Preprint of: Rohan Khizer, M., Saddique, Z., Imran, M., Javaid, A., Latif, S., Mantzavinos, D., Momotko, M., & Boczkaj, G. (2024). Polymer and graphitic carbon nitride based nanohybrids for the photocatalytic degradation of pharmaceuticals in wastewater treatment – A review. SEPARATION AND PURIFICATION TECHNOLOGY, 350, 127768. https://doi.org/10.1016/j.seppur.2024.127768

Polymer and graphitic carbon nitride based nanohybrids for the photocatalytic degradation of pharmaceuticals in wastewater treatment – a review

Muhammad Rohan Khizer[1], Zohaib Saddique[1], Muhammad Imran [1,*], Ayesha Javaid[1], Shoomaila Latif [2], Dionissios Mantzavinos[4], Malwina Momotko[3,*], Grzegorz Boczkaj[3,5,*]

[1] Centre for Inorganic Chemistry, School of Chemistry, University of the Punjab, Lahore 54000, Pakistan.

[2] School of Physical Sciences, University of the Punjab, Lahore 54000, Pakistan.

[3] Department of Sanitary Engineering, Faculty of Civil and Environmental Engineering, Gdańsk University of Technology, 11/12 Narutowicza Str., Gdańsk 80-233, Poland.

[4] Department of Chemical Engineering, University of Patras, Caratheodory 1, University Campus, GR-26504 Patras, Greece.

[5] EkoTech Center, Gdańsk University of Technology, G. Narutowicza St. 11/12, Gdansk 80-233, Poland

*Corresponding author email:

imran.hons@pu.edu.pk (M. Imran); malwina.momotko@pg.edu.pl (M. Momotko); grzegorz.boczkaj@pg.edu.pl (G.Boczkaj)

ABSTRACT

Pharmaceuticals, including antibiotics and anti-inflammatory drugs, have been.frequently detected in water reservoirs, in concentrations ranging from ng/L to µg/L, owing to their wide use in treatment of human and animal disease. Their uncontrolled use results in their increased release into the environment which is harmful for humans, animals, aquatic life and aquatic system. To remove these pollutants from water bodies, various processes including adsorption, membrane and bioreactors have been employed. Among them photocatalysis is one of the most advantageous treatment. Application of advanced chemical treatment, including advanced oxidation or reduction processes (AOPs or ARPs) based on organic-inorganic nanohybrids (OINHs) as photocatalysts revealed high effectiveness. OINHs are combination of two or more components which are organic and inorganic in nature. These materials have been synthesized by various methods and offers novel features owing to synergistic effect of their component. These materials are synthesized through sol-gel, surface functionalization, one pot synthesis, wrapping, and electrospinning methods. Organic components are essential in enhancing photocatalytic activity through increasing stability, surface area, functionality and light responsiveness of nanohybrid. Reports suggest >99% degradation of studied pharmaceuticals by these type of photocatalysts in time range of 30-60 minutes. High effectiveness was reported for carbamazepine, ciprofloxacin, diclofenac, ibuprofen, naproxen, paracetamol, sulfamethoxazole and tetracycline. This review summarizes recent literature on application of OINHs i.e. graphene oxide, g-C_3N_4, and polymer based nanohybrids, in photocatalytic removal of pharmaceuticals from wastewater via AOPs while elaborating on toxicity of pharmaceuticals, synthesis of OINHs and degradation mechanism of pharmaceutical drugs. Current challenges faced in this field as well as future recommendations are also discussed.

Keywords: Organic-inorganic Nanohybrids; Z-scheme Heterojunction; Photocatalytic Degradation; Water Treatment; Electrospinning; Environmental Pollutants; Emerging Organic Contaminants EOCs; Radicals; Metal Oxides; TiO_2.

1. Introduction

Pharmaceuticals are defined in broad term as therapeutic drugs that are used to cure and/or prevent diseases in human beings; antibiotics, nonsteroidal anti-inflammatory drugs (NSAIDs), anticonvulsants, analgesics, chemotherapeutics, and β-blockers are common classes of pharmaceutical products that are used commonly [1, 2]. Uncontrolled and excessive use of pharmaceuticals results in their untreated release into the environment. Main sources of pharmaceuticals release into aquatic systems are untreated effluents from hospitals, municipal plants, landfill leachate, surface run off, and illegal disposal[3-6]. Recent studies report release of 30-90% active and non-metabolized antibiotics into environment through urine and feces[7, 8]. This emerging class of water pollutants negatively affect human life and aquatic environment. For instance, excess of acetaminophen results in deadly liver damage as well as skin problem [9, 10]. Presence of antibiotics such as amoxicillin, tetracycline, and ampicillin in aquatic system results in generation of antibiotics resistance strains of bacteria [11-17]. Conclusively pharmaceuticals in water bodies are highly hazardous for human and aquatic life as well. These pollutants accumulate in ecosystem owing to their persistent nature and slow degradation rate. Their removal is further necessitated by their recalcitrant chemical and physical properties and accumulation in environmental food chain [18, 19]. To protect human and animal in particular and ecosystem in general, elimination of such persistent and eco-toxic pharmaceutically active compounds from water bodies is a crucial step that needs immediate attention. Typically, pharmaceuticals are present in treated water bodies in the range of ng/L to μg/L [20, 21]. Owing to their physiochemical properties, such as high volatility, polarity, lipophilicity, and persistence, and quantity in water, conventional treatments are not suitable for their removal[22].

In recent decades, advanced treatment processes for water treatment have gained increasing interest among researchers and these include electrochemical reduction[23], membrane filtration [24, 25], precipitation [26], electrodialysis [27], photocatalysis [28, 29], cavitation[30, 31], percarbonate-[32] and persulfate-based processes[33], and electrodeionization [34]. Photocatalysis is one of the advanced oxidation processes (AOPs) that has been regarded as a promising technology due to its high efficiency[29, 35, 36]. In photocatalysis, pharmaceuticals are degraded into simple molecules through their reaction with photogenerated reactive chemical species on the surface of photocatalyst. Photocatalyst is a substance or material that determines the rate of photocatalytic reaction, thus, its design and fabrication are crucial steps and have been considered a challenge that is being faced with deep interest by the research community [37-39].

There is a lot of research on synthesis of photocatalysts and their application in removal of pharmaceuticals from water through advanced oxidation processes and these photocatalysts include TiO_2, ZnS, NiS, CuS, HgO, Bi_2O_3, BiOBr, Fe_2O_3, $BiVO_2$, BiS, ZnO and organic-inorganic nanohybrids (OINHs) [39-45]. Among all these photocatalysts, OINHs are unique a class of materials with efficient catalytic activity due to certain features that result from combination of their organic and inorganic components. Organic component provide enlarged surface area of OINHS which increases photoactive sites and promote charge carrier production. Organic components are high light absorbing materials and this property is enhanced by inorganic component. Structural stability is one of prerequisite of photocatalysis, OINHs offer high structural stability owing to its highly stable organic component. Last but not least, structural tunability is crucial for optimizing performance of photocatalysts aimed at introducing such properties that can be instrumental for industrial scale applications, long term stability, good adsorption, and large surface area[46-48]. These features make them highly suitable candidates for industrial scale removal of pharmaceuticals from wastewater through AOPs. Since these materials are combination of two or more components into single domain while reflecting the properties of each material, they are named as hybrid materials [49]. In specific terms, hybrid materials are made up of at least two molecularly dispersed components and these component are essentially organic and inorganic in nature [50]. OINHs have been synthesized by sol-gel method, surface functionalization, one pot synthesis, wrapping method, and electrospinning of nanohybrids [51].

There is absence of elaborative studies that can summarize recent developments in the field of OINHs for photocatalytic degradation of pharmaceuticals in wastewater. This paper attempts to fill this gap by providing vital information of toxicity, sources, chemical nature of pharmaceuticals. It also introduces OINHs, elaborates their synthesis and application in removal of pharmaceuticals from wastewater while providing to the reader with their novel features and tunability for optimization of these materials aimed at their application at industrial scale. A necessary information of mechanisms of degradation assisted by these functional materials is also provided. Besides, current challenges faced by these materials and future possibilities are also recommended in last.

2. Sources and health risks of pharmaceuticals

Pharmaceuticals and their metabolites or residues enter into environment from various sources including pharmaceutical industry, hospital and municipal wastewater, and illegal disposal, as presented in Figure 1[11]. These micropollutants cannot be degraded by conventional water treatment plants, therefore, they are released continuously into the water bodies [52]. One of the major pathways for pharmaceuticals to enter into the environment is from human and animal excretion that is released into sewage system. Reports suggest that about 70% of pharmaceutical active ingredients and their metabolites enter into the environment from feces and elevate their level in wastewater[53]. Conventional wastewater treatment plants cannot remove these pollutants and as a result these pollutants enter into freshwater streams[54, 55].

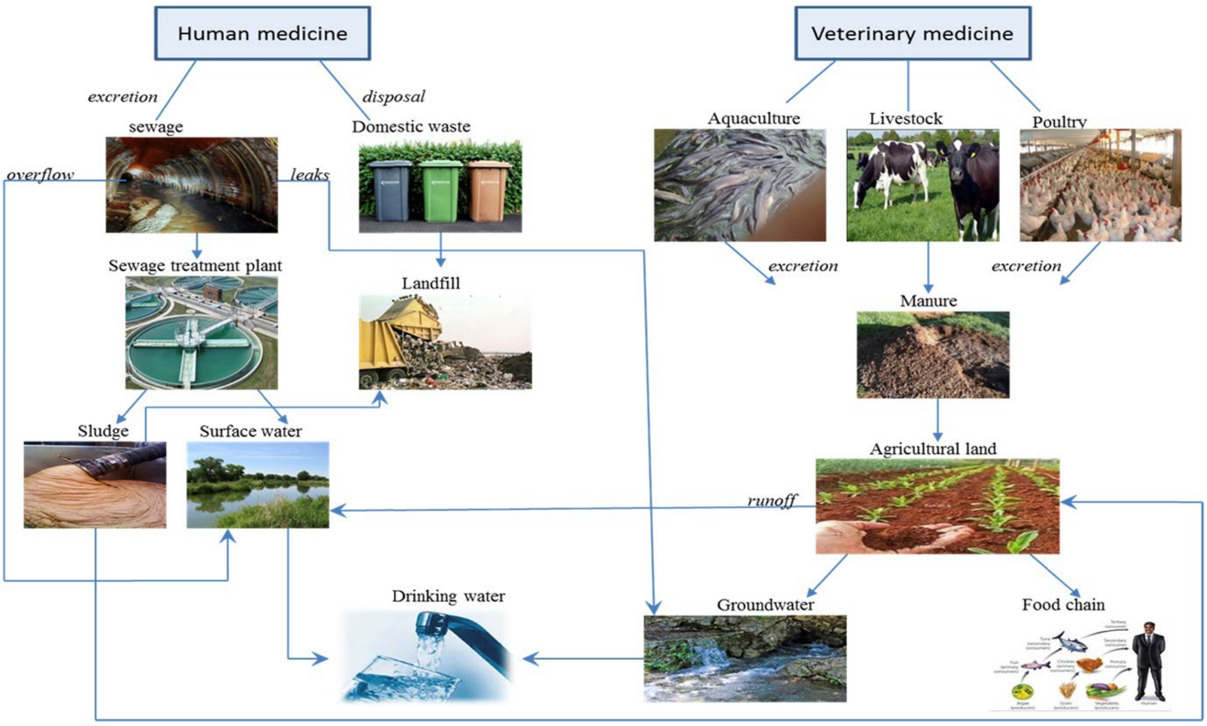

Figure 1: Sources of pharmaceutical pollutants and their pathway into environment. Reproduced from [11]. This is an open access article under the CC BY-NC-ND license (http:// creativecommons.org/licenses/by-nc-nd/4.0/).

Pharmaceutical micropollutants are hardly biodegradable, highly toxic, and persistent at low levels and as a result, they cause serious environmental concern for aquatic and human life[56]. Reportedly, the main sink of these pollutants in the environment includes effluents from wastewater treatment plants, sewage water, and ground water supply, causing feminization of male fish, and human health, by creating antibiotic resistant bacteria[1, 57, 58].

Although, non-steroidal anti-inflammatory drugs (NSAIDs) are present in the range of ng/L to µg/L, they pose various health threats including DNA damage, oxidative stress, behavioral changes, and bioaccumulation tissues in aquatic algae, fish and mollusks [52, 59, 60]. Diclofenac (DCF) is one of the commonly used NSAIDs, its continuous intake leads to several adverse effects on fish including cytotoxicity of gills and in human it can cause liver problems[61]. Risk of continuous use of DCF can be estimated from its classification by the United States Food and Drug Administration (US-FDA) as pregnancy risk class C [53, 62-65]. Another NSAID, ibuprofen, is one of the commonly used drugs for relieving pain in humans since 1960s and it is an emerging pollutant due to its refractory and persistent nature. Reports suggest its concentration around 20 ng/L in surface water and 3.8μg/L in sewage water. Its prolonged exposure for humans is cytotoxic, genotoxic and it can cause oxidative stress [39, 52]. Salicylic acid is one of the intermediates of ibuprofen and it is highly toxic, even it can delay postembryonic development among amphibians [39, 66]. Paracetamol overdose causes covalent modification in thiol group of proteins and ultimately death through nucleic acids damage, cell necrosis, and lipid oxidation [52]. Antibiotics presence in the environment causes generation of antibiotic resistant bacteria [67]. Many concerns relates also to tetracycline antibiotics [45]. Similarly there are other pharmaceuticals, such as norfloxacin (NOR) and carbamazepine (CBZ), highly hazardous for human health and disrupting embryonic development of aquatic organisms [68-70]. Fish grown in pharmaceutical-contaminated water may pose a serious health threat if they are consumed by humans. Unmetabolized or active ingredients of pharmaceuticals accumulate in fish that are not only harmful for themselves but also for human beings. Excellent reviews are referenced here for detailed information on sources, chemical nature, toxicity and potential risk of pharmaceuticals in water bodies [11, 67, 71-74]. To protect ecosystem from this existential threat, there is immediate need to remove or degrade these pollutants for water bodies.

3. Organic-inorganic nanohybrids (OINHs)

The term "hybrid" is defined as combination of two or more different components into a single material, while properties of both materials are reflected in that single material [49]. Organic-inorganic nanohybrids can be defined in more specific terms as combination of two components, organic and inorganic, to form a molecularly dispersed single material [50]. In terms of type, OINHs are classified into homogenous and heterogeneous materials. In homogenous nanohybrid, miscible organic and inorganic components are combined. While, in case of heterogeneous, these components are not miscible. Inorganic components are commonly a nanomaterials that have size dimension in the range of 1-100 nm [75]. In OINHs, the core material is of prime importance for its photocatalytic properties, particularly the band gap is a determining factor for performance. It is essential to critically analyze changes in band gap induced by doping with various materials. Typically, doping introduces an intra-band electronic energy level which reduces energy dissipation and is instrumental in enhancing separation of charges, i.e. an essential phenomenon for reaction initiation for the degradation of pharmaceuticals[76]. Secondly, g-C_3N_4 which is a metal-free polymeric system has been discussed. It has a band gap of 2.7 eV with a slight response to visible light. Another strategy to adjust band gap is formation of Z-scheme heterojunction where different energy levels are introduced leading to narrowing of band gap. Z-scheme heterostructures impart photocatalytic materials with higher separation efficiency of electrons-holes, wide range of light response, and strong redox ability[77]. For instance, Prabhavathi *et al.* synthesized Z-scheme heterostructures based on $CoWO_4$/ g-C_3N_4 and investigated its effectiveness against photocatalytic degradation of norfloxacin. Formation of Z-scheme heterostructures was instrumental in narrowing band gap from 2.7 to 1.90 eV leading to higher photocatalytic activity[68]. A similar phenomenon was observed in Z-scheme heterostructure of rGO/BSO/g-C_3N_4 where band gap was reduced from 2.7 to 2.34 eV [78]. There are several other reports, where Z-scheme heterostructures were synthesized aimed at narrowing band gap and enhancing catalytic performance [78-83]. Table 1 demonstrates the band gap of pristine core material in the range of 1-1.7 eV and 1.0-2.7 eV for rGO and g-C_3N_4, respectively. Compared to pristine core material, band gap of synthesized material may decrease [79, 84, 85] or increase[86-88] depending on several factors including synthesis, doping, and morphological features. Conventionally, decrease in band gap of material is desired for their efficient application in the degradation of pharmaceuticals. Although an increase in band gap was observed in some cases, this was not high enough to alter the photocatalytic properties of materials and, hence, reduce the photocatalytic activity for different pharmaceuticals degradation which remained high (88-97%). To make the material responsive in visible light range, a doping and heterostructure formation was found to be a successful strategy. Various studies reports changes in the band gap of these materials[89, 90]. More detailed information is discussed in another excellent review [91].

Table 1: Comparison of band gap values of core material before and after formation of OINHs.

OINHs material	Band Gap (eV)		Reference
	Pristine	Doped	
rGO/BSO/g-C_3N_4	2.7	2.34	[78]
$CoWO_4$/ g-C_3N_4	2.7	1.92	[68]
$SmVO_4$/g-C_3N_4	2.7 [91]	2.41	[85]
rGO/ Fe_2O_3/g-C_3N_4	2.7	1.82	[92]
Fe_3O_4/CeO_2/g-C_3N_4	2.7	1.50	[93]
g-C_3N_4@ZnO	2.7	2.27	[94]
g-C_3N_4/NiO/ZnO/ Fe_3O_4	2.7	2.8	[86]

In history of nanohybrids, clay-based nanohybrids were first materials of this class to be reported[95]. In OINHs, commonly employed inorganic components are metals, metal oxides, ceramics, layered double hydroxides, and magnetite whereas common organic components are polymers, and micelles [96, 97]. This unique class of materials is developed by self-assembly or grafting connection of inorganic clusters and organic components [98]. Sometimes, fragments of inorganic and organometallic complexes are used to construct OINHs [99]. In OINHs, beneficial properties of organic and inorganic materials are combined by discretely joining them into single domain [94]. In addition to beneficial properties of individual components, synergistic effect between the two components is also induced which results in excellent magnetic, electrical, and optical properties. Synergistically-induced optoelectrical properties widen the scope of these materials in various fields including photocatalysis [96, 100]. In OINHs, organic and inorganic components are joined through diverse interfaces and on that basis OINHs are divided into two classes. Class I include OINHs in which components are joined by weak interfaces such as hydrogen, electrostatic bonds, or Van de Waals forces. Unlike class I, in class II nanohybrids organic and inorganic components are joined by strong covalent or ionic-covalent bonds. Much of OINHs contain both type of interfaces but strong bonds dominate in determining the properties of class II materials[101]. Other than synthetic OINHs, nature is full of these materials, in fascinating forms, including shells, ivory, bones, ferritin, magnetotactic bacteria, and chitons. Nanohybrids biopolymers such as collagen and chitin are combined with inorganic materials including iron oxides, silica calcium compounds, and other composites through a variety of interfacial bonding [95]. Owing to unique and novel features of OINHs, they are used in biomedical application such as gene delivery, drug delivery, antimicrobial and imaging, while photocatalysis is an important application for environmental remediation[94, 102-104]. Owing to large surface area, structural stability and tunability, and excellent charge transfer properties, these are promising materials for photocatalytic removal of pharmaceuticals from wastewater through advanced oxidation process. For the systematic study of OINHs, we divided them into two classes on the basis of organic components, which are elaborated on following pages.

3.1 g-C_3N_4 based OINHs

Graphitic carbon nitride (g-C_3N_4) is a fascinating carbon-base conjugated polymer. Morphologically and structurally, it is a sheet like material with regular pattern of triazine units. Owing to its metal-free and highly light responsive nature, it has been under intensive attention of material scientists to harness its intrinsic properties for the development of novel materials for a variety of applications [105-107]. Particularly, its metal-free semiconductor nature and tri-s-triazine units are a game changers for photocatalytic applications, while it has a moderate band gap of 2.70 eV and responds in visible region up to 460 nm [108]. There are various studies that report on development of visible light responsive OINHs photocatalysts based on

$g-C_3N_4$ and other inorganic components. For instance, Hu *et al.* fabricated a binary OINH of $TiO_2/g-C_3N_4$ for the degradation of DCF and carbamazepine (CBZ) in wastewater. The synthesized photocatalyst was ecofriendly in nature and capable of degrading 98.9 % and 99.8% of DCF and CBZ within 90 min, respectively [70, 109]. Recovery of photocatalyst has been a challenging task in photocatalytic degradation of pharmaceutical pollutants in wastewater; to this end, Kumar *et al.* synthesized $C_3N_4/TiO_2/Fe_3O_4@SiO_2$ OINH having the feature of higher photoactivity with Z-scheme heterojunction system and magnetic recovery. The synthesized photocatalyst was employed for the degradation of ibuprofen (IBP) and the catalyst was able to remove 98% of ibuprofen (IBP) in 15 min under irradiation of visible light. Photocatalyst was recovered and reused revealing only 11% loss of photoactivity after three cycles, which indicates its stability and possibility of reuse [83]. For practical applications, structural stability is of prime importance. Liu *et al.* combined graphitic carbon nitride and graphene oxide in a ternary OINH $g-C_3N_4/Bi_2WO_6$/rGO and employed it for the photocatalytic degradation of IBP. An ecofriendly microwave assisted method was used to synthesize the photocatalyst. The as-synthesized photocatalyst led to 93% degradation of IBP. Crystal and morphological structure was observed after three cycles and photocatalyst showed no change of properties. To evaluate the activity of photocatalyst in real matrices, river water containing IBP was used for photocatalytic activity testing under sunlight and the result was promising for practical applications[110]. A comprehensive comparison of $g-C_3N_4$ based OINHs for the photocatalytic removal of pharmaceuticals from wastewater, alongside their synthesis strategy are presented in this review. Conclusively, $g-C_3N_4$ based photocatalysts offer highly suitable band gap, high chemical stability, and good electron carriers capability with cost effective and ecofriendly synthetic methods; these aspects present $g-C_3N_4$ based OINHs photocatalysts highly suitable for photocatalytic degradation of pharmaceutical in wastewater.

3.2 Polymer based OINHs

Polymers are large structural entities joined by same linkage between similar units. These are different form g-C_3N_4 in terms of offer better processibility, dispersibility and fine tuning for electron transfer process. In polymer based OINHs, polymer matrices with different size and shape are coupled with a variety of organic and inorganic materials. Such nanohybrids offer distinctive chemical and physical properties owed to synergistic effects between the two components[111]. Polymer based nanohybrids are excellent photocatalytic materials when coupled with nanomaterial semiconductors and one of the main advantages they offer is large surface area to volume ratio [112]. There are several polymers which have been employed to develop OINHs for photocatalytic applications including polyaniline[113], polypyrrole[114], polythiophene[115], and polyfuran [116]. Among these polymers, polyaniline attracted intensive attention from researchers owing to its higher stability, redox properties, tunable electrical conductivity, and low cost and easy synthesis [117]. To study the synergistic effect of polyaniline on photocatalytic properties, Kumar *et al.* fabricated magnetic ternary PANI/$LaFeO_3$/$CoFe_2O_4$ (PLC) nanohybrid through in situ polymerization of aniline and employed it for the photocatalytic degradation of pharmaceutical pollutant clozapine (CZP). Polymer based composites degraded 94.2 % of pharmaceutical pollutant in 120 min. The photocatalytic activity of the polymer based OINHs was far greater than its individual components [82]. Polypyrrole is another polymer which has been employed for the preparation of core-shell nanohybrid with ZnO and employed for the degradation of DCF. Ppy-ZnO degraded 81% of DCF under sunlight irradiation which was higher than individual polypyrrole and ZnO. Higher photocatalytic activity was attributed to large surface area, mesoporous structure and narrow band gap of nanocomposite [19]. For the degradation of ibuprofen (IBP), poly (o-phenylenediamine)/antimony oxide nanohybrid was fabricated. POPD/Sb_2O_3 nanohybrid degraded 92% of pharmaceutical pollutant in 60 min under sunlight irradiation. Polymer nanohybrid lost only 5.3% of its initial photocatalytic activity, which indicates that it is highly stable and can be employed for practical applications [118]. Summarized data elaborated further on polymer based OINHs for photocatalytic removal of pharmaceuticals from wastewater. In summary, polymer based OINHs offer large surface area, higher stability, narrow band gap, and cost effectiveness.

4. Synthesis Approaches of OINHs

Several various methods are used to synthesize organic-inorganic nanohybrids including sol-gel method, one pot synthesis, surface functionalization, and wrapping method. The most commonly used methods for the development of OINHs are presented in Figure 2 *[94]*. The advantages and drawbacks of each method are discussed in detail in following parts of this section. The selection of method mainly depends on target application, while the less time consuming, cheaper and more ecofriendly methods are given priority.

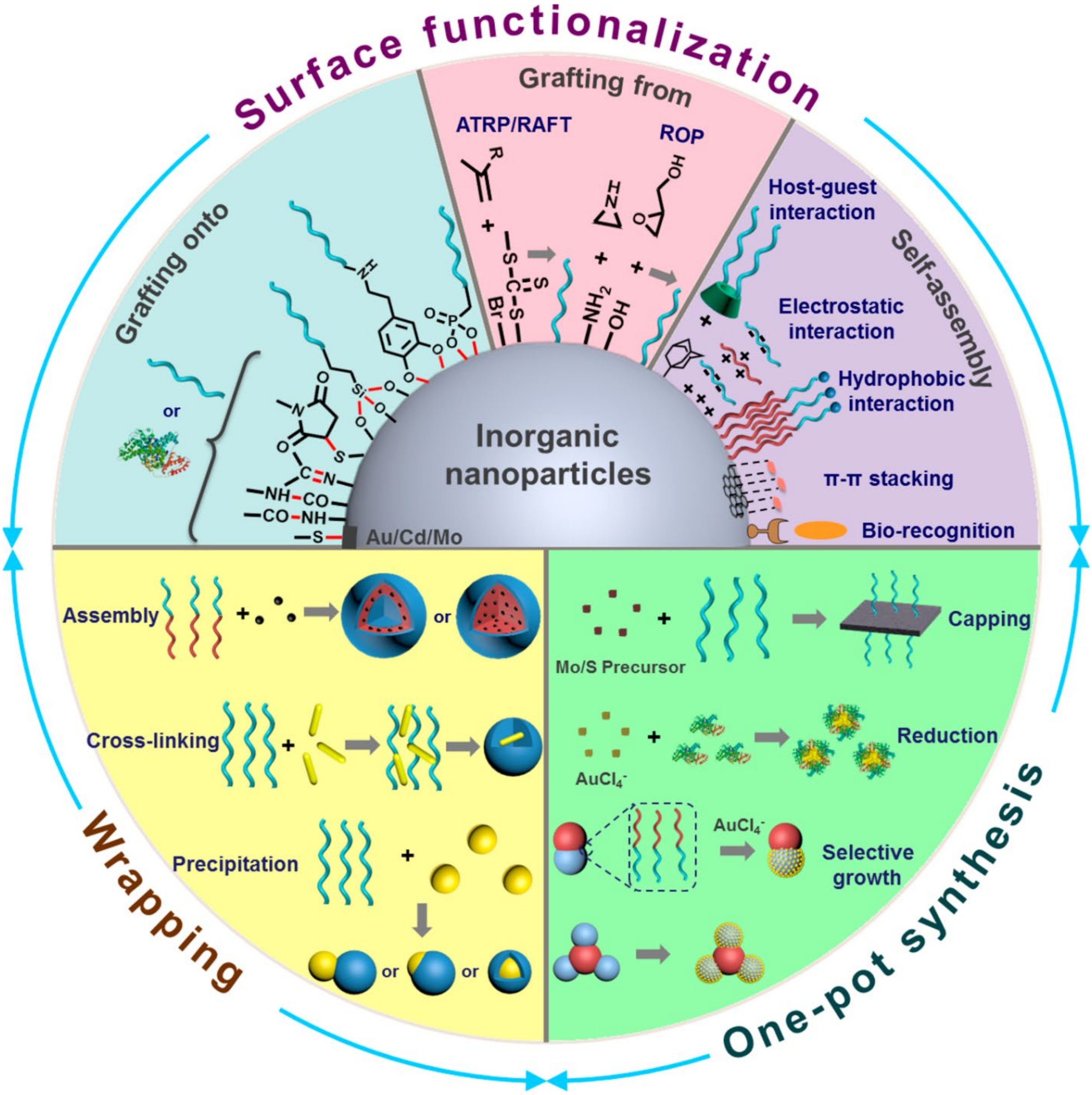

Figure 2: Most commonly employed methods for the development of OINHs. Reproduced with permission from [94]. Copyright ©2018, American Chemical Society.

4.1 Sol-Gel method

In sol-gel method, organic and inorganic components are chemically mixed at nanometric scale [119, 120]. Typically, inorganic components are dispersed homogenously in organic solvent which results in the formation of metal-oxo polymers. Sol-gel method is advantageous in terms of energy efficiency and control of chemical structure of product; this method requires mild temperature (80-100°C) for synthesis of OINHs [121, 122]. Typically, sol-gel method constitutes five steps including hydrolysis, polycondensation, aging, drying, and thermal decomposition, as exhibited in Figure 3 [123].

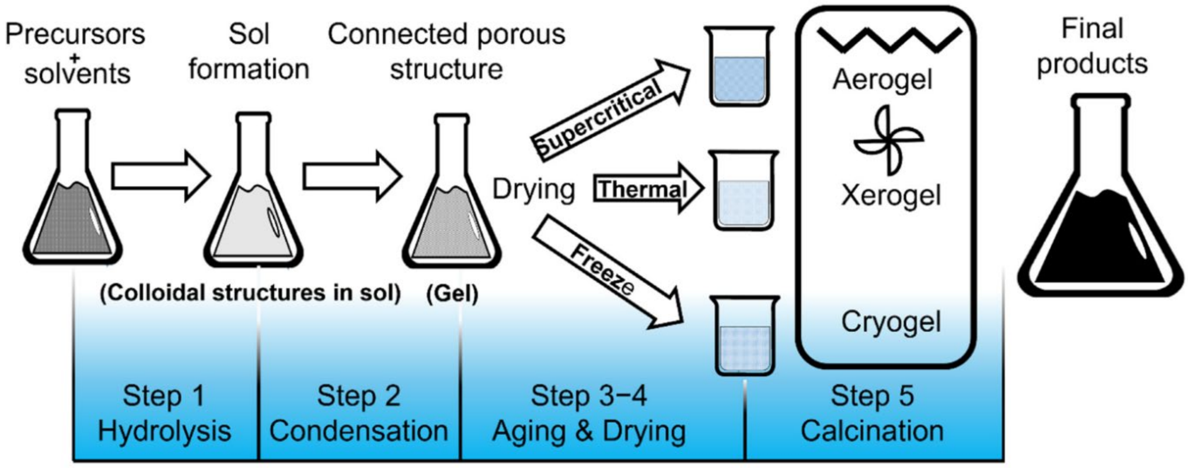

Figure 3: A schematic diagram of sol-gel method for synthesis of organic inorganic nanohybrids[123] This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Chemical reaction starts from sol which is gradually converted into gel-like material. After gel formation, the reaction mixture forms a biphasic system in which sol and gel co-exist while having diverse morphology with presence of discrete particles to continuous network of polymers. Next step involves the removal of solvent followed by drying of the product. During this step, the solvent is evaporated and the reaction mixture undergoes shrinkage and densification. During drying, porosity of the product can be controlled through rate at which the solvent is removed and so can the distribution of the pores. Super critical drying is considered to be the best method as it results in uniformly distributed product and prevents aggregation [124]. Zinc oxide doped polythiophene and polyimide-polydiphenylsiloxane (PI-PDPS) nanohybrids were prepared through the same method [51, 125]. Sol-gel process is advantageous in terms of low temperature requirement, high purity product, structural control, and control of the size of material.

4.2 Surface functionalization technique

Surface functionalization is one of the most widely used techniques for the synthesis of OINHs as well as the target oriented functionalization of any surface. Basically, there are three strategies that are employed in surface functionalization including grafting from, grafting on, and the self-assembly. For integration of nanoparticles and polymers, grafting on is the easiest way in which polymer is grafted on surface of synthesized NPs. A fixed molecular weight of grafted polymer is utilized and, in case of steric hindrance, chemical substitution is employed to enhance grafted density. To obtain best performance from gold NPs, various stabilization strategies are employed[126-128]. Thiol group is well known for its attraction toward metals, thiol-ended polyethylene glycol has been used to stabilize gold NPS and this is a good example of grafting on approach [94]. Grafting on based surface functionalization offers synthesis convenience and higher levels of effectiveness. Grafting from is a type of bottom up type of surface functionalization. In this strategy, organic layer of polymers is formed through polymerization in which polymer chains are bound to functional materials [129]. In situ polymerization is also considered as grafting from strategy. Examples include clay base OINHs for various applications [130, 131]. Grafting from strategy offers control over architecture, molecular weight and composition of nanohybrids. Self-assembly is a process in which specific interaction of organic and inorganic components is employed for the spontaneous bottom up organization of OINHs. β-CD and hydroxypropyl-β-cyclodextrin (HP-β-CD) are commonly used materials to initiate synthesis of self-assembled OINHs. β-CD possesses hydrophilic and hydrophobic moieties for such interactions and also has favorable size. This is also employed for gate mechanism to introduce host-guest recognition for trapping of specific molecules for catalysis [132, 133]. Surface functionalization is easy and cost effective, while providing much better control over properties of synthesized material.

4.3. One-pot synthesis

One pot synthesis nanohybrids are prepared simultaneously in a single reaction. It is simple and efficient in terms of cost and strategy for synthesis of OINHs and other functional materials[134]. Generally, in one pot synthesis all components are subjected to a series of successive chemical reactions in single reaction chamber. Owing to absence of formation any intermediate chemical compounds, this method helps in avoiding lengthy separation or purification process[135]. Organic molecules act as structure directing groups and it is convenient, simple and time saving method for synthesis of OINHs. In one pot synthesis, a variety of functional groups can be introduced to modify functionality of nanoparticles, which generate desirable properties in produced material. For instance, precipitation of iron oxide nanoparticles in the presence of carboxymethyl cellulose (CMC) enhances hydrophilicity and biocompatibility of the product [136]. There is no need for introduction of additional chemical reagents such as surfactants and emulsifiers in one pot synthesis and this makes it cheap and ecofriendly method [137]. It has been also used for binding of folate molecule on the surface of Mn_3O_4 without employing any linker molecule and this method proved to be cost effective [138]. Many molecules of interest can be combined in single domain through one pot synthesis without compromising on binding affinity of any molecule [139, 140]. Liang *et al.,* synthesized g-C_3N_4-Fe_2O_3 through one-pot synthetic method and employed in photocatalytic dyes degradation for wastewater treatment along with investigation of magnetic properties. While outlining drawbacks of other methods, it has been mentioned that one pot synthesis is highly advantageous in hindering electron-hole recombination ultimately leading to higher photocatalytic properties [141]. One pot synthesis is cost effective, easy, ecofriendly and offers a higher level of control of structural and functional properties.

4.4 Method of wrapping

In the wrapping method, inorganic molecules are encapsulated in organic matrix through self-assembly or direct encapsulation. In this method, noncovalent interactions are employed as binder for generation of OINHs. Basically, a core is generated around which organic or polymer molecules start wrapping, thus ultimately resulting in a core-shell structure. In wrapping method, diversity of functional group can be added; for instance, addition of organic functional groups in metal organic frames containing metal ions and their core around inorganic nanoparticles result in core shell nanohybrids. Synthesis of Fe_3O_4@OCMC@IRMOF-3 proceeds through wrapping method in which ferrites and chitosan composites are prepared separately and then added into the organic solvent with metal organic framework precursor. The reaction mixture is poured in autoclave and placed in a heating oven at 100°C for 6 h after thorough sonication. A deep reddish-brown color product was obtained which was washed with ethanol and water and dried [142]. Through similar procedures, a polysacchrides@iron oxide has been prepared having core shell structure [143]. There is another technique in which solution intercalation phenomenon is used. It is widely used in wrapping of silicate where silicates are exfoliated into monolayers in the presence of polymers/prepolymers. Polymers wrap around monolayers of exfoliated silicates and produce a covered nanohybrid [130, 131, 144]. Melt intercalation is a similar phenomenon except that layered silicates are in molten state and this permits higher quality interactions between the two components, thus producing exfoliated nanocomposite [145]. Although various components can be introduced in nanohybrids through wrapping method, it does not offer control over structure and composition of product and can lead to compromise on properties.

4.5 Electrospinning of nanohybrids

In this case, the polymer to be deposited is dissolved in suitable solvent and then potential difference is applied, causing charge deposition on the polymer solution droplets. Next, charge on liquid droplet overcomes the surface tension of polymers solution and jumps toward metal plate, thus forming nanofibers [146]. There is no need for extra step of drying since, during the process, the solvent is evaporated and the product is collected. Electrospinning offers formation of high surface area materials, tunable porosity and control over functionalization [147]. OINHs are synthesized by mixing of nanofibers material, polymers in suitable organic solvent to prepare a homogenized slurry. Volatile organic solvent is employed to obtain a stable and viscous slurry which is ejected through syringe, while potential difference is applied [148, 149]. There are several reported reviews that elaborate on recent advancements and application of electrospinning technique in nanofabrication. Electrospinning is cheap, simple, ecofriendly and versatile technique, which is used to prepare particularly nanofibers based nanohybrids for a variety of applications. Electrospinning results in formation of nanofibers that offer expanded surface area and porosity with excellent reusability. Li *et al.,* elaborated recent developments in field of electrospinning with outlining emerging technologies while discussing, single needle, multi-needle, needle less technologies for electrospinning. A detailed discussion on fibre structure, molecular orientation, optical and mechanical properties of electrospun material has been elucidated with their application in relevant field [150]. An excellent reviews on detailed discussion on electrospun fibres and their application in wastewater treatment technologies are available [151, 152].

Based on analysis of all synthetic method for OINHs, following table present advantages and disadvantages of these methods

Table 2: Advantages and disadvantages of different methods for synthesis of OINHs.

Synthesis Method	Advantages	Disadvantages
Sol-gel method	Low temperature, high purity, structure and size control.	Highly sensitive to environmental conditions.

Surface functionalization	Easy to handle, cost effective with comparable control over product feature.	Limited to surface only, intrinsic features cannot be improved.
One-pot synthesis	Cost effective, higher control over structural and morphological properties.	For better performance, the product may require post-synthetic modification.
Method of wrapping	Excellent for combination of various components.	Offer less control on composition and structure of product.
Electrospinning of nano-hybrids	Cheap, eco-friendly, and versatile technique, ideal for nanofibers.	Compromised surface and physical properties, available for limited number of materials.

5. Photocatalysis

In photocatalysis, when light photon (hυ) with energy greater than or equal to band gap (Eg) of semiconductor photocatalyst irradiates the material, electrons (e^-) are excited from valence band (VB) to conduction band (CB) leaving an electron hole (h^+) in valence band. Photogenerated electrons migrate toward the surface of photocatalyst and react with water to produce highly reactive chemical species such as $O_2^{\bullet -}$ and $HO^\bullet$. These radical species react with pharmaceutical molecules and degrade them into simple molecules (Figure 4) [153]. There are two phenomena that control photocatalytic activity of semiconductor, which are the photoexcitation rate of charged carriers and their recombination rate. These two act oppositely, higher photoexcitation means higher photocatalytic activity, while higher recombination rate means loss of energy and lower photocatalytic activity. For efficient photocatalytic activity, first prerequisite is to prevent the $e-/h^+$ recombination. The following equations represent the reactions occurring during the entire photocatalytic process [154, 155].

$$OINH + h\upsilon \rightarrow OINH\ (h^+_{(VB)} + e-_{(CB)}) \quad (1)$$

$$h^+ + H_2O \rightarrow HO^\bullet + H^+ \quad (2)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (3)$$

$$2e^- + 2H^+ + O_2^{\bullet -} \rightarrow HO^\bullet + OH^- \quad (4)$$

$$h^+ + OH^- + H_2O \rightarrow HO^\bullet + H^+ \quad (5)$$

$$^\bullet O_2- + {}^\bullet OH + h^+ + Drug \rightarrow \text{Intermediate product} \rightarrow \text{Degraded product} \quad (6)$$

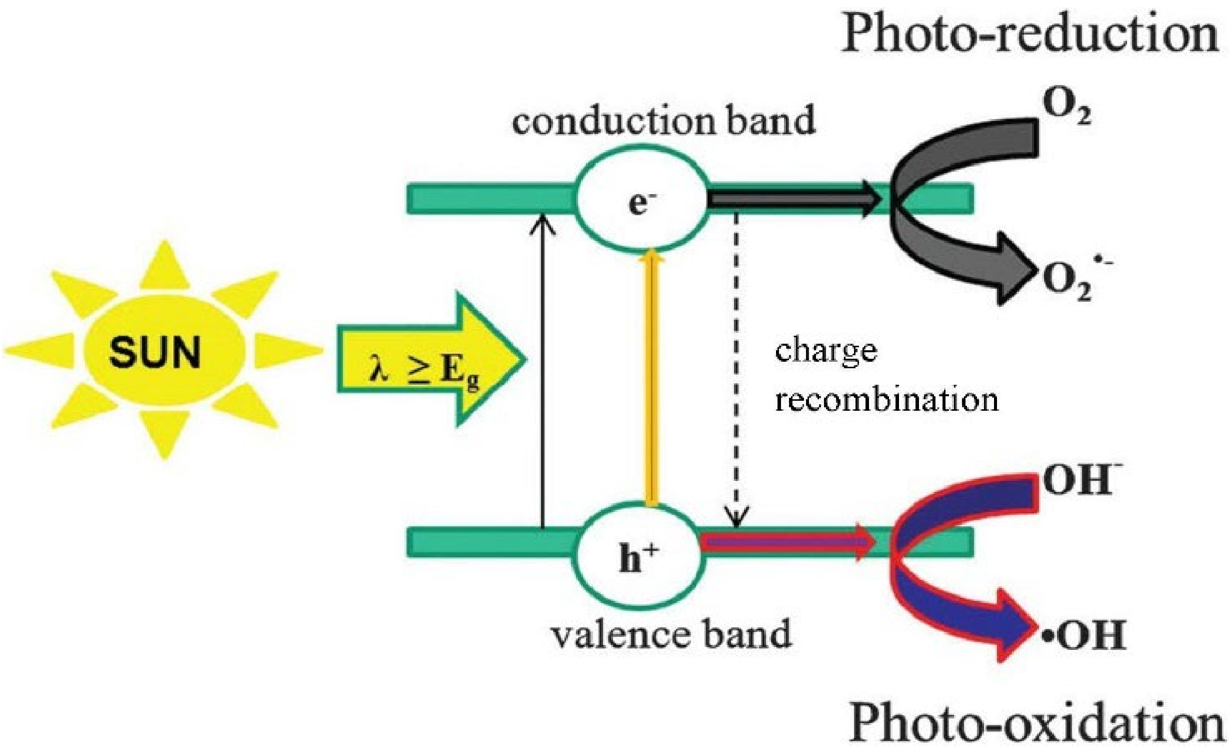

Figure 4: Schematic representation of photocatalytic process [153]. This is an open access article under the Creative Commons Attribution 3.0 Unported License (https://creativecommons.org/licenses/by/3.0/).

OINHs based photocatalysts undergo same reaction steps (1-6) for photocatalytic mineralization of pharmaceutical drugs. There are many research papers which report photocatalytic mineralization of various pharmaceuticals such as DCF [84], ibuprofen, sulfamethoxazole [156], paracetamol [157], ciprofloxacin [158], naproxen [78], tetracycline [81] etc. Owing to complex chemistry and different chemical structure there are different mechanisms of photocatalytic degradation of different pharmaceuticals. To investigate degradation reaction pathways, intermediates are determined and on the basis of their chemistry, the respective mechanism is developed. On the other hand, reactive oxygen species (ROSs), as well as h^+ and e^- contribution to the degradation mechanism are studied by means of scavenging tests as well as EPR technique.

Mechanism of degradation of TC is determined first based on the proportion of formed reactive oxygen species. Later degradation by-products (typically by chromatographic techniques coupled to mass spectrometry) are analyzed to define degradation pathways. As photocatalytic mineralization is determined by analysis of intermediates, different pathways are possible owing to diversity of intermediates. Shanavas *et al.* proposed two mechanisms for the visible light driven degradation of tetracycline using Cu/$Bi_2Ti_2O_7$/rGO (*Figure 5*). The process produces hydroxyl and superoxide radicals and electron holes after sunlight radiation of the surface of the photocatalyst. These radicals attack TC molecules and its intermediates ultimately leading to the formation of carbon dioxide, water and ammonium ion. To be specific, there are four active species that are produced by photocatalyst on incessant striking of sunlight on its surface and these include $^{\bullet}OH$, $^{\bullet}O_2^-$, h^+ and e^-. These active species attack TC and convert it into by-products with lower molecular weight. The degradation mechanism starts with cycloaddition of $^{\bullet}OH$ radical at 11C-12C double bond of TC leading to the formation of T1 intermediate with m/z of 461. Two methyl groups are removed from tertiary amine of T1 and T2 intermediate having m/z of 434. T3 intermediate having m/z of 394 is formed through the removal of formamide and T4 with m/z of 375 is formed by further removal of hydroxyl group. T5 (m/z; 172) and T6 (m/z; 209) intermediates are formed by cleavage of 5C-6C and 11C-12C of T4, respectively. In a final step, these intermediates are converted into water, carbon dioxide, and ammonium ions. Second mechanism of degradation starts with removal of methyl groups from TC and Produce a T7 with m/z of 416. Further degradation proceeds with removal of amino group from 5C and formamide leading to formation of T8 (m/z; 402) and T9 (m/z; 358), respectively. Second, last step is similar in both mechanism as thy involve cleavage of 5C-6C and 11C-12C leading to formation of T10 (m/z; 173) and T11 (m/z; 191), respectively. A CO_2, H_2O, and NH_4^+ are final products in both mechanisms (Figure 5) [159]. Along with these two possible mechanism of TC degradation, the literature reports several other routes where photocatalyst of different nature involved and produce varying proportion of reactive species. Tan *et al.* reported two different degradation pathways taking place during application of Z-scheme β-Bi2O3/ZrO2 heterojunctions with 3D mesoporous SiO2 nanospheres as photocatalyst where deamination and demethylataion has been the first step of two methods initiating a series of steps toward formation of mineralized product [160]. In another study, degradation of TC was assisted by carbon quantum dots-decorated BiOCl nanosheet/carbonized eggshell membrane composite. In this study a three different pathways were reported. A dehydration, dealkylation, and hydroxylation has been reported as first step [161]. There is also a study where a synergistic effect between photocatalysis and adsorption for TC degradation has been reported [162]. In this case a 1D/2D $La(OH)_3/(BiO)_2OHCl$ heterostructures were used. Although, all these studies reported different pathways for degradation of TC, at the end, they all result in the total mineralization with formation of CO_2, H_2O, and NH_4^+.

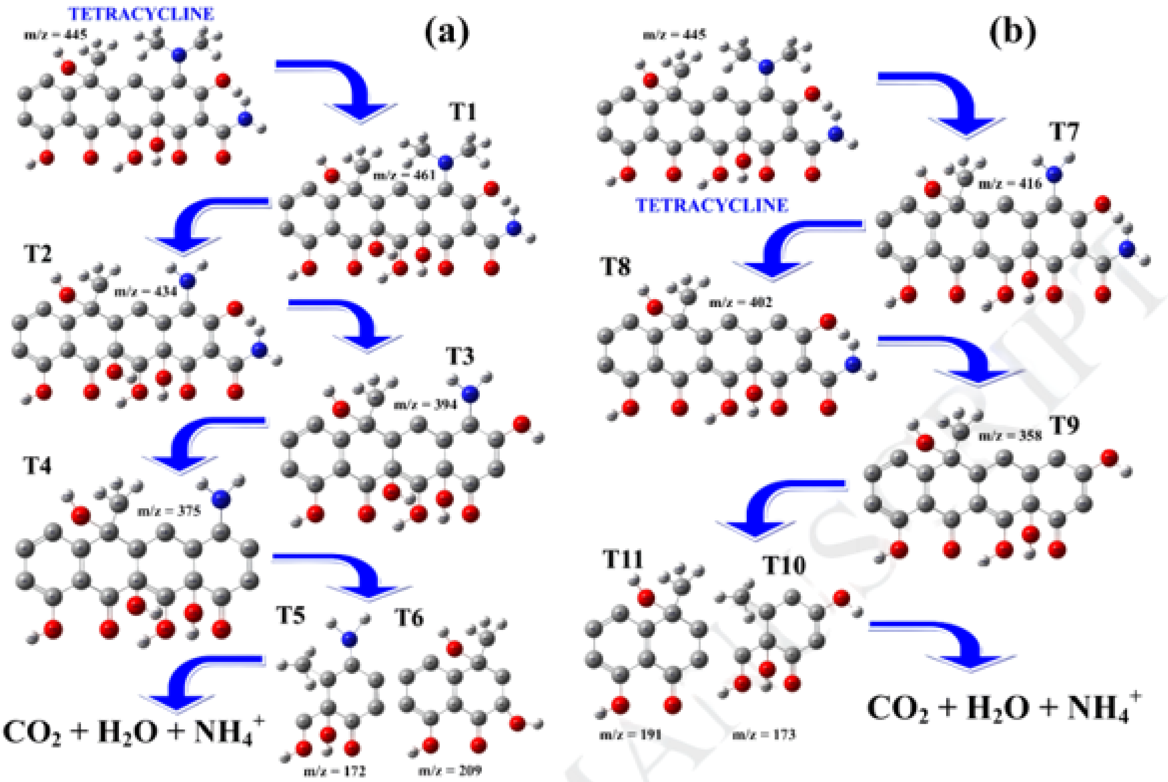

Figure 5: Two possible degradation reaction pathways for the photocatalytic degradation of TC. Reproduced from [159] with permission from Elsevier. License number: 5607760983949.

6. Application of OINHs for the removal of pharmaceuticals

OINHs are classified into three classes on the basis of their organic component. Among g-C_3N_4 based OINHs, nitrogen doped carbon dot decorated Bi_2MoO_6/g-C_3N_4 showed highest photodegradation efficiency for the removal of ciprofloxacin (CIP). Synthesized photocatalyst had band gap of 2.07 eV and showed 99% photocatalytic degradation of model pollutant in aqueous solution, in 30 min. There are five factors that make this photocatalyst better than others: (1) hydrophilicity, (2) large surface area (43.7 m^2/g), (3) higher light absorption, (4) low impedance, (5) good crystallinity. Hydrophilicity coupled with oxygenated surface enhances the adsorption of target pollutant for degradation. Large surface area is beneficial in terms of providing more active sites and enhanced photocatalytic activity. Photoexcitation of charged carriers solely depends upon absorption of sunlight, higher sunlight absorption means higher rate of photocatalytic activity. Photoexcitation of electrons is not the only factor that heavily influences photocatalytic efficiency. Migration of charged carriers and prevention of their recombination are also an important factor. Moreover, low impedance supports a robust electron-hole pairs migration and good crystallinity facilitates the prevention of their recombination[163]. Coupling of conducting polymers and functional material has been widely used for a variety of applications including photocatalytic removal of pharmaceuticals from wastewater. Mohamed *et al.* synthesized PAN-MWCNT/TiO_2–NH_2 OINHs to combine individual properties of polyaniline as an excellent stabilizer, MWCNT to improve tensile strength and electron conduction and cost effectiveness, ecofriendly nature and higher photocatalytic activity of TiO_2 [164-168]. As synthesized photocatalyst was employed for the degradation of three pharmaceutical pollutants that are commonly present in wastewater including ibuprofen, naproxen, and cetirizine, 99% of pollutants were degraded in the presence of UV irradiation. Different parameters were studied and optimized conditions were reported for practical applications. Photocatalyst was highly stable as it showed minor loss of its activity even after 5th cycle[169].

In a nutshell, production of OINHs for photocatalytic degradation of pharmaceuticals in wastewater is an excellent technique for environmental remediation that needs to be executed at large scale. In OINHs, synergistic impact of each component is vital factor that mainly promotes photocatalytic activity of the material.

 Table 3: Application of OINHs in photocatalytic degradation of pharmaceuticals with performance parameters and conditions

Graphitic carbon nitride based OINHs

Nanohybrid Photocatalyst	Method of synthesis	Band Gap (eV)	Pollutant	Conditions					Degradation Effectiveness (%)	Rate Constant	References
				Catalyst Dosage	Pollutant concentration	pH	Irradiation Time (min)	Light Source			
$CeVO_4$/g-C_3N_4	Hydrothermal method	1.99	CIP	0.5 g/L	6.6 mg/L	3	70	Visible light	92	0.2504 min^{-1}	[85]
CdS-g-C_3N_4	Chemical precipitation method	2.45	CTX	0.06 g/L	15 mg/L	10.5	81	Visible light	93	0.0336 min^{-1}	[170]
N-doped Carbon dot/g-C_3N_4/ $BiMoO_6$	Hydrothermal method	2.07	CIP	1 g/L	5 mg/L	8	30	Visible light	99	0.13 min^{-1}	[163]
$SmVO_4$/g-C_3N_4	Hydrothermal method	2.41	CP	0.4g/L	20 mg/L	3	105	Visible light	94	0.2704 min^{-1}	[85]
g-C_3N_4/TiO_2/Fe_3O_4@SiO_2	Sol-gel route	N/A	IBP	1 g/L	2 mg/L	7	15	Visible light	97	N/A	[83]
rGO/ Fe_2O_3/g-C_3N_4	Hydrothermal	1.82	TC CIP	0.1 g/L	50 mg/L	7	60	500 W halogen lamp	98 97	0.7088 min^{-1} 0.5187 min^{-1}	[92]

Fe_3O_4/CeO_2/g-C_3N_4	Hydrothermal	1.50	TCH	1 g/L	50 mg/L	2.7	180	300 W xenon lamp	97	0.0533 min^{-1}	[93]
g-C_3N_4/Bi_2WO_6/rGO	Microwave-assisted rout	N/A	IBP	0.5 g/L	5 mg/L	4.3	60	Visible light	93	0.011 min^{-1}	[110]
g-C_3N_4/NiO/ZnO/ Fe_3O_4	Hydrothermal	2.8	ESP	0.7 g/L	30 mg/L	6	70	23 W white LED bulb	95	0.06616 min^{-1}	[86]
CdS/g-C_3N_4/4AZ	Chemical precipitation method	2.10	CFP	0.4 g/L	17 mg/L	9	80	Visible light	93	3.71×10^{-2} min^{-1}	[171]
Ultrathin porous P-doped g-C_3N_4	One-step thermal polymerization method	N/A	DCF	0.4 g/L	5 mg/L	4.34	20	LED light	99	0.1248 min^{-1}	[172]
g-C_3N_4@ZnO	Thermal atomic layer deposition method	2.27	CEX	0.3 g/L	10 mg/L	N/A	60	Sunlight	99	0.0735 min^{-1}	[94]
Fe_3O_4/g-C_3N_4/MoO_3	Calcination method	N/A	TC	0.4 g/L	40 mg/L	7	120	1000 W xenon lamp	94	$1.63 \text{ x } 10^{-2}$ min^{-1}	[173]
$Ce_2(WO_4)_3$@ g-C_3N_4	Hydrothermal route	2.69	MXF	0.5 g/L	10 mg/L	N/A	60	Visible light	94	0.0594 min^{-1}	[174]
TiO_2/g-C_3N_4	Solvothermal method	2.76	IBF	1 g/L	5 mg/L	N/A	60	Visible light	95	0.03833 min^{-1}	[175]
TiO_2/g-C_3N_4	Ultrasonication method	2.02	DCF	0.1 g/L	10 mg/L	6.4	30	Visible light	98.2	0.1796 min^{-1}	[176]
$CoWO_4$/g-C_3N_4	Hydrothermal method, followed by ultra-sonication	1.85	NOR	0.5 g/L	10 mg/L	N/A	80	Visible light	97	0.000471 min^{-1}	[68]

MoS_2/g-C_3N_4/ $Bi_{24}O_{31}Cl_{10}$	Impregnation-calcination method	N/A	TC	0.01 g/L	20 mg/L	N/A	50	Visible light	98	0.06429 min^{-1}	[80]
g-C_3N_4/Zn doped Fe_3O_4	Solvothermal route	N/A	CEX	0.5 g/L	10 mg/L	6	30	Visible light	91	0.0645 min^{-1}	[177]
Polymer based OINHs											
PPy-ZnO	Polymerization method	1.81	DCF	1 g/L	10 mg/L	6	60	UV-Vis Light	81	0.986 min^{-1}	[19]
PANI/$LaFeO_3$/$CoFe_2O_4$	In situ polymerization	2.25	CZP	0.3 g/L	50 mg/L	6	120	Visible light	94	0.0248 min^{-1}	[82]
Chitosan-glyoxal/Polyvinylpyrrolidone/MoS_2 (CSG/PVP/MoS_2)	Hydrothermal-ultrasonic method	2.12	DCF	0.1 g/L	100 mg/L	5	50	UV-light	95	0.0195 min^{-1}	[178]
$ZnFe_2O_4$@CMC	Hydrothermal	1.4	CIP	0.3 g/L	5 mg/L	7	100	6 W UV lamp	87	0.277 min^{-1}	[179]
POPD/Sb_2O_3	In-situ oxidative polymerization method	1.35	IBP	N/A	50 mg/L	N/A	60	Sunlight	91	0.1725 min^{-1}	[118]
Pt@PPy-C/ZnO	Sol-gel route and ultrasonication methodology	2.65	LIZ	0.1	20 mg/L	N/A	40	Visible light	94	0.066 min^{-1}	[122]
PAN-MWCNT/TiO_2–NH_2	Polymerization method	N/A	IBP	0.3 g/L	5 mg/L	2	120	UV Light	99	N/A	[169]
			NPX				25				

			CIZ				45				
rGO/PANI/C-ZnO	Polymerization method	2.80	ACP	0.1 g/L	10 mg/L	N/A	100	Solar light	47	0.0055 min^{-1}	[180]
Fe_2O_3@PPy/rGO	Chemical reflux	N/A	ACP	0.6 g/L	1 mg/L	7.4	120	UV- Light	84	N/A	[181]
PANI/ZrO_2	Hydrothermal method	3.16	CIP	1g/L	13 mg/L	N/A	120	UV-light	96	N/A	[182]

7. Current challenges and future recommendations

Although there has been a lot of developments in the OINHs field for photocatalytic degradation of pharmaceutical pollutants from water bodies, these developments are far from practical application. Currently this field faces challenges from two sides, one issue is related to synthesis of photocatalysts and mechanism of photocatalysis, while the second is the diversity of pharmaceuticals. Synthesis is highly expensive, complicated and time consuming. These are big challenges that must be addressed through the development of properly optimized synthesis methods. In many cases, such aspects are not reported in the papers; authors omit to discuss the issues and limitations of developed materials. In the current review work, only lab scale applications have been studied and there has been no investigation of OINHs in real water matrices which are highly complex mixtures of various compounds, this needs to be addressed for practical applications. Photocatalysts efficiency can be enhanced by preventing recombination of electron and hole pairs and this can be achieved by band engineering and selection of suitable semiconductor materials. Second major challenge comes from diverse structure of pharmaceuticals that may be treated by a limited number of photocatalysts. There is a limited number of reports in which photocatalytic degradation of more than one pharmaceutical pollutant was investigated. It seems that only best results are reported, instead of critical evaluation of universal character/selectivity of the catalyst. Diverse structure of pharmaceutical and resulting intermediates are huge challenges, which can create more toxicity in comparison to the parent chemicals. To overcome this challenge there is need of development of methodology to control nature of intermediates and end product. Currently, risks of nitro-derivatives as by-products in AOPs are widely reported[183, 184]. This aspect should be addressed in respect to OINHs based processes. Table 1 reveal that most studies report photocatalytic degradation of NSAIDs [118, 169], no doubt they are widely used pharmaceuticals but there is need to work on degradation of other pharmaceutical and related pollutants such as antineoplastic, beta blockers, steroids, hormones, psychotropic, and personal care products. To address current challenges and advancement in the field, future researches should be focused on development of cost effective, ecofriendly, simple, and mild condition method for synthesis of OINHs having fully optimized crystallinity and band structure. For practical application, work should be done on diversification of pharmaceuticals.

8. Conclusions

Diseases are integral part of life which are cured through pharmaceuticals. Excessive and uncontrolled use of these pharmaceutical results in their release in environment particularly in water bodies and cause harms to human, animals, aquatic life and ecosystems. This review summarizes latest literature on removal of these toxic pharmaceutical from water bodies via advanced oxidation process based on photocatalysis. This review provides reader with vital information about OINHs as photocatalyst for photocatalytic removal of pharmaceutical from water bodies. OINHs are excellent photocatalytic materials owing to their novel properties for photocatalytic removal of pharmaceuticals and they can be optimized for large scale application. We believe, this review provides enough information for future researchers and we hope future researches will be focused on synthesis of OINHs photocatalyst and diversification of pharmaceutical to achieve industrial scale applications.

Acknowledgements

The authors gratefully acknowledge financial support from the National Science Centre, Warsaw, Poland for project OPUS nr UMO-2021/41/B/ST8/01575.

References

1. Corcoran, J., M.J. Winter, and C.R. Tyler, *Pharmaceuticals in the aquatic environment: a critical review of the evidence for health effects in fish.* Critical reviews in toxicology, 2010. **40**(4): p. 287-304.
2. Boxall, A.B., et al., *Pharmaceuticals and personal care products in the environment: what are the big questions?* Environmental health perspectives, 2012. **120**(9): p. 1221-1229.
3. Desbiolles, F., et al., *Occurrence and ecotoxicological assessment of pharmaceuticals: is there a risk for the Mediterranean aquatic environment?* Science of the Total Environment, 2018. **639**: p. 1334-1348.
4. Tran, N.H. and K.Y.-H. Gin, *Occurrence and removal of pharmaceuticals, hormones, personal care products, and endocrine disrupters in a full-scale water reclamation plant.* Science of the Total Environment, 2017. **599**: p. 1503-1516.
5. Tran, N.H., M. Reinhard, and K.Y.-H. Gin, *Occurrence and fate of emerging contaminants in municipal wastewater treatment plants from different geographical regions-a review.* Water research, 2018. **133**: p. 182-207.
6. Xie, H., et al., *Pharmaceuticals and personal care products in water, sediments, aquatic organisms, and fish feeds in the Pearl River Delta: Occurrence, distribution, potential sources, and health risk assessment.* Science of the total Environment, 2019. **659**: p. 230-239.
7. Javid, N., Z. Honarmandrad, and M. Malakootian, *Ciprofloxacin removal from aqueous solutions by ozonation with calcium peroxide.* Desalination and Water Treatment, 2020. **174**: p. 178-185.
8. Sun, X., et al., *A review on hydrodynamic cavitation disinfection: The current state of knowledge.* Science of the Total Environment, 2020. **737**: p. 139606.
9. Boxall, A.B., *Pharmaceuticals in the Environment and Human Health.* Health Care and Environmental Contamination, 2018: p. 123-136.
10. Robinson, A.A., J.B. Belden, and M.J. Lydy, *Toxicity of fluoroquinolone antibiotics to aquatic organisms.* Environmental Toxicology and Chemistry: An International Journal, 2005. **24**(2): p. 423-430.
11. Ebele, A.J., M.A.-E. Abdallah, and S. Harrad, *Pharmaceuticals and personal care products (PPCPs) in the freshwater aquatic environment.* Emerging contaminants, 2017. **3**(1): p. 1-16.
12. Honarmandrad, Z., et al., *Activated persulfate and peroxymonosulfate based advanced oxidation processes (AOPs) for antibiotics degradation–A review.* Water Resources and Industry, 2022: p. 100194.
13. Khataee, A., M. Fathinia, and S. Joo, *Simultaneous monitoring of photocatalysis of three pharmaceuticals by immobilized TiO2 nanoparticles: chemometric assessment, intermediates identification and ecotoxicological evaluation.* Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2013. **112**: p. 33-45.
14. Yang, L., E.Y. Liya, and M.B. Ray, *Degradation of paracetamol in aqueous solutions by TiO2 photocatalysis.* Water research, 2008. **42**(13): p. 3480-3488.
15. Sangion, A. and P. Gramatica, *Hazard of pharmaceuticals for aquatic environment: prioritization by structural approaches and prediction of ecotoxicity.* Environment International, 2016. **95**: p. 131-143.
16. Quadra, G.R., et al., *Do pharmaceuticals reach and affect the aquatic ecosystems in Brazil? A critical review of current studies in a developing country.* Environmental Science and Pollution Research, 2017. **24**: p. 1200-1218.
17. Cleuvers, M., *Aquatic ecotoxicity of pharmaceuticals including the assessment of combination effects.* Toxicology letters, 2003. **142**(3): p. 185-194.
18. Khasawneh, O.F.S. and P. Palaniandy, *Occurrence and removal of pharmaceuticals in wastewater treatment plants.* Process Safety and Environmental Protection, 2021. **150**: p. 532-556.

19. Silvestri, S., et al., *Synthesis of PPy-ZnO composite used as photocatalyst for the degradation of diclofenac under simulated solar irradiation.* Journal of Photochemistry and Photobiology A: Chemistry, 2019. **375**: p. 261-269.
20. Khasawneh, O.F.S. and P. Palaniandy, *Photocatalytic Degradation of Pharmaceuticals Using TiO Based Nanocomposite Catalyst-Review.* Civil and Environmental Engineering Reports, 2019. **29**(3): p. 1-33.
21. Lee, C.M., P. Palaniandy, and I. Dahlan, *Pharmaceutical residues in aquatic environment and water remediation by TiO 2 heterogeneous photocatalysis: a review.* Environmental Earth Sciences, 2017. **76**: p. 1-19.
22. Majumder, A., B. Gupta, and A.K. Gupta, *Pharmaceutically active compounds in aqueous environment: A status, toxicity and insights of remediation.* Environmental research, 2019. **176**: p. 108542.
23. Mousset, E. and K. Doudrick, *A review of electrochemical reduction processes to treat oxidized contaminants in water.* Current Opinion in Electrochemistry, 2020. **22**: p. 221-227.
24. Zazouli, M.A. and L.R. Kalankesh, *Removal of precursors and disinfection by-products (DBPs) by membrane filtration from water; a review.* Journal of Environmental Health Science and Engineering, 2017. **15**(1): p. 1-10.
25. Janjhi, F.A., et al., *MXene-based materials for removal of antibiotics and heavy metals from wastewater–a review.* Water Resources and Industry, 2023: p. 100202.
26. Azimi, A., et al., *Removal of heavy metals from industrial wastewaters: a review.* ChemBioEng Reviews, 2017. **4**(1): p. 37-59.
27. Zularisam, A., A. Ismail, and R. Salim, *Behaviours of natural organic matter in membrane filtration for surface water treatment—a review.* Desalination, 2006. **194**(1-3): p. 211-231.
28. Yu, C., et al., *Thermal stability, microstructure and photocatalytic activity of the bismuth oxybromide photocatalyst.* Chinese Journal of Chemistry, 2012. **30**(3): p. 721-726.
29. Fernandes, A., et al., *Synergistic effect of TiO2 photocatalytic advanced oxidation processes in the treatment of refinery effluents.* Chemical Engineering Journal, 2020. **391**: p. 123488.
30. Wang, L., et al., *Bibliometric analysis and literature review of ultrasound-assisted degradation of organic pollutants.* Science of The Total Environment, 2023. **876**: p. 162551.
31. Fedorov, K., et al., *Synergistic effects of hybrid advanced oxidation processes (AOPs) based on hydrodynamic cavitation phenomenon–a review.* Chemical Engineering Journal, 2022. **432**: p. 134191.
32. Fedorov, K., et al., *Activated sodium percarbonate-ozone (SPC/O3) hybrid hydrodynamic cavitation system for advanced oxidation processes (AOPs) of 1, 4-dioxane in water.* Chemical Engineering Journal, 2023. **456**: p. 141027.
33. Lin, D., et al., *Application of persulfate-based oxidation processes to address diverse sustainability challenges: A critical review.* Journal of Hazardous Materials, 2022: p. 129722.
34. Arar, Ö., et al., *Various applications of electrodeionization (EDI) method for water treatment—A short review.* Desalination, 2014. **342**: p. 16-22.
35. Khan, J.A., et al., *Synthesis of eosin modified TiO2 film with co-exposed {001} and {101} facets for photocatalytic degradation of para-aminobenzoic acid and solar H2 production.* Applied Catalysis B: Environmental, 2020. **265**: p. 118557.
36. Fernandes, A., et al., *Integrated photocatalytic advanced oxidation system (TiO2/UV/O3/H2O2) for degradation of volatile organic compounds.* Separation and Purification Technology, 2019. **224**: p. 1-14.
37. Priya, A., et al., *Occurrences and removal of pharmaceutical and personal care products from aquatic systems using advanced treatment-A review.* Environmental Research, 2022. **204**: p. 112298.
38. Koe, W.S., et al., *An overview of photocatalytic degradation: photocatalysts, mechanisms, and development of photocatalytic membrane.* Environmental Science and Pollution Research, 2020. **27**(3): p. 2522-2565.

39. Sruthi, L., B. Janani, and S.S. Khan, *Ibuprofen removal from aqueous solution via light-harvesting photocatalysis by nano-heterojunctions: A review.* Separation and Purification Technology, 2021. **279**: p. 119709.
40. Ahmed, S.F., et al., *Nanomaterials as a sustainable choice for treating wastewater.* Environmental Research, 2022. **214**: p. 113807.
41. Zia, J., J. Kashyap, and U. Riaz, *Facile synthesis of polypyrrole encapsulated V2O5 nanohybrids for visible light driven green sonophotocatalytic degradation of antibiotics.* Journal of Molecular Liquids, 2018. **272**: p. 834-850.
42. Song, Y., et al., *Synergistic effect of persulfate and g-C3N4 under simulated solar light irradiation: implication for the degradation of sulfamethoxazole.* Journal of hazardous materials, 2020. **393**: p. 122379.
43. Silva, E.C., et al., *The effect of an external magnetic field on the photocatalytic activity of CoFe2O4 particles anchored in carbon cloth.* Journal of Photochemistry and Photobiology A: Chemistry, 2021. **416**: p. 113317.
44. Saddique, Z., et al., *Band engineering of BiOBr based materials for photocatalytic wastewater treatment via advanced oxidation processes (AOPs)–A review.* Water Resources and Industry, 2023: p. 100211.
45. Soltani, R.D.C., et al., *Sonocatalytic degradation of tetracycline antibiotic using zinc oxide nanostructures loaded on nano-cellulose from waste straw as nanosonocatalyst.* Ultrasonics Sonochemistry, 2019. **55**: p. 117-124.
46. Yang, H., et al., *Inorganic-organic hybrid photocatalysts: Syntheses, mechanisms, and applications.* Chinese Journal of Catalysis, 2022. **43**(8): p. 2111-2140.
47. Liras, M. and M. Barawi, *Hybrid materials based on conjugated polymers and inorganic semiconductors as photocatalysts: from environmental to energy applications.* Chemical Society Reviews, 2019. **48**(22): p. 5454-5487.
48. Chongdar, S., et al., *Porous organic–inorganic hybrid materials for catalysis, energy and environmental applications.* Chemical Communications, 2022. **58**(21): p. 3429-3460.
49. Ashby, M.F. and Y.J. Bréchet, *Designing hybrid materials.* Acta materialia, 2003. **51**(19): p. 5801-5821.
50. Kickelbick, G., *Hybrid materials-past, present and future.* 2014.
51. Alam, S.M.M., A.H. Ashik, and A.N. Ul-Hossain, *Preparation and Performances of Polyimide-Insitu formed Polydiphenylsiloxane Nano hybrids.* Materials Today: Proceedings, 2021.
52. Żur, J., et al., *Organic micropollutants paracetamol and ibuprofen—toxicity, biodegradation, and genetic background of their utilization by bacteria.* Environmental Science and Pollution Research, 2018. **25**(22): p. 21498-21524.
53. Tiwari, D., *Efficient use of hybrid materials in the remediation of aquatic environment contaminated with micro-pollutant diclofenac sodium.* Chemical Engineering Journal, 2015. **263**: p. 364-373.
54. Yang, Y. and G.S. Toor, *Contaminants in the Urban Environment. Pharmaceuticals and Personal Care Products (PPCPs) Part 2*. 2015, Department of Soil and Water Sciences, Center for Landscape Conservation and ….
55. Kallenborn, R., et al., *Pharmaceuticals and personal care products (PPCPs) in Arctic environments: indicator contaminants for assessing local and remote anthropogenic sources in a pristine ecosystem in change.* Environmental Science and Pollution Research, 2018. **25**(33): p. 33001-33013.
56. Fabbri, E. and S. Franzellitti, *Human pharmaceuticals in the marine environment: focus on exposure and biological effects in animal species.* Environmental toxicology and chemistry, 2016. **35**(4): p. 799-812.
57. Kim, H.-Y., I.-S. Lee, and J.-E. Oh, *Human and veterinary pharmaceuticals in the marine environment including fish farms in Korea.* Science of the Total Environment, 2017. **579**: p. 940-949.

58. Ojemaye, C.Y. and L. Petrik, *Occurrences, levels and risk assessment studies of emerging pollutants (pharmaceuticals, perfluoroalkyl and endocrine disrupting compounds) in fish samples from Kalk Bay harbour, South Africa.* Environmental Pollution, 2019. **252**: p. 562-572.
59. Bort, R., et al., *Diclofenac toxicity to hepatocytes: a role for drug metabolism in cell toxicity.* Journal of Pharmacology and Experimental Therapeutics, 1999. **288**(1): p. 65-72.
60. Haap, T., R. Triebskorn, and H.-R. Köhler, *Acute effects of diclofenac and DMSO to Daphnia magna: immobilisation and hsp70-induction.* Chemosphere, 2008. **73**(3): p. 353-359.
61. Zhang, Y., S.-U. Geißen, and C. Gal, *Carbamazepine and diclofenac: removal in wastewater treatment plants and occurrence in water bodies.* Chemosphere, 2008. **73**(8): p. 1151-1161.
62. Martínez, C., et al., *Aqueous degradation of diclofenac by heterogeneous photocatalysis using nanostructured materials.* Applied Catalysis B: Environmental, 2011. **107**(1-2): p. 110-118.
63. Zhang, N., et al., *Diclofenac photodegradation under simulated sunlight: effect of different forms of nitrogen and kinetics.* Journal of hazardous materials, 2011. **192**(1): p. 411-418.
64. Mehinto, A.C., E.M. Hill, and C.R. Tyler, *Uptake and biological effects of environmentally relevant concentrations of the nonsteroidal anti-inflammatory pharmaceutical diclofenac in rainbow trout (Oncorhynchus mykiss).* Environmental science & technology, 2010. **44**(6): p. 2176-2182.
65. Chae, J.-P., et al., *Evaluation of developmental toxicity and teratogenicity of diclofenac using Xenopus embryos.* Chemosphere, 2015. **120**: p. 52-58.
66. Vaja, R., et al., *The COVID-19 ibuprofen controversy: a systematic review of NSAIDs in adult acute lower respiratory tract infections.* British journal of clinical pharmacology, 2021. **87**(3): p. 776-784.
67. Yang, X., et al., *Recent advances in photodegradation of antibiotic residues in water.* Chemical Engineering Journal, 2021. **405**: p. 126806.
68. Prabavathi, S.L., et al., *Construction of heterostructure CoWO4/g-C3N4 nanocomposite as an efficient visible-light photocatalyst for norfloxacin degradation.* Journal of Industrial and Engineering Chemistry, 2019. **80**: p. 558-567.
69. Yang, T., T.-J. Fan, and B. Xu, *Norfloxacin induces apoptosis and necroptosis in human corneal epithelial cells.* Toxicology in Vitro, 2020. **66**: p. 104868.
70. Anku, W.W., et al., *Photocatalytic degradation of pharmaceuticals using graphene based materials*, in *A New Generation Material Graphene: Applications in Water Technology*. 2019, Springer. p. 187-208.
71. Zhao, X.-L., et al., *Effects of environmental norfloxacin concentrations on the intestinal health and function of juvenile common carp and potential risk to humans.* Environmental Pollution, 2021. **287**: p. 117612.
72. Kovalakova, P., et al., *Occurrence and toxicity of antibiotics in the aquatic environment: A review.* Chemosphere, 2020. **251**: p. 126351.
73. Rathi, B.S., P.S. Kumar, and P.-L. Show, *A review on effective removal of emerging contaminants from aquatic systems: current trends and scope for further research.* Journal of Hazardous Materials, 2021. **409**: p. 124413.
74. Parolini, M., *Toxicity of the Non-Steroidal Anti-Inflammatory Drugs (NSAIDs) acetylsalicylic acid, paracetamol, diclofenac, ibuprofen and naproxen towards freshwater invertebrates: A review.* Science of the Total Environment, 2020. **740**: p. 140043.
75. Ha, C.-S. and S. Nagappan, *Hydrophobic and Superhydrophobic Organic-Inorganic Nanohybrids*. 2018: Jenny Stanford Publishing.
76. Smith, A.M. and S. Nie, *Semiconductor nanocrystals: structure, properties, and band gap engineering.* Accounts of chemical research, 2010. **43**(2): p. 190-200.
77. Zhang, G., Z. Wang, and J. Wu, *Construction of a Z-scheme heterojunction for high-efficiency visible-light-driven photocatalytic CO 2 reduction.* Nanoscale, 2021. **13**(8): p. 4359-4389.

78. Oluwole, A.O. and O.S. Olatunji, *Enhanced photocatalytic degradation of naproxen in aqueous matrices using reduced graphene oxide (rGO) decorated binary BSO/g-C3N4 heterojunction nanocomposites.* Chemical Engineering Journal Advances, 2022. **12**: p. 100417.
79. Hassandoost, R., et al., *Hierarchically structured ternary heterojunctions based on Ce3+/Ce4+ modified Fe3O4 nanoparticles anchored onto graphene oxide sheets as magnetic visible-light-active photocatalysts for decontamination of oxytetracycline.* Journal of hazardous materials, 2019. **376**: p. 200-211.
80. Kang, J., et al., *Dual Z-scheme MoS2/g-C3N4/Bi24O31Cl10 ternary heterojunction photocatalysts for enhanced visible-light photodegradation of antibiotic.* Journal of Alloys and Compounds, 2020. **825**: p. 153975.
81. Fakhri, H. and H. Bagheri, *Two novel sets of UiO-66@ metal oxide/graphene oxide Z-scheme heterojunction: Insight into tetracycline and malathion photodegradation.* Journal of Environmental Sciences, 2020. **91**: p. 222-236.
82. Kumar, A., et al., *Robust visible light active PANI/LaFeO3/CoFe2O4 ternary heterojunction for the photo-degradation and mineralization of pharmaceutical effluent: Clozapine.* Journal of Environmental Chemical Engineering, 2021. **9**(5): p. 106159.
83. Kumar, A., et al., *Development of g-C3N4/TiO2/Fe3O4@ SiO2 heterojunction via sol-gel route: a magnetically recyclable direct contact Z-scheme nanophotocatalyst for enhanced photocatalytic removal of ibuprofen from real sewage effluent under visible light.* Chemical Engineering Journal, 2018. **353**: p. 645-656.
84. Li, W., et al., *Photocatalytical degradation of diclofenac by Ag-BiOI-rGO: Kinetics, mechanisms and pathways.* Chemosphere, 2019. **218**: p. 966-973.
85. Leeladevi, K., et al., *Fabrication of 3D pebble-like CeVO4/g-C3N4 nanocomposite: A visible light-driven photocatalyst for mitigation of organic pollutants.* Diamond and Related Materials, 2021. **116**: p. 108424.
86. Raha, S. and M. Ahmaruzzaman, *Enhanced performance of a novel superparamagnetic g-C3N4/NiO/ZnO/Fe3O4 nanohybrid photocatalyst for removal of esomeprazole: Effects of reaction parameters, co-existing substances and water matrices.* Chemical Engineering Journal, 2020. **395**: p. 124969.
87. Ahmad, M., et al., *Graphene oxide supported Fe2 (MoO4) 3 nano rods assembled round-ball fabrication via hydrothermal route and photocatalytic degradation of nonsteroidal anti-inflammatory drug.* Journal of Molecular Liquids, 2020. **301**: p. 112343.
88. Su, G., et al., *Magnetic Fe3O4@ SiO2@ BiFeO3/rGO composite for the enhanced visible-light catalytic degradation activity of organic pollutants.* Ceramics International, 2021. **47**(4): p. 5374-5387.
89. Liu, Y., et al., *Tuning band structure of graphitic carbon nitride for efficient degradation of sulfamethazine: Atmospheric condition and theoretical calculation.* Chinese Chemical Letters, 2022. **33**(3): p. 1385-1389.
90. Ragupathi, V., P. Panigrahi, and N.G. Subramaniam, *Bandgap engineering in graphitic carbon nitride: Effect of precursors.* Optik, 2020. **202**: p. 163601.
91. Gao, R.-H., et al., *Graphitic carbon nitride (g-C3N4)-based photocatalytic materials for hydrogen evolution.* Frontiers in Chemistry, 2022. **10**: p. 1048504.
92. Shanavas, S., et al., *Computationally guided synthesis of (2D/3D/2D) rGO/Fe2O3/g-C3N4 nanostructure with improved charge separation and transportation efficiency for degradation of pharmaceutical molecules.* Applied Catalysis B: Environmental, 2019. **255**: p. 117758.
93. Wang, S., et al., *Magnetic Fe3O4/CeO2/g-C3N4 composites with a visible-light response as a high efficiency Fenton photocatalyst to synergistically degrade tetracycline.* Separation and Purification Technology, 2021. **278**: p. 119609.

94. Zhao, N., et al., *Versatile types of organic/inorganic nanohybrids: from strategic design to biomedical applications.* Chemical reviews, 2018. **119**(3): p. 1666-1762.

95. Faustini, M., et al., *History of organic–inorganic hybrid materials: prehistory, art, science, and advanced applications.* Advanced Functional Materials, 2018. **28**(27): p. 1704158.

96. Manatunga, D.C., et al., *Recent developments in the use of organic–inorganic nanohybrids for drug delivery.* Wiley Interdisciplinary Reviews: Nanomedicine and Nanobiotechnology, 2020. **12**(3): p. e1605.

97. Foong, L.K., et al., *Applications of nano-materials in diverse dentistry regimes.* Rsc Advances, 2020. **10**(26): p. 15430-15460.

98. Shi, Z., et al., *A 3D inorganic-organic hybrid constructed from Strandberg-type polyoxometalates and silver complexes: Synthesis, structure and properties.* Inorganic Chemistry Communications, 2019. **102**: p. 104-107.

99. Hajizadeh, F., et al., *Synthesis and investigation of two new crystalline organic inorganic nano-hybrids based on Wells-Dawson vanadotungstates and 1H-1, 2, 4-triazole as electro- and photocatalysts.* Journal of Molecular Structure, 2021. **1224**: p. 129003.

100. Guo, K., et al., *Organic/inorganic nanohybrids as multifunctional gene delivery systems.* The Journal of Gene Medicine, 2019. **21**(5): p. e3084.

101. Mir, S.H., et al., *Organic-inorganic hybrid functional materials: An integrated platform for applied technologies.* Journal of The Electrochemical Society, 2018. **165**(8): p. B3137.

102. Mohammed, L.A., et al. *Synthesis, Characterization and Antimicrobial Activities of Silver Nanoparticles coated [1, 3] Thiazin-4-One derivatives*. in *Journal of Physics: Conference Series*. 2019. IOP Publishing.

103. Loyo, C., et al., *PLA/CaO nanocomposites with antimicrobial and photodegradation properties.* Polymer Degradation and Stability, 2022. **197**: p. 109865.

104. Ahadi, N., A. Mobinikhaledi, and M.A. Bodaghifard, *One-pot synthesis of 1, 4-dihydropyridines and N-arylquinolines in the presence of copper complex stabilized on MnFe2O4 (MFO) as a novel organic–inorganic hybrid material and magnetically retrievable catalyst.* Applied Organometallic Chemistry, 2020. **34**(10): p. e5822.

105. Hao, Q., et al., *Graphitic carbon nitride with different dimensionalities for energy and environmental applications.* Nano Research, 2020. **13**: p. 18-37.

106. Liao, G., et al., *Emerging graphitic carbon nitride-based materials for biomedical applications.* Progress in Materials Science, 2020. **112**: p. 100666.

107. Wang, J. and S. Wang, *A critical review on graphitic carbon nitride (g-C3N4)-based materials: Preparation, modification and environmental application.* Coordination Chemistry Reviews, 2022. **453**: p. 214338.

108. Jiang, L., et al., *Doping of graphitic carbon nitride for photocatalysis: a reveiw.* Applied Catalysis B: Environmental, 2017. **217**: p. 388-406.

109. Nawaz, M., et al., *One-step hydrothermal synthesis of porous 3D reduced graphene oxide/TiO2 aerogel for carbamazepine photodegradation in aqueous solution.* Applied Catalysis B: Environmental, 2017. **203**: p. 85-95.

110. Liu, S.-H. and W.-T. Tang, *Photodecomposition of ibuprofen over g-C3N4/Bi2WO6/rGO heterostructured composites under visible/solar light.* Science of The Total Environment, 2020. **731**: p. 139172.

111. Enesca, A. and C. Cazan, *Polymer Composite-Based Materials with Photocatalytic Applications in Wastewater Organic Pollutant Removal: A Mini Review.* Polymers, 2022. **14**(16): p. 3291.

112. Khairy, M. and M. Gouda, *Electrical and optical properties of nickel ferrite/polyaniline nanocomposite.* Journal of advanced research, 2015. **6**(4): p. 555-562.

113. Sirajudheen, P., et al., *Tunable photocatalytic oxidation response of ZnS tethered chitosan-polyaniline composite for the removal of organic pollutants: a mechanistic perspective.* Materials Today: Proceedings, 2021. **47**: p. 2553-2559.

114. Selvakumar, K., et al., *Facile construction of sandwich-like composited Sm2MoO6/ZnO/rGO and its activity in photodecomposition of ibuprofen.* Colloids and Surfaces A: Physicochemical and Engineering Aspects, 2022. **650**: p. 129545.
115. Zia, J., F. Fatima, and U. Riaz, *A comprehensive review on the photocatalytic activity of polythiophene-based nanocomposites against degradation of organic pollutants.* Catalysis Science & Technology, 2021. **11**(20): p. 6630-6648.
116. Ozkazanc, E., H. Ozkazanc, and O. Gundogdu, *Characterization and charge transport mechanism of multifunctional polyfuran/tin (IV) oxide composite.* Journal of Inorganic and Organometallic Polymers and Materials, 2018. **28**: p. 2108-2120.
117. Shah, A.-u.-H.A., et al., *Synthesis and characterization of polyaniline–zirconium dioxide and polyaniline–cerium dioxide composites with enhanced photocatalytic degradation of rhodamine B dye.* Chemical Papers, 2018. **72**(10): p. 2523-2538.
118. Zia, J. and U. Riaz, *Photocatalytic degradation of anti-inflammatory drug using POPD/Sb2O3 organic-inorganic nanohybrid under solar light.* Journal of Materials Research and Technology, 2019. **8**(5): p. 4079-4093.
119. Manocha, L., et al., *Sol-gel processing of carbidic glasses.* Bulletin of Materials Science, 2000. **23**(1): p. 1-4.
120. Wang, D. and G.P. Bierwagen, *Sol–gel coatings on metals for corrosion protection.* Progress in organic coatings, 2009. **64**(4): p. 327-338.
121. Díaz-Sánchez, M., et al., *Nanohybrids based on F-doped titanium dioxides and carbon species with enhanced dual adsorption-photodegradation activity for water decontamination.* Catalysis Communications, 2022. **169**: p. 106477.
122. Faisal, M., et al., *Rapid photodegradation of linezolid antibiotic and methylene blue dye over Pt nanoparticles/polypyrrole-carbon black/ZnO novel visible light photocatalyst.* Journal of Environmental Chemical Engineering, 2021. **9**(6): p. 106773.
123. Navas, D., et al., *Review on sol-gel synthesis of perovskite and oxide nanomaterials.* Gels, 2021. **7**(4): p. 275.
124. Ansari, F., A. Sobhani, and M. Salavati-Niasari, *Simple sol-gel synthesis and characterization of new CoTiO3/CoFe2O4 nanocomposite by using liquid glucose, maltose and starch as fuel, capping and reducing agents.* Journal of colloid and interface science, 2018. **514**: p. 723-732.
125. Faisal, M., et al., *Polythiophene doped ZnO nanostructures synthesized by modified sol-gel and oxidative polymerization for efficient photodegradation of methylene blue and gemifloxacin antibiotic.* Materials Today Communications, 2020. **24**: p. 101048.
126. Wang, Y., et al., *Enhanced dispersion stability of gold nanoparticles by the physisorption of cyclic poly (ethylene glycol).* Nature communications, 2020. **11**(1): p. 6089.
127. El-Batal, A.I., et al., *Gum Arabic polymer-stabilized and Gamma rays-assisted synthesis of bimetallic silver-gold nanoparticles: Powerful antimicrobial and antibiofilm activities against pathogenic microbes isolated from diabetic foot patients.* International Journal of Biological Macromolecules, 2020. **165**: p. 169-186.
128. da Silva, A.B., et al., *Composite materials based on chitosan/gold nanoparticles: From synthesis to biomedical applications.* International Journal of Biological Macromolecules, 2020. **161**: p. 977-998.
129. Zhang, Y., et al., *Polymer-coated hollow mesoporous silica nanoparticles for triple-responsive drug delivery.* ACS applied materials & interfaces, 2015. **7**(32): p. 18179-18187.
130. Jafarbeglou, M., et al., *Clay nanocomposites as engineered drug delivery systems.* RSC advances, 2016. **6**(55): p. 50002-50016.
131. Patil, A.J. and S. Mann, *Self-assembly of bio–inorganic nanohybrids using organoclay building blocks.* Journal of Materials Chemistry, 2008. **18**(39): p. 4605-4615.
132. Liu, X., et al., *Development of a promising drug delivery for formononetin: Cyclodextrin-modified single-walled carbon nanotubes.* Journal of Drug Delivery Science and Technology, 2018. **43**: p. 461-468.

133. Wang, H., et al., *Design and synthesis of core–shell–shell upconversion nanoparticles for NIR-induced drug release, photodynamic therapy, and cell imaging.* ACS applied materials & interfaces, 2016. **8**(7): p. 4416-4423.
134. Ali, N., et al., *Fabrication strategies for functionalized nanomaterials*, in *Nanomaterials: Synthesis, Characterization, Hazards and Safety*. 2021, Elsevier. p. 55-95.
135. Mandal, K., et al., *Notes on useful materials and synthesis through various chemical solution techniques*, in *Chemical Solution Synthesis for Materials Design and Thin Film Device Applications*. 2021, Elsevier. p. 29-78.
136. Carvalho, S.M., et al., *Bifunctional magnetopolymersomes of iron oxide nanoparticles and carboxymethylcellulose conjugated with doxorubicin for hyperthermo-chemotherapy of brain cancer cells.* Biomaterials science, 2019. **7**(5): p. 2102-2122.
137. Tian, J., et al., *Environmentally friendly, one-pot synthesis of Ag nanoparticle-decorated reduced graphene oxide composites and their application to photocurrent generation.* Inorganic chemistry, 2012. **51**(8): p. 4742-4746.
138. Mondal, S., et al., *Novel one pot synthesis and spectroscopic characterization of a folate-Mn 3 O 4 nanohybrid for potential photodynamic therapeutic application.* RSC advances, 2019. **9**(52): p. 30216-30225.
139. Wang, J., et al., *One-pot synthesis of multifunctional magnetic ferrite–MoS 2–carbon dot nanohybrid adsorbent for efficient Pb (ii) removal.* Journal of Materials Chemistry A, 2016. **4**(10): p. 3893-3900.
140. Hoseini, A.-A., et al., *An organic–inorganic hybrid nanomaterial composed of a Dowson-type (NH 4) 6 P 2 Mo 18 O 62 heteropolyanion and a metal–organic framework: synthesis, characterization, and application as an effective adsorbent for the removal of organic dyes.* RSC Advances, 2020. **10**(66): p. 40005-40018.
141. Liang, Q., et al., *One-pot synthesis of magnetic graphitic carbon nitride photocatalyst with synergistic catalytic performance under visible-light irradiation.* Journal of Photochemistry and Photobiology A: Chemistry, 2017. **335**: p. 165-173.
142. Chowdhuri, A.R., et al., *Carbon dots embedded magnetic nanoparticles@ chitosan@ metal organic framework as a nanoprobe for pH sensitive targeted anticancer drug delivery.* ACS applied materials & interfaces, 2016. **8**(26): p. 16573-16583.
143. Song, W., et al., *Magnetic alginate/chitosan nanoparticles for targeted delivery of curcumin into human breast cancer cells.* Nanomaterials, 2018. **8**(11): p. 907.
144. García-Guzmán, P., et al., *Characterization of hybrid microparticles/Montmorillonite composite with raspberry-like morphology for Atorvastatin controlled release.* Colloids and Surfaces B: Biointerfaces, 2018. **167**: p. 397-406.
145. Campbell, K., D.Q. Craig, and T. McNally, *Poly (ethylene glycol) layered silicate nanocomposites for retarded drug release prepared by hot-melt extrusion.* International journal of pharmaceutics, 2008. **363**(1-2): p. 126-131.
146. Hu, X., et al., *Electrospinning of polymeric nanofibers for drug delivery applications.* Journal of controlled release, 2014. **185**: p. 12-21.
147. Haider, A., S. Haider, and I.-K. Kang, *A comprehensive review summarizing the effect of electrospinning parameters and potential applications of nanofibers in biomedical and biotechnology.* Arabian Journal of Chemistry, 2018. **11**(8): p. 1165-1188.
148. Gao, Y., et al., *Electrospun organic–inorganic nanohybrids as sustained release drug delivery systems.* Journal of Materials Chemistry B, 2017. **5**(46): p. 9165-9174.
149. El Gohary, M.I., et al., *Electrospinning of doxorubicin loaded silica/poly (ε-caprolactone) hybrid fiber mats for sustained drug release.* Advances in Natural Sciences: Nanoscience and Nanotechnology, 2018. **9**(2): p. 025002.
150. Li, Y., et al., *Developments of advanced electrospinning techniques: A critical review.* Advanced Materials Technologies, 2021. **6**(11): p. 2100410.

151. Sarkodie, B., et al., *Photocatalytic degradation of dyes by novel electrospun nanofibers: A review.* Chemosphere, 2023. **313**: p. 137654.
152. Nasir, A.M., et al., *Recent progress on fabrication and application of electrospun nanofibrous photocatalytic membranes for wastewater treatment: A review.* Journal of Water Process Engineering, 2021. **40**: p. 101878.
153. Colmenares, J.C. and R. Luque, *Heterogeneous photocatalytic nanomaterials: prospects and challenges in selective transformations of biomass-derived compounds.* Chemical Society Reviews, 2014. **43**(3): p. 765-778.
154. Mestre, A.S. and A.P. Carvalho, *Photocatalytic degradation of pharmaceuticals carbamazepine, diclofenac, and sulfamethoxazole by semiconductor and carbon materials: a review.* Molecules, 2019. **24**(20): p. 3702.
155. Leeladevi, K., et al., *Investigation on photocatalytic degradation of hazardous chloramphenicol drug and amaranth dye by SmVO4 decorated g-C3N4 nanocomposites.* Materials Science in Semiconductor Processing, 2021. **123**: p. 105563.
156. Nawaz, M., et al., *Reduced graphene oxide− TiO2/sodium alginate 3-dimensional structure aerogel for enhanced photocatalytic degradation of ibuprofen and sulfamethoxazole.* Chemosphere, 2020. **261**: p. 127702.
157. Pham, T.H., J.-W. Park, and T. Kim, *Enhanced photodegradation of paracetamol from water by cobalt doped graphitic carbon nitride.* Solar Energy, 2021. **215**: p. 151-156.
158. Raja, A., et al., *Visible active reduced graphene oxide-BiVO4-ZnO ternary photocatalyst for efficient removal of ciprofloxacin.* Separation and purification technology, 2020. **233**: p. 115996.
159. Shanavas, S., et al., *High efficient catalytic degradation of tetracycline and ibuprofen using visible light driven novel Cu/Bi2Ti2O7/rGO nanocomposite: kinetics, intermediates and mechanism.* Journal of Industrial and Engineering Chemistry, 2019. **72**: p. 512-528.
160. Xu, C., et al., *Constructing Z-scheme β-Bi2O3/ZrO2 heterojunctions with 3D mesoporous SiO2 nanospheres for efficient antibiotic remediation via synergistic adsorption and photocatalysis.* Rare Metals, 2022. **41**(6): p. 2094-2107.
161. Zhou, Q., et al., *Novel hierarchical carbon quantum dots-decorated BiOCl nanosheet/carbonized eggshell membrane composites for improved removal of organic contaminants from water via synergistic adsorption and photocatalysis.* Chemical Engineering Journal, 2021. **420**: p. 129582.
162. Tan, Y., et al., *Highly efficient photocatalytic degradation over rose-like 1D/2D La (OH) 3/(BiO) 2 OHCl heterostructures boosted by rich oxygen vacancies and enhanced interfacial charge transfer.* Environmental Science: Nano, 2023. **10**(1): p. 215-228.
163. Adorna Jr, J., et al., *Indirect Z-scheme nitrogen-doped carbon dot decorated Bi2MoO6/g-C3N4 photocatalyst for enhanced visible-light-driven degradation of ciprofloxacin.* Chemical Engineering Journal, 2021. **422**: p. 130103.
164. Bundschuh, M., et al., *Nanoparticles in the environment: where do we come from, where do we go to?* Environmental Sciences Europe, 2018. **30**(1): p. 1-17.
165. Aboamera, N.M., et al., *An effective removal of organic dyes using surface functionalized cellulose acetate/graphene oxide composite nanofibers.* Cellulose, 2018. **25**: p. 4155-4166.
166. Kamel, B.M., et al., *Tribological behaviour of calcium grease containing carbon nanotubes additives.* Industrial Lubrication and Tribology, 2016.
167. Mohamed, A., et al., *Surface functionalized composite nanofibers for efficient removal of arsenic from aqueous solutions.* Chemosphere, 2017. **180**: p. 108-116.
168. Mohamed, A., et al., *A novel and highly efficient photocatalytic degradation of malachite green dye via surface modified polyacrylonitrile nanofibers/biogenic silica composite nanofibers.* Separation and Purification Technology, 2019. **210**: p. 935-942.

169. Mohamed, A., et al., *Photodegradation of Ibuprofen, Cetirizine, and Naproxen by PAN-MWCNT/TiO 2–NH 2 nanofiber membrane under UV light irradiation.* Environmental Sciences Europe, 2018. **30**(1): p. 1-9.

170. AttariKhasraghi, N., et al., *Achieving the enhanced photocatalytic degradation of ceftriaxone sodium using CdS-g-C3N4 nanocomposite under visible light irradiation: RSM modeling and optimization.* Journal of Inorganic and Organometallic Polymers and Materials, 2021. **31**(7): p. 3164-3174.

171. AttariKhasraghi, N., et al., *Zeolite 4A supported CdS/g-C3N4 type-II heterojunction: A novel visible-light-active ternary nanocomposite for potential photocatalytic degradation of cefoperazone.* Journal of Molecular Liquids, 2021. **342**: p. 117479.

172. Li, D., et al., *High-efficiency ultrathin porous phosphorus-doped graphitic carbon nitride nanosheet photocatalyst for energy production and environmental remediation.* Applied Catalysis B: Environmental, 2022. **307**: p. 121099.

173. He, T., et al., *Novel magnetic Fe3O4/g-C3N4/MoO3 nanocomposites with highly enhanced photocatalytic activities: Visible-light-driven degradation of tetracycline from aqueous environment.* PloS one, 2020. **15**(8): p. e0237389.

174. Prabavathi, S.L., et al., *Enhanced photoactivity of cerium tungstate-modified graphitic carbon nitride heterojunction photocatalyst for the photodegradation of moxifloxacin.* Journal of Materials Science: Materials in Electronics, 2020. **31**(14): p. 11434-11447.

175. Chen, X., et al., *Multiphase TiO2 surface coating g-C3N4 formed a sea urchin like structure with interface effects and improved visible-light photocatalytic performance for the degradation of ibuprofen.* International Journal of Hydrogen Energy, 2018. **43**(29): p. 13284-13293.

176. Hu, Z., et al., *Construction of carbon-doped supramolecule-based g-C3N4/TiO2 composites for removal of diclofenac and carbamazepine: A comparative study of operating parameters, mechanisms, degradation pathways.* Journal of hazardous materials, 2019. **380**: p. 120812.

177. Nguyen, X.S., et al., *Photocatalytic degradation of cephalexin by g-C3N4/Zn doped Fe3O4 under visible light.* Environmental Technology, 2021. **42**(8): p. 1292-1301.

178. Li, X., et al., *Adsorption and photocatalysis assisted optimization for drug removal by chitosan-glyoxal/Polyvinylpyrrolidone/MoS2 nanocomposites.* International journal of biological macromolecules, 2019. **136**: p. 469-475.

179. Malakootian, M., et al., *Facile and green synthesis of ZnFe2O4@ CMC as a new magnetic nanophotocatalyst for ciprofloxacin degradation from aqueous media.* Process Safety and Environmental Protection, 2019. **129**: p. 138-151.

180. Shankar, E.G., et al., *Efficient solar light photocatalytic degradation of commercial pharmaceutical drug and dye using rGO-PANI assisted c-ZnO heterojunction nanocomposites.* Ceramics International, 2021. **47**(17): p. 23770-23780.

181. Kumar, R.S., et al., *Fe3O4 nanorods decorated on polypyrrole/reduced graphene oxide for electrochemical detection of dopamine and photocatalytic degradation of acetaminophen.* Applied Surface Science, 2021. **556**: p. 149765.

182. Vijayalakshmi, S., et al., *Preparation of zirconium oxide with polyaniline nanocatalyst for the decomposition of pharmaceutical industrial wastewater.* Ionics, 2020. **26**(3): p. 1507-1513.

183. Rayaroth, M.P., et al., *Advanced oxidation processes (AOPs) based wastewater treatment-unexpected nitration side reactions-a serious environmental issue: A review.* Chemical Engineering Journal, 2022. **430**: p. 133002.

184. Gągol, M., et al., *Hydrodynamic cavitation based advanced oxidation processes: Studies on specific effects of inorganic acids on the degradation effectiveness of organic pollutants.* Journal of Molecular Liquids, 2020. **307**: p. 113002.