Environmental Applications of TiO_2-Based Photocatalytic Nanostructures

Subjects: Environmental Sciences

Contributor: Maria-Anna Gatou, Athanasia Syrrakou, Nefeli Lagopati, Evangelia A. Pavlatou

Contemporary technological and industrial advancements have led to increased reliance on chemicals for product innovation, leading to heightened contamination of water sources by traditional pollutants (organic dyes, heavy metals) and disease-causing microorganisms. Wastewater treatment processes now reveal “emerging pollutants”, including pharmaceuticals, endocrine disruptors, and agricultural chemicals. While some are benign, certain emerging pollutants can harm diverse organisms. Researchers seek cost-effective water purification methods that completely degrade pollutants without generating harmful by-products. Semiconductor-based photocatalytic degradation, particularly using titanium dioxide (TiO_2), is popular for addressing water pollution.

Keywords: titanium dioxide ; nanostructures ; synthesis methods ; photocatalytic mechanism ; dyes ; heavy metals ; pesticides ; microbes ; environmental applications

1. Introduction

The World Water Development Report (2020) [1] underscores the critical environmental priority of protecting water reserves amidst global climate change challenges. Currently, natural aquatic environments face vulnerability to various hazardous substances from multiple sources, including civic society, the public sector and, notably, industrial activities.

Various industries (textile, pharmaceutical, agricultural, papermaking, printing, cosmetics, and food processing) generate extensive wastewater laden with diverse organic pollutants, such as pharmaceuticals, dyes, heavy metals, endocrine disruptors (EDCs), pesticides, and herbicides, leading to contamination. Additionally, water contamination results from a multitude of microorganisms thriving in raw household sewage, containing fecal matter and other decomposable substances. This conducive environment for microbial proliferation contributes to the onset and transmission of diseases. Notably, prevalent waterborne bacteria, like *Escherichia coli*, originating from the excrement of both farm animals and humans, cause ailments like diarrhea, renal failure, colitis, and hemolytic uremic syndrome [2]. *Salmonella*, inducing illnesses such as typhoid fever and salmonellosis [3], and cholera, caused by *Vibrio cholera*’s cholera toxin production [4], are severe diseases. Bacterial pathogens, like *Pseudomonas aeruginosa*, contribute to conditions like diarrhea and Shanghai fever [5], while Legionella, a primary agent in transmitting Legionnaire’s disease [6], can proliferate in water sources.

Several treatment methods, including chemical precipitation, separation, adsorption, coagulation, biological treatment, and Fenton oxidation techniques, are currently employed [7]. Despite their application, these methods often result in partial pollutant degradation, transferring contaminants between phases and producing secondary by-products requiring additional treatment [8][9]. Biological treatment, reliant on microbial metabolism [10][11][12], is reliable, cost-effective, and safe but exhibits lower efficacy in suspended solids removal, necessitating improved operational management. Coagulation and precipitation methods form flocs using polymer or inorganic coagulants (e.g., Fe, Al), aiding pollutant coagulation for subsequent removal through water-soluble metal salts, pH adjustment, or polymer coagulants producing sludge flocs to effectively precipitate or separate solids from wastewater [13][14][15]. While these techniques enhance treatment effectiveness, chemical use raises environmental concerns, and the resulting biological sludge contributes to pipe blockages and water quality deterioration. Fenton oxidation, leveraging Fenton’s reagent for oxidative capabilities, generates hydroxyl radicals (•OH) through hydrogen peroxide and iron salt reactions [16][17][18][19][20]. This involves minimal additional device use compared to other oxidation methods, making it easy to implement. However, drawbacks include significant sludge generation and increased operating expenses for subsequent processing.

Currently, there is a growing emphasis on advanced oxidation processes (AOPs) utilizing semiconductor materials as a promising alternative to conventional methods [21]. These processes offer advantages, such as simplified equipment requirements, indiscriminate oxidation, straightforward operational management, cost efficiency, and comprehensive

decomposition of organic dyes into harmless byproducts [22]. A unique aspect of AOPs involves the generation of reactive species, like •OH radicals, enabling rapid and indiscriminate oxidation of organic, inorganic, and biological contaminants. Heterogeneous photocatalysis, employing oxide-based nanomaterials, is particularly effective in eliminating water-soluble pollutants from both water and wastewater under light exposure [23].

Metal oxide semiconductors, like titanium dioxide (TiO_2), demonstrate enhanced adsorption ability and act as effective catalysts due to increased reactivity, high photosensitivity, extensive specific surface area, cost-efficiency, non-toxicity, and biocompatibility [24]. TiO_2, notably one of the most widely used photocatalysts, owes its extensive utilization to advantageous characteristics, including heightened photocatalytic activity, chemical stability, cost-effectiveness, and abundance [25][26]. Existing in crystal structures. like anatase and rutile, TiO_2 exhibits distinct band-gaps and surface attributes, significantly influencing its photocatalytic activity and selectivity. Anatase TiO_2 is generally recognized as the most active among these structures [26][27]. Given their widespread application and exploration, TiO_2-based nanostructures have undergone diverse means of optimization and chemical modifications to enhance efficiency and broaden their application scope. Efforts have particularly focused on improvement in TiO_2's absorption of visible light through doping with non-metal or transition metal ions, combination with other semiconductor materials or deposition of noble metal nanoparticles with a surface plasmonic resonance (SPR) effect [28][29][30].

2. TiO_2-Based Photocatalysts for Effective Elimination of Pharmaceutical Pollutants from Water and Wastewater

During the last few years, numerous new organic pollutants have emerged in the environment [31][32][33]. Various sources contribute to the environmental occurrence of drug residuals, including hospital and manufacturing wastewater, as well as landfill leachates [34][35]. The rapid increase in human population, accelerated industrialization, as well as increased pharmaceutical dependence, have remarkably enhanced environmental pollution [36][37]. Even though the release of pharmaceutical remnants into the environment may seem negligible initially, they tend to accumulate over time and pose severe threats to humans and both terrestrial and aquatic organisms. Such compounds have been detected in multiple origins, as hospital effluents, municipal wastewater treatment plants, groundwater, surficial water, as well as drinking water [38]. Due to their robust nature, these compounds resist degradation through the typical biological procedures used in municipal wastewater treatment plants. As a consequence, they remain untreated for prolonged periods, posing hazards to ecosystems [39]. Previous studies have indicated that even at extremely low concentrations (50 ng/L), the occurrence of pharmaceutical agents in surficial water and groundwater systems implies a significant risk to humans and animals by contaminating their main source of drinking water [40]. In addition, the increase in various types of antibiotics notably adds to the escalation of resistance among bacteria and microbes against medicinal substances, consequently raising the likelihood of increased risk to human populations [41]. Pharmaceutical substances enter aquatic environments, like wastewater, through various mechanisms subsequent to their usage, whether in their original state or as by-products of metabolism. The illustration in **Figure 1** depicts the pathways through which these substances are released during the phase of drug administration.

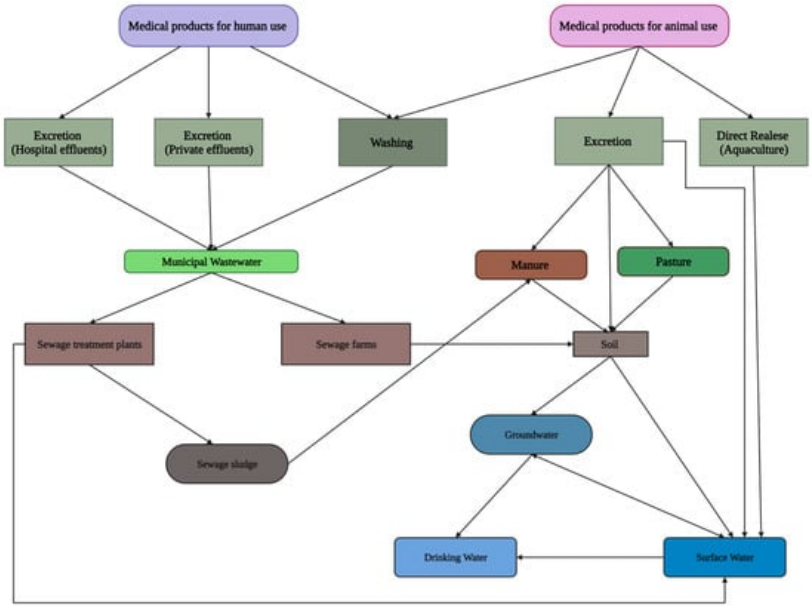

Figure 1. Distribution pathways of medical products/pharmaceutical substances into the environment.

The utilization stage in the pharmaceuticals' lifecycle significantly contributes to their environmental release. Distinguishing if residuals found within the environment originate from human or veterinary usage can be challenging, particularly when certain products are used by both, due to specific product characteristics or misuse. The primary avenue for pharmaceuticals entering the environment during consumption is through human and agricultural animal waste, like urine and feces, which consistently find their way into sewage or soil. Despite the fact that excretion constitutes the predominant approach, substantial amounts of products administered topically, like anti-inflammatory gels, can be rinsed away during bathing. As a result, the quantity and nature of drug residuals discharged post-consumption vary based on parameters, like the quantity and type of substance ingested, administration method and metabolic degree [42].

Up to now, a variety of methods have been utilized for eliminating pharmaceutical substances from water and wastewater effluents. These techniques encompass activated sludge treatment, membrane reactors, algal and microbial reactors, alongside other biological procedures, like biological aerated filters, sequencing batch reactors, trickling filters, rotating biological contactors, biofilm reactors, membrane bioreactors, constructed wetlands, biological activated carbon filters, anaerobic digestion, bio-electrochemical systems, and phytoremediation [43][44]. Several crucial parameters, entailing physical and chemical properties, contaminants' biodegradability, solubility, robustness, as well as operational conditions (such as temperature, pH, and duration), significantly influence the fate of pharmaceutical pollutants in water bodies. Furthermore, attempts have been undertaken to utilize indirect optical decomposition methods employing •OH, produced via sunlight-mediated activation of nitrate and humic acid, acting as light sensitizers [45]. The decay of optical properties in wastewater treatment processes depends on various parameters, like intensity of solar irradiation, geographical location, depth of water, climate, and water's organic composition. High turbidity levels caused by increased sludge concentration limit light penetration, minimizing optical degradation within traditional wastewater treatment plants [46]. In these facilities, impurity removal primarily relies on absorption facilitated by particulate matter and microbial degradation. However, the effectiveness of adsorption in eliminating pharmaceutical compounds is limited. Adsorption efficacy depends on factors like electrostatic interactions, hydrophobic drug properties, and their interactions with biological substances, like microorganisms. Additionally, factors like the type of reactor (fixed bed or continuous system), flow rate, and adsorbent concentration play significant roles. The literature suggests that acidic drugs (e.g., Ibuprofen, Clo-fibric acid, Phenoprofen, and Bezafibrate) with pK_a ranging between 3.6 and 4.9 have minimal adsorption capacity to activated sludge [47]. While some drugs partially degrade and get removed from water and wastewater, others undergo complete degradation, forming various by-products [48]. Biodegradation includes the use of anaerobic or aerobic digestion by varied microorganisms found in sewage sludge, typically used for handling it. This process facilitates the breakdown of pharmaceutical substances present within the sludge. However, some medications may persist without changing, leading to potential contamination of water bodies, like surface or groundwater. Additionally, the membrane process is being considered as a biological treatment method. Ongoing research is exploring various biological approaches to eliminate pharmaceutical pollutants. For instance, a previous study found that activated sludge had the capability to remove steroid hormone E2 at a percentage equal to ≈70–80% [49].

Given the limitations of traditional techniques in eliminating pharmaceutical pollutants, such as low effectiveness, substantial energy usage, and the generation of detrimental by-products, researchers have introduced advanced oxidation processes as an auspicious and efficient alternative approach [50]. AOP methods include ozonation, photocatalysis and Fenton/photo-Fenton approaches. The aforementioned methods aim to thoroughly degrade and mineralize various pharmaceutical compounds, as per the available literature [51]. AOPs involve generating extremely reactive species as free radicals ($•O_2^-$, •OH and $•HO_2$), focusing particularly on •OH. The as-mentioned radicals, especially •OH, possess significant ability in eliminating pollutants' molecules [52]. Based on the drug effluent's characteristics, as well as the preferred treatment goal, AOPs are able to be utilized either separately or along with other biological and physical processes [53]. Among AOP methods, TiO_2-based photocatalysis has arisen as a hopeful and effective method for eradicating pharmaceutical contaminants from water-based settings [54][55].

Manasa and his team investigated the effectiveness of four distinct titanium dioxide photocatalysts doped with boron and cerium (0.1 wt.% and 1 wt.% Ce-TiO_2, as well as 1 wt.% and 2 wt.% B-TiO_2), prepared via the EDTA-citrate approach, for breaking down typical fluoroquinolone-based antibiotics (ciprofloxacin and norfloxacin) using sunlight irradiation. The observed band-gap values ranged from 2.5 to 2.9 eV, indicating the presence of a new energy level towards efficient charge separation and recombination's decrease. At optimized conditions, 1 wt.% Ce-TiO_2 and 1 wt.% B-TiO_2 exhibited superior photocatalytic performance, potentially because of enhanced cerium adsorption rate and the boron occupying interstitial lattice positions, along with a reduced band-gap. These catalysts showcased 93% decomposition for both ciprofloxacin and norfloxacin, coupled with increased disinfection effectiveness of the order of 95–99.99% [56]. Conversely, Suwannaruang and co-researchers investigated the impact of several N-doping concentrations on surficial features, crystalline phase structure, optical and textural attributes, chemical state, and photocatalytic performance of N-doped titanium dioxide nano-rice particles. Under the examined parameters, the highest and lowest decomposition percentages

of ciprofloxacin were 94.3% and 70% for 12.5 wt.% N and 1 wt.% N, respectively, upon UV irradiation for 4 h, indicating an enhancement of photocatalytic activity with increasing nitrogen dopant concentrations [57].

Furthermore, Martins and co-researchers examined the decomposition of ciprofloxacin through photocatalysis upon UV and visible light irradiation, utilizing high-efficiency Au@TiO_2 photocatalytic nanostructures. They achieved this by refining synthetic factors, adjusting photocatalysis parameters, and employing computational modeling. They observed that the resulting nanocomposites absorbed 40–55% more irradiation within the visible spectrum compared to pure TiO_2. Experimental assessments revealed a higher decomposition of ciprofloxacin (91%) under UV light irradiation, while a percentage equal to 49% was achieved under visible light irradiation [58]. In another study, Cabrera-Reina and colleagues investigated the elimination of the antibiotics imipenem and meropenem from various aqueous solutions (distilled water, river water, and simulated wastewater treatment plant effluents) using TiO_2 photocatalysis at a pilot plant scale. They demonstrated favorable decomposition rates under the specific experimental conditions employed [59].

Moreover, Truppi and his team developed a photocatalytic nanocomposite (Au@TiO_2 nanorods) via a co-precipitation approach, followed by calcination at ascending temperatures (250–650 °C). Their research focused on investigating the photocatalytic efficiency of the as-mentioned nanocomposites in degrading an antibiotic molecule (nalidixic acid) utilizing visible light irradiation [60]. Notably, nanocomposites calcined at 450 °C exhibited degradation rates up to 3.2 times more rapid than that of TiO_2 Evonik P25, a commercially available reference material, towards decomposing the targeted compound.

In addition, Gomez-Aviles and co-researchers achieved total decomposition of acetaminophen using C-TiO_2 nanotubes calcined at 400 and 500 °C under solar light irradiation in 1 h. They utilized lignin as a carbon precursor, in order to alter the anatase TiO_2 lattice via a hydrothermal process followed by thermal treatment. The hydrothermal method allowed the production of TiO_2 nanotubes possessing a relatively well-developed surface area, while the resulting C-TiO_2 exhibited an E_g value equal to 2.95 eV, given the existence of the lignin-derived material [61]. Lately, Penas-Garzon and co-researchers studied activated carbon-TiO_2 heterostructures prepared via different methods (solvothermal, microwave-assisted, and sol–gel) utilizing lignin as the carbon source. Among these methods, the microwave-assisted route demonstrated superior performance towards the photocatalytic degradation of acetaminophen, ibuprofen and antipyrine upon solar light irradiation [62].

Additionally, Ahmadpour and colleagues showcased the efficacy of a TiO_2@Zn-Fe_2O_4/Pd photocatalyst produced via the photo-deposition method. They optimized pH, catalyst concentration, and diclofenac's initial concentration, demonstrating its excellent performance in degrading this pharmaceutical substance under solar light exposure. The catalyst exhibited super magnetic properties, facilitating its magnetic separation for facile recovery from the reaction mixture [36].

In a pioneering effort, the same researchers developed $ZnFe_2O_4$@TiO_2/Cu nanocomposites for naproxen removal, achieving an 80.7% degradation efficiency under sunlight irradiation. DRS analysis of the nanocomposites revealed heightened light absorption in the visible spectrum, resulting in reduced electron-hole recombination. Copper's inclusion, possessing an enhanced specific surface area, fostered increased Cu-semiconductor charge and energy transfer. The nanocomposites displayed notable stability and recyclability, maintaining a 72.3% removal rate after 5 cycles of catalyst use [34].

Then, Murgolo and his team investigated a photocatalyst composed of hydroxyapatite and TiO_2 for eliminating diclofenac in water. Their findings indicated a remarkable 95% degradation of the targeted compound within 24 h using the as-mentioned catalyst under UV light exposure [63].

In a separate study, Czech and colleagues examined novel TiO_2 nanocomposites integrating pristine carbon nanotubes (MWCNTs) at varying concentrations (0.15–8.78 wt.%) for the removal of acetaminophen from water. The most effective photocatalytic performance was observed with the nanocomposite containing 1.72 wt.% MWCNTs, enabling 81.6% elimination of acetaminophen elimination from water [64].

Payan and his team also conducted a synthesis of Cu-doped TiO_2 functionalized with SWCNTs using a novel process combining sol–gel and hydrothermal methods. The characterization analysis confirmed the successful integration of Cu ions into the TiO_2 structure and surficial attachment of nanoparticles onto SWCNTs without altering the TiO_2 lattice structure. Regarding photocatalytic performance, total decomposition of sulfamethazine was accomplished under a pH value equal to 7, 10 wt.% SWCNT content, 4 wt.% Cu content, sulfamethazine concentration equal to 30 mg/L and duration of reaction equal to 135 min [65].

Furthermore, Abdelraheem and colleagues carried out a comprehensive study involving the solar light-mediated remediation of domestic wastewater effluents using N,B-co-doped TiO_2. This study focused on the decomposition of bisphenol A, ibuprofen, triclosan, diclofenac, and estrone in double distilled water and various treated wastewater samples. The investigation also considered the impact of typical wastewater components, such as NO_3^-, Cl^-, Br^- and HCO_3^- characterized by recognized ROS quenching attributes. The obtained data demonstrated the successful removal of all examined compounds from individual and combined systems, even in the occurrence of naturally present, typical inorganic quenching agents [66].

Carbuloni and his team explored metformin's decomposition using TiO_2@ZrO_2 nanocomposites upon UV light irradiation. Their study revealed the effective removal of metformin from water under optimized conditions of pH and concentration of the utilized catalyst. The enhanced performance of the TiO_2@ZrO_2 nanocomposites towards the photocatalytic degradation of the model pharmaceutical pollutant was linked to the textural and structural characteristics' alteration, like increased specific surface area, reduced size of the particles, enhanced anatase phase concentration and E_g variations [67].

Additionally, Escudeiro de Oliveira and colleagues employed nanotubes developed on a Ti-0.5 wt.% W alloy for eliminating estrone (E1) and 17a-ethinylestradiol (EE2), which constitute important drugs listed in the EU Watch List, upon both UV and visible light irradiation. Based on their results, the doped samples presented enhanced photocatalytic activity in comparison to samples without doping, as well as other semiconductors, when subjected to both types of light irradiation. This superiority was attributed to reduced recombination rates of photo-produced charges and a flat-band potential's shift towards more negative values [68].

Finally, Gurung and his team investigated the elimination of typically utilized pharmaceutics (carbamazepine and diclofenac) utilizing a Ag_2O@TiO_2 (P25) photocatalyst. Optimal removal percentages of the order of 89.10% for carbamazepine and 93.5% for diclofenac were achieved after 180 min under UV irradiation and a photocatalyst dose equal to 0.4 g/L in distilled water [69].

It is widely accepted that the formation of a Schottky heterojunction through the combination of noble metals with TiO_2 can effectively boost photocatalytic activity [70]. To elaborate, the majority of noble metals possess Fermi levels lower than TiO_2's conduction band, leading to the suppression of charge carrier recombination [71]. Simultaneously, the surface plasmon resonance (SPR) effect exhibited by nano-sized metals, such as Cu, Ag, and Au, enhances the material's absorption of visible light [72]. This SPR effect is characterized by the collective oscillation of electrons on the surface of nano-sized metals, and the controllable manipulation of SPR further augments photocatalytic activity [73]. More precisely, semiconductors loaded with plasmonic metals can significantly boost the generation of photogenerated carriers while concurrently elevating the concentration of superoxide or hydroxyl radicals on the semiconductor's surface. Consequently, this results in a robust capability to degrade various pollutants [74].

Generally, it is proposed that plasmonic metals share common features in their ability to enhance semiconductors through three mechanisms. Initially, metal nanoparticles exhibit a robust light absorption capacity within the visible spectrum and possess a significant scattering cross-section at the resonant wavelength. Both these characteristics substantially amplify the catalytic efficiency of proximal semiconductors. Secondly, the presence of metal nanoparticles on semiconductors results in a more potent electromagnetic field when subjected to localized surface plasmon resonance (LSPR) excitation compared to individual nanoparticles. This intensification facilitates the generation and separation of photogenerated electron-hole pairs within the semiconductor. Finally, the LSPR absorption wavelength of metal nanoparticles can be adjusted by manipulating particle size and shape. Consequently, catalyst performance can be enhanced by modifying the metal composition, morphology, and the contact interface between semiconductors [74].

Kaur and his team [75] fabricated Ag-modified TiO_2 catalysts with distinct morphologies and examined the effect on salicylic acid degradation. It was proposed that the morphological variations led to the difference in both interface and contact areas, which affected the performance of the catalyst.

Moreover, Gang and co-researchers [76] synthesized Ag nanoparticles of 24, 27 and 30 nm through a controlled chemical reduction and these were subsequently loaded onto TiO_2. The Ag/TiO_2 plasmonic photocatalysts displayed superior stability and exceptionally improved the photocatalytic efficiency for visible-light degradation of tetracycline. Ag nanoparticles played a significant role and indicated size-dependent SPR effects, while Ag nanoparticles of 30 nm presented the highest photocatalytic efficiency (90 %) within 90 min.

3. TiO_2-Based Photocatalysts for Effective Elimination of Heavy Metals from Water and Wastewater

Metal ions present in water can undergo reduction to their lower energy state when electrons generated via TiO_2 photo-excitation are available, particularly when the reduction potentials align favorably (Equation (1)). Alternatively, enhancing the reductive elimination of metallic ions can occur indirectly by introducing sacrificial electron donors, like methanol or formaldehyde (Equations (2) and (3)). Moreover, under specific circumstances where the existing oxidation state of the metal ions is not the highest attainable, they can be further oxidized to higher states through the influence of •OH or h^+ (holes) (Equation (4)) [77].

$$M^{n+} + ne^- \rightarrow M$$

$$R - CH_2OH + \bullet OH \rightarrow R - CH^{\bullet} - OH + H_2O$$

$$M^{n+} + R - CH^{\bullet} - OH \rightarrow M^{(n-1)} + R - CHO$$

$$M^{n+} \xrightarrow{\bullet OH\,/h^+} M^{n+1}$$

Heavy metals are typically characterized by their increased atomic weight and density, far surpassing that of H_2O. Due to their relatively lower reactivity and strong properties, they have been extensively utilized across various industries. Nevertheless, noxious heavy metals, like Pb, tend to accumulate swiftly in the environment, proving resistant to biological degradation [78]. Extensive reports highlight the severe toxicity of heavy metals to various human organs, leading to severe consequences, like mutations and cancer [79]. It is crucial to note that, while heavy metals are essential for proper bodily functions in specific quantities, their excess presence can be detrimental. Studies indicate significant adverse effects of heavy metals on plants, involving decreased uptake of nutrients and reduced productivity, when grown in soil where these metals are present [80]. Titanium dioxide has emerged as a cost-effective and time-effective method for heavy metal removal, with primal research proposing their reduction to decreased oxidative states subsequent to their surficial deposition onto the photocatalyst [81].

Titanium dioxide has been effectively employed in the reduction of heavy metal ions through photocatalysis, such as Ni^{2+}, Cd^{2+}, Pb^{2+}, and Cu^{2+}, following first-order kinetics. Enhanced removal of these metals was observed in more acidic conditions, suggesting TiO_2's adaptability to function in such environments. Research indicates that the mechanism primarily involved in heavy metal removal was adsorption, facilitated by the substantial specific surface area of the nano-TiO_2 particles [82]. These nano-TiO_2 particles demonstrated promise for reusability and operation under room temperature conditions. Their adsorption capacity conformed to established isotherms, like the Langmuir isotherm, showcasing TiO_2 nanoparticles as a promising alternative for the removal of heavy metal ions from wastewater [83].

Moreover, titanium dioxide has exhibited effectiveness in photo-catalytically eliminating As from industrial wastewater. The material displayed capability for multiple cycles and retained its effectiveness after regeneration. Simultaneously, other heavy metal ions, like Cu^{2+}, Cd^{2+}, and Pb^{2+}, also presented reduced concentrations, indicating the potential for simultaneous removal without sludge generation [84].

Ti nanotube arrays, altered with the coupling agent KH-570, proved highly effective in degrading Pb^{2+}, Cu^{2+}, and Cr^{6+} present in water. The array's arrangement enhanced specific surface area, as well as photocatalytic effectiveness, while the coupling agent augmented interaction between Ti and the heavy metals' ions. Nevertheless, this altered photocatalyst necessitated UV irradiation for effective operation, while its performance was influenced by wastewater turbidity [85]. Despite these limitations, further evaluation of this catalyst is warranted due to its beneficial aspects.

Titanium dioxide has established a significant history in eliminating Hg (Hg^{2+} to Hg^0) from wastewater, serving as both a photocatalyst [86] and an assisting agent [87]. Research indicates photocatalytic efficacy within a pH range of 3 to 7, notably highlighting the effectiveness of the sol–gel method in producing particles with substantial surface area. Enhancements in catalyst efficiency were observed when increasing pH levels in this range, displaying considerable kinetics [88].

TiO_2 nanotubes have proven remarkably efficient in eliminating Cu^{2+} ions from water while concurrently generating hydrogen. Their enhanced catalytic activity stems from the significantly larger surface area compared to traditional

nanoparticles, attributed to their distinctive shape and structure. The volume of hydrogen produced correlates with the quantity of Cu^{2+}, with an initial concentration of 10 mol % of Cu^{2+} in titanium dioxide demonstrating optimal performance [89]. Furthermore, the transformation of Cr^{6+} ions to Cr^{3+} is achievable using doped TiO_2 photocatalysts. Achieving >99% elimination effectiveness was possible by doping with Fe and exposing the catalyst to visible irradiation. Enhanced electron transfer among the doped titanium dioxide and the ions of heavy metal, compared to pure TiO_2, significantly contributed to the supreme performance [90].

Another method for Cr^{3+} ion removal involved doping TiO_2 developed on graphene oxide with Mn. This process commences with electron transfer from Cr^{6+} towards the photocatalyst, yielding Cr^{3+}, accompanied by subsequent electron transfer resulting in Cr^0 atoms [91]. The co-doping process involving Ag and Mn in TiO_2 has demonstrated remarkable effectiveness in eliminating Cr^{6+} and Cu^{3+} ions from water using a thermodynamically spontaneous adsorption mechanism. The as-mentioned photocatalyst exhibited the ability to eliminate even negligible quantities of these heavy metal ions [92]. Another approach, that of doping with Gd, also displayed positive outcomes in removing Cr^{6+} ions. However, the observations were not as encouraging as those acquired from Fe and Ag@Mn-co-doped TiO_2 photocatalysts [93]. Furthermore, the elimination of Cr^{6+} from wastewater was attained by creating a composite material consisting of titanium dioxide with EDTA on a carbon sheet substrate, showcasing exceptional photodegradation efficiency. This composite exhibited enhanced coordination, while the carbon sheet substrate acted as a dispersion matrix both for nano-TiO_2 particles and EDTA molecules [94].

The inclusion of MnO_2 alongside TiO_2 remarkably enhanced the elimination of Pb^{2+} ions, despite a reduction in surface area. This alteration fostered appealing interactions between the dopant and ions, resulting in heightened ion adsorption by the photocatalyst [95]. Furthermore, the elimination of heavy metals present in nuclear wastes, like Cs^+ and Sr^{2+}, was achieved through doping titanium dioxide nanotubes with chromium ions. The charged nanotubes significantly bolstered removal efficiency, capitalizing on the increased specific surface area [96][97]. In addition, studies indicate the effective reduction of arsenic, a common groundwater contaminant, through iron-doped TiO_2. The incorporation of Fe ions enabled both adsorption and photocatalytic activity under visible irradiation through decreasing the E_g value. Optimal results were achieved with 1 wt.% of Fe at a pH value equal to 7, showcasing its potential as a promising agent for As removal [98].

Nanocomposites have emerged as viable solutions for removing heavy metal ions from water. One proposed method towards the elimination of Pb from wastewater involved the utilization of TiO_2 bio-nanocomposites, crafted through a procedure combining sol–gel fabrication of nano-TiO_2 particles and mixing with a polymeric solution. The as-proposed method presented a notable benefit, as it avoided introducing any by-pollutants into the treated water [99].

The photo-electrocatalytic elimination of Cr^{6+} was found to proceed nearly thrice faster compared to the conventional photocatalysis using TiO_2. Incorporating spherical nanostructures greatly expanded the reaction area, resulting in additional improvements [100]. Another effective approach for Cr^{6+} removal involved integrating Ag_3PO_4 into TiO_2 nanotube arrays, which exhibited equal efficacy in removing organic dyes [101].

The combination of mesoporous hollow TiO_2 nanospheres with 3-aminopropyl triethoxy-silane significantly enhanced the photodegradation effectiveness towards Cu^{2+}, Cd^{2+}, and Pb^{2+}. The resulting composite demonstrated degradation efficiencies 12.7, 17.5, and 1.8 times higher, respectively, than those achieved by bare hollow nano-TiO_2 spheres [102]. Furthermore, the integration of reduced graphene oxide (rGO) with titanium dioxide nanospheres effectively removed Ag^+ ions from water, where rGO contributed to increased charge carrier recombination. The maximum adsorption efficiency recorded was equal to 34.8 mg/g [103]. Additionally, a graphene-like TiO_2@C nanocomposite was utilized to eliminate Pb^{2+} ions from water, displaying an adsorption efficiency of the order of 331.7 mg/g [104].

4. TiO_2-Based Photocatalysts for Effective Elimination of Organic Dyes from Water and Wastewater

A method of removing dyes from the water is photodegradation. There are two potential mechanisms that explain the process. One is the indirect path, where the dye molecule is excited by visible light energy, causing it to enter its triplet excited state. Subsequently, it is further transformed into a semi-oxidized radical by injecting electrons into the conduction band of titanium dioxide (Equations (5) and (6)) [105].

$$\mathrm{dye} + \mathrm{hv} \rightarrow \mathrm{dye}^{*}\ (\mathrm{intermediate})$$

$$\mathrm{dye}^{*} + \mathrm{TiO_2} \rightarrow \mathrm{dye}^{+} + \mathrm{TiO_2^{-}}$$

The second proposed mechanism is direct. In this process, dye molecules interact with the hydroxyl radicals produced, as well as with the electrons and holes formed due to excitation in the conduction band. This interaction leads to the reduction and oxidation of the dyes, respectively [106]. The indirect mechanism is observed to predominate over the direct mechanism, and the photodegradation is higher and requires less time [107] (**Figure 2**).

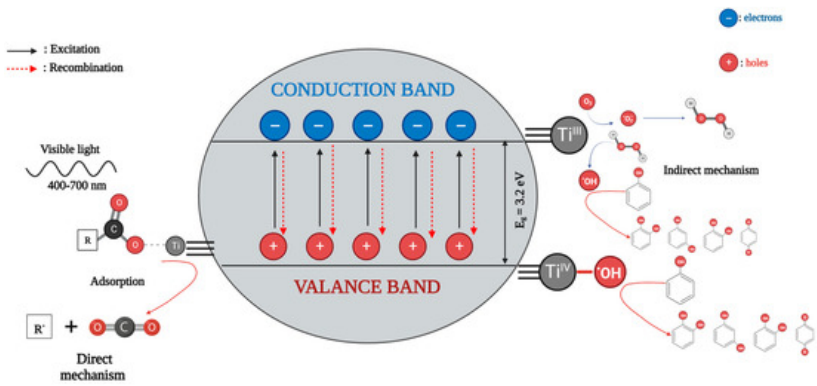

Figure 2. Schematic representation of the direct and indirect mechanism of the photocatalytic degradation of dyes using TiO_2.

The pollution of water sources by dyes has been increasing over the years, mainly because of industrial processes, endangering aquatic organisms and indirectly affecting humans. These dyes are frequently non-biodegradable, accumulating in the body over time [108]. Very often, industrial waste contains both dyes and heavy metals, which meaning that it is impractical to remove them with different processes [109]. It would be ideal to find an efficient and cost-effective way to remove both [110]. A type of dye that is dangerous and difficult to decay is azo [111]. Accumulation of dyes in the water and soil alter their characteristics, which presents a significant problem, being responsible for significant degradation of the water and soil.

Traditionally, techniques like flocculation, adsorption filtration, and dialysis have been employed to eliminate dye molecules from solution. Nevertheless, these techniques frequently lack consistency and reliability, often resulting in incomplete structural degradation and color removal. The discharge of inadequately processed waste into the environment contributes to higher pollution levels [112]. TiO_2 nanomaterials have also drawn attention, in the case of water pollution, as possible solution.

The immobilization of TiO_2 nanomaterials on a matrix has been identified as an effective catalyst. Different azo dyes have been degraded with this type of catalyst. The process resulted in complete removal of color, with dye type AO10 being the easier to degrade. The concentration of organic carbon was significantly reduced in a few hours. TiO_2 nanoparticles proved to be very promising for industrial waste degradation. The degradation is caused by the conversion of the double bond between two nitrogen atoms in the dye molecule to an NH_4^+ ion [9].

Using Rhodamine blue as a pollutant, researchers tested the viability of a zeolite matrix containing TiO_2. They noted higher efficiency, while the composite was easier to recover and reuse [113]. Similar dyes, like methylene blue, have been used to test the difference between the use of micro-sized particles of TiO_2 and nano-sized ones. As expected, the nanosized particles are much more efficient. There are also reports that solutions with higher pH are favorable for the degradation reaction [114]. A composite using a naturally sourced support matrix for the nanoparticles was synthesized using eggshells. The composite was tested on the same dyes as in the previous examples and had positive results. The synthesis was based on the solvothermal method, which is found to play a role in the performance of the produced nanoparticles [115].

Simple TiO_2 nanoparticles have been used to degrade different dyes under sunlight. Solar radiation contains a percentage of UV light, making pure nanoparticles an effective option, if not the most efficient. Nevertheless, complete removal of the dyes was achieved [116]. Other nanostructures, like nanotubes, have also been tested yielding significant results. These can vary depending on the synthetic method and the target dye. For Orange II, the hydrothermal method had better results. Physical adsorption is the mechanism of degradation. Elevating the temperature lowered the time needed [117].

Doping is an easy method to increase the performance of the photocatalyst. Nickel and platinum as doping agents produce remarkable results. It should also be noted that, these metals make the nanoparticles magnetic, which helps recovery. They also proved to be very stable when they were reused [118]. Making the TiO_2 photocatalyst work effectively under visible light irradiation is often the point of the doping, by lowering the band-gap value. Manganese proved to be very effective as dopant, while zirconia and cobalt had negative results [119]. An increase in surface area with doping is

also an important consideration. Metals like iron, copper and chromium have been tested. Doping with copper was found to be most effective at removing methylene blue. The surface area and the lower band-gap are both important factors in this result [120]. Reactive Red dye 198 was successfully degraded, using TiO_2 doped with Fe and N. A first-order reaction was observed, and the improved activity of the catalyst is attributed to the generation of superoxide species, as suggested by Kaur and colleagues [121]. Another doping element which has been tested is strontium. The doped TiO_2, successfully degraded brilliant green, which is an antiseptic and antibacterial dye [122].

The incorporation of elements that are not metals, such as nitrogen and sulfur, has proven to enhance the photocatalytic efficiency of TiO_2, improving the performance under visible light irradiation. The band-gap is reduced by the creation of N^{2+} and S^{2+} levels. A graphene matrix, containing TiO_2 nanoparticles co-doped with these, proved to be a very efficient catalyst for a number of different dyes [123][124].

Carbon doping has also been tested with TiO_2 nanorods. This resulted in a very efficient photocatalyst for dye removal, although the very high temperature requirements limit the potential for large scale applications [125]. The rare earth ytterbium, recovered from waste cathode ray tubes (CRT), was used to dope TiO_2 nanosheets. Recycling the material is an efficient way to make the process more environmentally friendly. The experiments proved that dye degradation is possible, while also degrading heavy metals (chromium) as reported by Zhang and his team [126].

MgO/TiO_2 nanocomposites are used in the photocatalytic methanation of CO_2 through reduction [127], as well as in the production of biodiesel [128]. These composites can be used in dye removal applications. Transition metals can also enhance the photocatalytic behavior of TiO_2. Using sol–gel synthesis, TiO_2 nanoparticles doped with iron were produced and demonstrated high efficiency under visible light irradiation, at basic conditions [129].

Pure TiO_2 nanoparticles, which work under UV light irradiation, have been immobilized on polymer matrixes, retaining their efficiency, while exhibiting enhanced reusability. The incorporation is achieved using a dehydration reaction [130].

Electro-spinning has been used to synthesize nanofibers from TiO_2/CuO. The photodegradation of an azo dye was tested, using the nanofibers. Enhanced adsorption capabilities and the ability to work under visible and UV light were noted. A TiO_2 nanocomposite with zinc sulfide has proven to be a potent photocatalyst. Even at small doses, it can degrade many different dyes when irradiated with ultra-violet light [131].

A TiO_2/SiO_2 nanocomposite, characterized by a high anatase content, has been developed. There are many experiments using methylene blue which test this composite, with some studies using green synthetic methods [132].

Furthermore, a TiO_2/SiO_2 nanocomposite, doped with copper, was created using a simple sol–gel technique. The presence of SiO_2 in the composite enhances the adsorption of organic compounds, while the addition of copper reduces the band-gap. High efficiency in the degradation of Rhodamine B was reported [133]. In order to create TiO_2/SiO_2 aerogels that work under visible light irradiation, researchers used tungsten and fluorine as doping agents. The high pore capacity and lower band-gap helped in the degradation of Rhodamine B [134]. Composites that use the same oxides, immobilized on the polymers polydimethylsiloxane and chitosan, have also been tested [135].

Phosphor-containing nanocomposites have been synthesized for UV and visible light photocatalysis. These $NaYF_4$:(Gd, Si)/TiO_2 nanocomposites exhibited enhanced absorption of UV/visible light and the separation of electron and hole pairs for efficient photocatalysis. Similar $NaYF_4$:Yb,Tm-TiO_2 nanocomposites exhibit photocatalytic activity under near-infrared irradiation [136].

Palygorskite, a fibrous clay material, has also been used. Another usable clay is montmorillonite, a cheap and non-toxic way to add a support structure to TiO_2 nanoparticles. Under ultra-violet light irradiation, the composite proved effective for dye degradation [137].

Other nanocomposites that have been tested are based on TiO_2@SnO_2. Their mesoporous structure and high surface area make them efficient catalysts for photodegradation [138]. Combining two catalysts often results in an improved composite material. Researchers also noted that this material exhibits anti-microbial activity [139]. The conditions of synthetic process can affect the properties of the resulting material. This was demonstrated by researchers using a microwave hydrothermal process to synthesize CdS/$CdTiO_3$-TiO_2 nanocomposites [140].

A novel TiO_2 composite consisting of anatase interacting with a rutile phase containing Ti^{3+} was synthesized by heating a mixture of TiO_2 and Ti_2O_3 at high temperatures. For this composite to degrade some dyes, requires other elements as co-catalysts, like Cu or Pt [141]. A nanocomposite that exhibited great photocatalytic performance under both UV and visible

light irradiation was based on a zeolite matrix, which has the ability to adsorb dyes. The composite was made by $BiVO_4/TiO_2$-NaY [142].

Graphene nanoplates incorporated with Ag_2O/TiO_2 were tested under visible light and UV conditions. Hydrogen peroxide was used to enhance the catalysis. Anions, like carbonate, nitrate, hydrogen phosphate, chloride, and sulfate, can affect the reaction [143].

TiO_2 was used to enhance the surface area of fly ash by a factor of ten. This novel material was used to successfully remove a heavy metal, a dye and a hazardous chemical used in detergents, under ultra-violet light irradiation [144].

Titanium dioxide immobilized onto electro-spun fibers from PVA was employed for the selective removal of methylene blue from a mixture of two dyes [145]. The polymer structures make possible the recovery and reuse of the nanoparticles. This composite demonstrated high photocatalytic efficiency in the decomposition of dye, attributed to the rapid swelling of the hydrogel in acidic conditions [146].

Enzymes have also been used alongside nanomaterials for water treatment. Researchers synthesized polydopamine tethered CPO/HRP-TiO_2 nanocomposites with high biocatalytic activity, stability and reusability. The synthetic method used was in situ polymerization along with an ultrasound bombardment size reduction technique. The enzyme is responsible for the biochemical degradation of the chromophore part of the dye. It has been employed in the degradation of aniline blue, crystal violet, and 2,4-dichlorophenol [147].

Multi walled carbon nanotubes have also been impregnated with TiO_2 nanoparticles. The composite has similar positives as other immobilization matrixes [148]. TiO_2 nanoparticles have also been used in combination with activated carbon. This composite has been successful in degrading various dyes, in batches or with continuous flow [149]. Enhanced photocatalytic properties have also been achieved with silver doping on C-TiO_2 [150].

Graphene oxide (GO) has also been investigated when combined with TiO_2, as water filter, in order to remove dyes [151]. Higher presence of graphene oxide seems to positively affect the removal capabilities [152]. Reduced graphene oxide (rGO) has also been employed alongside TiO_2 for dye degradation. Researchers utilized car bumpers as a recycled source of carbon, showcasing a method of upcycling waste into a novel and high-performance carbon-based photocatalyst. The technology holds the potential for improvement by investigating the possibility of using different plastics for their carbon [153]. A hybrid rGO-TiO_2/Co_3O_4 nanomaterial was synthesized through co-precipitation and utilized for dye removal from wastewater. Reduced graphene oxide proved effective in narrowing the TiO_2/Co_3O_4 band-gap, allowing reaction under visible light. Furthermore, the rGO component inhibited electron-hole recombination, promoting dye degradation [154].

The g-C_3N_4/TiO_2 nanocomposite was able to perform under visible light irradiation. The nanotube-shaped nanomaterial exhibited the highest level of degradation compared to other structures and shapes derived from the experiments [155]. A graphitic carbon nitride-titanium dioxide-graphene aerogel was also an efficient catalyst under visible light irradiation [156] [157]. A membrane made by g-C_3N_4/TiO_2/PAA/PTFE was successfully used to filtrate waste under UV and visible light [158]. Another way to immobilize TiO_2 nanoparticles is on glass beads. These methods have been tested for dye and phenol removal [159][160].

Nanosheets of TiO_2/g-C_3N_4 with dispersed Fe_3O_4 particles demonstrated high photocatalytic activity [161]. Similar results were observed for g-C_3N_4-TiO_2 composites independently [162]. Additionally, a composite of TiO_2 (MNTC nanosheets) formed from nanorods co-doped with Mo/N on carbon nanofibers was relatively successful [163]. Carbon nanosheets, similar to graphene with TiO_2, demonstrated high adsorption capacity [104]. TiO_2 nanosheets also served as the foundation for a composite with Cu-biphenyl-amine, which achieved complete degradation of the dyes in under 3 h [164]. Another composite of TiO_2 nanosheets with silver completely removed the dye in 20 min [165].

Carbon dots are a zero-dimensional nanomaterial. SnO_2 carbon dots have been attached onto TiO_2 nanospheres to create a highly effective catalyst [166]. Three-dimensional nanomaterials containing nanorods have been used to create nanospheres of TiO_2 doped with platinum towards the visible light-assisted degradation of dyes [167].

Fe_3O_4 has also been tested with TiO_2. The experiments were performed under ultrasound to enhance performance [168]. In addition, the embedding of Fe_3O_4 has been proven to be extremely useful, in order to provide TiO_2 with magnetic separation ability [169]. Moreover, the combination of oleic acid with TiO_2 was tested [170].

Photo-electrocatalysis has proven to be an efficient method for treating water containing methylene blue. Doping TiO_2 with fluorine enabled degradation under visible light and improved the generation of electron-hole pairs, enhancing performance [171]. In another study, met-anil yellow and Remazol red B dyes were successfully degraded through photo-electrocatalysis [172]. Furthermore, Pd-doped TiO_2 nanorods showed the ability to produce hydrogen as a byproduct during the removal of Rhodamine B through photo-electrocatalysis under solar irradiation. The unique structure of platinum atoms in the rod configuration contributed to its enhanced performance, particularly in retaining charges [173].

The use of TiO_2 as a photonic crystal has been demonstrated to enhance the degradation ability of catalysts in various studies. Titanium dioxide inverse opals have been proven to be effective in degrading dyes and phenols under ultra-violet light [174]. Photonic crystals coated with gold nanoparticles were able to remove phenols using visible light [175]. Inverse TiO_2 opal photonic crystals coupled with TiO_2/poly(3-hexylthiophene) have demonstrated the ability to remove dyes with visible light sources [176]. TiO_2@SiO_2 photonic crystals have been employed for the degradation of acetaldehyde and dyes [174][177]. An nc-TiO_2/SnO_2 inverse opal composite membrane and Cu_2O/TiO_2 have also been used as photocatalysts [178]. Inverse TiO_2/Pt opals Schottky structures on the Ti substrate have proven effective in degrading phenols [179]. Additionally, a novel photonic crystal structural-induced Cu_3SnS_4/Ti^{3+}-TiO_2 p-n coaxial heterojunction array was proved able to degrade dyes [180].

5. TiO_2-Based Photocatalysts for Effective Elimination of Pesticides from Water and Wastewater

The imperative need to remove pesticide residuals from water stems from their remarkably enhanced toxicity. One method for achieving this is mineralization, a process that involves the complete release of all inorganic components from organic pesticides through degradation. TiO_2 demonstrates the capacity for photocatalytic degradation of pesticides. Resulting radicals from this reaction subsequently interact with dissolved oxygen, generating organic peroxyl radicals (ROO•), crucial for achieving total pesticide mineralization (Equations (7) and (8)) [181].

$$\text{organic pesticides} \xrightarrow{TiO_2 \text{ photo-excitation / adsorption}} \text{intermediates}$$

$$\text{intermediates} \rightarrow CO_2 + SO_4^{2-} + SO_4^{3-} + SO_3^{-}$$

The use of pesticides in the agriculture sector has proved extremely necessary, in order to fulfill the rising food requirements driven by a significant enhancement of the population globally. While pesticides effectively enhance production and prevent agricultural losses, they come with various environmental drawbacks [182]. Similar to dyes and pharmaceuticals, pesticides pose significant threats to aquatic organisms, given their exceptionally increased biological toxicity. These substances not only cause fatalities but also lead to a notable reduction in aquatic organisms' activity [183]. Moreover, their non-biodegradable nature contributes to their accumulation within various organisms. Pesticides can induce acute and chronic health effects, ranging from immune system disruption to improper endocrine function [184]. Moreover, there has been significant attention paid to the potential carcinogenicity of pesticides [185]. Like dyes and pharmaceuticals, traditional wastewater treatment approaches are unable to thoroughly eliminate pesticides, resulting in the potential accumulation of noxious substances in various organisms within the environment [186]. Nevertheless, titanium dioxide has exhibited remarkable effectiveness in degrading pesticides, both in its pure form and when doped.

For instance, chlorpyrifos, a phosphate-based pesticide, underwent photocatalytic degradation utilizing TiO_2 nanoparticles. Approximately 80% of the pesticide was decomposed within 24 h, while the photocatalyst proved effective whether bacteria were present or not, although bacterial presence slightly reduced the degradation rate of the examined pesticide. The as-mentioned photocatalytic procedure necessitated UV light irradiation, as visible irradiation lacked sufficient energy for the utilization of the reaction [187]. Similarly, profenofos and quinalphos have been reduced by TiO_2 nanoparticles using a comparable mechanism upon UV light irradiation. The photocatalyst displayed promising reusability potential under multiple cycles without substantial activity decrease. Its performance was influenced by various factors, such as TiO_2 concentration, radiation duration, and system pH [188]. Additionally, titanium dioxide has demonstrated effectiveness in treating a stream, including a pesticide combination (diuron, alachlor, isoproturon and atrazine).

The efficiency of TiO_2 as a photocatalyst was observed in treating pure, as well as ordinary, water. However, when additional pollutants in normal water were present, there was a notable decline in TiO_2′s effectiveness, attributed to the hindrance of radical formation that accelerates the photocatalytic reaction [189]. The exceptional efficacy of TiO_2 nanowires in atrazine degradation has been evidenced because of their significant specific surface area, as well as pore volume.

These nanowires also present advantages such as cost-effectiveness in synthesis and potential reusability across multiple cycles [190].

Imidacloprid degradation by nano-TiO_2 particles within a cylindrical reactor has been reported as highly effective. The reactor's structure, featuring coaxial cylinders, facilitated enhanced contact among the photocatalyst and polluted water, thereby enhancing photocatalytic performance. Additionally, the reactor demonstrated applicability in both batch and continuous modes, underscoring its adaptability and effectiveness [191]. TiO_2 P25 has been widely recognized as a photocatalyst for pesticide elimination. In one research project, typically found pesticides and insecticides, such as malathion, fenitrothion, quinalphos, vinclozolin, dimethoate and fenarimol, have been decomposed utilizing TiO_2 P25 under solar light irradiation. Another commercially available form, Kronos VLP 7000, was examined but proved to be less efficient than P25, because of inferior specific surface area and pore volume attributes [192]. Additionally, TiO_2 P25 has demonstrated increased efficacy in removing diazinon from water, achieving >99% pesticide decomposition at a pH value equal to 6.

The reaction primarily depended on the supplied UV amount and reaction time. Additionally, TiO_2 concentration and aeration have been identified as improving the photocatalytic process [193]. Altering the structure of titanium dioxide nanotubes significantly improved the elimination effectiveness of simazine pesticide. The proposed approach involved structural modification by varying the anodization time, with a time equal to 10 min yielding the optimal outcomes [194].

Incorporating Fe into TiO_2 demonstrated exceptional performance in diazinon decomposition, achieving an optimal decomposition efficiency of ≈85%. The presence of Fe notably accelerated the reaction under UV light and ultrasonic irradiation. Ultrasonic irradiation demonstrated better degradation efficacy when used individually. However, the highest efficiency was achieved when both UV and ultrasonic irradiation were combined with Fe-TiO_2 [195]. Introducing cerium (Ce) doping yielded excellent outcomes in removing metolachlor, a typically used pesticide. The magnetic properties of Ce facilitated the dopant–TiO_2 separation. Cerium doping enhanced porosity and decreased charge carrier recombination, significantly enhancing effectiveness [196]. Ce dopant also proved effective in removing another common pesticide, glyphosate. A Ce loading of 0.45 wt.% was determined as optimal. In addition, Mn and La were studied as potential dopants towards glyphosate elimination. Among the three, Mn exhibited the optimal performance, followed by Ce and then La, all with an optimal loading of the order of 0.45 wt.%. Concentrations surpassing the optimum value led to a great efficiency loss [197].

Ce has been utilized as a dopant in the photocatalytic elimination of dicamba pesticide under visible light irradiation. An optimal loading of Ce equal to 1 wt.% led to complete degradation within 2 h, particularly effective in conditions where pH values were greater than 7, generating non-toxic by-products easily removable from water. Ce aggregation increased specific surface area and pore volume, enhancing the photocatalytic effectiveness of Ce-TiO_2 compared to the bare photocatalyst [198]. Boron (B) doping exhibited superior degradation of various pesticides compared to the undoped photocatalyst, significantly enhancing robustness and reusability. The presence of B atoms within the TiO_2 lattice contributed to improved functionality and stability of the doped photocatalyst. Combining photocatalysis with ozonation accelerated pesticide elimination [199]. Furthermore, doping TiO_2 with non-metals, like C, N, and F, enhanced its degradation capability, notably preventing electron and hole pair recombination under visible light. Thiamethoxam and imidacloprid insecticides were completely degraded using doped photocatalysts under different wavelengths, showing stability across multiple cycles, promising for industrial applications [200].

Finally, the method of TiO_2 photo-electrocatalysis has proven effective in eliminating the herbicide atrazine from water samples. Almost total elimination of the contaminant occurred within 30 min reaction time, displaying a first-order kinetics trend [201]. Atrazine removal from groundwater has been also accomplished through employing TiO_2-graphite photo-electrocatalysts, exhibiting an impressive reduction effectiveness of up to 99.7% [202], slightly surpassing the efficacy observed in the earlier study.

6. TiO_2-Based Photocatalysts for Effective Elimination of Microbes from Water and Wastewater

TiO_2 has been studied extensively for its anti-microbial activity [203]. It can be used on surfaces or to disinfect water. When the bacteria *E. coli* suffers membrane damage, malondialdehyde is produced, due to lipid peroxidation. Bactericidal activity can be measured in this way. TiO_2 activated by light, can cause cell death after a short time (30 min), by damaging the cell membranes. The creation of radicals causes lipid peroxidation. The by-product malondialdehyde is also oxidated further facilitating the easy cell access [204]. Cancer cells are also vulnerable to this type of damage [205].

The efficiency of bactericidal methods depends on their effective disinfection time (EDT), representing the duration needed for complete bacterial inactivation in the absence of irradiation, and without the possibility of regrowth. In the case of TiO_2, no regrowth is observed within the subsequent 60 h in the absence of irradiation, as the bacterial concentration continues to decrease in the dark [206].

Photo-induced bactericidal methods have attracted research attention. TiO_2 nanoparticles are very effective, due to their decreased size [207]. In order for the nanoparticles to be reused, they need to be recovered. Immobilizing them on a matrix is a good solution, but decreases their efficiency. Enhanced permeability of ions through cell membranes has been proposed as a potential disinfection method. TiO_2 has also been shown to degrade the toxins that are released from the dying bacterial cells [208].

Various harmful microorganisms, including *Escherichia coli*, constitute a threat to water bodies worldwide. In general, these microbes produce noxious substances upon entering the human body [209]. Temperature, water turbidity, pH, and the presence of competing microorganisms affect their lifespan [210]. While sunlight has been found efficient in inactivating a plethora of microorganisms, scaling up this method for industrial use presents significant challenges. Alternative approaches, like chlorine treatment, have been explored; however, impracticality arises from the production of noxious substances associated with these approaches [211].

Microbes in aquatic bodies, can negatively affect the fish population [212]. Infected water has also been a major factor for the spread of diseases throughout history, like cholera caused by *Vibrio cholerae*, and typhoid caused by *Salmonella typhi* [213].

In this context, it is essential to research and develop photocatalysts that are efficient and environmentally friendly. Utilizing thin films consisting of TiO_2 nanoparticles has demonstrated remarkable efficacy in the elimination of *E. coli* from water through photocatalysis. The swift and efficient inactivation of cells is attributed to the expansion of the cell membrane upon adsorption by titanium dioxide and illumination. The potential effects include the loss of protoplasm, speculated to result from membrane expansion and cell distortion. Additionally, acids' fast degradation further contributes to the membrane's expansion [214]. TiO_2 nanotubes have also demonstrated comparable anti-microbial applications in water purification, targeting organisms such as *E. coli* and *Staphylococcus aureus*. Exposure to UV irradiation for 24 h in the presence of the photocatalyst resulted in the degradation of both organisms by more than 97%. The effect was greater than that exhibited by simple TiO_2 P25 nanoparticles. The shape of the nanomaterial seems to be an important factor for anti-microbial capabilities [215].

Nevertheless, TiO_2 P25 has proven exceptionally efficient against microbes under specific parameters. *Salmonella typhimurium* and *Listeria monocytogenes* were both inactivated by the photocatalyst when exposed to UV irradiation. *Listeria* was proven to be more resistant than *Salmonella*. The mechanism seems to be membrane damage, as in other cases. The catalytic reaction was significantly influenced by the concentration of the nanoparticles, with the most favorable results obtained at a concentration equal to 1 g/L [216].

Doping of the nanoparticles has also been extensively studied. Nitrogen doping is an easy and effective way to increase the bactericidal properties. Different nitrogen containing compounds have been used and, depending on the target microorganism, the optimal chemical can differ. For example, the removal of *B. cereus* was achieved completely when triethyl amine was used. In other cases, urea was better [217]. Nitrogen doping lowers the band-gap, making the photocatalyst more effective even when irradiated with visible light. Doping with fluorine has also bene investigated, yielding a comparable outcome in terms of the E_g. However, a distinction was observed in the distribution of atoms. More specifically, N atoms were detected in the interstices, while F atoms were observed surficially [218].

Research has demonstrated that TiO_2 doped with Fe, Mn and Mg is an extremely effective method for eliminating the virus H1N1 from water. The catalytic process proved viable even in the presence of a weak source of visible light irradiation, achieving over 99% elimination effectiveness within 30 min. Additionally, elimination utilizing UV irradiation was also feasible, but it is considered less practical, since the reaction can be conducted utilizing visible irradiation [219]. Likewise, TiO_2 nanofibers doped with Cu exhibited impressive capabilities in removing the f2 virus and *E. coli*. The concurrent elimination of both microorganisms was demonstrated upon visible light irradiation and the reaction proved to be unaffected by pH variations. The elimination of the virus was directly correlated with the photocatalyst's concentration, as well as the light's intensity, showing an inverse relationship with the quantity of the virus. Nevertheless, it was observed that the elimination of the virus was more enhanced when present alone, compared to its presence alongside bacteria, indicating competition for adsorption spaces as a contributing factor [220].

Silver, which itself is considered to have anti-microbial properties, can be used to greatly enhance the TiO_2 efficiency. Nanowires doped with silver demonstrated superior performance to other doping elements against the bacteria *E. coli*. The processed water was determined as safe to drink, therefore this nanomaterial has potential for large scale applications [221].

Other doping agents that lower the band-gap of TiO_2 and make it efficient for visible light photocatalysis are manganese and cobalt. The best results were produced by co-doping, which resulted in a 99% concentration reduction for the viruses that were tested, within 20 min. Sunlight contains the UV spectrum and is superior to artificial light [222].

In general, the mode of toxicity of TiO_2 nanoparticles towards harmful microorganisms is depicted in **Figure 3**.

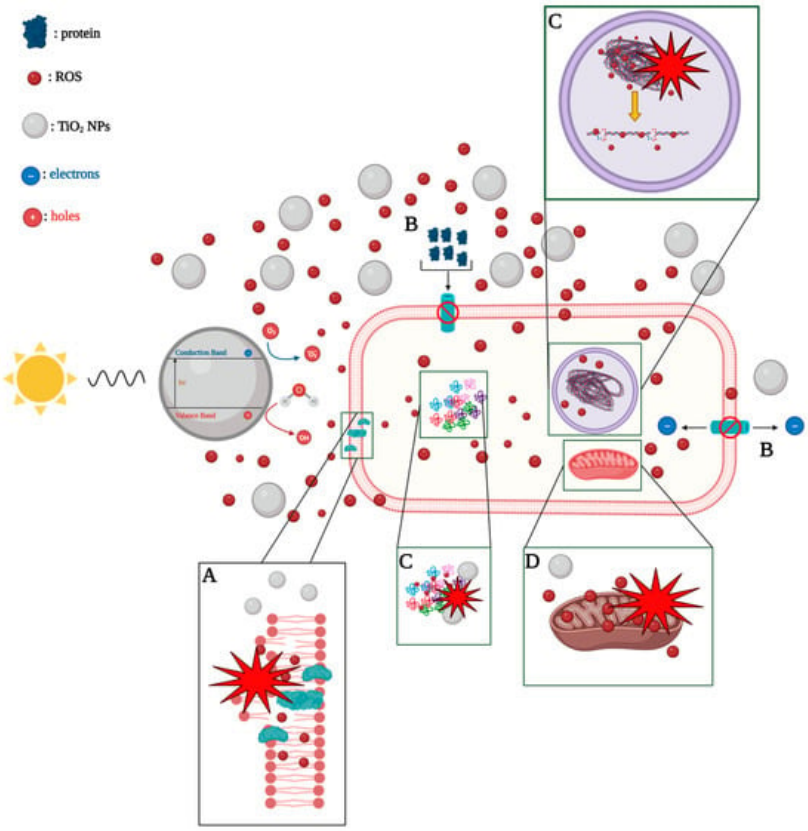

Figure 3. Schematic representation of the TiO_2 nanoparticles' toxicity mechanism towards pathogenic microorganisms. In general, the toxicity mechanism can be attributed to the following procedures: (**A**) infliction of cellular damage and lipid oxidation arising from the attachment of nano-particles through electrostatic interaction with the cell wall, (**B**) disruption of the cytoplasmic flow, due to nanoparticle hindrance of nutrient carriers, leading to (**C**) photocatalytic decomposition of biological macromolecules, and (**D**) impairment of intracellular organelles [223].

7. TiO_2-Based Photocatalysts for Effective Elimination of Hormones and Endocrine Disrupting Compounds (EDCs) from Water and Wastewater

Endocrine-disrupting chemicals (EDCs) are natural or human-made chemicals that may mimic, block, or interfere with the body's hormones, which are part of the endocrine system. These chemicals are associated with a wide array of health issues. They are found in wastewater from some industries and from households. Drugs, pesticides and cosmetics can be a source of these chemicals, as well as living organisms [224]. They can have significant negative effects on humans, especially on the development of children [225]. It is also possible to affect the fetus in pregnant women [226]. Negative effects have also been found on aquatic life. An example of this is the feminization of fish, from high estrogen levels in their environment [227].

Hormones and some drugs are endocrine disrupting compounds. Hormones, even in very small amounts, can affect humans and other organisms [228]. Heavy metals can also affect the endocrine system. Some common chemicals found in the wastes of certain industries are phthalates, which are considered carcinogenic [229], and bisphenol, which is linked to sexual dysfunction in males [230].

It is difficult to completely remove these compounds from water, which means they often end up in the aquatic environment. It is very important to find ways to degrade these chemicals during wastewater treatment. TiO_2 has shown

promise as a viable and clean method to remove endocrine disrupting compounds from wastewater [231].

TiO_2 nanomaterials have been used for the degradation of many hormones and other similar compounds. The use of TiO_2 thin films was very effective for the removal of steroidal hormones after light irradiation. Faster degradation was achieved with the addition of hydrogen peroxide [232].

Pure TiO_2 nanoparticles have been used successfully for the removal of estrogens (female hormones: estrone, estradiol, estriol, estetrol) and mimic chemicals, like bisphenol A. UV light is required for efficient degradation and acidic conditions are favorable [233]. The photodegradation often has more than one stage. By-products, like hydroxylated estrones, are produced first and then they are further degraded [234]. From this class of hormones, estradiol seems to be easier to remove with pure TiO_2 nanoparticles [235], while estriol and estrone require higher concentrations of the catalyst to be efficiently removed [236]. Compounds that belong to this class of chemicals have also been degraded with the use of stacked TiO_2 thin films in reactors where the wastewater flows through. The removal of Bisphenol A in comparison to the other chemicals was the most challenging when using this method. The by-products produced are not as similar to estrogens, which means they are much safer [237].

Testosterone, which is a male hormone, can also be degraded be TiO_2 nanoparticles. A study found that the resulting by-products are similar to those produced by natural metabolism [238]. The nanoparticles, under irradiation, can transfer electrons and also cause the formation of hydroxyl radicals in the solution. Both mechanisms are responsible for the degradation of the hormone.

Doping the nanoparticles with silver and adding hydrogen peroxide in the solution during photodegradation resulted in good performance under visible light irradiation. The test was carried out with dexamethasone as a pollutant [239].

TiO_2 has also been used in conjunction with phytoremediation. Phytoremediation is a technique that uses plants to clean polluted ground. By combining these two methods, researchers were able to remove the pollutant decabromodiphenyl ether. The byproducts were nontoxic. The TiO_2 increased its efficiency by helping uptake by the plants [240].

Titanium dioxide has also been used in hybrid composites in an effort to synthesize a more efficient catalyst. Porphyrins are a class of organic compounds that are often used in photodynamic therapy. Researchers used cardanols, a toxic byproduct of the cashew industry, to synthesize porphyrins, that were then impregnated with TiO_2 nanoparticles. Metals such as zinc and iron were also used to create metallo-porphyrins. This conjugate was used to degrade 4-nitrophenol [241].

In general, an effective way to use TiO_2 nanoparticles is to immobilize them into a matrix. In this way, they can easily be used inside a recirculation reactor. TiO_2-coated clay beads were used in this way, to degrade the pollutant monocrotophos [242].

Other TiO_2 nanomaterials that have been tested, are nanotubes, doped with C_3N_4. Using electro-photocatalysis, the researchers reported that the degradation of phenolic compounds was much faster compared to pure TiO_2. The doping lowered the band-gap [243]. Other complex nano-structures that have been synthesized are hydrogels with graphene and TiO_2. The tests showed outstanding performance during photo-electrocatalysis for the degradation of bisphenol A and no significant decline in performance after 10 cycles [156][157]. The method of photo-electrocatalysis has also been used to degrade propyl paraben using TiO_2 nanotubes doped with WO_3 [244].

References

1. UNESCO. The United Nations World Water Development Report 2020 Water and Climate Change; UNESCO: Paris, France, 2020.
2. Chart, H. VTEC enteropathogenicity. Symp. Ser. Soc. Appl. Microbiol. 2000, 29, 12S–23S.
3. Fowler, C.C.; Galán, J.E. Decoding a Salmonella typhi regulatory network that controls typhoid toxin expression within human cells. Cell Host Microbe 2018, 23, 65–76.
4. Rivera-Chávez, F.; Mekalanos, J.J. Cholera toxin promotes pathogen acquisition of host-derived nutrients. Nature 2019, 572, 244–248.
5. Chuang, C.-H.; Wang, Y.-H.; Chang, H.-J.; Chen, H.-L.; Huang, Y.-C.; Lin, T.-Y.; Ozer, E.A.; Allen, J.P.; Hauser, A.R.; Chiu, C.-H. Shanghai fever: A distinct Pseudomonas aeruginosa enteric disease. Gut 2014, 63, 736–743.

6. Rajasurya, V.; Surani, S. Legionnaires Disease in Immunocompromised Host; IntechOpen: London, UK, 2020.
7. Sansenya, T.; Masri, N.; Chankhanittha, T.; Senasu, T.; Piriyanon, J.; Mukdasai, S.; Nanan, S. Hydrothermal synthesis of ZnO photocatalyst for detoxification of anionic azo dyes and antibiotic. J. Phys. Chem. Solids 2022, 160, 110353.
8. Vaez, Z.; Javanbakht, V. Synthesis, characterization and photocatalytic activity of ZSM-5/ZnO nanocomposite modified by Ag nanoparticles for methyl orange degradation. J. Photochem. Photobiol. A 2020, 388, 112064.
9. Khataee, A.R.; Pons, M.N.; Zahraa, O. Photocatalytic degradation of three azo dyes using immobilized TiO2 nanoparticles on glass plates activated by UV light irradiation: Influence of dye molecular structure. J. Hazard. Mater. 2009, 168, 451–457.
10. Liberatore, L.; Bressan, M.; Belli, C.; Lustrato, G.; Ranalli, G. Chemical and biological combined treatments for the removal of pesticides from wastewaters. Water Air Soil Pollut. 2012, 223, 4751–4759.
11. Ballesteros Martín, M.M.; Sánchez Pérez, J.A.; Casas López, J.L.; Oller, I.; Malato Rodríguez, S. Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation. Water Res. 2009, 43, 653–660.
12. Bressan, M.; Liberatore, L.; d'Alessandro, N.; Tonucci, L.; Belli, C.; Ranalli, G. Improved combined chemical and biological treatments of olive oil mill wastewaters. J. Agric. Food Chem. 2004, 52, 1228–1233.
13. Tahir, M.S.; Saleem, M.; Malik, S.R.; Khan, J.R.; Siebenhofer, M. An innovative and advanced oxidation process for effluent treatment through wet tube-type electrostatic precipitation. Chem. Eng. Process. Process Intensif. 2012, 52, 16–20.
14. Ben Mansour, L.; Kesentini, I. Treatment of effluents from cardboard industry by coagulation-electroflotation. J. Hazard. Mater. 2008, 153, 1067–1070.
15. Hanay, Ö.; Hasar, H. Effect of anions on removing Cu2+, Mn2+ and Zn2+ in electrocoagulation process using aluminum electrodes. J. Hazard. Mater. 2011, 189, 572–576.
16. Centi, G.; Perathoner, S.; Torre, T.; Verduna, M.G. Catalytic wet oxidation with H2O2 of carboxylic acids on homogeneous and heterogeneous Fenton-type catalysts. Catal. Today 2000, 55, 61–69.
17. Ghosh, P.; Samanta, A.N.; Ray, S. Reduction of COD and removal of Zn2+ from rayon industry wastewater by combined electro-Fenton treatment and chemical precipitation. Desalination 2011, 266, 213–217.
18. Lin, S.H.; Chang, C.C. Treatment of landfill leachate by combined electro-Fenton oxidation and sequencing batch reactor method. Water Res. 2000, 34, 4243–4249.
19. Ayodele, O.B.; Hameed, B.H. Synthesis of copper pillared bentonite ferrioxalate catalyst for degradation of 4-nitrophenol in visible light assisted Fenton process. J. Ind. Eng. Chem. 2013, 19, 966–974.
20. Monteagudo, J.M.; Durán, A.; San Martín, I.; Aguirre, M. Effect of light source on the catalytic degradation of protocatechuic acid in a ferrioxalate-assisted photo-Fenton process. Appl. Catal. B 2010, 96, 486–495.
21. John Peter, I.; Praveen, E.; Vignesh, G.; Nithiananthi, P. ZnO nanostructures with different morphology for enhanced photocatalytic activity. Mater. Res. Express 2017, 4, 124003.
22. Zhang, D.E.; Ren, L.Z.; Hao, X.Y.; Pan, B.B.; Wang, M.Y.; Ma, J.J.; Li, F.; Li, S.A.; Tong, Z.W. Synthesis and photocatalytic property of multilayered Co3O4. Appl. Surf. Sci. 2015, 355, 547–552.
23. Ani, I.J.; Akpan, U.G.; Olutoye, M.A.; Hameed, B.H. Photocatalytic degradation of pollutants in petroleum refinery wastewater by TiO2- and ZnO-based photocatalysts: Recent development. J. Clean. Prod. 2018, 205, 930–954.
24. Tanji, K.; Navio, J.A.; Chaqroune, A.; Naja, J.; Puga, F.; Hidalgo, M.C.; Kherbeche, A. Fast photodegradation of rhodamine B and caffeine using ZnO-hydroxyapatite composites under UV-light illumination. Catal. Today 2022, 388–389, 176–186.
25. Lagopati, N.; Tsilibary, E.P.; Falaras, P.; Papazafiri, P.; Pavlatou, E.A.; Kotsopoulou, E.; Kitsiou, P. Effect of nanostructured TiO2 crystal phase on photoinduced apoptosis of breast cancer epithelial cells. Int. J. Nanomed. 2014, 9, 3219–3230.
26. Lagopati, N.; Kitsiou, P.; Kontos, A.; Venieratos, P.; Kotsopoulou, E.; Kontos, A.; Dionysiou, D.; Pispas, S.; Tsilibary, E.; Falaras, P. Photo-induced treatment of breast epithelial cancer cells using nanostructured titanium dioxide solution. J. Photochem. Photobiol. A Chem. 2010, 214, 215–223.
27. Anitha, B.; Khadar, M.A. Anatase-rutile phase transformation and photocatalysis in peroxide gel route prepared TiO2 nanocrystals: Role of defect states. Solid State Sci. 2020, 108, 106392.
28. Lagopati, N.; Kotsinas, A.; Veroutis, D.; Evangelou, K.; Papaspyropoulos, A.; Arfanis, M.; Falaras, P.; Kitsiou, P.V.; Pateras, I.; Bergonzini, A.; et al. Biological effect of silver-modified nanostructured titanium dioxide in cancer. Cancer Genom. Proteom. 2021, 18 (Suppl. S3), 425–439.

29. Nur, A.S.M.; Sultana, M.; Mondal, A.; Islam, S.; Robel, F.N.; Islam, A.; Sumi, M.S.A. A review on the development of elemental and codoped TiO2 photocatalysts for enhanced dye degradation under UV–vis irradiation. J. Water Process. Eng. 2022, 47, 102728.
30. Kowalska, E.; Mahaney, O.O.P.; Abe, R.; Ohtani, B. Visible-light-induced photocatalysis through surface plasmon excitation of gold on titania surfaces. Phys. Chem. Chem. Phys. 2010, 12, 2344–2355.
31. Kümmerer, K. Antibiotics in the aquatic environment—A review–part I. Chemosphere 2009, 75, 417–434.
32. Rasouli, S.; Rezaei, N.; Hamedi, H.; Zendehboudi, S.; Duan, X. Superhydrophobic and superoleophilic membranes for oil-water separation application: A comprehensive review. Mater. Des. 2021, 204, 109599.
33. Zareei Pour, F.; Sabzehmeidani, M.M.; Karimi, H.; Madadi Avargani, V.; Ghaedi, M. Superhydrophobic–superoleophilic electrospun nanofibrous membrane modified by the chemical vapor deposition of dimethyl dichlorosilane for efficient oil-water separation. J. Appl. Polym. Sci. 2019, 136, 47621.
34. Ahmadpour, N.; Sayadi, M.H.; Sobhani, S.; Hajiani, M. A potential natural solar light active photocatalyst using magnetic ZnFe2O4@TiO2/Cu nanocomposite as a high performance and recyclable platform for degradation of naproxen from aqueous solution. J. Clean. Prod. 2020, 268, 122023.
35. Kumar, A.; Kumar, A.; Sharma, G.; Al-Muhtaseb, A.H.; Naushad, M.; Ghfar, A.A.; Stadler, F.J. Quaternary magnetic BiOCl/g-C3N4/Cu2O/Fe3O4 nano-junction for visible light and solar powered degradation of sulfamethoxazole from aqueous environment. Chem. Eng. J. 2018, 334, 462–478.
36. Ahmadpour, N.; Sayadi, M.H.; Sobhani, S.; Hajiani, M. Photocatalytic degradation of model pharmaceutical pollutant by novel magnetic TiO2@ZnFe2O4/Pd nanocomposite with enhanced photocatalytic activity and stability under solar light irradiation. J. Environ. Manag. 2020, 271, 110964.
37. Naushad, M. Surfactant assisted nano-composite cation exchanger: Development, characterization and applications for the removal of toxic Pb2+ from aqueous medium. Chem. Eng. J. 2014, 235, 100–108.
38. Sayadi, M.H.; Ahmadpour, N.; Homaeigohar, S. Photocatalytic and antibacterial properties of Ag-CuFe2O4@WO3 magnetic nanocomposite. Nanomaterials 2021, 11, 298.
39. Liu, F.; Liang, J.; Chen, L.; Tong, M.; Liu, W. Photocatalytic removal of diclofenac by Ti doped BiOI microspheres under visible light irradiation: Kinetics, mechanism, and pathways. J. Mol. Liq. 2019, 275, 807–814.
40. Comber, S.; Gardner, M.; Sörme, P.; Ellor, B. The removal of pharmaceuticals during wastewater treatment: Can it be predicted accurately? Sci. Total Environ. 2019, 676, 222–230.
41. Awfa, D.; Ateia, M.; Fujii, M.; Johnson, M.S.; Yoshimura, C. Photodegradation of pharmaceuticals and personal care products in water treatment using carbonaceous-TiO2 composites: A critical review of recent literature. Water Res. 2018, 142, 26–45.
42. Mudgal, S.; De Toni, A.; Lockwood, S.; Sales, K.; Backhaus, T.; Sorensen, B.H. Study on the environmental risks of medicinal products. In BIO Intelligence Service; European Commission: Brussels, Belgium, 2013; Available online: https://hal.science/hal-03859880 (accessed on 12 January 2024).
43. Sheng, C.; Agwu Nnanna, A.G.; Liu, Y.; Vargo, J.D. Removal of trace pharmaceuticals from water using coagulation and powdered activated carbon as pretreatment to ultrafiltration membrane system. Sci. Total Environ. 2016, 550, 1075–1083.
44. Bai, X.; Acharya, K. Removal of trimethoprim, sulfamethoxazole, and triclosan by the green alga Nannochloris sp. J. Hazard. Mater. 2016, 315, 70–75.
45. Williams, R.T.; Cook, J.C. Exposure to pharmaceuticals present in the environment. Ther. Innov. Regul. Sci. 2007, 41, 133–141.
46. Oluwole, A.O.; Omotola, E.O.; Olatunji, O.S. Pharmaceuticals and personal care products in water and wastewater: A review of treatment processes and use of photocatalyst immobilized on functionalized carbon in AOP degradation. BMC Chem. 2020, 14, 62.
47. Kümmerer, K.; Steger-Hartmann, T.; Meyer, M. Biodegradability of the anti-tumour agent ifosfamide and its occurrence in hospital effluents and communal sewage. Water Res. 1997, 31, 2705–2710.
48. Kumar, A.; Sharma, G.; Naushad, M.; Ahamad, T.; Cataluña Veses, R.; Stadler, F.J. Highly visible active Ag2CrO4/Ag/BiFeO3@RGO nano-junction for photoreduction of CO2 and photocatalytic removal of ciprofloxacin and bromate ions: The triggering effect of Ag and RGO. Chem. Eng. J. 2019, 370, 148–165.
49. Layton, A.; Gregory, B.; Seward, J.; Schultz, T.; Sayler, G. Mineralization of steroidal hormones by biosolids in wastewater treatment systems in Tennessee USA. Environ. Sci. Technol. 2000, 34, 3925–3931.

50. Kokkinos, P.; Venieri, D.; Mantzavinos, D. Advanced oxidation processes for water and wastewater viral disinfection. a systematic review. Food Environ. Virol. 2021, 13, 283–302.

51. Kanakaraju, D.; Glass, B.D.; Oelgemöller, M. Titanium dioxide photocatalysis for pharmaceutical wastewater treatment. Environ. Chem. Lett. 2014, 12, 27–47.

52. Zhang, Y.; Zhou, Z.; Chen, T.; Wang, H.; Lu, W. Graphene TiO2 nanocomposites with high photocatalytic activity for the degradation of sodium pentachlorophenol. J. Environ. Sci. 2014, 26, 2114–2122.

53. Sharma, G.; Alothman, Z.A.; Kumar, A.; Sharma, S.; Kumar Ponnusamy, S.; Naushad, M. Fabrication and characterization of a nanocomposite hydrogel for combined photocatalytic degradation of a mixture of malachite green and fast green dye. Nanotechnol. Environ. Eng. 2017, 2, 4.

54. Akter, S.; Islam, S.; Kabir, H.; Shaikh, A.A.; Gafur, A. UV/TiO2 photodegradation of metronidazole, ciprofloxacin and sulfamethoxazole in aqueous solution: An optimization and kinetic study. Arab. J. Chem. 2022, 15, 103900.

55. Sharma, M.; Yadav, A.; Mandal, M.K.; Dubey, K.K. TiO2 based photocatalysis: A valuable approach for the removal of pharmaceuticals from aquatic environment. Int. J. Environ. Sci. Technol. 2023, 20, 4569–4584.

56. Manasa, M.; Chandewar, P.R.; Mahalingam, H. Photocatalytic degradation of ciprofloxacin & norfloxacin and disinfection studies under solar light using boron & cerium doped TiO2 catalysts synthesized by green EDTA-citrate method. Catal. Today 2020, 375, 522–536.

57. Suwannaruang, T.; Kidkhunthod, P.; Chanlek, N.; Soontaranon, S.; Wantala, K. High anatase purity of nitrogen-doped TiO2 nanorice particles for the photocatalytic treatment activity of pharmaceutical wastewater. Appl. Surf. Sci. 2019, 478, 1–14.

58. Martins, P.; Kappert, S.; Nga Le, H.; Sebastian, V.; Kühn, K.; Alves, M.; Pereira, L.; Cuniberti, G.; Melle-Franco, M.; Lanceros-Méndez, S. Enhanced photocatalytic activity of Au/TiO2 nanoparticles against ciprofloxacin. Catalysts 2020, 10, 234.

59. Cabrera-Reina, A.; Martínez-Piernas, A.B.; Bertakis, Y.; Xekoukoulotakis, N.P.; Agüera, A.; Sánchez-Pérez, J.A. Ti photocatalysis under natural solar radiation for the degradation of the carbapenem antibiotics imipenem and meropenem in aqueous solutions at pilot plant scale. Water Res. 2019, 166, 115037.

60. Truppi, A.; Petronella, F.; Placido, T.; Margiotta, V.; Lasorella, G.; Giotta, L.; Giannini, C.; Sibillano, T.; Murgolo, S.; Mascolo, G.; et al. Gram-scale synthesis of UV-vis light active plasmonic photocatalytic nanocomposite based on TiO2/Au nanorods for degradation of pollutants in water. Appl. Catal. B Environ. 2019, 243, 604–613.

61. Gómez-Avilés, A.; Peñas-Garzón, M.; Bedia, J.; Rodriguez, J.J.; Belver, C. C-modified TiO2 using lignin as carbon precursor for the solar photocatalytic degradation of acetaminophen. Chem. Eng. J. 2019, 358, 1574–1582.

62. Peñas-Garzón, M.; Gómez-Avilés, A.; Belver, C.; Rodriguez, J.J.; Bedia, J. Degradation pathways of emerging contaminants using TiO2-activated carbon heterostructures in aqueous solution under simulated solar light. Chem. Eng. J. 2020, 392, 124867.

63. Murgolo, S.; Moreira, I.S.; Piccirillo, C.; Castro, P.M.L.; Ventrella, G.; Cocozza, C.; Mascolo, G. Photocatalytic degradation of diclofenac by hydroxyapatite–TiO2 composite material: Identification of transformation products and assessment of toxicity. Materials 2018, 11, 1779.

64. Czech, B.; Tyszczuk-Rotko, K. Visible-light-driven photocatalytic removal of acetaminophen from water using a novel MWCNT-TiO2-SiO2 photocatalysts. Separ. Purif. Technol. 2018, 206, 343–355.

65. Payan, A.; Akbar Isari, A.; Gholizade, N. Catalytic decomposition of sulfamethazine antibiotic and pharmaceutical wastewater using Cu-TiO2@functionalized SWCNT ternary porous nanocomposite: Influential factors, mechanism, and pathway studies. Chem. Eng. J. 2019, 361, 1121–1141.

66. Abdelraheem, W.H.M.; Nadagouda, M.N.; Dionysiou, D.D. Solar light-assisted remediation of domestic wastewater by N,B-TiO2 nanoparticles for potable reuse. Appl. Catal. B Environ. 2020, 269, 118807.

67. Carbuloni, C.F.; Savoia, J.E.; Santos, J.S.P.; Pereira, C.A.A.; Marques, R.G.; Ribeiro, V.A.S.; Ferrari, A.M. Degradation of metformin in water by TiO2–ZrO2 photocatalysis. J. Environ. Manag. 2020, 262, 110347.

68. Escudeiro de Oliveira, M.; Barroso, B.L.; de Almeida, J.; Moraes, M.L.L.; de Arruda Rodrigues, C. Photoelectrocatalytic degradation of 17a-ethinylestradiol and estrone under UV and visible light using nanotubular oxide arrays grown on Ti-0.5wt%W. Environ. Res. 2020, 191, 110044.

69. Gurung, K.; Ncibi, M.C.; Thangaraj, S.K.; Jänis, J.; Seyedsalehi, M.; Sillanpää, M. Removal of pharmaceutically active compounds (PhACs) from real membrane bioreactor (MBR) effluents by photocatalytic degradation using composite Ag2O/P-25 photocatalyst. Separ. Purif. Technol. 2019, 215, 317–328.

70. Gomathi Devi, L.; Kavitha, R. A review on plasmonic metal TiO2 composite for generation, trapping, storing and dynamic vectorial transfer of photogenerated electrons across the Schottky junction in a photocatalytic system. Appl. Surf. Sci. 2016, 360, 601–622.

71. Yin, X.; Que, W.; Liao, Y.; Xie, H.; Fei, D. Ag-TiO2 nanocomposites with improved photocatalytic properties prepared by a low temperature process in polyethylene glycol. Colloids Surf. A 2012, 410, 153–158.

72. Fei, J.; Li, J. Controlled preparation of porous TiO2-Ag nanostructures through supramolecular assembly for plasmon-enhanced photocatalysis. Adv. Mater. 2015, 27, 314–319.

73. Hou, W.; Cronin, S.B. A review of surface plasmon resonance-enhanced photocatalysis. Adv. Funct. Mater. 2013, 23, 1612–1619.

74. Wang, T.; Wang, H.-J.; Lin, J.-S.; Yang, J.-L.; Zhang, F.-L.; Lin, X.-M.; Zhang, Y.-J.; Jin, S.; Li, J.-F. Plasmonic photocatalysis: Mechanism, applications and perspectives. Chin. J. Struct. Chem. 2023, 42, 100066.

75. Kaur, R.; Pal, B. Co-catalysis effect of different morphological facets of as prepared Ag nanostructures for the photocatalytic oxidation reaction by Ag-TiO2 aqueous slurry. Mater. Chem. Phys. 2013, 143, 393–399.

76. Gang, R.; Xia, Y.; Xu, L.; Zhang, L.; Ju, S.; Wang, Z.; Koppala, S. Size controlled Ag decorated TiO2 plasmonic photocatalysts for tetracycline degradation under visible light. Surf. Interfaces 2022, 31, 102018.

77. Litter, M.I. Mechanisms of removal of heavy metals and arsenic from water by TiO2-heterogeneous photocatalysis. Pure Appl. Chem. 2015, 87, 557–567.

78. Zhang, D.; Zhang, C.L.; Zhou, P. Preparation of porous nano-calcium titanate microspheres and its adsorption behavior for heavy metal ion in water. J. Hazard. Mater. 2011, 186, 971–977.

79. Shaheen, N.; Irfan, N.M.; Khan, I.N.; Islam, S.; Islam, M.S.; Ahmed, M.K. Presence of heavy metals in fruits and vegetables: Health risk implications in Bangladesh. Chemosphere 2016, 152, 431–438.

80. Khan, A.; Khan, S.; Khan, M.A.; Qamar, Z.; Waqas, M. The uptake and bioaccumulation of heavy metals by food plants, their effects on plants nutrients, and associated health risk: A review. Environ. Sci. Pollut. Res. 2015, 22, 13772–13799.

81. Kyung, H.; Lee, J.; Choi, W. Simultaneous and synergistic conversion of dyes and heavy metal ions in aqueous TiO2 suspensions under visible-light illumination. Environ. Sci. Technol. 2005, 39, 2376–2382.

82. Mahdavi, S.; Jalali, M.; Afkhami, A. Heavy metals removal from aqueous solutions using TiO2, MgO, and Al2O3 nanoparticles. Chem. Eng. Commun. 2013, 200, 448–470.

83. Poursani, A.S.; Nilchi, A.; Hassani, A.; Shariat, S.M.; Nouri, J. The synthesis of nano TiO2 and its use for removal of lead ions from aqueous solution. J. Water Resour. Protect. 2016, 8, 438–448.

84. Luo, T.; Cui, J.; Hu, S.; Huang, Y.; Jing, C. Arsenic removal and recovery from copper smelting wastewater using TiO2. Environ. Sci. Technol. 2010, 44, 9094–9098.

85. Yan, M.; Zeng, G.; Li, X.; Zhao, C.; Yang, G.; Gong, J.; Chen, G.; Tang, L.; Huang, D. Titanium dioxide nanotube arrays with silane coupling agent modification for heavy metal reduction and persistent organic pollutant degradation. New J. Chem. 2017, 41, 4377–4389.

86. Skubal, L.R.; Meshkov, N.K. Reduction and removal of mercury from water using arginine-modified TiO2. J. Photochem. Photobiol. A Chem. 2002, 148, 211–214.

87. Zhang, F.-S.; Nriagu, J.O.; Itoh, H. Photocatalytic removal and recovery of mercury from water using TiO2-modified sewage sludge carbon. J. Photochem. Photobiol. A Chem. 2004, 167, 223–228.

88. Dou, B.; Chen, H. Removal of toxic mercury(II) from aquatic solutions by synthesized TiO2 nanoparticles. Desalination 2011, 269, 260–265.

89. Xu, S.; Du, A.J.; Liu, J.; Ng, J.; Sun, D.D. Highly efficient CuO incorporated TiO2 nanotube photocatalyst for hydrogen production from water. Int. J. Hydrogen Energy 2011, 36, 6538–6545.

90. Xu, S.C.; Pan, S.S.; Xu, Y.; Luo, Y.Y.; Zhang, Y.X.; Li, G.H. Efficient removal of Cr (VI) from wastewater under sunlight by Fe(II)-doped TiO2 spherical shell. J. Hazard. Mater. 2014, 283, 7–13.

91. Chen, Z.; Li, Y.; Guo, M.; Xu, F.; Wang, P.; Du, Y.; Na, P. One-pot synthesis of Mn-doped TiO2 grown on graphene and the mechanism for removal of Cr(VI) and Cr (III). J. Hazard. Mater. 2016, 310, 188–198.

92. Gullipilli, S.; Rupakula, R.B. Adsorption studies of Cr(VI) and Cu(II) metal ions from aqueous solutions by synthesized Ag and Mg co-doped TiO2 nanoparticles. Separ. Sci. Technol. 2018, 54, 2983–2992.

93. Eddy, D.R.; Rahayu, I.; Wyantuti, S.; Hartati, Y.W.; Firdaus, M.L.; Bahti, H.H. Photocatalytic activity of gadolinium doped TiO2 particles for decreasing heavy metal chromium (VI) concentration. J. Phys. Conf. Ser. 2018, 1080, 012013.

94. Luo, Z.; Qu, L.; Jia, J.; Wang, J.; Jiang, S.; Wu, Z.; Wu, X. TiO2/EDTA-rich carbon composites: Synthesis, characterization and visible-light-driven photocatalytic reduction of Cr(VI). Chin. Chem. Lett. 2018, 29, 547–550.
95. Kobayashi, Y.; Kanasaki, R.; Nozaki, T.; Shoji, R.; Sato, K. Improving effect of MnO2 addition on TiO2-photocatalytic removal of lead ion from water. J. Water Environ. Technol. 2017, 15, 35–42.
96. Zhang, Y.; Hu, H.; Chang, M.; Chen, D.; Zhang, M.; Wu, L.; Li, X. Nonuniform doping outperforms uniform doping for enhancing the photocatalytic efficiency of Au-doped TiO2 nanotubes in organic dye degradation. Ceram. Int. 2017, 43, 9053–9059.
97. Zhang, Y.; Hu, Z.; Cui, X.; Yao, W.; Duan, T.; Zhu, W. Capture of Cs+ and Sr2+ from aqueous solutions by using Cr doped TiO2 nanotubes. J. Nanosci. Nanotechnol. 2017, 17, 3943–3950.
98. Garza-Arévalo, J.I.; García-Montes, I.; Reyes, M.H.; Guzmán-Mar, J.L.; Rodríguez-González, V.; Reyes, L.H. Fe doped TiO2 photocatalyst for the removal of As (III) under visible radiation and its potential application on the treatment of As-contaminated groundwater. Mater. Res. Bull. 2016, 73, 145–152.
99. Seema, K.M.; Mamba, B.B.; Njuguna, J.; Bakhtizin, R.Z.; Mishra, A.K. Removal of lead (II) from aqeouos waste using (CD-PCL-TiO2) bio-nanocomposites. Int. J. Biol. Macromol. 2018, 109, 136–142.
100. Zhao, Y.; Chang, W.; Huang, Z.; Feng, X.; Ma, L.; Qi, X.; Li, Z. Enhanced removal of toxic Cr(VI) in tannery wastewater by photoelectrocatalysis with synthetic TiO2 hollow spheres. Appl. Surf. Sci. 2017, 405, 102–110.
101. Wang, Q.; Zheng, Q.; Jin, R.; Gao, S.; Yuan, Q.; Rong, W.; Wang, R. Photoelectrocatalytic removal of organic dyes and Cr(VI) ions using Ag3PO4 nanoparticles sensitized TiO2 nanotube arrays. Mater. Chem. Phys. 2017, 199, 209–215.
102. Hang, Y.; Yin, H.; Ji, Y.; Liu, Y.; Lu, Z.; Wang, A.; Shen, L.; Yin, H. Adsorption performances of naked and 3-aminopropyl triethoxysilane-modified mesoporous TiO2 hollow nanospheres for Cu2+, Cd2+, Pb2+, Cr(VI) ions. J. Nanosci. Nanotechnol. 2017, 17, 5539–5549.
103. Abbas, K.K.; Al-Ghaban, A.M.H.A. Enhanced solar light photoreduction of innovative TiO2 nanospherical shell by reduced graphene oxide for removal silver ions from aqueous media. J. Environ. Chem. Eng. 2019, 7, 103168.
104. Gan, W.; Shang, X.; Li, X.H.; Zhang, J.; Fu, X. Achieving high adsorption capacity and ultrafast removal of methylene blue and Pb2+ by graphene-like TiO2@C. Colloids Surf. A 2019, 561, 218–225.
105. Ajmal, A.; Majeed, I.; Malik, R.N.; Idriss, H.; Nadeem, M.A. Principles and mechanisms of photocatalytic dye degradation on TiO2-based photocatalysts: A comparative overview. RSC Adv. 2014, 4, 37003–37026.
106. Konstantinou, I.K.; Albanis, T.A. TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetic and mechanistic investigations: A review. Appl. Catal. B Environ. 2004, 49, 1–14.
107. Zhang, F.; Zhao, J.; Shen, T.; Hidaka, H.; Pelizzetti, E.; Serpone, N. TiO2-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO2 dispersions under visible light irradiation. Appl. Catal. B Environ. 1998, 15, 147–156.
108. Sakthivel, S.; Neppolian, B.; Shankar, M.V.; Arabindoo, B.; Palanichamy, M.; Murugesan, V. Solar photocatalytic degradation of azo dye: Comparison of photocatalytic efficiency of ZnO and TiO2. Sol. Energy Mater. Sol. Cells 2003, 77, 65–82.
109. Chen, C.; Li, X.; Ma, W.; Zhao, J.; Hidaka, H.; Serpone, N. Effect of transition metal ions on the TiO2-assisted photodegradation of dyes under visible irradiation: A probe for the interfacial electron transfer process and reaction mechanism. J. Phys. Chem. B 2002, 106, 318–324.
110. Gola, D.; Malik, A.; Namburath, M.; Ahammad, S.Z. Removal of industrial dyes and heavy metals by Beauveria bassiana: FTIR, SEM, TEM and AFM investigations with Pb(II). Environ. Sci. Pollut. Res. 2018, 25, 20486–20496.
111. Chung, K.T. Azo dyes and human health: A review. J. Environ. Sci. Health Part C Environ. Carcinog. Ecotoxicol. Rev. 2016, 34, 233–261.
112. Raman, C.D.; Kanmani, S. Textile dye degradation using nano zero valent iron: A review. J. Environ. Manag. 2016, 177, 341–355.
113. Chandra, R.; Mukhopadhyay, S.; Nath, M. TiO2@ZIF-8: A novel approach of modifying micro-environment for enhanced photo-catalytic dye degradation and high usability of TiO2 nanoparticles. Mater. Lett. 2016, 164, 571–574.
114. Dariani, R.S.; Esmaeili, A.; Mortezaali, A.; Dehghanpour, S. Photocatalytic reaction and degradation of methylene blue on TiO2 nano-sized particles. Optik 2016, 127, 7143–7154.
115. Singh, R.; Kumari, P.; Chavan, P.D.; Datta, S.; Dutta, S. Synthesis of solvothermal derived TiO2 nanocrystals supported on ground nano egg shell waste and its utilization for the photocatalytic dye degradation. Opt. Mater. 2017, 73, 377–383.

116. Ljubas, D.; Smoljanić, G.; Juretić, H. Degradation of Methyl Orange and Congo Red dyes by using TiO2 nanoparticles activated by the solar and the solar-like radiation. J. Environ. Manag. 2015, 161, 83–91.

117. Zulfiqar, M.; Chowdhury, S.; Sufian, S.; Omar, A.A. Enhanced photocatalytic activity of Orange II in aqueous solution using solvent-based TiO2 nanotubes: Kinetic, equilibrium and thermodynamic studies. J. Clean. Prod. 2018, 203, 848–859.

118. Pol, R.; Guerrero, M.; García-Lecina, E.; Altube, A.; Rossinyol, E.; Garroni, S.; Baró, M.D.; Pons, J.; Sort, J.; Pellicer, E. Ni-, Pt- and (Ni/Pt)-doped TiO2 nanophotocatalysts: A smart approach for sustainable degradation of Rhodamine B dye. Appl. Catal. B Environ. 2016, 181, 270–278.

119. Gnanasekaran, L.; Hemamalini, R.; Saravanan, R.; Ravichandran, K.; Gracia, F.; Gupta, V.K. Intermediate state created by dopant ions (Mn, Co and Zr) into TiO2 nanoparticles for degradation of dyes under visible light. J. Mol. Liq. 2016, 223, 652–659.

120. Kerkez-Kuyumcu, Ö.; Kibar, E.; Dayioɔlu, K.; Gedik, F.; Akin, A.N.; Özkara Aydinoğlu, S. A comparative study for removal of different dyes over M/TiO2(M ¼ Cu, Ni, Co, Fe, Mn and Cr) photocatalysts under visible light irradiation. J. Photochem. Photobiol. A Chem. 2015, 311, 176–185.

121. Kaur, N.; Kaur, S.; Singh, V. Preparation, characterization and photocatalytic degradation kinetics of Reactive Red dye 198 using N, Fe codoped TiO2 nanoparticles under visible light. Desalin. Water Treat. 2016, 57, 9237–9246.

122. Sood, S.; Umar, A.; Kumar Mehta, S.; Sinha, A.S.K.; Kansal, S.K. Efficient photocatalytic degradation of brilliant green using Sr-doped TiO2 nanoparticles. Ceram. Int. 2015, 41, 3533–3540.

123. Brindha, A.; Sivakumar, T. Visible active N, S co-doped TiO2/graphene photocatalysts for the degradation of hazardous dyes. J. Photochem. Photobiol. A Chem. 2017, 340, 146–156.

124. McManamon, C.; O'Connell, J.; Delaney, P.; Rasappa, S.; Holmes, J.D.; Morris, M.A. A facile route to synthesis of S-doped TiO2 nanoparticles for photocatalytic activity. J. Mol. Catal. A Chem. 2015, 406, 51–57.

125. Shao, J.; Sheng, W.; Wang, M.; Li, S.; Chen, J.; Zhang, Y.; Cao, S. In situ synthesis of carbon-doped TiO2 single-crystal nanorods with a remarkably photocatalytic efficiency. Appl. Catal. B Environ. 2017, 209, 311–319.

126. Zhang, Q.; Fu, Y.; Wu, Y.; Zhang, Y.N.; Zuo, T. Low-cost Y-doped TiO2 nanosheets film with highly reactive facets from CRT waste and enhanced photocatalytic removal of Cr(VI) and methyl orange. ACS Sustain. Chem. Eng. 2016, 4, 1794–1803.

127. Li, Q.; Zong, L.; Li, C.; Yang, J. Reprint of photocatalytic reduction of CO2 on MgO/TiO2 nanotube films. Appl. Surf. Sci. 2014, 319, 16–20.

128. Dahl, M.; Liu, Y.; Yin, Y. Composite titanium dioxide nanomaterials. Chem. Rev. 2014, 114, 9853–9889.

129. Anwar, D.I.; Mulyadi, D. Synthesis of Fe-TiO2 composite as a photocatalyst for degradation of methylene blue. Procedia Chem 2015, 17, 49–54.

130. Lei, P.; Wang, F.; Gao, X.; Ding, Y.; Zhang, S.; Zhao, J.; Liu, S.; Yang, M. Immobilization of TiO2 nanoparticles in polymeric substrates by chemical bonding for multi-cycle photodegradation of organic pollutants. J. Hazard. Mater. 2012, 227–228, 185–194.

131. Talebi, S.; Chaibakhsh, N.; Moradi-Shoeili, Z. Application of nanoscale ZnS/TiO2 composite for optimized photocatalytic decolorization of a textile dye. J. Appl. Res. Technol. 2017, 15, 378–385.

132. Hui, C.; Lei, Z.; Xitang, W.; Shujing, L.; Zhongxing, L. Preparation of nanoporous TiO2/SiO2 composite with rice husk as template and its photocatalytic property. Rare Met. Mater. Eng. 2015, 44, 1607–1611.

133. Li, J.; Zhen, D.; Sui, G.; Zhang, C.; Deng, Q.; Jia, L. Nanocomposite of Cu-TiO2-SiO2 with high photoactive performance for degradation of rhodamine B dye in aqueous wastewater. J. Nanosci. Nanotechnol. 2012, 12, 6265–6270.

134. Liu, J.; Liu, J.; Shi, F.; Hu, S.; Jiang, S.; Liu, S.; Liu, D.; Tian, X. F/W codoped TiO2-SiO composite aerogels with improved visible light-driven photocatalytic activity. J. Solid State Chem. 2019, 275, 8–15.

135. Shao, L.; Liu, H.; Zeng, W.; Zhou, C.; Li, D.; Wang, L.; Lan, Y.; Xu, F.; Liu, G. Immobilized and photocatalytic performances of PDMS-SiO2-chitosan@TiO2 composites on pumice under simulated sunlight irradiation. Appl. Surf. Sci. 2019, 478, 1017–1026.

136. Tang, Y.; Di, W.; Zhai, X.; Yang, R.; Qin, W. NIR-responsive photocatalytic activity and mechanism of NaYF4:Yb,Tm@TiO2 core-shell nanoparticles. ACS Catal. 2013, 3, 405–412.

137. Djellabi, R.; Ghorab, M.F.; Cerrato, G.; Morandi, S.; Gatto, S.; Oldani, V.; Di Michele, A.; Bianchi, C.L. Photoactive TiO2-montmorillonite composite for degradation of organic dyes in water. J. Photochem. Photobiol. A Chem. 2015, 295, 57–63.

138. Alagarasi, A.; Rajalakshmi, P.U.; Shanthi, K.; Selvam, P. Solar light photocatalytic activity of mesoporous nanocrystalline TiO2, SnO2, and TiO2-SnO2 composites. Mater. Today Sustain. 2019, 5, 100016.

139. Magdalane, C.M.; Kanimozhi, K.; Arularasu, M.V.; Ramalingam, G.; Kaviyarasu, K. Self-cleaning mechanism of synthesized SnO2/TiO2 nanostructure for photocatalytic activity application for waste water treatment. Surf. Interfaces 2019, 17, 100346.

140. Li, Y.; Zhang, W.; Li, L.; Yi, C.; Lv, H.; Song, Q. Litchi-like CdS/CdTiO3-TiO2 composite: Synthesis and enhanced photocatalytic performance for crystal violet degradation and hydrogen production. RSC Adv. 2016, 6, 51374–51386.

141. Hamdy, M.S.; Saputera, W.H.; Groenen, E.J.; Mul, G. A novel TiO2 composite for photocatalytic wastewater treatment. J. Catal. 2014, 310, 75–83.

142. Rahimi, B.; Jafari, N.; Abdolahnejad, A.; Farrokhzadeh, H.; Ebrahimi, A. Application of efficient photocatalytic process using a novel BiVO/TiO2-NaY zeolite composite for removal of acid orange 10 dye in aqueous solutions: Modeling by response surface methodology (RSM). J. Environ. Chem. Eng. 2019, 7, 103253.

143. Saleh, R.; Taufik, A.; Prakoso, S.P. Fabrication of Ag2O/TiO2 composites on nanographene platelets for the removal of organic pollutants: Influence of oxidants and inorganic anions. Appl. Surf. Sci. 2019, 480, 697–708.

144. Visa, M.; Isac, L.; Duta, A. New fly ash TiO2 composite for the sustainable treatment of wastewater with complex pollutants load. Appl. Surf. Sci. 2015, 339, 62–68.

145. Jaseela, P.K.; Garvasis, J.; Joseph, A. Selective adsorption of methylene blue (MB) dye from aqueous mixture of MB and methyl orange (MO) using mesoporous titania (TiO2)-poly vinyl alcohol (PVA) nanocomposite. J. Mol. Liq. 2019, 286, 110908.

146. Yun, J.; Jin, D.; Lee, Y.S.; Kim, H. Photocatalytic treatment of acidic waste water by electrospun composite nanofibers of pH-sensitive hydrogel and TiO2. Mater. Lett. 2010, 64, 2431–2434.

147. Cheng, H.; Hu, M.; Zhai, Q.; Li, S.; Jiang, Y. Polydopamine tethered CPO/HRPTiO2 nano-composites with high bio-catalytic activity, stability and reusability: Enzyme-photo bifunctional synergistic catalysis in water treatment. Chem. Eng. J. 2018, 347, 703–710.

148. Saleh, T.A.; Gupta, V.K. Photo-catalyzed degradation of hazardous dye methyl orange by use of a composite catalyst consisting of multi-walled carbon nanotubes and titanium dioxide. J. Colloid Interface Sci. 2012, 371, 101–106.

149. Rajamanickam, D.; Shanthi, M. Photocatalytic degradation of an azo dye Sunset Yellow under UV-A light using TiO2/CAC composite catalysts. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2014, 128, 100–108.

150. Hassan, M.E.; Liu, G.; Omer, E.O.M.; Goja, A.M.; Acharya, S. Silver embedded C-TiO2 exhibits improved photocatalytic properties with potential application in waste water treatment. Arab. J. Chem. 2018, 12, 1134–1140.

151. Xu, C.; Cui, A.; Xu, Y.; Fu, X. Graphene oxide-TiO2 composite filtration membranes and their potential application for water purification. Carbon 2013, 62, 465–471.

152. Ahmed, A.S.; Ahamad, T.; Ahmad, N.; Khan, M.Z. Removal enhancement of acid navy blue dye by GO-TiO2 nanocomposites synthesized using sonication method. Mater. Chem. Phys. 2019, 238, 121906.

153. Mohamed, H.H.; Alsanea, A.A. TiO2/carbon dots decorated reduced graphene oxide composites from waste car bumper and TiO2 nanoparticles for photocatalytic applications. Arab. J. Chem. 2018, 13, 3082–3091.

154. Ranjith, R.; Renganathan, V.; Chen, S.M.; Selvan, N.S.; Rajam, P.S. Green synthesis of reduced graphene oxide supported TiO2/Co3O4 nanocomposite for photocatalytic degradation of methylene blue and crystal violet. Ceram. Int. 2019, 45, 12926–12933.

155. Monga, D.; Basu, S. Enhanced photocatalytic degradation of industrial dye by g-C3N4/TiO2 nanocomposite: Role of shape of TiO2. Adv. Powder Technol. 2019, 30, 1089–1098.

156. Zhang, J.J.; Fang, S.S.; Mei, J.Y.; Zheng, G.P.; Zheng, X.C.; Guan, X.X. High-efficiency removal of rhodamine B dye in water using g-C3N4 and TiO2 co-hybridized 3D graphene aerogel composites. Separ. Purif. Technol. 2018, 194, 96–103.

157. Zhang, Y.; Cui, W.; An, W.; Liu, L.; Liang, Y.; Zhu, Y. Combination of photoelectrocatalysis and adsorption for removal of bisphenol A over TiO2-graphene hydrogel with 3D network structure. Appl. Catal. B Environ. 2018, 221, 36–46.

158. Chi, L.; Qian, Y.; Guo, J.; Wang, X.; Arandiyan, H.; Jiang, Z. Novel g-C3N4/TiO2/PAA/PTFE ultrafiltration membrane enabling enhanced antifouling and exceptional visible-light photocatalytic self-cleaning. Catal. Today 2019, 335, 527–537.

159. Daneshvar, N.; Salari, D.; Niaei, A.; Rasoulifard, M.H.; Khataee, A.R. Immobilization of TiO2 nanopowder on glass beads for the photocatalytic decolorization of an azo dye C.I. Direct Red 23. J. Environ. Sci. Health 2005, 40, 1605–1617.

160. Cunha, D.L.; Kuznetsov, A.; Achete, C.A.; Machado, A.E.d.H.; Marques, M. Immobilized TiO2 on glass spheres applied to heterogeneous photocatalysis: Photoactivity, leaching and regeneration process. PeerJ 2018, 6, e4464.

161. Abbasi, Z.; Farrokhnia, A.; García-López, E.I.; Zargar Shoushtari, M. Codeposition of Fe3O4 nanoparticles sandwiched between g-C3N4 and TiO2 nanosheets: Structure, characterization and high photocatalytic activity for efficiently degradation of dye pollutants. Phys. Chem. Res. 2019, 7, 65–80.

162. Gu, W.; Lu, F.; Wang, C.; Kuga, S.; Wu, L.; Huang, Y.; Wu, M. Face-to-Face interfacial assembly of ultrathin g-C3N4 and anatase TiO2 nanosheets for enhanced solar photocatalytic activity. ACS Appl. Mater. Interfaces 2017, 9, 28674–28684.

163. Qiu, J.; Liu, F.; Yue, C.; Ling, C.; Li, A. A recyclable nanosheet of Mo/N-doped TiO2 nanorods decorated on carbon nanofibers for organic pollutants degradation under simulated sunlight irradiation. Chemosphere 2019, 215, 280–293.

164. Khan, M.A.; Mutahir, S.; Wang, F.; Lei, W.; Xia, M. Sensitization of TiO2 nanosheets with Cu-biphenylamine framework to enhance photocatalytic degradation performance of toxic organic contaminants: Synthesis, mechanism and kinetic studies. Nanotechnology 2018, 29, 375605.

165. Nair, A.K.; Jagadeesh Babu, P.E. Ag-TiO2 nanosheet embedded photocatalytic membrane for solar water treatment. J. Environ. Chem. Eng. 2017, 5, 4128–4133.

166. Du, F.; Zuo, X.; Yang, Q.; Yang, B.; Li, G.; Ding, Z.; Wu, M.; Ma, Y.; Jin, S.; Zhu, K. Facile assembly of TiO2 nanospheres/SnO2 quantum dots composites with excellent photocatalyst activity for the degradation of methyl orange. Ceram. Int. 2016, 42, 12778–12782.

167. Wang, H.; Xiao, L.; Wang, C.; Lin, B.; Lyu, S.; Chu, X.; Chi, Y.; Yang, X.; Wang, X. Pd/TiO2 nanospheres with three-dimensional hyperstructure for enhanced photodegradation of organic dye. Chem. Res. 2019, 35, 667–673.

168. Ghaforyan, H.; Ghaffary, T.; Pincak, R.; Ebrahimzadeh, M. Effects of ultrasound waves intensity on the removal of Congo Red color from the textile industry wastewater by Fe3O4@TiO2 core-shell nanospheres. arXiv 2017, arXiv:1708.04683.

169. Tetteh, E.K.; Rathilal, S.; Asante-Sackey, D.; Chollom, M.N. Prospects of synthesized magnetic TiO2-based membranes for wastewater treatment: A review. Materials 2021, 14, 3524.

170. Cao, J.; Song, X.Z.; Kang, X.; Dai, Z.; Tan, Z. One-pot synthesis of oleic acid modified monodispersed mesoporous TiO2 nanospheres with enhanced visible light photocatalytic performance. Adv. Powder Technol. 2018, 29, 1925–1932.

171. Liu, D.; Tian, R.; Wang, J.; Nie, E.; Piao, X.; Li, X.; Sun, Z. Photoelectrocatalytic degradation of methylene blue using F doped TiO2 photoelectrode under visible light irradiation. Chemosphere 2017, 185, 574–581.

172. Nurdin, M.; Azis, T.; Maulidiyah, M.; Aladin, A.; Hafid, N.A.; Salim, L.O.A.; Wibowo, D. Photocurrent responses of metanil yellow and remazol red B organic dyes by using TiO2/Ti electrode. IOP Conf. Ser. Mater. Sci. Eng. 2018, 367, 12048.

173. Yilmaz, P.; Lacerda, A.M.; Larrosa, I.; Dunn, S. Photoelectrocatalysis of rhodamine B and solar hydrogen production by TiO2 and Pd/TiO2 catalyst systems. Electrochim. Acta 2017, 231, 641–649.

174. Likodimos, V. Photonic crystal-assisted visible light activated TiO2 photocatalysis. Appl. Catal. B Environ. 2018, 230, 269–303.

175. Lu, Y.; Yu, H.; Chen, S.; Quan, X.; Zhao, H. Integrating plasmonic nanoparticles with TiO2 photonic crystal for enhancement of visible-light-driven photocatalysis. Environ. Sci. Technol. 2012, 46, 1724–1730.

176. Liao, G.; Chen, S.; Quan, X.; Chen, H.; Zhang, Y. Photonic crystal coupled TiO2/polymer hybrid for efficient photocatalysis under visible light irradiation. Environ. Sci. Technol. 2010, 44, 3481–3485.

177. Wang, Y.; Li, P.; Chen, S.L.; Wang, A.J. Dual-bandgap effect of photonic crystals on TiO2 photocatalytic activity in ultraviolet and visible light regions. Catal. Surv. 2019, 23, 23–32.

178. Geng, Z.; Zhang, Y.; Yuan, X.; Huo, M.; Zhao, Y.; Lu, Y.; Qiu, Y. Incorporation of Cu2O nanocrystals into TiO2 photonic crystal for enhanced UV-visible light driven photocatalysis. J. Alloys Compd. 2015, 644, 734–741.

179. Chen, H.; Chen, S.; Quan, X.; Zhang, Y. Structuring a TiO2-based photonic crystal photocatalyst with Schottky junction for efficient photocatalysis. Environ. Sci. Technol. 2010, 44, 451–455.

180. Li, Y.; Chang, Y.; Liu, F.T.; Zhao, Y.; Wang, J.; Wang, C.W. Photonic crystal structural-induced Cu3SnS4/Ti3+-TiO2 p-n coaxial heterojunction arrays for light-driven H2 production and pollutant degradation. Mater. Des. 2017, 133, 426–434.

181. Vela, N.; Pérez-Lucas, G.; Fenoll, J.; Navarro, S. Recent overview on the abatement of pesticide residues in water by photocatalytic treatment using TiO2. In Application of Titanium Dioxide; IntechOpen: London, UK, 2017.

182. Liu, Y.; Liu, F.; Pan, X.; Li, J. Protecting the environment and public health from pesticides. Environ. Sci. Technol. 2012, 46, 5658–5659.

183. Shuman-Goodier, M.E.; Propper, C.R. A meta-analysis synthesizing the effects of pesticides on swim speed and activity of aquatic vertebrates. Sci. Total Environ. 2016, 565, 758–766.

184. Blair, A.; Ritz, B.; Wesseling, C.; Beane Freeman, L. Pesticides and human health. Occup. Environ. Med. 2015, 72, 81–82.

185. Alavanja, M.C.R.; Bonner, M.R. Occupational pesticide exposures and cancer risk: A review. J. Toxicol. Environ. Health Part B 2012, 15, 238–263.

186. Vanraes, P.; Ghodbane, H.; Davister, D.; Wardenier, N.; Nikiforov, A.; Verheust, Y.P.; Van Hulle, S.W.H.; Hamdaoui, O.; Vandamme, J.; Van Durme, J.; et al. Removal of several pesticides in a falling water film DBD reactor with activated carbon textile: Energy efficiency. Water Res. 2017, 116, 1–12.

187. Farner Budarz, J.; Cooper, E.M.; Gardner, C.; Hodzic, E.; Ferguson, P.L.; Gunsch, C.K.; Wiesner, M.R. Chlorpyrifos degradation via photoreactive TiO2 nanoparticles: Assessing the impact of a multi-component degradation scenario. J. Hazard. Mater. 2019, 372, 61–68.

188. Amalraj, A.; Thirumalaisamy, S.; Rajeswari, A.; Pius, A. Photocatalytic degradation of quinalphos and profenofos pesticides using UV irradiated TiO2 nanoparticles-a kinetic study. Mater. Focus 2016, 5, 377–384.

189. Cruz, M.; Gomez, C.; Duran-Valle, C.J.; Pastrana-Martínez, L.M.; Faria, J.L.; Silva, A.M.T.; Faraldos, M.; Bahamonde, A. Bare TiO2 and graphene oxide TiO2 photocatalysts on the degradation of selected pesticides and influence of the water matrix. Appl. Surf. Sci. 2017, 416, 1013–1021.

190. Zhang, Y.; Han, C.; Zhang, G.; Dionysiou, D.D.; Nadagouda, M.N. PEG-assisted synthesis of crystal TiO2 nanowires with high specific surface area for enhanced photocatalytic degradation of atrazine. Chem. Eng. J. 2015, 268, 170–179.

191. Ahmari, H.; Heris, S.Z.; Khayyat, M.H. The effect of titanium dioxide nanoparticles and UV irradiation on photocatalytic degradation of Imidaclopride. Environ. Technol. 2018, 39, 536–547.

192. Vela, N.; Calín, M.; Yáñez-Gascón, M.J.; Garrido, I.; Pérez-Lucas, G.; Fenoll, J.; Navarro, S. Photocatalytic oxidation of six pesticides listed as endocrine disruptor chemicals from wastewater using two different TiO2 samples at pilot plant scale under sunlight irradiation. J. Photochem. Photobiol. A Chem. 2018, 353, 271–278.

193. Kalantary, R.R.; Dadban Shahamat, Y.; Farzadkia, M.; Esrafili, A.; Asgharnia, H. Photocatalytic degradation and mineralization of diazinon in aqueous solution using nano-TiO2 (Degussa, P25): Kinetic and statistical analysis. Desalin. Water Treat. 2015, 55, 555–563.

194. Suhaimy, S.H.M.; Lai, C.W.; Tajuddin, H.A.; Samsudin, E.M.; Johan, M.R. Impact of TiO2 nanotubes' morphology on the photocatalytic degradation of simazine pollutant. Materials 2018, 11, 66.

195. Tabasideh, S.; Maleki, A.; Shahmoradi, B.; Ghahremani, E.; McKay, G. Sonophotocatalytic degradation of diazinon in aqueous solution using iron-doped TiO2 nanoparticles. Separ. Purif. Technol. 2017, 189, 186–192.

196. Mermana, J.; Sutthivaiyakit, P.; Blaise, C.; Gagné, F.; Charnsethikul, S.; Kidkhunthod, P.; Sutthivaiyakit, S. Photocatalysis of S-metolachlor in aqueous suspension of magnetic cerium-doped mTiO2 core-shell under simulated solar light. Environ. Sci. Pollut. Res. 2017, 24, 4077–4092.

197. Umar, K.; Aris, A.; Ahmad, H.; Parveen, T.; Jaafar, J.; Majid, Z.A.; Reddy, A.V.B.; Talib, J. Synthesis of visible light active doped TiO2 for the degradation of organic pollutants-methylene blue and glyphosate. J. Anal. Sci. Technol. 2016, 7, 29.

198. Maddila, S.; Oseghe, E.O.; Jonnalagadda, S.B. Photocatalyzed ozonation by Ce doped TiO2 catalyst degradation of pesticide Dicamba in water. J. Chem. Technol. Biotechnol. 2016, 91, 385–393.

199. Quiñones, D.H.; Rey, A.; Álvarez, P.M.; Beltrán, F.J.; Li Puma, G. Boron doped TiO2 catalysts for photocatalytic ozonation of aqueous mixtures of common pesticides: Diuron, o-phenylphenol, MCPA and terbuthylazine. Appl. Catal. B Environ. 2014, 178, 74–81.

200. Joseph, A.I.J.; Thiripuranthagan, S. Non-metal doped titania photocatalysts for the degradation of neonicotinoid insecticides under visible light irradiation. J. Nanosci. Nanotechnol. 2018, 18, 3158–3164.

201. Komtchou, S.; Dirany, A.; Drogui, P.; Delegan, N.; El Khakani, M.A.; Robert, D.; Lafrance, P. Degradation of atrazine in aqueous solution with electrophotocatalytic process using TiO2-x photoanode. Chemosphere 2016, 157, 79–88.

202. Turan, N.B.; Sari Erkan, H.; Çaglak, A.; Bakırdere, S.; Engin, G.O. Optimization of atrazine removal from synthetic groundwater by electrooxidation process using titanium dioxide and graphite electrodes. Separ. Sci. Technol. 2019, 55, 3036–3045.

203. Matsunaga, T.; Tomoda, R.; Nakajima, T.; Wake, H. Photoelectrochemical sterilization of microbial cells by semiconductor powders. FEMS Microbiol. Lett. 1985, 29, 211–214. Available online: https://www.sciencedirect.com/science/article/pii/0378109785903003 (accessed on 12 January 2024).

204. Maness, P.-C.; Smolinski, S.; Blake, D.M.; Huang, Z.; Wolfrum, E.J.; Jacoby, W.A. Bactericidal activity of photocatalytic TiO2 reaction toward an understanding of its killing mechanism. Appl. Environ. Microbiol. 1999, 65, 4094–4098.

205. Cai, R.; Hashimoto, K.; Itoh, K.; Kubota, Y.; Fujishima, A. Photokilling of malignant cells with ultrafine TiO2 powder. Bull. Chem. Soc. Jpn. 1991, 64, 1268–1273.

206. Karunakaran, C. Solar Photocatalytic Disinfection of Bacteria. In New and Future Developments in Catalysis; Suib, S.L., Ed.; Elsevier B.V.: Amsterdam, The Netherlands, 2013.

207. Prasad, G.K.; Ramacharyulu, P.V.R.K.; Merwyn, S.; Agarwal, G.S.; Srivastava, A.R.; Beer Singh, G.P.R.; Vijayaraghavan, R. Photocatalytic inactivation of spores of Bacillus anthracis using titania nanomaterials. J. Hazard. Mater. 2011, 185, 977–982.

208. Nasser, A.M.; Paulman, H.; Sela, O.; Ktaitzer, T.; Cikurel, H.; Zuckerman, I.; Meir, A.; Aharoni, A.; Adin, A. UV disinfection of wastewater effluents for unrestricted irrigation. Water Sci. Technol. 2006, 54, 83–88.

209. Egli, T.; Köster, W.; Meile, L. Pathogenic microbes in water and food: Changes and challenges. FEMS Microbiol. Rev. 2002, 26, 111–112.

210. Laxma Reddy, P.V.; Kavitha, B.; Kumar Reddy, P.A.; Kim, K.H. TiO2-based photocatalytic disinfection of microbes in aqueous media: A review. Environ. Res. 2017, 154, 296–303.

211. Mahmood, M.A.; Baruah, S.; Anal, A.K.; Dutta, J. Heterogeneous photocatalysis for removal of microbes from water. Environ. Chem. Lett. 2012, 10, 145–151.

212. Leung, T.L.F.; Bates, A.E. More rapid and severe disease outbreaks for aquaculture at the tropics: Implications for food security. J. Appl. Ecol. 2013, 50, 215–222.

213. Ashbolt, N.J. Microbial contamination of drinking water and disease outcomes in developing regions. Toxicology 2004, 198, 229–238.

214. Joost, U.; Juganson, K.; Visnapuu, M.; Mortimer, M.; Kahru, A.; Nõmmiste, E.; Joost, U.; Kisand, V.; Ivask, A. Photocatalytic antibacterial activity of nano-TiO2 (anatase)-based thin films: Effects on Escherichia coli cells and fatty acids. J. Photochem. Photobiol. B Biol. 2015, 142, 178–185.

215. Podporska-Carroll, J.; Panaitescu, E.; Quilty, B.; Wang, L.; Menon, L.; Pillai, S.C. Antimicrobial properties of highly efficient photocatalytic TiO2 nanotubes. Appl. Catal. B Environ. 2015, 176–177, 70–75.

216. Long, M.; Wang, J.; Zhuang, H.; Zhang, Y.; Wu, H.; Zhang, J. Performance and mechanism of standard nano-TiO2 (P-25) in photocatalytic disinfection of foodborne microorganisms-Salmonella typhimurium and Listeria monocytogenes. Food Control 2014, 39, 68–74.

217. Makropoulou, T.; Panagiotopoulou, P.; Venieri, D. N-doped TiO2 photocatalysts for bacterial inactivation in water. J. Chem. Technol. Biotechnol. 2018, 93, 2518–2526.

218. Milosevic, I.; Jayaprakash, A.; Greenwood, B.; van Driel, B.; Rtimi, S.; Bowen, P. Synergistic effect of fluorinated and N doped TiO2 nanoparticles leading to different microstructure and enhanced photocatalytic bacterial inactivation. Nanomaterials 2017, 7, 391.

219. Choi, S.Y.; Cho, B. Extermination of influenza virus H1N1 by a new visible-light induced photocatalyst under fluorescent light. Virus Res. 2018, 248, 71–73.

220. Zheng, X.; Shen, Z.; Cheng, C.; Shi, L.; Cheng, R.; Yuan, D. Photocatalytic disinfection performance in virus and virus/bacteria system by Cu-TiO2 nanofibers under visible light. Environ. Pollut. 2018, 237, 452–459.

221. Rao, G.; Brastad, K.S.; Zhang, Q.; Robinson, R.; He, Z.; Li, Y. Enhanced disinfection of Escherichia coli and bacteriophage MS2 in water using a copper and silver loaded titanium dioxide nanowire membrane. Front. Environ. Sci. Eng. 2016, 10, 11.

222. Venieri, D.; Gounaki, I.; Binas, V.; Zachopoulos, A.; Kiriakidis, G.; Mantzavinos, D. Inactivation of MS2 coliphage in sewage by solar photocatalysis using metal-doped TiO2. Appl. Catal. B Environ. 2015, 178, 54–64.

223. De Pasquale, I.; Lo Porto, C.; Dell'Edera, M.; Petronella, F.; Agostiano, A.; Curri, M.L.; Comparelli, R. Photocatalytic TiO2-based nanostructured materials for microbial inactivation. Catalysts 2020, 10, 1382.

224. Tijani, J.O.; Fatoba, O.O.; Petrik, L.F. A review of pharmaceuticals and endocrinedisrupting compounds: Sources, effects, removal, and detections. Water. Air. Soil Pollut. 2013, 224, 1770.

225. Burkhardt-Holm, P. Endocrine disruptors and water quality: A state-of-the-art review. Int. J. Water Resour. Dev. 2010, 26, 477–493.

226. Monneret, C. What is an endocrine disruptor? Comptes Rendus Biol. 2017, 340, 403–405.

227. Tetreault, G.R.; Bennett, C.J.; Shires, K.; Knight, B.; Servos, M.R.; McMaster, M.E. Intersex and reproductive impairment of wild fish exposed to multiple municipal wastewater discharges. Aquat. Toxicol. 2011, 104, 278–290.

228. Tabata, A.; Kashiwada, S.; Ohnishi, Y.; Ishikawa, H.; Miyamoto, N.; Itoh, M.; Magara, Y. Estrogenic influences of estradiol-17 beta, p-nonylphenol and bis-phenol-A on Japanese medaka (Oryzias latipes) at detected environmental concentrations. Water Sci. Technol. 2001, 43, 109–116.

229. Villeneuve, S.; Cyr, D.; Lynge, E.; Orsi, L.; Sabroe, S.; Merletti, F.; Gorini, G.; Morales Suarez Varela, M.; Ahrens, W.; Baumgardt-Elms, C.; et al. Occupation and occupational exposure to endocrine disrupting chemicals in male breast cancer: A case-control study in Europe. Occup. Environ. Med. 2010, 67, 837–844.

230. Li, D.; Zhou, Z.; Qing, D.; He, Y.; Wu, T.; Miao, M.; Wang, J.; Weng, X.; Ferber, J.R.; Herrinton, L.J.; et al. Occupational exposure to bisphenol-A (BPA) and the risk of self-reported male sexual dysfunction. Hum. Reprod. 2009, 25, 519–527.

231. Tong, A.Y.C.; Braund, R.; Warren, D.S.; Peake, B.M. TiO2-assisted photodegradation of pharmaceuticals—A review. Cent. Eur. J. Chem. 2012, 10, 989–1027.

232. AlAani, H.; Hashem, S.; Karabet, F. Photocatalytic (UV-A/TiO2) and photolytic (UV-A) degradation of steroid hormones: Ethinyl estradiol, levonorgestrel, and progesterone. Int. J. Chem. Res. 2017, 10, 1061–1070.

233. Arlos, M.J.; Liang, R.; Hatat-Fraile, M.M.; Bragg, L.M.; Zhou, N.Y.; Servos, M.R.; Andrews, S.A. Photocatalytic decomposition of selected estrogens and their estrogenic activity by UV-LED irradiated TiO2 immobilized on porous titanium sheets via thermal-chemical oxidation. J. Hazard. Mater. 2016, 318, 541–550.

234. Sornalingam, K.; McDonagh, A.; Zhou, J.L.; Johir, M.A.H.; Ahmed, M.B. Photocatalysis of estrone in water and wastewater: Comparison between Au-TiO2 nanocomposite and TiO2, and degradation by-products. Sci. Total Environ. 2018, 610–611, 521–530.

235. Zatloukalová, K.; Obalová, L.; Koči, K.; Čapek, L.; Matěj, Z.; Šnajdhaufová, H.; Ryczkowski, J.; Słowik, G. Photocatalytic degradation of endocrine disruptor compounds in water over immobilized TiO2 photocatalysts. Iran. J. Chem. Chem. Eng. IJCCE 2017, 36, 29–38.

236. Ramírez-Sánchez, I.M.; Tuberty, S.; Hambourger, M.; Bandala, E.R. Resource efficiency analysis for photocatalytic degradation and mineralization of estriol using TiO2 nanoparticles. Chemosphere 2017, 184, 1270–1285.

237. Solcova, O.; Spacilova, L.; Maleterova, Y.; Morozova, M.; Ezechias, M.; Kresinova, Z. Photocatalytic water treatment on TiO2 thin layers. Desalin. Water Treat. 2016, 57, 11631–11638.

238. Ruokolainen, M.; Gul, T.; Permentier, H.; Sikanen, T.; Kostiainen, R.; Kotiaho, T. Comparison of TiO2 photocatalysis, electrochemically assisted Fenton reaction and direct electrochemistry for simulation of phase i metabolism reactions of drugs. Eur. J. Pharmaceut. Sci. 2016, 83, 36–44.

239. Pazoki, M.; Parsa, M.; Farhadpour, R. Removal of the hormones dexamethasone (DXM) by Ag doped on TiO2 photocatalysis. J. Environ. Chem. Eng. 2016, 4, 4426–4434.

240. Chow, K.L.; Man, Y.B.; Tam, N.F.Y.; Liang, Y.; Wong, M.H. Removal of decabromodiphenyl ether (BDE-209) using a combined system involving TiO2 photocatalysis and wetland plants. J. Hazard. Mater. 2017, 322, 263–269.

241. Vasapollo, G.; Mele, G.; Del Sole, R.; Pio, I.; Li, J.; Mazzetto, S.E. Use of novel cardanol-porphyrin hybrids and their TiO2-based composites for the photodegradation of 4-Nitrophenol in water. Molecules 2011, 16, 5769–5784.

242. Sraw, A.; Kaur, T.; Pandey, Y.; Sobti, A.; Wanchoo, R.K.; Toor, A.P. Fixed bed recirculation type photocatalytic reactor with TiO2 immobilized clay beads for the degradation of pesticide polluted water. J. Environ. Chem. Eng. 2018, 6, 7035–7043.

243. Wang, H.; Liang, Y.; Liu, L.; Hu, J.; Cui, W. Highly ordered TiO2 nanotube arrays wrapped with g-C3N4 nanoparticles for efficient charge separation and increased photoelectrocatalytic degradation of phenol. J. Hazard. Mater. 2018, 344, 369–380.

244. Martins, A.S.; Nuñez, L.; Lanza, M.R.d.V. Enhanced photoelectrocatalytic performance of TiO2 nanotube array modified with WO3 applied to the degradation of the endocrine disruptor propyl paraben. J. Electroanal. Chem. 2017, 802, 33–39.