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A CRITICAL REVIEW OF THE PHOTOCATALYTIC DEGRADATION OF PHARMACEUTICAL RESIDUES BY A TIO$_2$-BASED PHOTOCATALYST

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Creating photocatalytic materials to generate clean energy and for ecological detoxification has been a challenge as far as meeting the worldwide demand for energy and cutting pollution is concerned. Anti-inflammatory medicines and pharmaceutically active chemicals (PhACs) are frequently found in wastewater. Since conventional wastewater treatment facilities do not completely remove these micropollutants (pharmaceuticals), alternatives are required. It is still difficult to make an inert and efficient nano-photocatalyst like titanium dioxide (TiO_2). TiO_2 photocatalysts have been extensively utilized as innovative photocatalysts for treating contamination because of their distinctive physicochemical characteristics, less toxic nature, biological inertness, improved energy efficiency, low-temperature reaction conditions, insolubility in water, easy accessibility, highly stable chemical nature and natural environmentally friendliness. However, their large band gap energy, that can only be generated under UV light and quickly with charge carrier recombination, restricts their photocatalytic applications. Its band gap energy was additionally decreased in order to be active in visible light in a variety of methods. Recent research developments concerning the TiO_2-based heterostructure as a photocatalyst as well as its modifications, factors and removal method are summarized in this review which concludes with an overview and viewpoints on the present difficulties as well as fresh lines of inquiry in this developing field of study.

Keywords: photocatalysts, photocatalysis, TiO_2 nanoparticles, pharmaceutical residue, antibiotics

1. Introduction

Water is universally recognized as the most important factor in the development of civilization as well as for the survival of life on this planet. Obtaining clean and affordable water is one of our most fundamental needs which for the past 200 years has been a major global problem. The largest global problem affecting human health is the pollution of water. Numerous pharmaceutical medications have been continually made over recent years. Antibiotics are ingested in small doses, moreover, the majority of them are excreted in our urine and faeces, where they end up in aquatic environments. Antibiotic concentrations in hospitals and urban wastewater are typically between 0.3 and 100 mg/l [1]-[3], it is crucial to properly remove these chemicals from contaminated water. However, traditional approaches like coagulation, electrocoagulation and adsorption are inefficient with regard to the breakdown of pharmaceutical components. Although techniques that utilize biomembranes like reverse osmosis and nanofiltration result in the substantial removal of these impurities, they also have certain limitations because of fouling, which significantly lowers their efficiency [3].

Active pharmaceutical chemicals that leak into water are currently regarded as new growing contaminants since they have the potential to have detrimental impacts on the environment as well as on human health. There are two possible pathways of these pharmaceuticals into wastewater; (i) small amounts of these active pharmaceutical ingredients (APIs) enter the water systems by being excreted through our urine or faeces as unchanged metabolites or compounds, or (ii) disposal as surplus or expired medications into the environment. Pharmaceutical medications often fall into one of several major categories, including analgesics, antiseptics, antibiotics, contraceptives, antiepileptics, beta blockers, hormones, etc. Using TiO_2 as a photocatalyst proved to be the most effective treatment

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approach for removing such complicated contaminants like antibiotics [3]-[7].

1.1. Pharmaceutical residue in water systems

The extensive use of pharmaceuticals, which are not biodegradable, in human healthcare results in their heavy consumption. Pharmaceuticals continue to be found in the environment, which, despite their relatively low concentrations in drinking water and groundwater, can be detrimental to people and aquatic life. Because of their antipyretic, analgesic and anti-inflammatory effects, NSAIDs (non-steroidal anti-inflammatory drugs) are among the most frequently utilized pharmacological substances in both veterinary and human therapies. Ibuprofen, naproxen, paracetamol, acetylsalicylic acid and diclofenac are the only commonly used NSAIDs that have been found in water samples from both developed and developing countries as micropollutants. The majority of the time, these NSAIDs have a hazardous effect on ecosystems and aquatic organisms, which indirectly affects individuals through the food chain [8]-[14].

1.2. Common pharmaceutical compounds found in water

Pharmaceuticals, primarily antibiotics and cytostatic medications, have a history of environmental pollution, negative consequences on human health and harming aquatic ecosystems. However, given their crucial nature as far as sustaining a healthy society is concerned, they are significantly utilized. Antibiotics are commonly used to treat microbiological infections. A 2013 study found that over 248 thousand tons of antibiotics are used annually, with Asia accounting for about 70% of global antibiotic use. Antibiotic use in livestock is predicted to increase globally by 67% by 2030. The misuse of antibiotics leads to environmental pollution, notably in water bodies, which poses a serious hazard to human health. Therefore, it is important to reduce antibiotic usage and maintain a clean atmosphere [15].

Antibiotics are used as extremely significant antibacterial substances for the treatment as well as mitigation of transmittable illnesses in both people and animals. They also play a crucial role in livestock farming, fish farming and medical industries. Nevertheless, antibiotics pose serious risks to the aquatic ecosystem due to their misuse. Toxic levels of antibiotics and their poor biodegradability present major dangers to human life that must be addressed immediately [1].

Although TCH (Taxotere or Taxol, carboplatin and Herceptin) is a common antibiotic, because of its solid structure and poor ability to biodegrade, it has detrimental effects on both human and animal health. Effective ways to remove TCH from wastewater are urgently needed. Biological and physical adsorption techniques have both been used to remove TCH from wastewater, but they haven't been able to entirely get rid of this pollutant. According to reports, the photocatalytic degradation of TCH is the best method since it does not produce residual pollution, is highly efficient and simple. Feizpoor et al. used a simple hydrothermal process by placing Ag_3BiO_3 nanoparticles (NPs) on TiO_2 to create n-n heterojunctions. TiO_2/Ag_3BiO_3 yielded the best TCH photodegradation efficiency, 15.4 times better than TiO_2. TiO_2/Ag_3BiO_3's better light absorption capacity and decreased coupling of charged particles produced by light due to the creation of n-n heterojunctions are the main reasons for the increase in the photodegradation efficiency of TCH. Through the use of reactive species quenching studies, the mechanism enhancing the photodegradation efficiency of TCH was discovered [1].

Cytostatic or anti-cancer medications, another group of contaminants in the developing pharmaceutical industry, have also been detected in small concentrations on the surface of water, moreover, are toxic and carcinogenic to people. The use of cytostatic medication over an extended period could have a negative impact on the environment. Due to the rising number of cancer cases over recent years, the use of these medications, also referred to as anti-cancer or antineoplastic treatments, has surged. These medications impede chromosomal replication or damage DNA, killing cells. As a result, only a small number of such medications can be hydrolyzed or photolyzed biologically, making it extremely difficult to remove them from wastewater [15]-[17].

Additional detrimental effects are to be anticipated given the continued expansion in the manufacture and utilization of medications as well as the lack of effective methods to evaluate and decrease their ability to adversely effect the environment. Changes in antibiotics are possible when biotic and abiotic environmental variables are present. Numerous substances can modify their activity by producing secondary pollutants (SP) that are considerably more harmful than the original ones, making them resistant to natural degradation as well. Antibiotics and biological accumulation have long-term effects on living things that can prevent plants from growing as well as cause cancer in addition to liver and kidney diseases in mammals amongst other detrimental effects. These compounds from the surroundings can also enter our bodies in drinking water and food, leading to antibiotic resistance, allergic reactions, toxic and neurotoxic consequences, etc. [18]. *Figure 1* represents the major sources of antibiotics that cause water pollution.

2. Photocatalysis

The method of photocatalysis uses light energy to accelerate chemical reactions by making use of photocatalysts, which are able to absorb light and increase the rate of a chemical reaction. According to the fundamentals of photocatalysis, electron-hole pairs are produced when the photocatalyst is activated by photons with the appropriate amount of energy. These photoexcited charges can then participate in various reactions such as redox reactions or the degradation of organic compounds. The fundamental principles of

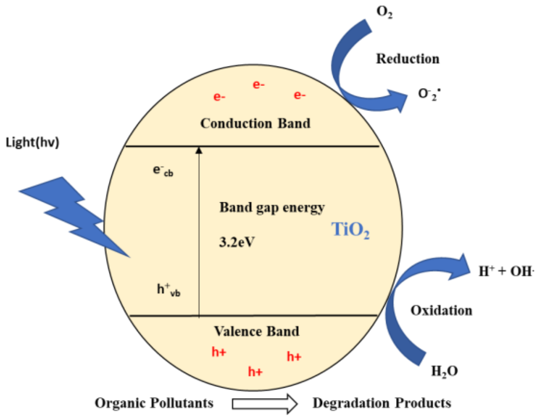

Figure 1: Mechanism of removing pollutants by the TiO_2 photocatalyst

photocatalysis are discussed in several of the referenced studies. According to Mandade, the primary distinction between a photocatalyst and a standard catalyst is the process of activation. While standard catalysts are activated by heating, photocatalysts are activated by photons of the right energy [19]. Gusain and Kumar et al. explain that photocatalysis relies on the increased surface exposure of the photocatalyst, which enhances its organic degradation activity. Moreover, photocatalysts are effective in reducing toxic heavy metals like hexavalent chromium from water systems [20]. Additionally, photocatalysis is a topic that encompasses diverse forms of implementation and a wide range of materials. When developing photocatalytic materials, factors like efficiency, stability, scalability and cost must be taken into account [21]. Due to their advantageous features, semiconductors are frequently used as photocatalysts, and different types of semiconductors have been investigated [22].

2.1. TiO_2 as a photocatalyst

TiO_2, a significant element that occurs in the form of its oxide, is used extensively in the commercial manufacture of numerous products and is significant in a number of industries. There are three primary crystal forms of TiO_2: (i) brookite; (ii) rutile and (iii) anatase. The characteristics of these vary, including the space group, the lattice constants, etc. The commercial demand for nanoscopic TiO_2 and its derivatives is driven by their large surface area and short diffusion paths. Greater comprehension of the functional characteristics of porous TiO_2 materials would enable the development of a number of desirable features for a variety of applications such as to promote photocatalytic processes like the splitting of water to make hydrogen gas, mineralization of pharmaceuticals, treatment of wastewater and degradation of organic contaminants to list just a few [23]. *Table 1* represents different TiO_2 photocatalysts for the removal of pharmaceutical pollutants, dyes and organic compounds.

2.2. Mechanisms of TiO_2 photocatalysis for the degradation of organic compounds

The mechanism of photocatalytic activities using TiO_2 as a photocatalyst has been covered in a number of studies. When light with a wavelength larger than or equal to the band gap strikes the surface of TiO_2, electrons from the valence band (VB) jump to the conduction band (CB), creating electrons and holes in the former (h^+_{vb}) and latter (e^-_{cb}), respectively. While the produced hole acts as a powerful oxidant, oxidizing the water molecule and surface hydroxyl ion to form OH•, the electrons act as a strong reductant, reducing the O_2 molecules to form

Table 1: TiO_2 nanomaterials for the removal of organic compounds
*PD = photodeposition synthesis

Organic compound	Material	Light Source	Catalyst amount	% degradation/time	Reference
Rhodamine B dyes	Ag-TiO_2-PD*	UV irradiation	--	99 % / 2 h	[2]
Reactive Red 120 (RR 120)	AC-TiO_2	365 nm UV-A light/32 W	50 mg / 100 ml	95 % / 50 min	[4]
ketoconazole (KNZ)	TiO_2-NPs	365 nm high pressure mercury lamp/250 W	120 mg / L	98.4 % / 60 min	[6]
Reactive Green-19 dye	TiO_2-NPs	630nm/UV-light	0.030 g /100 ml	98.88 % / 60 min	[8]
ornidazole (ODZ)	TiO_2-NPs	Hg vapor lamp/400 W	50 mg / L	66.15 % / 3 h	[10][10]
Rhodamine 6G	S-doped TiO_2	526nm/LED bulbs of 12 W	50 mg / 50 ml	91.7 % / 4 h	[12]
lomefloxacin	Au/TiO_2	--	10 mg / L	71.8 % / 180 min	[13]

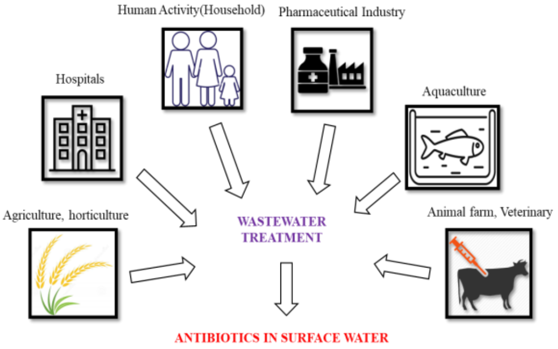

Figure 2: The principal origins of antibiotics found in water systems

O_2^{-}•. O_2^{-}•interacts with the H^+ ion to make HO_2•, which is then successively protonated to form H_2O_2. These processes take place on the TiO_2 surface of the photocatalyst. Photocatalytic degradation is aided by photogenerated ROSs (O_2^{-}•, OH•, HO_2• and H_2O_2) [24]. *Equations 1-6* show how electrons can interact with organic molecules to produce reduction products. Since oxygen can interact with the photogenerated electrons, its involvement is crucial. *Figure 2* represents the overall mechanism of removal of organic pollutants by the TiO_2 photocatalyst.

$$\mathrm{TiO_2} + h\nu \rightarrow e_{cb}^{-} + h_{vb}^{+} \tag{1}$$

$$h_{vb}^{+} + \mathrm{OH}_{surface}^{-} \rightarrow \mathrm{OH}\bullet \tag{2}$$

$$h_{vb}^{+} + \mathrm{H_2O}_{absorbed} \rightarrow \mathrm{OH}\bullet + \mathrm{H}^{+} \tag{3}$$

$$e_{cb}^{-} + \mathrm{O}_{absorbed} \rightarrow \mathrm{O}_2^{-}\bullet \tag{4}$$

$$h_{vb}^{+} + \mathrm{Organic} \rightarrow \mathrm{Oxidation\ products} \tag{5}$$

$$\mathrm{OH}\bullet + \mathrm{Organic} \rightarrow \mathrm{Degradation\ products} \tag{6}$$

2.3. Factors influencing the photocatalytic efficiency of TiO_2

The photocatalytic efficiency of TiO_2, a commonly used photocatalytic material, is influenced by various factors. Some of these factors affecting TiO_2 photocatalysis include its specific surface area, crystal phase, crystallite size and crystallinity. Although these structural characteristics of TiO_2 can impact its photocatalytic efficiency, there is some controversy over which factor is the most important [25].

Functionalization and doping: The functionalization and doping of TiO_2 with other materials or metal cations can influence its photocatalytic properties. Doping can create donor or acceptor energy levels, generate defects in TiO_2 and affect its crystallinity, thereby influencing the efficiency of charge carrier separation and recombination [26].

Structure and morphology: The morphology and structure of TiO_2 such as nanotubes or nanoparticles can have an impact on its surface area, light absorption capacity and charge carrier transport, thereby affecting its photocatalytic performance [27].

Band gap energy: The band gap energy of TiO_2 determines the wavelength of light it can absorb. The effective rate of light absorption and subsequent photocatalytic processes can be affected by the band gap energies of the various TiO_2 crystal shapes [28].

Co-catalysts and sensitizers: By adding co-catalysts or sensitizers to TiO_2, e.g. metals or organic dyes, the photocatalytic effectiveness of the material can be increased by increasing light absorption, the separation of charges and reaction kinetics [29].

Reaction conditions: The photocatalytic efficiency of TiO_2 can be influenced by variables like pH, temperature, reactant concentration and the oxygen content or other reactive species in the reaction environment [30].

3. Application of TiO_2 photocatalysis for the degradation of pharmaceutical residues

TiO_2 has been used effectively to remove pharmaceutical contaminants from water. The photocatalytic efficacy of TiO_2 during water treatment is hindered by the effective movement of low-charge carriers and its poor level of sensitivity to visible light. Numerous techniques such as the design of heterojunctions, alterations to its surface and doping are thought to be very successful in enhancing the photodegradation capacity of TiO_2. To increase the photodegradation efficiency and speed up the migration of photogenerated charge, p-n or n-n heterojunctions based on TiO_2 seem to be a great solution [1]. *Table 2* represents different TiO_2 photocatalysts for the removal of pharmaceutical pollutants and their photodegradation efficiency.

3.1. Experimental methods for evaluating TiO_2 photocatalysis

The evaluation of TiO_2 photocatalysis can involve various experimental methods. Here are some of the experimental methods commonly used to assess TiO_2 photocatalysis:

Decolorization of dyes: One commonly employed method is to evaluate the decolorization or degradation of dyes such as methylene blue (MB) under visible or UV light irradiation [31]. By decreasing the dye concentration or color intensity over time, the photocatalytic activity of TiO_2 can be determined.

Photocatalytic activity tests: These tests involve assessing the ability of TiO_2 to induce desired reactions under light irradiation. For instance, the conversion of organic pollutants or the degradation of target compounds can be measured using specific analytical techniques [32]. The reaction products can be analyzed using various spectroscopic or chromatographic techniques to determine the efficiency of TiO_2 photocatalysis.

Quantum efficiency measurements: Quantum efficiency measurements provide insights into the

Table 2: Comparison of photodegradation efficiency in the removal of different pharmaceutical residues
*PD = photodeposition synthesis; **MW = formaldehyde assisted microwave synthesis

Sample	Pollutant	Irradiation time (min)	Light source	Removal efficiency	Reference
TiO_2/Ag_3BiO_3	TCH	210	50W lamp	98.50%	[1]
TiO_2	Ciprofloxacin (CIP)	76	15W UV-C lamp	88.30%	[3]
ZnO-TiO_2-MXene	Carbamazepine (CBZ)	180	150W halogenated high pressure light	97.00%	[5]
AC/TiO_2	Ibuprofen (IBU)	180	220W UV lamp	95.32%	[7]
	Diclofenac (DFC)			83.14%	
	Paracetamol (PRC)			80.40%	
Fe/TiO_2-ZnO	Sumatriptan Succinate (STS)	60	250W high-pressure mercury vapor lamp	70.00%	[9]
UV/TiO_2	Paracetamol	150	UV light	72.50%	[11]
Ag-TiO_2-PD*	Naproxen Sodium, Flurbiprofen	10	UV light	80.00%	[2]
Ag-TiO_2-MW**		60		74.00%	
AC-TiO_2	Ofloxacin (OFL)	50	8W mercury UV lamps	82.00%	[4]

efficiency of TiO_2 in converting absorbed photons into photocatalytic reactions. This method involves measuring the amount of photons absorbed and the number of reactive species generated [33]. This information helps to evaluate the overall performance of TiO_2 photocatalysts.

Chemical probe tests: Chemical probes can be used to evaluate specific reactive species generated during photocatalysis. For example, the generation of hydroxyl radicals (OH•) or superoxide radicals (O_2^{-}•) can be measured using appropriate probe compounds. These tests provide insights into the photocatalytic pathways and mechanisms facilitated by TiO_2 [34].

Transient absorption spectroscopy and time-correlated single photon counting are two examples of time-resolved spectroscopic methods that can be used to study the dynamics and kinetics of charge carriers in TiO_2 photocatalysts. These techniques offer details concerning the lifetime of photogenerated charge carriers and recombination rates, two important variables affecting photocatalytic effectiveness [26].

Approaches for surface characterization: The structural characteristics and morphology of TiO_2 photocatalysts can be evaluated using surface characterization techniques like XRD, SEM, TEM and specific surface area measurements. These methods help the relationship between structural characteristics and photocatalytic efficiency to be comprehended [35].

It is crucial to remember that the selection of the experimental approach depends on the precise objectives of the study and the details sought regarding the TiO_2 photocatalytic performance. For a thorough knowledge of TiO_2 photocatalysis, researchers frequently combine these techniques.

3.2. Comparison with other techniques

TiO_2 photocatalysis can be contrasted with other advanced oxidation processes (AOPs), in addition to photocatalysis. AOPs include a variety of processes that use strong oxidants to break down contaminants. Through these processes, highly reactive species are produced, including hydroxyl radicals (OH•), which are capable of quickly destroying organic molecules. Ozonation, Fenton's reagent (H_2O_2/Fe^{2+}) and oxidation procedures utilizing ultraviolet (UV) radiation are a few examples of AOPs. TiO_2 photocatalysis can be compared to other AOPs in terms of efficiency, reaction kinetics, energy requirements and the suitability of particular procedures regarding various types of pollutants [36]. AOPs can cause photodegradation in a variety of methods, including deterioration brought about by photolysis, photosensitizers and ROS. For example, among AOPs, it is possible to distinguish between photochemical reactions including the breakdown by UV photons, the combined effect of UV / H_2O_2, UV / O_3, UV / H_2O_2 / O_3, the breakdown by photocatalysis in liquid semiconductor solutions, both ultrasonic procedures and Fenton photoreactions, as well as radiological procedures involving ionizing radiation either by itself or in conjunction with O_3 and/or H_2O_2 [37],[38]. AOPs can use semiconductor nanoparticles as catalysts which are stimulated by light of different wavelengths, from UV to near-IR, determined by the band gap energy [39].

3.3. *Efficiency and limitations of TiO_2 photocatalysis for the degradation of pharmaceutical residues*

The factors that affect the efficiency of the catalyst are:

1) TiO_2 photocatalytic effectiveness is inhibited by the transfer limitations of pairs of electrons and holes, which primarily occur on the surface of TiO_2. Titania is prone to electrode and hole charge carrier recombination, which inhibits photocatalytic activity. The inadequate adsorption of organic contaminants on the TiO_2 surface resulted in poor rates of photocatalytic degradation.
2) Photocatalysts have a weak affinity for organic contaminants. Immobilization of the photocatalyst may facilitate selective affinity for the target pollutants.
3) Due to the volatile nature of nanoparticles, the TiO_2 nanoparticles may aggregate during photocatalytic degradation, thereby blocking the active centers from absorbing light radiation which would hinder the photocatalytic activity of TiO_2. TiO_2 aggregates as a result of organic ionizable molecules connected to the particles.
4) TiO_2 nanoparticles may cause higher scattering conditions that could reduce the photocatalytic activity of the material. To enhance the photocatalytic activity, the right UV wavelengths and TiO_2 concentration are essential [40].
5) The efficient and secure recovery of TiO_2 NPs from the water treated is a significant practical problem for the treatment of organic compounds in wastewater. An earlier study found that a TiO_2 nanopowder solution is better at dispersing the powder than a fixed support.
6) Due to the high band energy of the original TiO_2 photocatalyst and the fact that sunlight is used to facilitate its decomposition processes, it is thought to be less energy-efficient than conventional heterostructured photocatalysts [40].

To enable the creation of TiO_2-based photocatalysts that can be activated by visible or solar light, more research must be done to improve both the chemical and physical characteristics of the photocatalyst. The size of the TiO_2 particles, type of dopant and its concentration must be changed to take advantage of the visible light spectrum and increase its affinity to organic compounds in order to overcome these constraints. Secondly, the successful recovery and regeneration of suitable substrates that are very capable of separating TiO_2 nanoparticles is required. The structural design of substrates can also bring about the absorption of different organic contaminants. Thirdly, to optimize photocatalysis, its reaction conditions or other parameters like light intensity, calcination temperature, pH and significant amount of additives need to be assessed [39]. *Figure 3* represents the overall limitations of TiO_2 photocatalysts with regard to the degradation of organic compounds, that is, factors affecting the TiO_2 photocatalytic process.

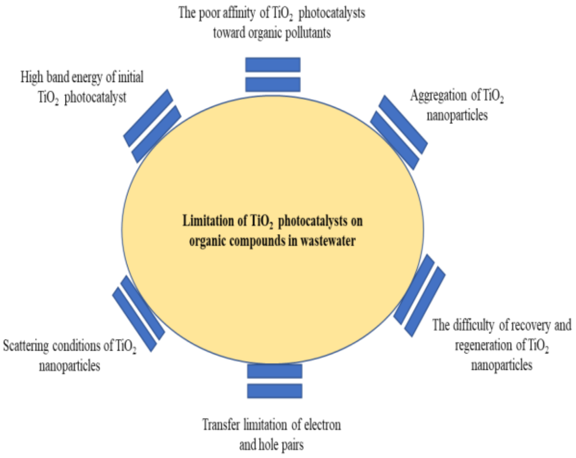

Figure 3: Limitations of TiO_2 photocatalysts

4. Factors affecting the TiO_2 photocatalytic process

4.1. *Properties and characteristics of the TiO_2 catalyst*

TiO_2 is a versatile compound that is extensively applied as a catalyst in various fields. Its properties and characteristics contribute to its effectiveness in catalytic reactions. Based on published research, below are some essential traits and features of TiO_2 catalysts: TiO_2 is used as a catalyst in thermo- and photo-catalytic processes [41]. It demonstrates catalytic activity in reactions like hydrolysis, oxidation and reduction. Due to its semiconductive, photocatalytic and catalytic properties, TiO_2 catalysts are used in a variety of industries, including the chemical industry [42].

The structural and physicochemical characteristics of TiO_2 have a considerable impact on the efficiency, specificity and sustainability of its catalytic performance. Particle size, surface area, surface flaws and crystal structure are all significant factors [41]. The redox dynamics of Pt and Cu nanoparticles on TiO_2 have been studied during photocatalytic oxidation, providing insights into the behavior of metal catalysts on TiO_2 surfaces [43]. TiO_2 catalysts exhibit strong metal-support interactions (SMSIs), which enhance their catalytic performance. SMSIs are characterized by the coverage of TiO_x over metal nanoparticles, resulting in an enhanced interaction between the metal and the support material

[44]. These interactions enhance the stability and performance of the catalyst.

The optical absorption properties of TiO_2 catalysts are important for their photocatalytic activity. Although bare TiO_2 primarily absorbs UV light, when doped with elements such as iron, a red shift can occur in its absorption band edge, expanding the range of light absorption [45]. TiO_2 is also a catalyst for hydrolysis and it is a superior catalyst-support material [42] due to its chemical stability and acid-base characteristics.

4.2. Influence of pH, temperature and dissolved oxygen on photocatalysis

A catalyst and light energy are used in the process known as photocatalysis to promote chemical reactions. Numerous variables, including pH, temperature and dissolved oxygen, might affect how well photocatalysis works. Here is a detailed breakdown of how these parameters affect photocatalysis based on the literature:

pH: Photocatalytic activity can be considerably impacted by the pH of the reaction environment. For instance, it was discovered that the crystalline structure and fraction of hydroxyl oxygen in TiO2-based photocatalysts are pH-dependent [46],[47]. It has been noted that lowering the pH in some systems accelerates the photodegradation of organic molecules [48]. Aqueous pH-responsive photocatalysts have also been investigated for controlling polymer synthesis [49]. The specific pH range and its influence may vary depending on the catalyst and reaction system.

Temperature: Temperature has a significant role in photocatalysis as it affects the reaction kinetics and energy transfer processes. Because reactants and intermediates move more quickly at higher temperatures, photocatalytic activity is typically improved when heated [37]. Each photocatalytic system may have a preferred temperature range, above which the activity may decline due to thermal deactivation or other temperature-dependent effects.

Dissolved oxygen: Dissolved oxygen can affect how photocatalytic reactions proceed. In photocatalysis, oxygen can participate in the oxidation reactions as an electron acceptor. The overall effectiveness and selectivity of the photocatalytic process might be impacted by the presence of oxygen. In other instances, oxygen defects on the catalyst surface have been suggested to increase its photoactivity [38].

It is crucial to keep in mind that the precise effects of pH, temperature and dissolved oxygen on photocatalysis might change based on the catalytic material, reaction conditions and target reaction. The performance of photocatalysis can also be influenced by additional factors such as the kind of reactants, catalyst loading and light intensity.

4.3. Impact of organic and inorganic species on TiO_2 photocatalysis

When analyzing the efficiency of TiO_2-based photocatalysts, it is crucial to take both organic and inorganic species into account. Depending on their type and concentration, organic chemicals can have either positive or negative effects on TiO_2 photocatalysis. By using TiO_2-based photocatalysts, certain organic pollutants, including formaldehyde, toluene, benzene, phenol and trichloroethene, can be successfully destroyed [46]. However, the physical and structural characteristics of the TiO_2 photocatalyst during the oxidation process might be impacted by the presence of natural organic matter (NOM) [47]. The efficacy of the photocatalyst and the production of byproducts can be influenced by the quantity and type of organic species as well as how they interact with TiO_2.

Species that are inorganic can also significantly affect TiO_2 photocatalysis. For example, soluble substances like chloride ions (Cl^-), phosphate ions (PO_4^{3-}) and sulfate ions (SO_4^{2-}) have been found to impact the efficiency of photocatalytic degradation in water matrices [48]. In some cases, inorganic ions present in wastewater such as Cl^-, NO_3^-, SO_4^{2-} and PO_4^{3-} can serve as scavengers of reactive oxygen species, thereby competing with the target organic pollutants for these species and impeding the photocatalytic process [49]. According to their type and concentration, different inorganic species may have varying effects.

It is significant to highlight that both organic and inorganic compounds can have complex, system-dependent effects on TiO_2 photocatalysis. Different results can be obtained depending on the concentration, type and interactions of these species with the photocatalyst. Therefore, when evaluating the effect of organic and inorganic species on TiO_2 photocatalysis, it is imperative to take into account the particular experimental circumstances and the target pollutants. TiO_2-based photocatalysts can destroy organic pollutants, moreover, the nature of the aqueous matrix and natural organic matter can affect the efficiency and generation of byproducts by the photocatalytic reaction. Similar to how organic species can scavenge reactive oxygen species, inorganic species can do likewise, altering the overall effectiveness of the photocatalytic process. TiO_2 photocatalysis must be optimized in order to create effective methods for water treatment and pollutant degradation. This requires an understanding of the interactions and effects of these species.

4.4. Strategies for enhancing the efficiency of TiO_2 photocatalysis

Utilizing modifying agents is a favorable strategy for enhancing the photocatalytic performance of TiO_2. Anionic or cationic additives are both acceptable. The long-term viability of the anatase phase, particle size and other characteristics can all be impacted by the addition of modifying agents. This enables the band gap to be reduced and light to be absorbed in the visible spectrum. Due to the expensive nature of f-metals, p- or d-metal cations are typically utilized in cationic doping. Metal ions can modify the photoreactivity of the photocatalyst by controlling the recombination process and acting as photoinduced charge traps. Amoxicillin is virtually destroyed (94%) by 300 minutes of irradiation under visible light with even a small amount (0.5%) of TiO_2 doped with cobalt ion. The use of commercially available Degussa P25 and undoped materials results in antibiotic removal efficiencies of 21% and 16%, respectively over the same irradiation time [37].

5. Future perspectives and challenges

Research into TiO_2 photocatalysis has been a rapidly evolving field and several emerging trends have gained a significant amount of attention. A substantial area of study has been the production and use of nanostructured TiO_2 photocatalysts. To improve photocatalytic activity, many approaches, including sol-gel, hydrothermal and template-assisted processes, are being used to change the morphology and structure of TiO_2 on the nanoscale. UV light, which only makes up a minor portion of the solar spectrum, is primarily absorbed by conventional TiO_2 photocatalysts. Therefore, attempts should be made to expand the range of visible light (wavelength > 400 nm) absorbed by TiO_2 photocatalysts.

- Strategies include doping TiO_2 with transition metal ions, coupling it with other semiconductors and surface modifications with organic dyes or carbon-based materials. These approaches can enhance the absorption of visible light and improve overall photocatalytic performance.
- The introduction of co-catalysts onto the TiO_2 surface can enhance charge separation and transfer kinetics.
- The development of heterojunctions and composite materials may also be promising to enhance photocatalysis.
- Energy efficiency and catalyst recovery are critical aspects regarding the practical applications of TiO_2 photocatalysis. Research should focus on methods to enhance energy efficiency by improving catalyst loading, reaction conditions and light sources.
- Since the efficiency and adaptability of the remedial process are greatly influenced by the design of the photocatalytic reactor, researchers should focus on designing more efficient reactors.
- TiO_2 photocatalysis depends on the photocatalyst being activated by light. The right choice of light source is essential to achieve optimal photocatalytic activity. UV light, particularly within the range of 300-400 nm, is most commonly used as it matches the absorption range of TiO_2. However, efforts are being made to extend the absorption range of light by incorporating visible light sources or using modified TiO_2 materials that exhibit photocatalytic activity in visible light.

TiO_2 photocatalysis can be used in conjunction with other treatments to enhance the removal of pollutants. Synergistic approaches include coupling TiO_2 photocatalysis with adsorption, membrane filtration, advanced oxidation processes or biological processes. These combinations can improve the efficiency of the treatment, reduce energy consumption and remove recalcitrant compounds. TiO_2 photocatalysis in wastewater treatment systems has the ability to remove a range of organic pollutants effectively and sustainably. The process is still being optimized and scaled up for usage in real-world applications, moreover, problems with regard to catalyst stability, cost and energy efficiency are being addressed.

By addressing these challenges and optimizing TiO_2 photocatalysis through continuous research and development, the efficiency, applicability and feasibility of this technology in wastewater treatment can be enhanced, leading to more sustainable and efficient removal of pollutants.

6. Conclusion

The elimination of organic pollutants from effluent was highlighted by this study. Common forms of organic pollutants were identified, the basic principles of TiO_2-based photocatalysts with regard to the removal of organic pollution outlined, and the first limitations of TiO_2 photocatalysis in this regard explored. A number of variables that are crucial for the photocatalytic degradation of TiO_2 were considered. For the future commercial usage of TiO_2-based photocatalysis, several process variables, including the concentration of the catalyst, particle size, pH adjustment and substrate choice, will be significant. The main benefits of photocatalysis were determined as follows: industrial waste can be indiscriminately converted into harmless substances by TiO_2-based photocatalysts without causing any additional pollution. Solar energy is a free, natural resource that supplies most of the energy needed. However, depending on the properties of effluent, further research needs to be carried out to develop photocatalytic systems and optimize their operation.

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REFERENCES

[1] Feizpoor, S.; Habibi-Yangjeh, A.; Luque, R.: Design of TiO_2/Ag_3BiO_3 n-n heterojunction for enhanced degradation of tetracycline hydrochloride under visible-light irradiation, *Environ. Res.*, 2022, **215-2**, 114315, DOI: 10.1016/j.envres.2022.114315

[2] Nyankson, E.; Yeboah, N.; Jnr, S.O.; Onaja, S.; Mensah, T.; Efavi, J.K.: The effect of synthesis route on the photocatalytic performance of Ag-TiO_2 using rhodamine b dyes, pesticides, and pharmaceutical waste as model pollutants, *Mater. Res. Express*, 2022, **9**(9), 094001, DOI: 10.1088/2053-1591/ac871f

[3] Parmar, N.; Srivastava, J.K.: Process optimization and kinetics study for photocatalytic ciprofloxacin degradation using TiO_2 nanoparticle: A comparative study of Artificial Neural Network and Surface Response Methodology, *J. Indian Chem. Soc.*, 2022, **99**(8), 100584, DOI: 10.1016/j.jics.2022.100584

[4] Alghamdi, Y.G.; Krishnakumar, B.; Malik, M.A.; Alhayyani, S.: Design and preparation of biomass-derived activated carbon loaded TiO_2 photocatalyst for photocatalytic degradation of reactive red 120 and ofloxacin, *Polymers*, 2022, **14**(5), 880, DOI: 10.3390/polym14050880

[5] Rdewi, E.H.; Abbas, K.K.; Abdulkadhim Al-Ghaban, A.M.: Removal pharmaceutical carbamazepine from wastewater using ZnO-TiO_2-MXene heterostructural nanophotocatalyst under solar light irradiation, *Mater. Today: Proc.*, 2022, **60**(3), 1702–1711, DOI: 10.1016/j.matpr.2021.12.229

[6] Azizi, A.; Khodabakhshi, A.; Jamshidifar, S.: Biosynthesis of TiO_2 nanoparticles as a suitable photocatalyst for degradation of ketoconazole: characterization, efficiency, toxicity evaluation and degradation pathways, *J. Mater. Sci. Mater. Electron.*, 2022, **33**(8), 5938–5952, DOI: 10.1007/s10854-022-07774-0

[7] Üstün Odabaşi, S.; Boudraà, Í.; Aydin, R.; Büyükgüngör, H.: Photocatalytic removal of pharmaceuticals by immobilization of TiO_2 on activated carbon by LC–MS/MS monitoring, *Water Air Soil Pollut.*, 2022, **233**(4), 111, DOI: 10.1007/s11270-022-05579-9

[8] Kaur, H.; Kaur, S.; Kumar, S.; Singh, J.; Rawat, M.: Eco-friendly approach: synthesis of novel green TiO_2 nanoparticles for degradation of reactive green 19 dye and replacement of chemical synthesized TiO_2, *J. Clust. Sci.*, 2021, **32**, 1191–1204, DOI: 10.1007/s10876-020-01881-w

[9] Alizadeh, E.; Baseri, H.: Photocatalytic degradation of sumatriptan succinate by ZnO, Fe doped ZnO and TiO_2-ZnO nanocatalysts, *Mater. Chem. Horiz.*, 2022, **1**(1), 7–21, DOI: 10.22128/mch.2022.534.1002

[10] Ahmad, W.; Singh, A.; Jaiswal, K.K.; Gupta, P.: Green synthesis of photocatalytic TiO_2 nanoparticles for potential application in photochemical degradation of ornidazole, *J. Inorg. Organomet. Polym. Mater.*, 2021, **31**, 614–623, DOI: 10.1007/s10904-020-01703-6

[11] Shinde, M.A.; Sul, M.G.S.; Kapdi, M.S.S.: Removal of paracetamol from pharmaceutical waste water by using UV/TiO_2 and UV/ZnO_2, *Int. J. Res. Pub. Rev.*, 2022, **3**(11), 3107–3114

[12] Sharotri, N.; Gupta, S.; Sud, D.: Visible light responsive S-doped TiO_2 nanoparticles: synthesis, characterization and photocatalytic degradation of pollutants, *Nanotechnol. Environ. Eng.*, 2022, **7**(2), 503–515, DOI: 10.1007/s41204-022-00228-2

[13] Duo, J.; Li, W.; Wang, Y.; Wang, S.; Wufuer, R.; Pan, X.: Photothermal catalytic degradation of lomefloxacin with nano Au/TiO_2, *Water*, 2022, **14**(3), 339, DOI: 10.3390/w14030339

[14] Saravanan, A.; Kumar, P.S.; Jeevanantham, S.; Anubha, M.; Jayashree, S.: Degradation of toxic agrochemicals and pharmaceutical pollutants: Effective and alternative approaches toward photocatalysis, *Environ. Pollut.*, 2022, **298**, 118844, DOI: 10.1016/j.envpol.2022.118844

[15] Kumar, S.; Sharma, R.; Gupta, A.; Dubey, K.K.; Khan, A.; Singhal, R.; Kumar, R.; Bharti, A.; Singh, P.; Kant, R.: TiO_2 based photocatalysis membranes: An efficient strategy for pharmaceutical mineralization, *Sci. Total Env.*, 2022, **845**, 157221, DOI: 10.1016/j.scitotenv.2022.157221

[16] Siedlecka, E.M.: Removal of cytostatic drugs from water and wastewater: Progress in the development of advanced treatment methods, in: Fate and effects of anticancer drugs in the environment, Heath, E.; Isidori, M.; Kosjek, T.; Filipič, M. (Eds), (Springer Cham), 2020, pp. 197–219, DOI: 10.1007/978-3-030-21048-9_9

[17] Evgenidou, E.; Ofrydopoulou, A.; Malesic-Eleftheriadou, N.; Nannou, C.; Ainali, N.M.; Christodoulou, E.; Bikiaris, D.N.; Kyzas, G.Z.; Lambropoulou, D.A.: New insights into transformation pathways of a mixture of cytostatic drugs using polyester-TiO_2 films: Identification of intermediates and toxicity assessment, *Sci. Total Env.*, 2020, **741**, 140394, DOI: 10.1016/j.scitotenv.2020.140394

[18] Bayan, E.M.; Pustovaya, L.E.; Volkova, M.G.: Recent advances in TiO_2-based materials for photocatalytic degradation of antibiotics in aqueous systems, *Env. Technol. Innov.*, 2021, **24**, 101822, DOI: 10.1016/j.eti.2021.101822

[19] Mandade, P.: Introduction, basic principles, mechanism, and challenges of photocatalysis, in: Handbook of nanomaterials for wastewater treatment, Bhanvase, B.; Sonawane, S.; Pawade, V.; Pandit, A. (Eds.) (Elsevier), 2021, pp. 137–154, DOI: 10.1016/B978-0-12-821496-1.00016-7

[20] Gusain, R.; Kumar, N.; Ray, S.S.: Factors influencing the photocatalytic activity of photocatalysts in wastewater treatment, in: Photocatalysts in advanced oxidation processes for wastewater treatment, Fosso-Kankeu, E.; Pandey, S.; Ray, S.S. (Eds.) (Wiley), 2020, pp. 229–270, DOI: 10.1002/9781119631422.ch8

[21] Yang, X.; Wang, D.: Photocatalysis: from fundamental principles to materials and applications, *ACS Appl. Energy Mater.*, 2018, **1**(12), 6657–6693, DOI: 10.1021/acsaem.8b01345

[22] Khan, M.M.: Principles and mechanisms of photocatalysis, in: Photocatalytic systems by design, Sakar, M.; Balakrishna, R.G.; Do, T. (Eds.) (Elsevier), 2021, pp. 1–22, DOI: 10.1016/B978-0-12-820532-7.00008-4

[23] Chen, Y.; Wang, M.; Yan, F.; Wang, W.; Qu, Y.; Fang, H.; Cui, Z.; He, B.; Li, J.: Enhanced UV–vis photoinduced hydrogen evolution of metalloporphyrin sensitized PSf/TiO_2 MMMs by varying center metal ion complexed in porphyrin, *Fuel*, 2022, **312**, 122810, DOI: 10.1016/j.fuel.2021.122810

[24] Chen, D.; Cheng, Y.; Zhou, N.; Chen, P.; Wang, Y.; Li, K.; Huo, S.; Cheng, P.; Peng, P.; Zhang, R.: Photocatalytic degradation of organic pollutants using TiO_2-based photocatalysts: A review, *J. Clean. Prod.*, 2020, **268**, 121725, DOI: 10.1016/j.jclepro.2020.121725

[25] Yamazaki, Y.; Takaki, D.; Nishiyama, N.; Yamazaki, Y.: Factors affecting photocatalytic activity of TiO_2, in: Current developments in photocatalysis and photocatalytic materials, Wang, X.; Anpo, M.; Fu, X. (Eds.) (Elsevier), 2020, pp. 23–38, DOI: 10.1016/B978-0-12-819000-5.00003-5

[26] Irfan, F.; Tanveer, M.U.; Moiz, M.A.; Husain, S.W.; Ramzan, M.: TiO_2 as an effective photocatalyst mechanisms, applications, and dopants: a review, *Eur. Phys. J. B*, 2022, **95**(11), 1–13, DOI: 10.1140/epjb/s10051-022-00440-8

[27] El-Gendy, R.A.; El-Bery, H.M.; Farrag, M.; Fouad, D.M.: Metal chalcogenides (CuS or MoS_2)-modified TiO_2 as highly efficient bifunctional photocatalyst nanocomposites for green H_2 generation and dye degradation, *Sci. Rep.*, 2023, **13**(1), 7994, DOI: 10.1038/s41598-023-34743-2

[28] Guo, Q.; Zhou, C.; Ma, Z.; Yang, X.: Fundamentals of TiO_2 photocatalysis: concepts, mechanisms, and challenges, *Adv. Mater.*, 2019, **31**(50), 1901997, DOI: 10.1002/adma.201901997

[29] Jeon, J.P.; Kweon, D.H.; Jang, B.J.; Ju, M.J.; Baek, J.B.: Enhancing the photocatalytic activity of TiO_2 catalysts, *Adv. Sustain. Syst.*, 2020, **4**(12), 2000197, DOI: 10.1002/adsu.202000197

[30] Ge, J.; Zhang, Z.; Ouyang, Z.; Shang, M.; Liu, P.; Li, H.; Guo, X.: Photocatalytic degradation of (micro)plastics using TiO_2-based and other catalysts: Properties, influencing factor, and mechanism, *Environ. Res.*, 2022, **209**, 112729, DOI: 10.1016/j.envres.2022.112729

[31] Rescigno, R.; Sacco, O.; Venditto, V.; Fusco, A.; Donnarumma, G.; Lettieri, M.; Fittipaldi, R.; Vaiano, V.: Photocatalytic activity of P-doped TiO_2 photocatalyst, *Photochem. Photobiol. Sci.*, 2023, **22**, 1223–1231, DOI: 10.1007/s43630-023-00363-y

[32] Kim, M.S.; Yoo, H.Y.; Choi, G.E.; Jo, S.; Shin, H.; Lim, J.: Visible light photocatalysis of TiO_2 complexed with albumin via a ligand-to-metal charge transfer (LMCT) pathway, *J. Phys. Chem. C*, 2023, **127**(11), 5408–5415, DOI: 10.1021/acs.jpcc.3c00445

[33] Minnekhanov, A.; Kytina, E.; Konstantinova, E.; Kytin, V.; Marikutsa, A.; Elizarov, P.: Photoinduced dynamics of radicals in N-and Nb-codoped titania nanocrystals with enhanced photocatalysis: experiment and modeling, *Cryst. Growth Des.*, 2022, **22**(7), 4288–4297, DOI: 10.1021/acs.cgd.2c00272

[34] Chakhtouna, H.; Benzeid, H.; Zari, N.; Qaiss, A.E.K.; Bouhfid, R.: Recent progress on Ag/TiO_2 photocatalysts: photocatalytic and bactericidal behaviors, *Environ. Sci. Pollut. Res.*, 2021, **28**, 44638–44666, DOI: 10.1007/s11356-021-14996-y

[35] Dell'Edera, M.; Porto, C.L.; De Pasquale, I.; Petronella, F.; Curri, M.L.; Agostiano, A.; Comparelli, R.: Photocatalytic TiO_2-based coatings for environmental applications, *Catal. Today*, 2021, **380**, 62–83, DOI: 10.1016/j.cattod.2021.04.023

[36] Hou, C.; Wang, L.; Zhang, W.; Zhu, Z.; Lu, S.; Zou, F.; Wang, C.: Construction of TiO_2–x confined by layered iron silicate toward efficient visible-light-driven photocatalysis–fenton synergistic removal of organic pollutants, *ACS Appl. Mater. Interfaces*, 2023, **15**(19), 23124–23135, DOI: 10.1021/acsami.3c01981

[37] Yılmaz, H.Ç.; Akgeyik, E.; Bougarrani, S.; El Azzouzi, M.; Erdemoğlu, S.: Photocatalytic degradation of amoxicillin using Co-doped TiO_2 synthesized by reflux method and monitoring of degradation products by LC–MS/MS, *J. Dispers. Sci. Technol.*, 2020, **41**(3), 414–425, DOI 10.1080/01932691.2019.1583576

[38] Khan, A.; Valicsek, Z.; Horváth, O.: Photocatalytic degradation rhodamine B in heterogeneous and homogeneous systems, *Hung. J. Ind. Chem.*, 2021, **49**(1), 9–16, DOI: 10.33927/hjic-2021-02

[39] Krakowiak, R.; Musial, J.; Bakun, P.; Spychała, M.; Czarczynska-Goslinska, B.; Mlynarczyk, D.T.; Koczorowski, T.; Sobotta, L.; Stanisz, B.; Goslinski, T.: Titanium dioxide-based photocatalysts for degradation of emerging contaminants including pharmaceutical pollutants, Appl. Sci., 2021, **11**(18), 8674, DOI: 10.3390/app11188674

[40] Raza, N.; Raza, W.; Gul, H.; Azam, M.; Lee, J.; Vikrant, K.; Kim, K.-H.: Solar-light-active silver phosphate/titanium dioxide/silica heterostructures for photocatalytic removal of organic dye, *J. Clean. Prod.*, 2020, **254**, 120031, DOI: 10.1016/j.jclepro.2020.120031

[41] Scirè, S.; Fiorenza, R.; Bellardita, M.; Palmisano, L.: Catalytic applications of TiO_2, in: Titanium dioxide (TiO_2) and its applications, Parrino, F.; Palmisanopp, L. (Eds.) (Elsevier), 2021, pp. 637–679, DOI: 10.1016/B978-0-12-819960-2.00006-7

[42] Byun, M.Y.; Kim, Y.E.; Baek, J.H.; Jae, J.; Lee, M.S.: Effect of surface properties of TiO_2 on the performance of Pt/TiO_2 catalysts for furfural hydrogenation, *RSC Adv.*, 2022, **12**(2), 860–868, DOI: 10.1039/D1RA07220J

[43] Chiarello, G.L.; Bernareggi, M.; Selli, E.: Redox dynamics of Pt and Cu nanoparticles on TiO_2 during the photocatalytic oxidation of methanol under aerobic and anaerobic conditions studied by in situ modulated excitation X-ray absorption spectroscopy, *ACS Catal.*, 2022, **12**(20), 12879–12889, DOI: 10.1021/acscatal.2c03025

[44] Macino, M.; Barnes, A.J.; Althahban, S.M.; Qu, R.; Gibson, E.K.; Morgan, D.J.; Freakley, S.J.; Dimitratos, N.; Kiely, C.J.; Gao, X.: Tuning of catalytic sites in Pt/TiO_2 catalysts for the chemoselective hydrogenation of 3-nitrostyrene, *Nat. Catal.*, 2019, **2**(10), 873–881, DOI: 10.1038/s41929-019-0334-3

[45] Valero-Romero, M.; Santaclara, J.; Oar-Arteta, L.; Van Koppen, L.; Osadchii, D.; Gascon, J.; Kapteijn, F.: Photocatalytic properties of TiO_2 and Fe-doped TiO_2 prepared by metal organic framework-mediated synthesis, *Chem. Eng. J.*, 2019, **360**, 75–88, DOI: 10.1016/j.cej.2018.11.132

[46] Talaiekhozani, A.; Rezania, S.; Kim, K.-H.; Sanaye, R.; Amani, A.M.: Recent advances in photocatalytic removal of organic and inorganic pollutants in air, *J. Clean. Prod.*, 2021, **278**, 123895, DOI: 10.1016/j.jclepro.2020.123895

[47] Gowland, D.C.; Robertson, N.; Chatzisymeon, E.: Photocatalytic oxidation of natural organic matter in water, *Water*, 2021, **13**(3), 288, DOI: 10.3390/w13030288

[48] Gao, L.; Zhou, B.; Wang, F.; Yuan, R.; Chen, H.; Han, X.: Effect of dissolved organic matters and inorganic ions on TiO_2 photocatalysis of diclofenac: mechanistic study and degradation pathways, *Environ. Sci. Pollut. Res.*, 2020, **27**, 2044–2053, DOI: 10.1007/s11356-019-06676-9

[49] Tang, T.; Lu, G.; Wang, W.; Wang, R.; Huang, K.; Qiu, Z.; Tao, X.; Dang, Z.: Photocatalytic removal of organic phosphate esters by TiO_2: Effect of inorganic ions and humic acid, *Chemosphere*, 2018, **206**, 26–32, DOI: 10.1016/j.chemosphere.2018.04.161