



Review

Composites for Aqueous-Mediated Heterogeneously Catalyzed Degradation and Mineralization of Water Pollutants on TiO₂—A Review

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Abstract: Wastewater incorporates a wide range of organic toxins, which have an adverse impact on the health of humans and other living things. In recent years, nanotechnology has promoted effective strategies for the photodegradation of industrial organic toxins and tenacious medical contaminants present in wastewater. Advanced composites based on photocatalysts can provide promising solutions for environmental cleanup without generating hazardous byproducts, because they promote the complete oxidation of contaminants. This survey article recaps the essentials of heterogeneous catalysis. Among the major players in heterogeneous catalysis, the metal oxide catalyst (e.g., TiO₂) groups cover photocatalysis of water toxins such as dyes, harmful organic molecules, and pharmaceutical contamination. The reasons for the proposal of TiO₂ as an active filler for heterogeneous photocatalysts include its superior surface area, significant activity for distinct oxidation and reduction reactions at low temperatures and pressures, effective interaction with metal supports, and chemical stability. Because of the aforementioned features, heterogeneous TiO₂ catalysts have a lot of potential in photocatalyst applications, and they can be improved even further by doping them with anionic or cationic dopants.

Keywords: heterogeneous photocatalysis; TiO₂ semiconductor; degradation and mineralization; dyes; pharmaceutical contaminants; biocomposites



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1. Introduction

Humanity currently faces real and crucial problems related to climate change and the deterioration of environmental resources [1,2]. Among the latter, ecological contamination due to millions of different colored compounds and effluent substances is one of the most important issues [3]. Worldwide, over 0.7 million organic coloring compounds and natural/synthetic dyes are produced annually in textiles, beauty aids, plastics and polymers, paper and printing, pesticides and insecticides, pharmaceuticals, gaseous products, and consumer electronics. The waste effluents of the aforementioned companies and industries, due to their harmful potential, persistence, and malignant activity, generate risks for the biosphere and human wellbeing [4–12]. It is becoming increasingly urgent to replace these refractory toxins with natural alternatives and, in any case, to degrade the poisons before reintroducing them into the environment and water sources. The materials and treatment procedures currently applied in wastewater treatment cannot always handle natural toxins. Often, the effluents released by these companies contain very high levels of toxic pollutants. Colored and colorless pollutants typically have complex atomic structures, making them eminently stable and complicated to biodegrade. Consequently, owing to their limited biodegradability, prevailing treatment measures are not proficient in managing wastewater pollutants. Photocatalytic mineralization has incredible potential to control pollutants or

toxins present in the aqueous environment. Photocatalysis using heterogeneous catalysts is an efficient technique for the decomposition of water pollutants.

In previous decades, numerous materials have been proposed for catalysis, generally classified into homogeneous and heterogeneous catalysts [13–15]. Homogeneous photocatalysts are molecular composites that are generated by coordination chemistry and consist of well-defined monoatomic metal centers. On the other hand, heterogeneous photocatalysts are typically fabricated using surface morphology science and semiconductors with solid-state chemistry, whose atoms over the surface assist as reaction sites. Both homogeneous and heterogeneous catalysts have distinct benefits and drawbacks that are influenced by their assorted designs and operating principles (Figure 1).

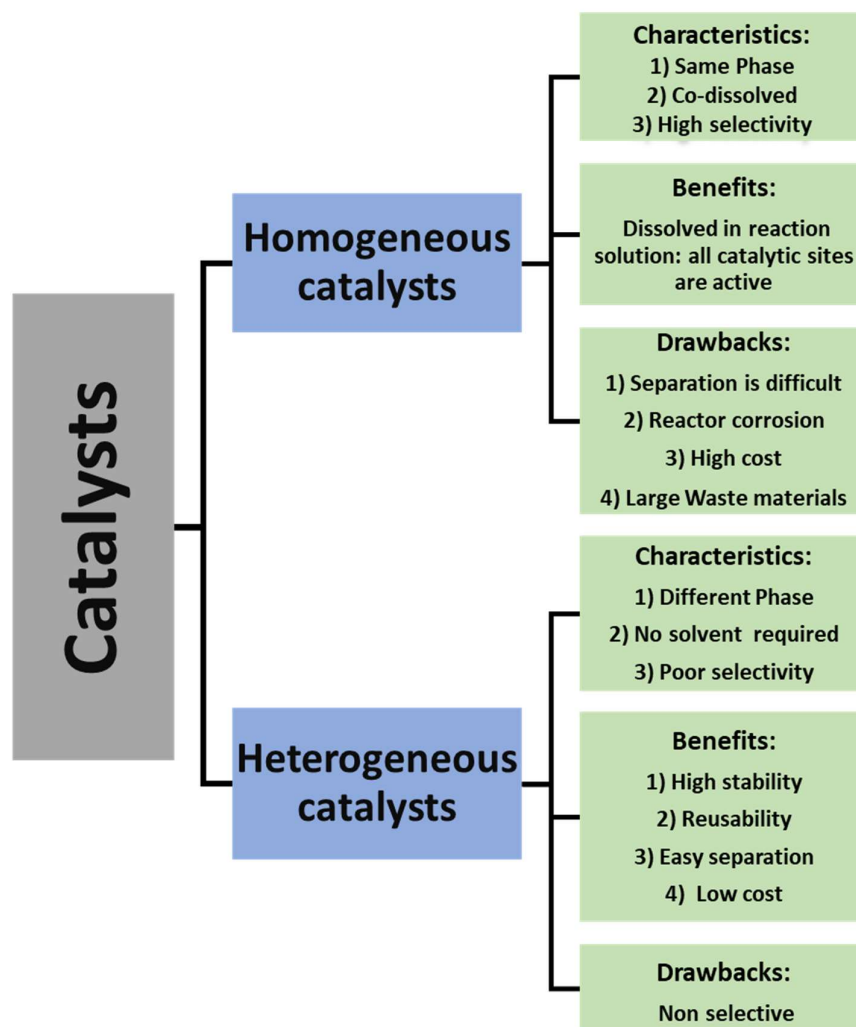


Figure 1. Characteristics, benefits, and drawbacks of homogeneous and heterogeneous catalysts.

Homogeneous catalysts' redox potentials, absorption coefficients, and electronic characteristics can all be modified by varying how the nuclei of the metal atoms coordinate with various organic ligands [2]. Consequently, the functional sites of homogeneous catalysts have been frequently chemically characterized, enabling the theoretical computing of reaction mechanisms and the rational construction of catalysts. Homogeneous catalysts, however, are challenging to retrieve and reclaim for long-term employment due to their comparably expensive prices.

Heterogeneous micro- and nanoscale composites provide benefits beyond those of homogeneous catalysts, including simplified catalyst and reaction byproduct isolation, versatility in consistent chemical industries, and recyclability. Heterogeneous catalysis is currently used in around 80% of all industrial operations, mainly for oxidation processes

and energy generation. An overview of the applications of heterogeneous catalysis in the industrial domain is shown in the graphical abstract.

In heterogeneous catalysis, water-splitting, photoreduction–oxidation, organic synthesis, hydrogen transfer, sanitization, anticancer therapy, metal deposition, gaseous pollutant eviction, water detoxification, and other reactions are all included [16–20]. The catalysts and reaction conditions occur in various circumstances in the heterogeneous catalysis process. Most heterogeneous catalysts consist of solids and either liquids or gases in the reaction mixture [21]. Simple phase separation at the end of the process greatly empowers the reaction's separation of the reactant(s), product substance(s), and catalyst(s).

Metal oxides, either as active phases or as substrates, are among the most significant and commonly employed types of solid catalysts. Metal oxides are employed extensively in heterogeneous catalysis by virtue of their acid–base and redox reaction aspects [22–25]. Metals and metal oxides constitute the majority of catalysts used in synthetic transformations. Metals from the transition and noble groups are commonly utilized as catalysts, and their performance has been associated with their outer electron configuration [26]. Metal oxide catalysts became conspicuous during the 1950s, when they were found to catalyze a wide assortment of oxidation, hydroelectric treatment, and acid–alkali responses—especially in synthetic and industrial science. The highlights on photocatalysis [27–36] and photochemical splitting of water [37–42] have appeared in many review publications. Among metal oxide catalysts, titanium dioxide catalysts are predominantly used, owing to their low cost of manufacture, ease of regeneration, and selective action. Moreover, TiO_2 has been implemented widely in catalytic reactions, including oxidation, reduction, photocatalysis, water-splitting, energy storage, and biological applications (Figure 2).

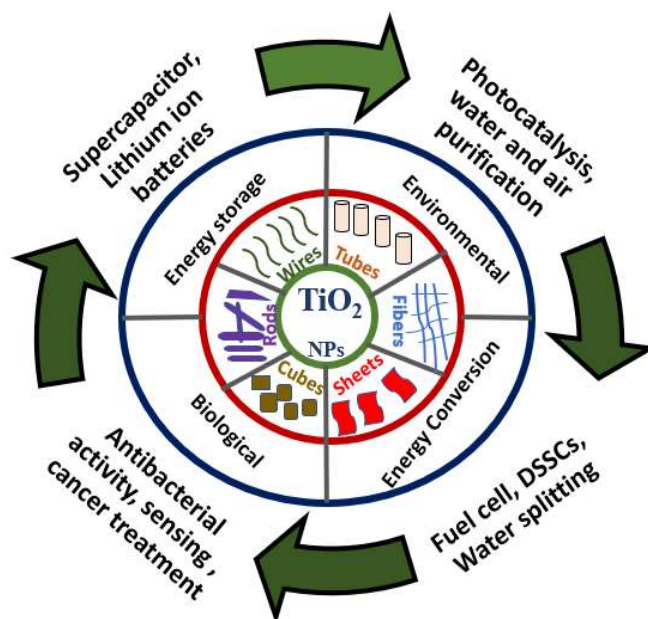


Figure 2. TiO_2 nanoparticles with distinct structures used in various applications.

1.1. TiO_2 as a Heterogeneous Photocatalyst

Mostly semiconducting materials such as metal oxides, including TiO_2 and doped titanium oxides, have been utilized for photocatalysis and the photosplitting of water (H_2O) into hydrogen (H_2) and oxygen (O_2). The majority of the catalysts show strong catalysis when scattered as particulates or as cathodes; thus, the abovementioned investigations are termed “heterogeneous photocatalysis”.

Owing to its wide bandgap (3.2 eV) under UV–visible light, TiO_2 has been evidenced to be among the most favorable n-type semiconductors. This material is also effectively improved because of its excellent chemical and physical stability and greater refractive index. Several novel TiO_2 photocatalysts have indeed been reported, most of which were

used to catalyze UV-illuminated photoreactions, and today TiO_2 is being modified to potentially sensitize visible light.

Furthermore, several types of TiO_2 —such as TiO_2 powders, nanotubes, nanorods, and nanofilms—have recently been produced. The decomposition of dyes and toxic organic compounds has been tested on composites containing and/or doped with TiO_2 . The increased efficacy of various types of TiO_2 employed for the removal of dyes and phenolic compounds in aqueous solutions was analyzed in this review.

1.2. Heterogeneous Photocatalysis—Advanced Oxidation Processes

Advancements regarding heterogeneous photocatalysis on TiO_2 surfaces in the presence of photons are steadily rising, showing the most elevated rate among all advanced oxidation processes (AOPs) [43–45]. The literature on the photocatalytic degradation of wastewater has shown the adequacy of photocatalysis as an advantageous method for wastewater treatment.

Photoreactions do not occur as a result of illumination with light alone. These responses frequently prefer the utilization of photocatalysts: a term that implies that photons helped in the generation of the chemically active species. Heterogeneous photocatalysis, by definition, is the oxidation of target molecules with the assistance of active species, utilizing nanostructures as a catalyst beneath the UV–visible photon stimulation. When the energy of UV–Vis radiation is comparable to or greater than the bandgap energy—the threshold energy required to transfer an electron from the valance band (VB) to the conduction band (CB)—at the surface of the photocatalyst, it results in the production of holes (h^+). On account of the TiO_2 semiconductor substance, photons' absorption leads to electron–hole pairs that participate in the resulting redox reactions with the adsorbed molecules over the surface to produce a definitive product(s). These electrons (e^-) and holes (h^+) can go through the resulting oxidation and reduction process with any species shown in Figure 3, which may be adsorbed over the TiO_2 surface to release the radical products, leading to high productivity in the photocatalytic measures.

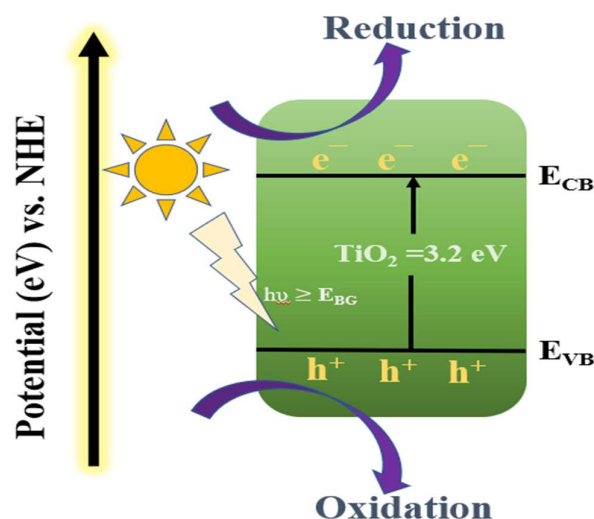


Figure 3. Schematic illustration of the reaction mechanism for a photon-induced reaction process in a TiO_2 semiconductor.

The electrons and holes created can subsequently be utilized to drive substance relations, as follows:

- The energy bandgap among electrons and holes is greater than the energy needed for the absolute reaction.
- The redox possibilities of the electrons and holes (the CB and VB positions, respectively) are reasonable for redox reaction activation.
- The redox processes are possibly quick enough to rival the electron–hole recombination.

An energy level diagram (ELD) can be built to simplify the photocatalytic component. Subsequently, the overall band-edge positions of the photocatalysts can be determined utilizing the following exact formulae [46]:

$$E_{CB} = \chi(A_a B_b C_c) - 1/2E_g + E_0 \quad (1)$$

$$E_{VB} = E_{CB} + E_g \quad (2)$$

where $\chi(A_a B_b C_c)$ represents the absolute electronegativity of semiconductor materials dictated by “Pearson’s Absolute Electronegativity” with the outright electronegativities of metal particles and anions. For the hydrogen dimensions, E_0 denotes the energy of free electrons (4.5 eV) versus NHE, while E_g presents the bandgap energy of the photocatalysts. Utilizing this condition, the positions of the VB and CB in the semiconductor nanostructure can be determined. In a heterogeneous photocatalysis mechanism, two reaction steps happen successively: the reduction of oxygen (O_2), and the oxidation of toxic pollutants by the hydroxyl ($OH^\bullet$) radicals. Throughout the excitation of TiO_2 , electrons are assembled in the conduction band, which causes the formation of a hole in the valence band. In this manner, it is important to devour electrons to expand the effectiveness of photocatalysis on TiO_2 . Herein, the electrons are engaged to reduce the oxygen. The general reaction of the sample is addressed in Figure 4. The holes metamorphose the water (H_2O) molecules into hydroxyl ($OH^\bullet$) radicals and hydrogen (H^+) cations in the presence of photoillumination, and $OH^\bullet$ is formed, which acts as an oxidizing agent and changes toxic organic compounds—principally those incorporated in wastewater—into water, carbon dioxide, and other innocuous byproducts.

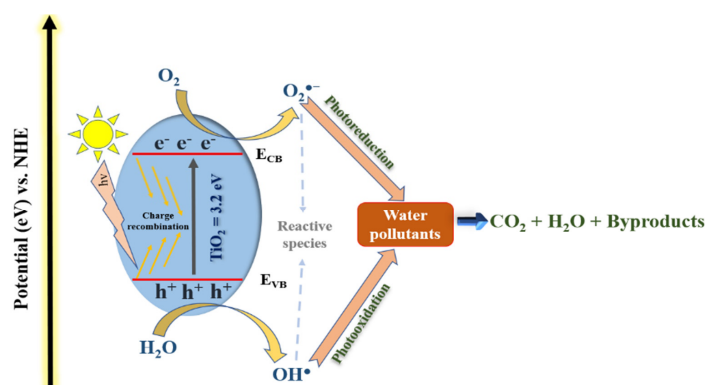


Figure 4. Mechanism of the photocatalytic action of a TiO_2 sample in wastewater treatment under the irradiation of distinct photon sources.

Furthermore, the mechanism of the overall photosensitization and decomposition of hazardous samples can be demonstrated by Equations (3)–(6):



1.3. Influence of the Semiconductor Edge Positions of the Valence Band (VB) and Conduction Band (CB) on Photocatalysis

In the photocatalysis method, the edge possibilities of the photocatalyst’s conduction band (CB) are lower, while those of the valence band (VB) are higher, compared to the redox pair potential available in the solution. The photogenerated e^- and h^+ will bring about reduction and oxidation measures. At the point when the redox capability of the species to be oxidized/reduced is resolved, the best photocatalyst with the best edge positions of the

bands can be chosen [47]. The thermodynamic motive force is relative to the divergence between the semiconductor's VB and CB possibilities and the target molecule's redox potential. For the reduction process, semiconductors with highly negative CB edges are more proficient, while semiconductors with highly positive VB edges are more compelling for oxidation responses.

In addition, the photogenerated holes at the VB can be shipped towards the adsorbed water pollutants and decompose them; however, they are not able to shape $\text{OH}^\bullet$ radicals by oxidizing water (H_2O), given the greater VB potential ($\text{EVB} = +2.39 \text{ eV}$ against NHE) than the related $\text{E}^\bullet_{\text{OH}/\text{H}_2\text{O}}$ ($+2.68 \text{ eV}$ vs NHE). The abovementioned suggestion from the energy level diagram (ELD) is similar to the scavenger trial results, demonstrating that superoxide radicals ($\text{O}_2^{\bullet-}$) and holes (h^+) are the most significant reactive species that effectively take part in wastewater mineralization.

Significantly, the $\text{OH}^\bullet$ radicals play a considerable role in the degradation of pollutants, and the fabrication of $\text{OH}^\bullet$ can start from two pathways: a multistep reduction by photo-generated charge carriers, as referenced above; and the holes' oxidization of water (OH^-). The essential point of interest of this approach likewise includes the thermodynamic aspect, which requires the VB position to be better than 2.38 eV (vs. NHE, $\text{pH} = 0$). The significance of producing superoxide radicals has been similarly clarified. On the off-chance that the photocatalysts cannot oxidize water (H_2O) to create $\text{OH}^\bullet$, the multistep decrease by photoelectrons brings out superoxide radicals, providing another conceivable technique to produce $\text{OH}^\bullet$ radicals. It is first initiated by the reaction of e^- with O_2 to create $\text{O}_2^{\bullet-}$, and then the $\text{O}_2^{\bullet-}$ combines with H^+ to produce $\text{HO}_2^{\bullet-}$. Hence, H_2O_2 is produced as the intermediate. Finally, $\text{OH}^\bullet$ radicals can be advanced through the separation of H_2O_2 . Thus, the $\text{O}_2^{\bullet-}$ and $\text{OH}^\bullet$ radicals promote the degradation of the water pollutants.

2. Advancements in the Field of Heterogeneous Photocatalytic Treatment

2.1. Influence of the Distinct Phase and Bandgap Energies of TiO_2 Semiconductors and Reactive Species over Photocatalysis

The TiO_2 catalyst is the most propitious n-type semiconductor because of its 3.2 eV bandgap width under UV light. Furthermore, the high chemical and physical stability of TiO_2 materials is generally explored in research [48,49]. Among various semiconducting materials, including carbides and nitrides, TiO_2 -based semiconductor assistance materials are known to have amazing properties, and TiO_2 -based semiconductor catalysts show remarkable resistance to corrosion in various electrolytic media. The investigation of TiO_2 nanoparticles as catalysts is significant during heterogeneous catalysis, owing to the size and essence of the interaction of the TiO_2 catalyst with the substrate. This interaction emphatically impacts the assurance of synergistic catalytic performance and the selectivity of the heterogeneous TiO_2 catalyst [50]. TiO_2 is widely utilized as a photocatalyst due to its superior effectiveness and adaptability in various response media, nontoxicity, compound dependability, and minimal effort [51]. TiO_2 has a wide bandgap, showing higher UV photon absorption than visible light. UV photons account for only about 4% in the general daylight range. This disadvantage profoundly restricts the productivity of TiO_2 in future applications for antitoxin wastewater degradation. Visible light accounts for over 40% in the general daylight range. Accordingly, TiO_2 with visible-light-observant capacity could be developed using various possible techniques [52–57].

TiO_2 exists in three phases: anatase, rutile, and brookite. Anatase TiO_2 ($\text{EBG} = 3.2 \text{ eV}$) is the most productive for photocatalytic applications, followed by the rutile phase TiO_2 ($\text{EBG} = 3.0 \text{ eV}$). In addition, anatase has the smallest average effective mass of photo-generated electron-hole pairs relative to rutile and brookite. It is never permitted for photogenerated electrons to transfer instantly from the anatase TiO_2 conduction band (CB) to the valence band (VB). As illustrated in Figure 5, anatase's indirect bandgap has a longer lifespan for photoexcited electrons and holes compared to rutile's and brookite's direct bandgaps. [58]

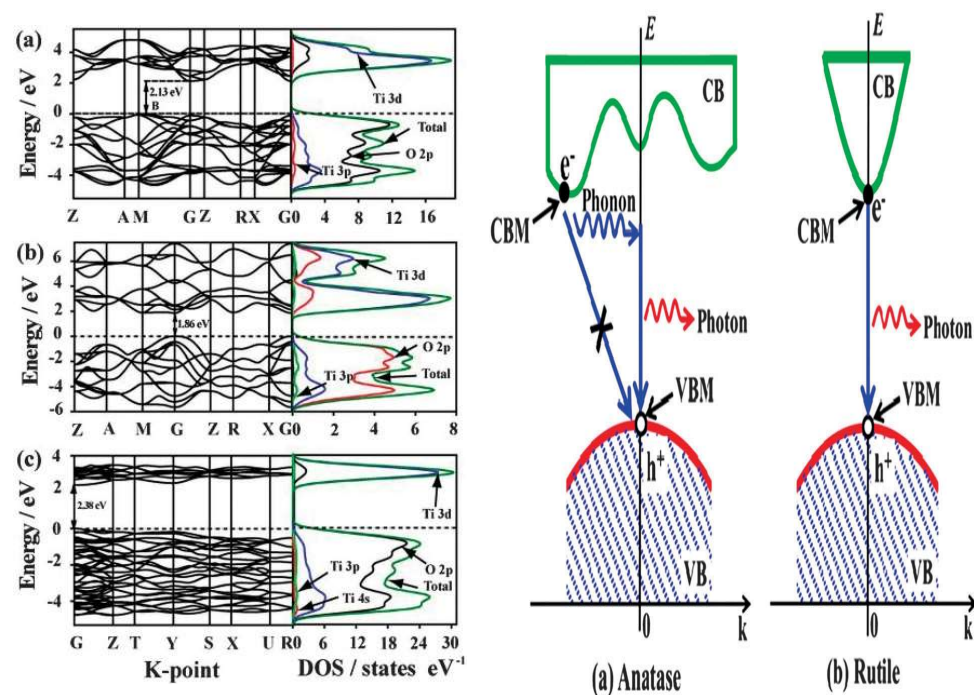


Figure 5. The band structure and DOS for (a) anatase, (b) rutile, and (c) brookite TiO₂, and comparison of the recombination processes of photogenerated electrons and holes within (a) indirect-gap anatase and (b) direct-gap rutile. Adapted from reference [58].

Weber and Kirchner confirmed the band shift within the sight of the ionic solution by conducting computational estimations on anatase TiO₂ [59]. For anatase and rutile, disputable outcomes were recorded for the positions of their CB and VB edges. Typically, it has been found that the anatase CB lies at a marginally lower potential than that of rutile [60,61], but certain researchers have found that the CB of rutile lies lower than that of anatase. As particles are diminished to quantum dots, the edges of their valence and conduction bands change fundamentally, causing huge changes in their optical values (quantum impact). For instance, bandgap fluctuation of TiO₂ has been found, with the VB and CB edges moving because of changing molecule size. The band tuning can also be acknowledged by doping the semiconductor. To overcome this problem, a few additional substances such as Fe²⁺, Fe³⁺, metal and non-metal doping, etc., have been added to the photocatalytic structure [62].

Titanium dioxide (TiO₂) is an n-type semiconductor that assimilates photons at wavelengths greater than 385 nm with the advancement of electrons from the valence band (VB) to the conduction band (CB). This excitation cycle leaves behind emphatically charged openings called holes (h⁺). Photoexcitation of semiconductor metal oxides such as TiO₂ results in hole aggregation in the charge carriers and electron production in the higher conduction band [48,63]. While several photoexcited charge carriers reassemble, others diffuse and enter the surface quickly, where they can be trapped or incorporated into other reactive species (Equations (7)–(15)).





The superior redox capacity of TiO_2 has made it the most well-known photocatalyst for many years. Its recorded applications are numerous, including energy generation and contaminant degradation. Accordingly, in the photocatalytic mineralization of toxic wastewater, TiO_2 has likewise attracted the interest of researchers.

2.2. Textiles and Colored Dyes

Different sorts of colored dyes are available in industrial sectors for dyeing/coloring objects—for example, methyl orange (MO), methyl red (MR), rhodamine-B (RhB), Congo red (CR) etc. The classification of dye pollutants is based on the molecules' component structure, dyeing, and their application. The overall classification of dye pollutants developed based on the chromophores in their molecular structure, including azo dyes, quinine–amine dyes, acridine dyes, anthraquinone dyes, xanthene, nitro dyes, etc. [64]. The investigation of photocatalytic degradation of dye pollutants mainly concerns factors such as the grouping of the dyes, the amount of photocatalyst utilized, the impact of the intensity of the illuminated photons, the light irradiation time, the impact of the dissolved oxygen, and various other parameters. The energy of photocatalytic degradation of toxic colored dyes is viewed as a pseudo-first-order response.

The direct oxidation of the dye sensitizer is a specific consequence of semiconductor photosensitization. By intentionally regulating the regeneration of cation radicals, the sensitizer goes through additional degradation. This self-sensitized oxidation mechanism is superior in the presence of visible photon degradation of colored contaminants [64–66]. Different coloring toxins—for instance, rhodamine B [67], cresyl violet [68], Congo red [69], reactive orange [70], orange G [71], erythrosine B [72], rose Bengal [73], etc.—have been utilized as sensitizers. This technique includes the excitation of dye pollutants from the HOMO/ground state (Dye) to the LUMO/triplet excited state (Dye*) under visible photons (>400 nm). The introduction of an electron into the TiO_2 conduction band converts this excited dye species into a semi-oxidized (Dye^{•+}) radical cation [74]. Superoxide radical ($O_2^{\bullet-}$) anions and $OH^\bullet$ radicals are created as a result of the reaction between this dissolved oxygen and trapped electrons in the system. The oxidation of organic molecules is mostly caused by these radicals [75]. A large body of work should be accounted for in the field of decomposition of toxic dyes into innocuous end products under UV–visible source illumination [76–79].

A huge number of mechanisms exist for the degradation of dye toxins, including both oxidizing (i.e., electron transfer from the dyes) and reducing (i.e., electron transfer towards the dyes) processes. The retention of light can be ensured in the dyes, the semiconductor, or both. Numerous dyes are produced today; azo dyes are predominant (~50–70%), followed by anthraquinone dyes. The estimation of photocatalytic execution is largely performed in the aqueous phase. The most frequently considered color pollutants are rhodamine B, methylene blue, Congo red, acid red 73, orange G, and methyl orange, among others. A summary of the huge body of literature [80–128] on the effects of heterogeneous photocatalysis on colored pollutants such as dye toxins is reported in the Supplementary Materials (Table S1).

2.3. Organic Molecules and Pharmaceutical Pollutants

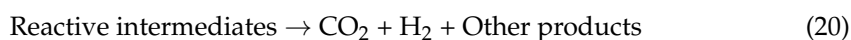
The production, use, and waste disposal of a variety of chemicals widely used in industry, pharmaceuticals, agriculture, and daily used organic substances are increasing, resulting in the unrestricted outflow of these substances into the water. Trace concentrations of these substances already show highly harmful impacts on aquatic ecosystems and human health. Because of their temporary resistance to the dissolution of pollutants in standard wastewater treatment plants (WWTPs), the presence of such trace compounds (mostly organic) has been extensively observed in effluents, surface waters, and drinking water, threatening the quality of water [129,130].

The pharmaceutical sector is an important part of the chemical industry. Pharmaceuticals include a broad category of human and veterinary medicines that are continuously used in huge quantities around the world. Some drug toxins (e.g., paracetamol, propylphenazone, diclofenac, clofibrilic acid, carbamazepine, and diazepam) escape degradation in WWTPs and enter the environment [131–135]. In addition to metabolic discharge, removal by flushing of unused or lapsed prescriptions and medication waste products from pre-fabricating facilities can likewise cause contamination in the environment [136,137]. The photocatalytic activity of pharmaceutical contaminants is regularly identified in wastewater bodies, known to be inefficiently removed in ordinary wastewater treatment reactors. To overcome these difficulties, a novel TiO₂ nanostructured catalyst sample can be utilized under various light sources, such as sunlight and UV light. Drug contaminants that can be oxidized by TiO₂-created hydroxyl (OH•) radicals include analgesics, (for example, sulfathiazole [138] and diclofenac [139]), antibiotics (for example, moxifloxacin [140] and amoxicillin [141]), and antiepileptics (for example, carbamazepine [142]).

Furthermore, pesticides/insecticides are generally used to shield agrarian yields from bugs, microorganisms, weeds, moths, organisms, etc. In any case, the constant use of pesticides brings about deficient soil quality, diminished nitrogen utilization by plants, and damage to food hotspots for animals. All the more critically, contamination due to pesticides in drinking water brings about serious health issues for humans and other animals. In this way, the degradation of pesticides should transform these unsafe compounds into harmless byproducts of N, P, and S, along with CO₂ and H₂O. Numerous investigations have clarified the progression of mineralization of widely utilized pesticides such as pyridaben [143], atrazine [144], triazophos [145], methyl parathion [146], dicofol [147], methamidophos [148], etc., utilizing TiO₂. It is additionally important to ensure that the decomposition of poisonous organic compounds is performed sufficiently until the total organic carbon (TOC) of the water is insignificant. This is because of the formation of poisonous organic intermediates upon the mineralization of the primary pollutants [149].

Advanced oxidation processes (AOPs) are considered to be eco-friendly techniques and depend on physicochemical methods that initiate decay, improve and simplify the chemical structure/composition of organic pollutants, and ultimately cause mineralization. The above techniques include the emergence of active charge-transient species such as the hydroxyl (OH•), alkoxyl (RO•), superoxide (O₂•[−]), sulfate (SO₄^{2−}), hydroperoxyl (HO₂•), and chlorine (Cl•) radicals, which mainly depend upon the photocatalyst or the oxidant utilized [150,151]. Hydroxy (OH•) radicals are normally created from reactions including oxidants—for example, ozone, hydrogen peroxide, or photocatalysts including semiconductors and metal ions—in the presence of UV–vis photons or various light sources. These species possess elevated oxidation potential with non-selectivity and elevated reaction kinetics, accomplishing the total mineralization of toxins to water, CO₂, and byproducts in distinct environments, changing them into further biodegradable particles [152].

The hydroxyl radicals produced by photoexcitation of photocatalyst (TiO₂) samples are proficient in oxidizing all electron-rich organic, toxic, and pharmaceutical compounds in water.



For instance, during the interaction of intermediates with hydrocarbons, the following reaction takes place:



In heterogeneous photocatalysis, the following reactions happen sequentially: the principal response is oxygen reduction, and the second is the oxidation of drug wastes and organic pollutants by the hydroxyl ($\text{OH}^\bullet$) radicals. In the process, upon excitation of the TiO_2 nanocatalyst, electrons are gathered in the conduction band, causing the production of holes. In this way, it is important for electrons to be consumed to increase the effectiveness of heterogeneous photocatalysis in the presence of a photocatalyst; as a result, the electrons are devoured by the broken-up oxygen.

A summary of the huge body of literature [153–190] on the efficacy of heterogeneous photocatalysts in the photocatalysis of colorless contaminants—e.g., organic toxic molecules, pharmaceutical pollutants, herbicides, and pesticides—is reported in the Supplementary Materials (Table S2).

2.4. Petroleum-Based Hydrocarbons

For many sectors, energy resources and raw materials produced from petroleum hydrocarbons are crucial. According to data gathered between 1970 and 2013 by the International Tanker Owners Pollution Federation Ltd., three oil leaks totaling more than 700 tons took place in 2013 [191]. Due to the catastrophic impacts of large-scale maritime oil spills and oil leak incidents, researchers devote a lot of attention to the avoidance or cleanup of oil spills. The pollutants of highest priority are persistent chemicals called petroleum hydrocarbon pollutants [192]. However, despite rising consumer demand, there are currently no commercially viable substitutes for petroleum products in everyday life [193]. Accidental leaks from the offshore and onshore petroleum industries cause contamination by petroleum hydrocarbons. Water bodies are directly impacted by this pollution. The unpleasant fact that water bodies are regarded as the ultimate and largest sinks for petroleum hydrocarbon pollution is widely recognized [194].

The wastewater from petroleum refineries (PRW) is notorious for having high concentrations of harmful chemicals that are bad for both humans and the environment. Due to the significant amounts of water utilized in petroleum refineries, the wastewater is mostly produced in massive volumes [195]. In nations where crude oil is processed, this issue frequently arises. Most treatments used by petroleum-refining companies are ineffective because persistent pollutants are still present in the discharged treated effluent, leading to secondary contamination of the environment. TiO_2 is the most stable photocatalyst due to its high mechanical, thermal, and chemical strength.

The Supplementary Materials (Table S3) contain an overview of the extensive literature [196–200] on the impact of heterogeneous photocatalysis on the photodegradation of petroleum-based hydrocarbon contaminants.

3. Interactions of Various Parameters Involved in Photocatalytic Applications

The heterogeneous photocatalytic process is a surface activity where the reaction takes place within the catalyst's active site in the presence of UV–visible source illumination. Similarly in each reaction, a few parameters—for instance, the pH of the medium, the concentrations of toxic substrates, the photocatalyst loading, the presence of other external parameters, etc.—regulate the reaction kinetics during photocatalytic mineralization. Many researchers have investigated these variables and their impacts on photocatalysis. In the following subsections, we review the favorable impacts of interaction parameters on the photocatalytic process.

3.1. Influence of the pH of the Reaction Medium

A significant aspect in photocatalytic decomposition processes occurring on particulate surfaces is the reaction medium's pH, which directs the charge attributes of the catalyst's surface and the aggregate size of its structures. Fluctuation in pH implies an alteration in the concentrations of H^+ and OH^- in the reaction composition. The hydroxyl ($\text{OH}^\bullet$) radical concentration plays an essential role in photocatalytic applications and is essential for oxidation. In this manner, the increase in pH implies an increase in the OH concentration

and its transformation to $\text{OH}^\bullet$ radicals. Consequently, the oxidation process intensifies further in the presence of $\text{OH}^\bullet$ radicals. This standard is somewhat relevant, yet real surface studies are more relevant to clarify the impact of pH. The efficiency rate thoroughly relies on the pH of the solution and can be clarified with the assistance of TiO_2 zero-point charges (pH_{zpc}) at $\text{pH} = 6.25$. In this fashion, the positively charged TiO_2 surface is in the acidic phase, while it is negatively charged in the basic solution.

At neutral pH (6.8), powerful adsorption of acidic toxic dyes onto the photocatalyst molecules takes place because of the electrostatic attraction of TiO_2 (positive charged) to the ionized toxic dye. Then again, at pH values above 6.8, a reduction in the reaction kinetics is observed, whereas increasing the pH of the substrate solution (pH 12) again causes the problem of anionic pollutants drawing closer to the negatively charged TiO_2 surface. Significant decolorization was accomplished at pH 6.8 (100% dye expulsion or TOC removal) with optimized Cu-Ni/ TiO_2 catalysts, whereas at pH 7.4 only 89.8% TOC removal was achieved [201].

The reaction pH is altered under light, and it is not controlled throughout the experiment. The impact of the pH increasing from 3 to 11 on the mineralization of RR, MB, and RB has been reported. At an acidic pH, hydroperoxyl ($\text{HO}_2^\bullet$) radicals can produce hydrogen peroxide (H_2O_2), which produces the hydroxyl ($\text{OH}^\bullet$) radicals for the mineralization of the colored anionic RR dye. In the case of MB—a cationic charged dye—the color expulsion rate was discovered to be high at basic pH [84].

The degradation kinetics of CR dye were found to be 98%, 80%, and 65% at pH 4, pH 6, and pH 9, respectively, within 420 min (Figure 6). These outcomes confirm that the higher degradation efficacy at acidic pH might be due to the effective production of CR anions via ionization of two sulfonic ions in CR dye. This illustrates that pH 6 is the optimal pH [113].

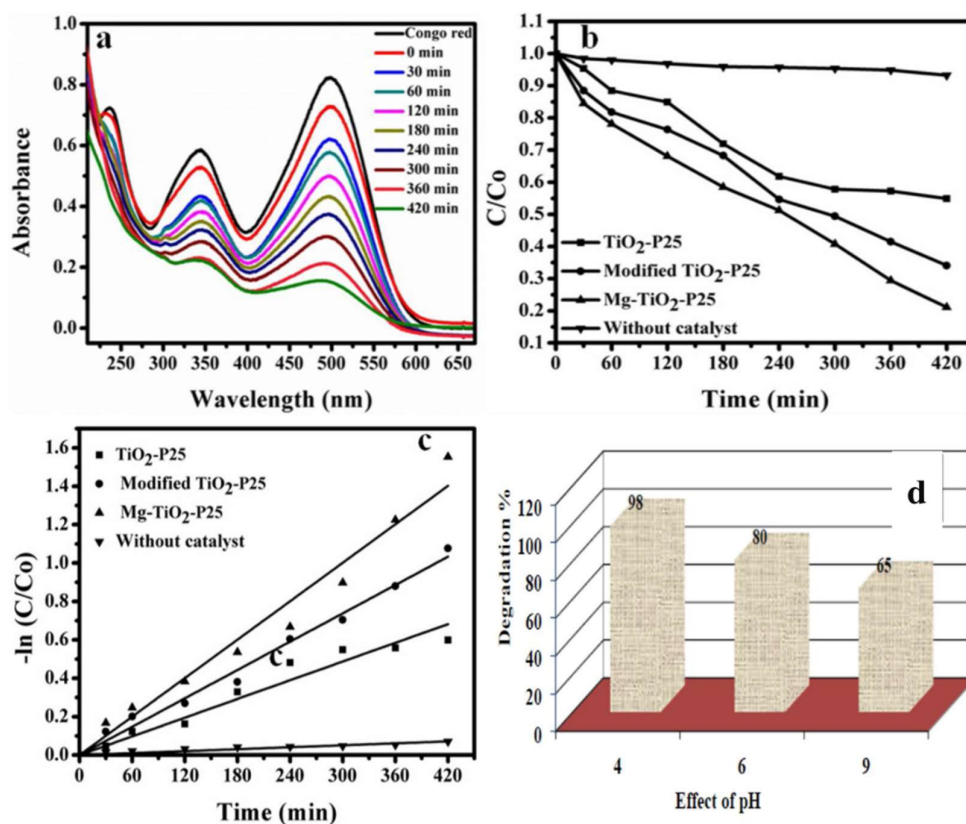


Figure 6. (a) Time-dependent UV-Vis absorption spectrum of $\text{Mg-TiO}_2\text{-P25}$ nanoparticles in the presence of persistent Congo red dye under illumination. (b) Photocatalytic degradation curve for different catalysts in the presence of Congo red. (c) First-order plot for the degradation of Congo red (2.5×10^{-5} , 50 mg $\text{Mg-TiO}_2\text{-P25}$ nanoparticles). (d) Effects of the variation of catalyst pH on photocatalysis. Adapted from reference [113].

The photocatalytic rate of MO dye is only 10.0% at pH = 6.4, 54.5% at pH = 4, and 93.2% at pH = 2. It can be observed that photodegradation efficacy diminishes with increasing pH for (TiO₂/PW12)10. The (TiO₂/PW12)10 shows the maximum photocatalytic rate at acidic pH. The decay of H3PW12O₄₀ is responsible for the somewhat minimal photodegradation productivity at pH = 7. Another explanation for the superior action of (TiO₂/PW12)10 in acidic media is that MO dye changes from an azo structure to a quinoid morphology at pH < 3.1. This reality can be demonstrated by the way in which the photodegradation of MO under UV photons increases from 1.9% to 12.9% when the pH is reduced from 6.4 to 2.0 [88].

Significantly less degradation efficacy was seen at pH = 10. A > 35% decrease in TOC and 92% decolorization was achieved at pH 2.0 via hydrodynamic cavitation (HC). The increase in the mineralization efficacy at acidic pH could be attributed to the fact that dye pollutants at lower pH are available in a molecular form whenever the pH is not precisely the pK_a = 10.7 [192]. The most elevated effectiveness was seen at pH 7.5; any further decrease or increase in pH (7 or 8) fundamentally diminishes the photocatalytic effectiveness of reduction. The adjustment of the medium's pH critically affects the photoreduction of 4-NP, as shown in Figure 6, directly influencing the properties of the photocatalyst's surface charges and the adsorption of toxic compounds [190].

3.2. The Impact of the Initial Pollutant Substrate Concentration on Photocatalysis

The initial pollutant substrate concentration is the essential requirement for the photocatalytic approach, and substrate samples are adsorbed over the reactive surface of the utilized catalyst. Photocatalysis depends on the adsorption of pollutants on the surface of the photocatalyst. In the photocatalysis process, only the amount of pollutants adsorbed on the surface of the photocatalyst contributes and not the concentration in the bulk of the solution. The adsorption of pollutants depends on the initial concentration of the dye. The initial concentration of pollutants in a given photocatalytic reaction is an important factor that needs to be considered. Increasing the substrate molecule concentration can decrease the kinetics of the mineralization reaction (k). The underlying substrate pollutant concentration can promote photocatalytic efficacy in two fundamental ways. At elevated concentrations of toxic pollutants, more reaction sites are observed on the TiO₂ surface for the pollutant substrates, diminishing the production of hydroxyl (OH•) radicals, since there are fewer active sites for anions such as hydroxyl ions to adhere to. Moreover, the foreign substances consume the photons prior to arriving at the photocatalyst surface, subsequently diminishing the photocatalytic efficiency.

The impact of the initial reactive brilliant red K-2BP concentration on photon-induced catalytic mineralization was investigated with a variety of concentrations of colored dyes, ranging from 0.5 mg/L to 8 mg/L. The observed photodegradation proficiency of K-2BP clearly decreased with increasing dye concentrations in the range from 4 to 8 mg/L after continuous photon illumination. Specifically, at dye pollutant concentrations over 6 mg/L, all photons were absorbed by the colored substrate mixtures, and fewer photons arrived at the TiO₂ surface. Subsequently, the production of charge carrier (electron-hole) sets was enormously decreased and, thus, the photon-induced catalysis of the dye was diminished because of the shortage of the oxidizing molecules [89].

With a specified concentration of 50 mg of Mg-TiO₂-P25 NPs and at different initial CR dye concentrations (1×10^{-5} to 2.5×10^{-5} M), photocatalytic mineralization was examined, and the outcomes were reported. It is clear from the outcomes that with the increase in the starting concentration of the dye, the evacuation effectiveness is diminished, which might be the reason that photon outreach to the catalyst surface declines at higher concentrations of the dye, because of the reduction in the activity of photons created with receptive radicals [113].

An investigation was conducted with various color toxin concentrations, i.e., AG-25 with 20, 40, 70, and 100 mg/L, as well as 10, 20, 30, and 50 mg/L RhB, with 1.0 g/L of GO/TiO₂ (10 wt%) photocatalyst. On the off-chance that the initial concentration of the color pollutants increased, the photocatalytic mineralization productivity diminished

because the amount of light consumed by the photocatalyst decreased. Light radiation experiences difficulties in penetrating high concentrations of color pollutants. The concentration of dye pollutants may be able to impact the photocatalytic mechanism [202].

Photodegradation investigations were carried out utilizing phenol-4-sulfonic acid (4-PSA) concentrations of 50, 80, and 150 mg/L with a 0.02% (*w/v*) photocatalyst under low pressure; 39.5 W UV lamps (λ -254 nm) with a length of 0.8 m were used to input the photons. The UV lamps used had identical output ratings (input rating of 39.5 W and output rating of 13.7 W). An increase in the 4-PSA concentration causes a reduction in the photocatalytic efficacy. With the increase in the initial 4-PSA concentration, the intermediate density also increases with time. The intermediates adhere to the photocatalyst surface. For consistent light power with a photocatalyst, the generation of hydroxy ($\text{OH}^\bullet$) radicals stays constant. Accordingly, the accessibility of the adsorbed substrates also decreases. The general impact decreases the mineralization of the substrate with the increase in its concentration in the feed [203].

The outcomes are correlated with the accompanying tentative environments. TiO_2/PAN nanofiber hybrid catalysts (30 mg) were independently introduced to 250 mL suspensions containing phenol concentrations of 10, 30, 60, and 120 mg/L, followed by UV photon illumination for 50 min; the reported photodegradation efficiencies of phenol were 98.3, 88.2, 75.5, and 59.3%, respectively (Figure 7). These outcomes exhibit that the mineralization effectiveness of phenol diminishes with an increase in the concentration of phenol under indistinguishable trail ambience. The amounts of $\text{OH}^\bullet$ and $\text{O}_2^{\bullet-}$ charge carriers produced on the remaining parts of the photocatalyst surface were consistent with the fixed states of the given light source. Thus, the available $\text{OH}^\bullet$ radicals were insufficient for phenol mineralization at elevated pollutant concentrations, bringing about a decrease in the photodegradation efficiency [177].

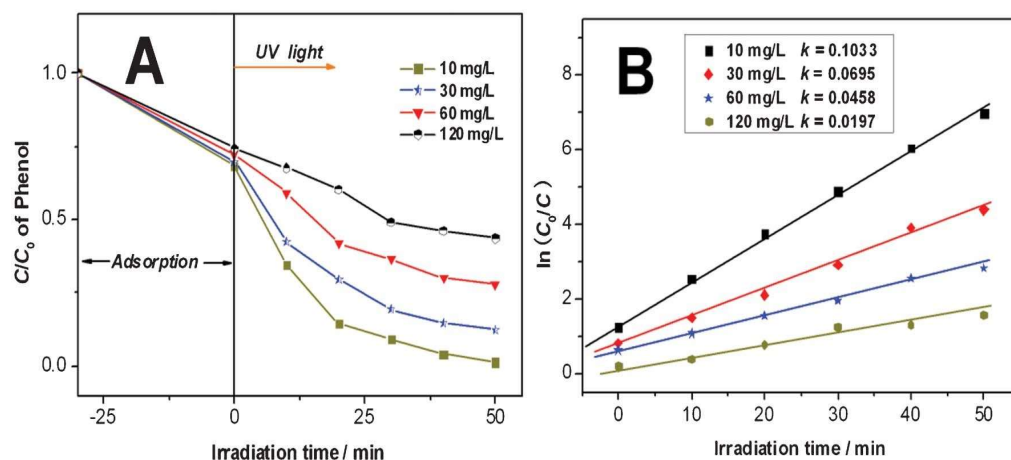


Figure 7. (A) Degradation profiles of various phenol concentrations over TiO_2/PAN hybrid nanofibers. (B) Kinetic linear simulation curves of photocatalytic phenol degradation with different phenol concentrations. Adapted from reference [177].

3.3. Influence of Photocatalyst Loading into the Reaction Suspension

To resist the abuse of photocatalysts, it is important to ascertain the loading or optimized dose of the catalyst sample for the proficient eradication of toxic organic and dye pollutants. The amount of photocatalyst required will rely upon the photocatalytic mechanism, the light source, the concentration of toxic pollutants, and the molecular morphology of the photocatalyst. Another perception in the literature is that the photocatalytic efficacy rate increases constantly with the increase in the photocatalyst to a certain weight; furthermore, the kinetics of photodegradation of the toxic pollutants diminish with the increase in the amount of the catalyst. This ensures that the uncovered photocatalyst surface area directly corresponds to the dose of the photocatalyst in the aqueous medium. Because organic pollutants are decreased in proportion to the amount adsorbed on a solid surface, there may be a saturation point beyond which the catalyst dose has no direct

relationship to the percentage of photodegradation. The kinetic rate of the photocatalysis process decreases with the photocatalyst dosage, reducing the number of photons retained. Reduced photocatalyst amounts increase the suspension's transparency, which extends the penetration of photon illumination in the photoreactor and, thus, reduces the photocatalytic degradation rate.

The impact of the quantity of chitosan/TiO₂ composite (CTC) on the decolorization of three dyes (RR, RB, and MB) has been explored utilizing various doses of CTC, ranging from 25 to 150 mg/L. At the point where all of the color particles are adsorbed on the CTC, no enhancement is accomplished by introducing further CTC. The most extreme levels of dye degradation were accomplished at 100 mg/L of CTC for RR, MB, and RB, showing 94.8%, 90.9%, and 80.6% efficiency, respectively, as after which they remained steady for additional examinations [84].

The mineralization of the sample of FD&C Yellow No. 5 (Y5) and the purified main component of FD&C Yellow No. 5 (MY5) in the presence of nano-TiO₂ was carried out under visible photons. Ref. [87] analyzed the impact of changing the dose of the TiO₂ NP catalyst on the decolorization efficiency. The initial MY5 concentration was 25 mg/L; during the addition of about 0.01, 0.02, 0.05, 0.1, and 0.2 mg/mL TiO₂ NPs, changes in the photocatalytic rate were observed. MY5 remained unaltered after 120 min, without TiO₂ NPs under visible light. An increase in the dose of TiO₂ brought about a maximum photocatalytic rate for MY5. At a TiO₂ NPs loading of 0.1 mg/mL, the color pollutant completely degraded after 30 min under visible photons. The most elevated rate, i.e., $k_{app} = 0.133$, was seen at a 0.2 mg/mL dosage of the catalyst [87].

The impact of photocatalyst loading on the photodegradation of RR4 dye was investigated in the range of 0.01–0.09 g/L at a fixed 0.3 mM concentration of RR4 dye. The outcomes confirmed the optimal photocatalyst dosage was 0.03 g, and further increases in the photocatalyst dosage appeared to diminish the photocatalytic mineralization of the RR4 dye. The extra increases most likely created more prominent turbidity in the solution, inhibiting the entrance of light and restraining the reaction [108].

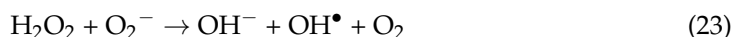
The minimum photocatalyst dose of 100 mg/L achieved 31.42% efficacy for pure anatase (Cat1) and 32.9% efficacy for Aeroxide P25 (Cat2). An additional increase in the loading of the Cat1 catalyst, under comparable procedure environments, led to an enhanced evacuation efficiency of 47.4% and 68.2% for catalyst material loadings of 400 and 200 mg/L, respectively. This increment was possible because of the abundance in the attainability of the site of action on the photocatalyst surface, which created active radicals for CHD (chlorhexidine digluconate) mineralization. The probability of agglomeration was greater with an increase in the catalyst dosage, which diminished the active photocatalyst surface for photon absorption and, consequently, brought about a decrease in the efficiency of photodegradation [154].

Investigations were carried out for amoxicillin trihydrate (AMT) mineralization under sunlight illumination with a TiO₂ photocatalyst dose of 0.25–2.5 g/L for 4 h. It was seen that the reaction kinetics expanded with the increase in the photocatalyst dosage up to 0.5 g/L and remained practically steady until 1 g/L, which enabled the optimal photon absorption. In any case, further increases in the TiO₂ dosage did not produce any huge increases in the photodegradation rate. AMT's photodegradation rate at 0.5–1.0 g/L showed a negligible difference; hence, 0.5 g/L was selected as the most reasonable photocatalyst dosage from an economic perspective [162].

3.4. Performance of Hydrogen Peroxide (H₂O₂) Oxidizing Species

The presence of reasonable oxidizing or electron-acceptor species obstructs the electron-hole recombination and, accordingly, impedes the quantum efficacy. Thus, the oxygen (O₂) molecule is typically utilized as an electron acceptor in the photocatalytic component. The incorporation of exterior oxidants as electron (e[−]) acceptors in semiconductor photocatalysts has been reported to enhance the mineralization efficacy of organic toxic contaminants.

The addition of excellent oxidizing agents—for example, hydrogen peroxide (H_2O_2)—to TiO_2 solutions is a notable strategy that is responsible for elevated kinetics of photo-oxidation. Hydrogen peroxide shows two functions in photocatalytic activity: it accepts an electron from the CB, along with influencing the charge detachment; and it forms active $\text{OH}^\bullet$ radicals.



Accordingly, attentive improvement of the oxidizing species concentration is important to ensure the greatest photocatalytic activity rates.

The effects of the increase in H_2O_2 concentration on the kinetics of photodegradation of AR88 were investigated by shifting the H_2O_2 concentration from 100 to 6000 μM at a constant color pollutant concentration of 100 μM and 5 bars of pressure. The rate was steady for the mineralization and decolorization of the pollutant AR88, and the rate was also found to decrease with TOC.

It was reported that the decolorization efficacy increases with an increase in the H_2O_2 concentration in the range of 0–4000 μM , and that practically complete decomposition takes place at 4000 μM . The reaction kinetics remained steady for the decomposition, which stayed constant with additional increases in the H_2O_2 concentration past 4000 μM (Figure 8). However, the TOC investigation revealed an optimal concentration of H_2O_2 at which the color pollutant's mineralization was greatest. The rate remained steady with the decrease in TOC and increases in the concentration of H_2O_2 up to 4000 μM , and it diminished thereon [204]. Photocatalytic efficacy was maximized easily with an increase in the concentration of H_2O_2 in the range of 0.3–0.53 mg/L and diminished continuously when the H_2O_2 concentration increased past 0.53 mg/L. The beneficial outcomes of the oxidant (H_2O_2) concentration might be ascribed to the hindrance of the recombination of electrons and holes at the photocatalyst sample surface by accepting the electron from the CB. In any case, higher H_2O_2 molarity can also accept electrons from the VB holes and hydroxyl ($\text{OH}^\bullet$) radicals. This pattern prompts H_2O_2 concentrations past the optimal value and does not increase the photodegradation proficiency of color pollutants [90].

The oxidizing species hydrogen peroxide enhanced the $\text{OH}^\bullet$ radical concentration, playing a significant role in the extent of photon-induced catalysis. In a solution of the pollutant AMT with natural pH, H_2O_2 was varied from 0.03 g/L to 0.21 g/L with TiO_2 loading of 0.5 g/L to contemplate its consequences on the photocatalytic kinetics. As anticipated, photodegradation increased as a result of raising the oxidant molarity, reaching up to 87%, yet increasing the H_2O_2 concentration past 0.12 g/L brought about a reduction in the rate of photocatalysis, as it acts as a scavenger [162].

The synergic effect of the possible photodegradation was investigated to reveal the contributions of a TiO_2 catalyst, microcellulose (MC), and H_2O_2 to color-pollutant decolorization. The photocatalytic rate kinetics of the independent treatments varied, and consolidated H_2O_2 helped in the photocatalysis of MB dye. The determined steady photodegradation proficiency for incorporated hydrogen peroxide helped achieve photocatalytic efficacy $k(\text{TiO}_2 + \text{H}_2\text{O}_2 + \text{MC})$ of 0.0297 min^{-1} . Moreover, the steady photodegradation rates for $k(\text{TiO}_2)$, $k\text{H}_2\text{O}_2$, and $k\text{MC}$ were 0.0015 min^{-1} , 0.0029 min^{-1} , and 0.004 min^{-1} , respectively [115]. The electron–hole (charge carrier) pair recombination was encouraged by introducing other (irrevocable) electron acceptors to the system. Considering this, the influence of H_2O_2 on the photon-induced catalysis of fluoroquinolones was explored increasing the concentration of H_2O_2 from 41.25 mg/L to 330 mg/L. The investigation was conducted with 500 mg/L TiO_2 at pH 6. The photodegradation rate increased with the amount of H_2O_2 , reaching the greatest activity at 82.5 mg/L. Further increasing the molar concentration of H_2O_2 caused a reduction in the photocatalytic efficiency. When the molar concentration of H_2O_2 was 0, 41.25, 82.5, 165, and 330 mg/L, the TOC evacuation was around 21%, 45%, 55%, 41%, and 37%, respectively [172].

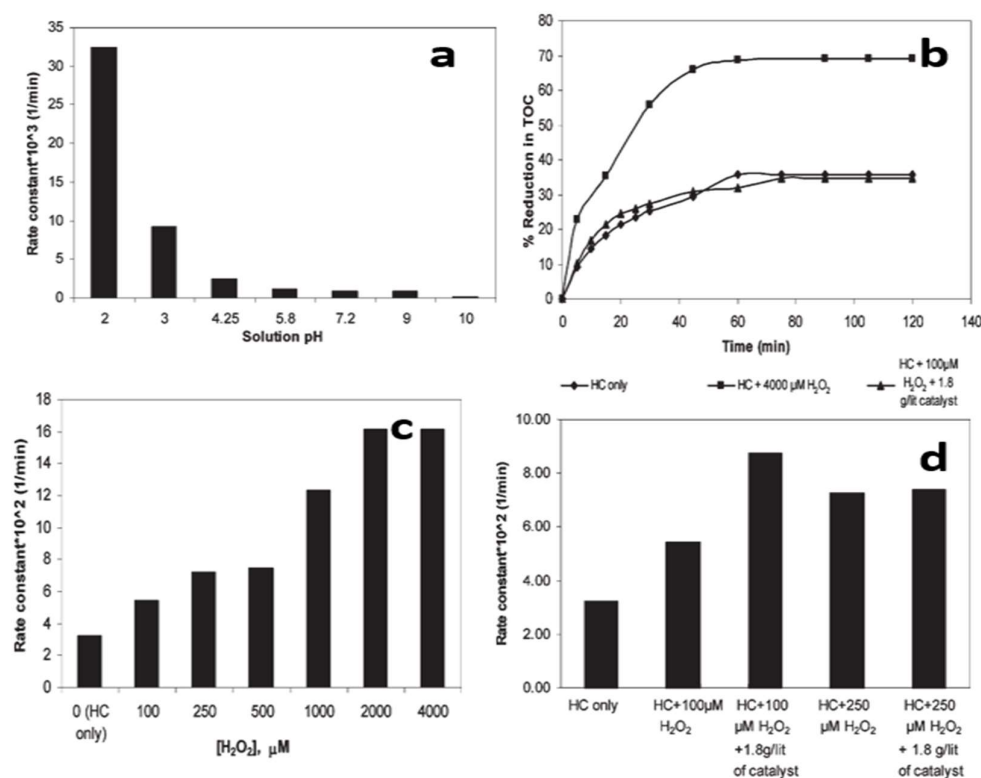


Figure 8. (a) Effects of solution pH on the decolorization rate of AR88. Conditions: volume of solution, 4 L; initial concentration, 100 μM ; inlet pressure, 5 bar. (b) Reduction (%) in TOC as a function of time under different optimized conditions: volume of solution, 4 L; initial concentration, 100 μM ; pH of the solution, 2.0; inlet pressure, 5 bar, (c) Effects of H_2O_2 addition on the decolorization rate of AR88. Conditions: volume of solution, 4 L; initial concentration, 100 μM ; pH of the solution, 2.0; inlet pressure, 5 bar. (d) Effects of catalyst addition on the decolorization rate of AR88. Conditions: volume of solution, 4 L; initial concentration, 100 μM ; pH of the solution, 2.0; inlet pressure, 5 bar. Adapted from reference [204].

3.5. Irradiation time, Light-Source Wavelength, and Intensity

The utilization of sunlight-based radiation is affordable, less dangerous, and produces more reproducible outcomes. The creation of electron-hole pairs and their recombination can vary when a UV-Vis source is utilized. The photon source wavelength can influence the electron-hole development rate, along with their recombination. The impact of UV-Vis illumination time influences the mineralization of aqueous pollutants when utilizing a TiO_2 photocatalyst in the photocatalytic chamber. As with all other parameters, source intensity plays a significant role in photocatalytic responses. The 3.2 eV bandgap energy of TiO_2 photocatalyst particles is provided by UV-Vis illumination or daylight energy. On certain occasions, visible photons fail to provide this amount of energy to photocatalytic activity. The decay rate directly corresponds with the addition of light illumination at low levels (first-order kinetics). Nonetheless, in addition to specific illumination levels, the mineralization rate also relies upon the square root of the photon intensity (half-order reaction).

The impact of illumination time on the decolorization of RR, MB, and RB pollutants was evaluated by estimating the levels of color evacuation in various timeframes, utilizing 50 mg/L toxic dye in a 50 mL solution and a 100 mg dose of CTC at ambient temperature under UV photon illumination. The outcomes confirmed that the level of color evacuation increased with the increase in the illumination time, reaching 94.8%, 90.9%, and 80.2% for RR, MB, and RB dyes, respectively, after 30 min of illumination [84].

The light flux is unavoidably associated with the photocatalytic performance. Setup and design practices distinctly insist that, in such a case, numerous appropriately conveyed light sources can bring about better inclusion (and usage) of the reactor's cross-area via the

occurrence of radiation. To evaluate this claim, the quantity of UV light sources was varied. Trials were carried out for an initial 4-PSA concentration of 80 mg/L with a consistent reactor stream rate of 55 mL/min. With an increase in the radiation intensity, as with the lights' distribution, the rate of evacuation of TOC expanded. At the point when a light flux of $0.594 \text{ mol of m}^2\text{h}^{-1}$ photons (i.e., if three lights were used, every light provided a radiation transition $0.198 \text{ mol of m}^2\text{h}^{-1}$ photons) was utilized, the rate of TOC evacuation was 57% [203].

At a specified wavelength, UV intensity determines the degree of radiation absorbed by the semiconductor sample. The photon power within the reactor likewise determines the conversion of the overall substrate and the degradation proficiency. In this investigation, CHD expulsion proficiency was found to increase with increasing light intensity in the $50\text{--}80 \text{ }\mu\text{W.cm}^{-2}$ range, likely as a direct result of the increased generation of electron–hole pairs, improving the photodegradation performance. Under such conditions, the charge carrier's recombination is inconsequential. The diminishing value of the CHD evacuation at $125 \text{ }\mu\text{W.cm}^{-2}$ could likely be explained by the rate of recombination of electrons and holes under elevated UV source flux [154].

The visible-photon-determined photocatalytic efficiency of $\text{ZnFe}_2\text{O}_4\text{--TiO}_2$ in the photodegradation of BPA was initially assessed by the illumination of three distinctive light sources: 365 nm UV, 465 nm visible light, and a sun-powered test system. The BPA photodegradation efficiency by unadulterated ST-01 TiO_2 semiconductors was in the range of 30–46%, in the following order: 465 nm visible source > sun-based light > 365 nm UV photons. The pseudo-first-order kinetics (k_{obs}) for the photodegradation of BPA under the illumination of UV (365 nm), visible light (465 nm), and the sunlight-based test system were 0.0052 min^{-1} , 0.218 min^{-1} , and 0.141 min^{-1} , respectively [175].

The mineralization efficiency was likewise investigated under a sun-powered source along with a lamp whose discharge extended for ca. 5% in the UV range. Although the photocatalytic process occurred more slowly than with the UV source, a limited level of decomposition was instigated, reaching 8.5% after around 420 min of stimulation. It ought to be highlighted that the photocatalyst was not elevated at all to support the ingestion of light under the visible irradiation, and that the effective light flux was a lot lower than that of the UV test lamp. Consequently, only the lamp with a UV tail could improve the photocatalytic properties, since anatase TiO_2 , with a 3.2 eV bandgap, has the edge of its absorption band at 386 nm [159].

4. Reaction Kinetics Incorporated in Photocatalytic Applications

Photocatalysis, like the decolorization/mineralization process, is a form of heterogeneous catalysis. It has been observed that the rate of kinetics fluctuates with various external parameters—for example, initial pollutant concentration, pH of the reaction medium, photocatalyst dosage, the influence of oxidants (hydrogen peroxide), irradiation time, light intensity/wavelength, etc. The impacts of these various parameters on photodegradation can be depicted as the kinetic rate constant. In this manner, it is vital to comprehend the kinetics of photon-induced catalysis. The components of heterogeneous photocatalytic reactions have been investigated by numerous specialists under Langmuir–Hinshelwood (L–H) kinetic rate conditions. This is because photocatalytic performance entails a sequence of steps, bringing about progressive degradation when illuminated with UV–Vis light. The expression of the first-order kinetic rate was illustrated when Houas and colleagues investigated photodegradation by examining the impact of the initial concentrations of water pollutants. The outcomes were demonstrated to be compatible with the kinetics of the first-order rate model [205]. The photocatalytic reaction with first-order rate kinetics was represented as follows:

$$-r_{\text{app}} = dC_s/dt = k_{\text{app}} C_s \quad (24)$$

where r_{app} and k_{app} denote the first-order kinetics reaction rate and the rate constant, respectively, while C_s indicates the concentration of the pollutant substrate at any reaction

time “*t*”. Because the reaction mixture contains TiO₂ as a photocatalyst, the photocatalytic rate kinetics can be assumed to be a pseudo-first-order response. The great concurrence between the hypothetical kinetics of the pseudo-first-order response model and practical observations aids in the depiction of the kinetics of photocatalysis, with the assistance of the following model:

$$-\ln(C_s/C_0) = k^*_{app} t \quad (25)$$

where *C*₀ is the initial toxic pollutant concentration and *C*_s is the degraded concentration of the toxic pollutant substrate after time “*t*”. The value of the rate constant was computed from the slope in the graph of $-\ln(C_s/C_0)$ versus time. The kinetic rate of heterogeneous photon-induced catalysis was deciphered utilizing the Langmuir–Hinshelwood (L–H) equation

5. Conclusions

The heterogeneous photocatalytic process has been frequently suggested as a promising approach for the removal of water contaminants. Nonetheless, 40 years of scientific studies and photocatalytic wastewater applications show great differences between lab research and the real requirements of wastewater purification with respect to different advances. In this domain, photocatalysis alone can barely exist outside research labs. Composites for heterogeneous photocatalytic mineralization/degradation utilizing TiO₂ photocatalysts remain a reasonable option for the decomposition of tenacious natural impurities in aqueous media. TiO₂ is a reducible metal oxide that responds strongly to pollutants compared with other metal oxides. Thus, TiO₂ has attracted much consideration for application as a heterogeneous catalytic support in aqueous reactions. At any rate, this promising innovation addresses the issue of changing organic toxic pollutants into nontoxic substances.

It can be concluded that catalysts supported on TiO₂ with various phase structures and morphologies may display distinctive physicochemical effects and catalytic reactions. Recently, nano-TiO₂ has set the norm as a benchmark aqueous-mediated heterogeneous photocatalyst for the mineralization and degradation of a wide scope of harmful organic mixtures, including chlorinated organics, color pollutants, pesticides, phenolics, drug mixtures, medications, and volatile organic compounds (VOCs). The photon-initiated movement of TiO₂ for the refinement of drinking water is likewise established. Many types of TiO₂—including anion-doped TiO₂, metal- and metal-oxide-doped TiO₂, core-shell TiO₂, polymer/TiO₂ composites, and co-catalyst-coupled TiO₂—have been created to boost the UV–Vis light action of original or pristine TiO₂. Several investigations confirmed that diverse trial parameters—for example, the initial analyte concentration, the pH of the suspension medium, and the wastewater grid—can change the photodegradation interactions of the TiO₂ photocatalyst and improve the economic feasibility and ecological impact of these exercises. The most ideal alternatives available for wastewater treatment based on photocatalytic procedures and the fabrication of photocatalysts were explored and their remarkable highlights explained, with TiO₂ photocatalysis being an exceptionally constructive wastewater treatment methodology. The huge body of existing literature and continuous exploration shows that this field of study is an exceptionally encouraging one, and further advancement is inevitable.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/jcs6110350/s1>, Table S1: Illustrative literature on the photocatalytic degradation of dyes; Table S2: Literature on the photodegradation of colorless hazardous organic toxin molecules and pharmaceutical contaminants.

Author Contributions: Conceptualization, M.C.M. and S.A.; methodology, S.A. and B.A.; data curation, M.C.M.; writing—original draft preparation, M.C.M.; writing—review and editing, S.A. and A.S.; supervision, S.A. All authors have read and agreed to the published version of the manuscript.

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