultraviolet (UV) radiation, the electrons in the valence band become energized and go to the conduction band. This process creates empty spaces, known as holes (h^+), as illustrated in Fig. 2. The electrons (e^-) in an excited state within the conduction band are currently in a 3D configuration. The probability of these electrons shifting to the valence band lowers due to their distinct characteristics. As a result, the chance of recombination between electrons (e^-) and holes (h^+) also decreases [41]. A redox reaction occurs at the surface of catalyst. The redox potential of the photogenerated valence band hole must be sufficiently high to produce $OH^{\bullet}$ radicals, which can then oxidize the organic pollutant. The redox potential of electron in the conductance band generated by light must be sufficiently

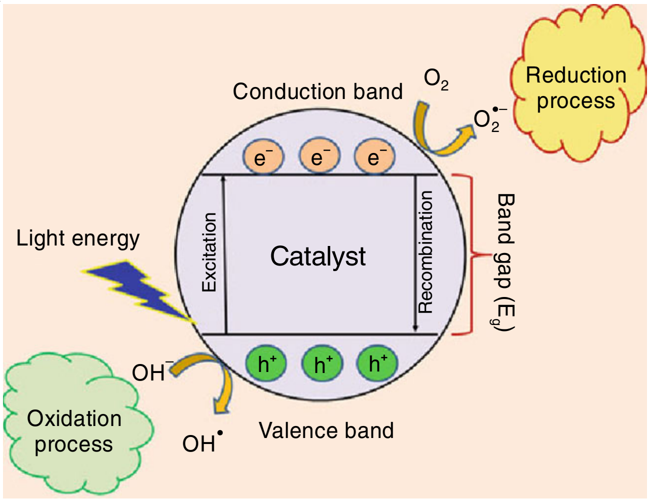

Fig. 2. Working of nanophotocatalyst

low in order to eliminate adsorbed superoxide (O_2^-) effectively [42].

Due to their large optical band gap, these materials have an ability to absorb ultraviolet (UV) radiation, which makes up less than 5% of the solar spectrum. However, they do not react to visible light, which accounts for 45% of the solar spectrum [43]. As a result, there has been considerable focus on the advancement of photocatalysts that can be activated by visible light. Doping is a commonly used method for making useful alterations. To develop active sites for the adsorption or catalysis of TiO_2, one can use heteroatoms such as iron and nitrogen. Nitrogen doping introduces a mid-gap state that serves as an electron donor or acceptor within the band gap. On the other hand, Fe^{3+} doping functions as a trap for the photogenerated electrons and holes, thereby inhibiting electron-hole recombination. The efficiency of the reaction is determined by the interplay between the surface charge carriers are transferred and the rate at which electrons and holes recombine [44]. The photocatalytic oxidation mechanism suggests that the $^{\bullet}OH$ and $^{\bullet}O_2^-$ radicals play a significant role in effectively removing contaminants and converting them into H_2O and CO_2 through mineralization [45].

Doped photocatalyst: The metallic oxide nanoparticles such as AgO, ZnO, MgO, CuO and TiO_2 [46,47] possess distinct characteristics such as electrical, magnetic, optical, thermal, efficacy against drug-resistant bacteria, viruses and fungal strains as well as catalytic activity [48]. Silver nanoparticles have a broad range of uses, surpassing other metal oxide nanoparticles [47]. However, TiO_2 stands out as the most remarkable nanomaterial due to its chemical stability, photocatalytic capabilities, high stability, biocompatibility and non-toxicity [49,50]. In addition to its various applications in water treatment, dye-sensitized solar cells, cosmetics, pigments and seed germination, TiO_2 is a crucial semiconductor photocatalyst [51,52].

Titanium dioxide (TiO_2) can be prepared using several methods [53] including hydrothermal [54,55], sol-gel [56-58], solvothermal [59-61], microwave-assisted synthesis [62,63], chemical vapour deposition [63,64] and others. The optimal nanoparticle size was found to be between 25 and 30 nm [65].

Catalytic activity of photocatalysts: Numerous doped TiO_2 photocatalysts were synthesized employing the aforementioned techniques and their efficacy in degrading cosmetic residues was assessed; the results are detailed in the subsequent Table-1.

In addition, ZnO as a photocatalyst exhibits the capability of degrading ethyl paraben in a solar-driven manner at a faster rate than P25 TiO_2 nanoparticles. Furthermore, the resulting compounds are less estrogenic in nature compared to ethyl paraben [77]. Shah *et al.* [78] investigated the degradation of methyl paraben using ZnO in conjunction with light, sonication or both. The maximal degradation achieved through sonication alone was 71%, whereas photocatalysis yielded 90%. Sheikhmohammadi *et al*. [79] examined the photocatalytic activity of butyl and benzyl paraben in absence of H_2O_2, which measured approximately 81% and 67.37%, respectively, whereas the presence of H_2O_2 led to an increase in degradation. Methyl paraben, a highly detrimental water pollutant originating from the cosmetic industry, was successfully degraded using silver nanoparticles affixed to reduced graphene oxide. Sheikhmohammadi *et al*. [80] and Khan *et al.* [81] fabricated the graphene oxide and reported its photocatalytic degradation activity to be 97.6%. Table-2 illustrates the application of diverse

TABLE-1
PHOTOCATALYTIC DEGRADATION OF COSMETIC POLLUTANTS USING METAL AND NON-METAL DOPED TiO_2 NANOMATERIAL AND THEIR METHODS OF SYNTHESIS

Photocatalyst	Method	Dopant precursor	Pollutant	Degradation efficiency (%)	Ref.
N-TiO_2	Sol-gel method	NH_3	Ethyl Paraben	98.0	[66]
N-TiO_2	Sol-gel method	NH_3	Methyl paraben	94.7	[67]
		Urea	Methyl paraben	61.2	
			Benzyl paraben	81.6	
N-TiO_2	Sol-gel method	NH_4OH	Methyl paraben	99.6	[68]
			Ethyl paraben	98.8	
			Propyl paraben	96.6	
rGO-TiO_2	Hydrothermal method	Natural graphite	Ethyl paraben	98.6	[69]
TiO_2 P-25			Methyl paraben	60.0	[70]
TiO_2 nanotubes			Methyl paraben	35.0	[71]
Al-TiO_2	Co-precipitation method		Propyl paraben	80.0	[72]
Pd-TiO_2	Photodeposition	$PdCl_2$	Benzyl paraben	75.0	[73]
Ag_2S-TiO_2	Sol-gel method	$AgNO_3$, thiourea	Ethyl paraben	95.0	[74]
Pure TiO_2	Sol-gel method		Benzyl paraben	10.0	[73]
Ag-TiO_2		$AgNO_3$		50.0	
Pt-TiO_2		H_2PtCl_6		40.0	
Pd-TiO_2		$PdCl_2$		75.0	
Au-TiO_2		$KAuCl_4$		10.0	
PbO/TiO_2 composite	Hydrothermal method	$Pb(NO_3)_2$	Benzophenone 3		[75]
Sb_2O_3/TiO_2		$SbCl_3$			
Pt@TiO_2	Reverse micelle sol-gel method	$H_2PtCl_6{\cdot}6H_2O$	Formaldehyde (gaseous)	98.3	[76]
TiO_2 (P25)				92.4	
TiO_2 (Home made)				75.2	
1 wt% Pt/TiO_2				85.6	

TABLE-2
PHOTOCATALYTIC DEGRADATION OF PHARMACEUTICAL POLLUTANTS USING METAL AND NON-METAL DOPED TiO_2 NANOMATERIAL AND THEIR METHODS OF SYNTHESIS

Photocatalyst	Type of pharmaceuticals	Summary	Degradation efficiency (%)	Method	Ref.
Cr-TiO_2	Amoxicilln (5 mg/L)	The optimal condition for the amoxicillin photo degradation is reached at pH 6 and an irradiation time at 90 min	100.00	Hydrothermal Process	[82]
Ag-TiO_2	Chloramphenicol (20 mg/L)	An optimum amount of Ag nanoparticles (0.96 wt%) in the calcination temperature 300°C. The highest removal efficiency of CAP (~100%) at the optimum conditions was observed in 20 min	100.00	Photo deposition technique	[83]
Cu-TiO_2	Levofloxacin (50 mg/L)	0.5 wt% Cu-TiO_2 photocatalyst has shown significant LFX degradation of 75.5% with catalyst loading of 1 g/L	75.50	Reverse micelle mediated modified sol-gel method	[84]
Sm-TiO_2	Ciprofloxacin (CIP)	1 wt.% Sm-loaded catalysts being the most active. More than 90% of CIP was degraded within 30 min	90.00	Hydrothermal method	[85]
N-TiO_2	Norfloxacin (NOR) (6.03 mg/L)	N-TiO_2 dose of 0.54 g/L and pH of 6.37 could be the proposed optimal degradation conditions, which resulted in a 99.53% removal of NOR within 30 min under visible light irradiation	99.53	Self-owned patent recipe	[86]
Bi, Ni co-doped TiO_2	Ofloxacin (OFL)	The photo-degradation kinetics follows a pseudo first-order reaction. Bi–Ni co-doped TiO_2 showed higher activity for photo catalytic degradation of OFL under solar light compared to Degussa TiO_2	86.00	Sol-gel method	[87]
N,S co-doped TiO_2	Ibufrofen	The N,S-TiO_2 nanoparticle is a well-developed mesoporous structure that contains both anatase and rutile phases and pH 6	85.00	Facile Sol-gel	[88]
N,S-TiO_2	Naproxen	N,S-TiO_2 nanoparticle contains both anatase and rutile phases and a large BET surface area (132 $m^2 g^{-1}$)	99.30	Facile Sol-gel	[88]
Mn, Ce co-doped	Diclofenac	The photo degradation rate of diclofenac can be approached by pseudo first-order kinetics	94.00	Sol-gel	[89]
Zn-TiO_2	Tetracyclin	The optimal degradation rate of tetracycline by Zn-doped TiO_2 and H_2O_2 modified Zn-doped TiO_2 was 85.27% and 88.14%	85.27	Sol-gel	[90]
Fe-TiO_2	Acetaminophen	The pseudo first order, pH 9 and UV irradiation time = 90.35 min)	90.35	Sol-gel	[91]

AOP photocatalytic techniques to address various pharmaceutical derived pollutants.

Conclusion

This review article provides an exhaustive enumeration of the diverse methodologies through which nanoparticles have purportedly been effectively employed to degrade the organic pollutants in the visible spectrum. The expansion of industrialization is contributing to the contamination of water bodies. The utilization of skin care products (cosmetics) and pharmaceuticals has increased in tandem with this pollution increase. Advanced oxidation processes are potentially among the most efficacious techniques utilized to treat wastewater that contains organic substances. In this context, the wastewater treatment is achieved *via* heterogeneous photocatalysis, an advanced oxidation process (AOP) that generates highly reactive free radical oxidants to convert organic pollutants to brief species or even to their complete mineralization. Multiple techniques, such as adsorption using activated carbon, biological processes, membrane filtration and advanced oxidation processes (AOPs), have been established to eliminate these pollutants from water and wastewater. TiO_2-based photocatalysts are regarded as one of the most prominent advanced oxidation process (AOP) methods due to their numerous advantages compared to alternative techniques, making them the most promising and suitable choices for the optical degradation of pharmaceutical pollutants in water. Research indicates that advanced oxidation processes (AOPs) are highly efficient in degrading pharmaceutical compounds; therefore, identifying degradation products and assessing their toxicity levels is crucial, as these byproducts may exhibit greater toxicity or biological activity than their parent compounds, potentially posing increased environmental risks. While water solutions or synthetic wastewater samples have predominantly been utilized for pharmaceutical degradation investigations, additional investigations employing actual wastewater samples is recommneded. The matrix of actual wastewater samples is complex due to the presence of inorganic and organic chemicals, necessitating a genuine AOP technique to guarantee its efficacy. Furthermore, the complex composition of wastewater samples complicates the identification of degradation products. Alongside single AOP approaches, hybrid methods are increasingly favored for attaining high removal efficiency. Furthermore, environmental planning, including pollutant concentration and the type of aquatic matrix, must be taken into account when devising experimental drug degradation designs.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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