Biodegradable Polymer-Supported Titanium Dioxide Photocatalysts

Subjects: Environmental Sciences
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During the past two decades, immobilization of titanium dioxide (TiO2), a well-known photocatalyst, on several polymeric substrates has extensively gained ground since it limits the need of post-treatment separation stages. Taking into account the numerous substrates tested for supporting TiO2 photocatalysts, the use of biodegradable polymer seems a hopeful option owing to its considerable merits, including the flexible nature, low price, chemical inertness, mechanical stability and wide feasibility.

biodegradable polymers | titanium dioxide | immobilization | photocatalysis | wastewater remediation

1. Introduction

Water contamination by organic compounds and metals has been outlined as one of the major global problems nowadays. In fact, due to their non-biodegradable nature, these harmful compounds remain for long time periods after their discharge into the environment, thus being characterized as persistent contaminants. Several techniques have been explored to remove these pollutants from water, including adsorption and photocatalysis, which comprise attractive and eco-friendly approaches. The nano-sized titanium dioxide (TiO2) is a famous photocatalyst among the metal oxides, due to its excellent efficiency, low price, physicochemical stability, extensive disposal, safety, and non-corrosive behavior. It has three crystal forms, anatase, rutile and brookite, while the first presents the most effective photocatalytic performance. Nevertheless, due to the challenges that arise from the very small particle size and the unfeasible reusability of the particles, including the post separation and recovery of the photocatalytic particles after water or wastewater treatment, the need of TiO2 immobilization is crucial [1] (**Figure 1**).

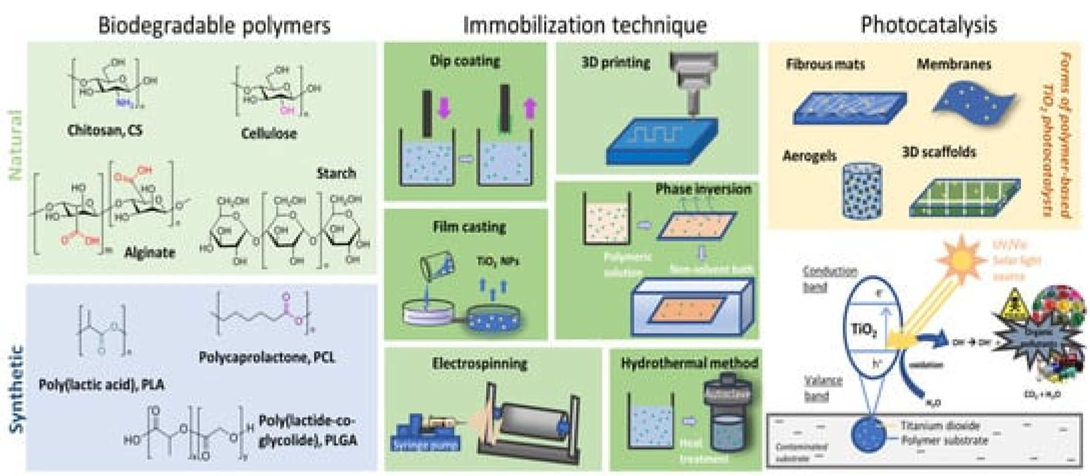

Figure 1. A brief illustration of the main synthetic routes fabricated for the immobilization of TiO2 nanoparticles onto biodegradable polymeric substrates for the photocatalytic degradation of organic pollutants.

2. Biodegradable Polymers Combined with TiO2 for Enhanced Photocatalytic Activity

2.1. Natural Biodegradable Polymers

2.1.1. Chitosan (CS)

Synthetic and Characterization Routes

A biodegradable polymer that has been widely explored in green pathways for waste remediation and photocatalytic activities is chitosan (CS). It is a linear polysaccharide and one of the most abundant biopolymers in the nature, with biodegradable, biocompatible and non-toxic character, derived from the deacetylation process of chitin, found in the exoskeletons of crustaceans and arthropods. Enzymes, such as chitosanase or lysozymes, are known to degrade chitosan. Its low-cost and the several versatile properties that chitosan possesses, render this polymer as an ideal candidate for environmental remediation purposes. Since CS is a great supporting material for the dispersion of TiO2 nanoparticles, CS/TiO2 is one of the most investigated composite photocatalysts, while their synergistic effects between them have also been studied. The immobilization of TiO2 in CS films has been widely investigated since it can be easily obtained owing to the miscibility between CS and hydrophilic TiO2. Chitosan contains in its structure amino and hydroxyl functional groups which act as coordination sites to form complexes with metals and several compounds, boosting by this means the effective removal of pollutants with special selectivity. However, the immobilization attempts require strong affinity between the TiO2 and the substrate, and thus, cross-linking processes with the aid of several alkaline agents (e.g., NaOH) are often selected [2]. A brief description of the studies reported herein for CS-supported photocatalysts is presented in **Table 1**.

Table 1. Summary of the chitosan-supported TiO2 photocatalysts enclosed in the presented literature.

	Biodegradable Polymeric Matrix					Photocatalysis Parameters.			Ref.
No.	Polymer Substrate	TiO_2 Precursor	Dopant	Immobilization Technique	Morphology of the Photocatalyst	Type of (Target) Pollutant	Light Source	Degradation Efficiency (Time Required)	
1	CS	TiO_2 nanopowders (Aeroxide; 80% anatase)	MT	CS-MT film casting & dip-coating in TiO_2 formulation	Bilayer photocatalyst	Methyl orange dye	45 W fluorescent lamp	98.7%	[3]
2	CS-grafted poly(vinyl imidazole)	Titanium isopropoxide	CDs	In situ deposition of TiO_2 NPs and CDs onto the polymeric surface under microwave irradiation	Nanocomposite hydrogel	2,4-dicholorophenol Reactive Blue 4 Reactive Red 15	Sunlight exposure for 30 min	95% (180 min) 95.8% (30 min) 98.2% (30 min)	[4]
3	CS	TiO_2 (P25)	-	Immobilization of TiO_2 in CS film by cross-linking process	Film	Tetracycline hydrochloride	UV lamp 30 W and λ = 360 nm	87% (240 min)	[2]
4	CS	Aeroxide P25-TiO_2	-	3D printing	3D printed scaffolds	Amoxicillin	UV irradiation (125 W), λ = 300–800 nm	90–60% (180 min)	[5]
5	CS	TiO_2 powder (P25)	-	One-step spray-drying synthesis	CS/TiO_2 nanocomposite particles	Organic dye, crystal violet	RPR-200 Photochemical Reactor (Rayonet), λ = 300 nm (8×, 21 W), and λ = 350 nm (8×, 24 W) lamps	58.3–15.5% (120 min) 95.7% pristine particles	[6]
6	CS	TiO_2	GO	Dopped-GO and CS impregnated in TiO_2 solution	-	cefixime trihydrate	4 × lamps UV-A irradiation, λ = 365 nm	95.34% (60 min)	[7]
7	CMCS	Butyl titanate	TiO_2/ZrO_2 composites	ZrO_2:TiO_2 were synthesized by a microwave hydrothermal method, CMCS as template	Composites	Rhodamine B	Photochemical reactor-UV irradiation (CEL-LPH120),	90.5–60.6% (60 min)	[8]

Biol. Macromol. 2020, 164, 3676–3686.

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Biodegradable Polymeric Matrix						Photocatalysis Parameters.			Ref.
No.	Polymer Substrate	TiO_2 Precursor	Dopant	Immobilization Technique	Morphology of the Photocatalyst	Type of (Target) Pollutant	Light Source	Degradation Efficiency (Time Required)	
8	CS + PVA	TiO_2 (anatase)	Ag	Loading algae cells on the TiO_2/Ag CS hybrid nanofiber mat prepared by electrospinning	Algae-TiO_2/Ag hybrid nanofiber membrane	Cr(VI) removal	500 W halogen tungsten lamp, λ > 400 nm	91–25% (180 min)	[9]
9	CS + CA	TiO_2 nanoparticles	SWCNTs + Fe_3O_4	Incorporated inorganics into electrospun nanofibers	Composite nanofibers	Cr(VI), As(V), Methylene blue and Congo red	4 × UV lamps, 30 W and λ = 365 nm	~99% (40–60 min)	[10]

Abbreviations: CS, chitosan; CMCS, carboxymethyl chitosan; PVA, polyvinyl alcohol; MT, montmorillonite; CDs, carbon dots; SWCNTs, single walled carbon nanotubes; GO, graphene oxide.

In other cases, the inclusion of organic or inorganic nanofillers, such as carbon dots (CDs) [4], graphene oxide (GO) [7], carbon nanotubes [10] and other metal oxides [8], into the polymer matrix has been also explored, providing nanocomposite materials with excellent architecture and dispersion of the nanofillers. Carbonaceous and inorganic materials not only perform as supporting materials for the new composites but also act as co-catalysts for the intensification of the photocatalytic efficiency of TiO_2 [7].

Bergamonti et al. [5] utilized a 3D printer to prepare CS scaffolds as the embedding matrix for TiO_2 nanoparticles. In order to prepare a stable polymeric network, the dried scaffolds after the 3D printing procedure were further proceeded with ammonia solution in order to eliminate the acetic acid used for the solution of CS and provide by this ionic gelation path a neutral and stable network.

ZabihiSahebi et al. [10] reported on the formation of cellulose acetate/chitosan/single walled carbon nanotubes/ferrite/titanium dioxide (CA/chitosan/SWCNT/Fe_3O_4/TiO_2) nanofibers for the removal of metals and dyes. Herein, the combination of these two polymers had a dynamic impact on the efficiency of the final matrix.

An additional study taking advantage of the electrospinning technique with CS as polymer nanofiber mat was conducted by Wang et al. [9] (**Figure 2**). In this work, ultrafine CS membranes doped with TiO_2/Ag, were loaded with green algae cells and the synergistic photocatalytic activity of the designed mats was investigated for the removal of Cr(VI). According to the authors, the inorganic addition enhanced the conductivity of the polymer solution and though the electrospinning efficiency of CS solution was improved. TEM images implied that the Ag in situ formed nanoparticles were homogeneously dispersed into the polymer matrix, whereas TiO_2 deposition was additionally assured by X-ray spectroscopy analysis. SEM images provided in the study illustrate the photo-degradation of the algae-cells on the surface of the prepared mats.

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1... esis of cellulose acetate/chitosan/SWCNT/Fe3O4/TiO2 composite nanofibers for the removal of Cr(VI), As(V), Methylene blue and Congo red from aqueous solutions. Int. J. Biol. Macromol. 2019, 140, 1296–1304.

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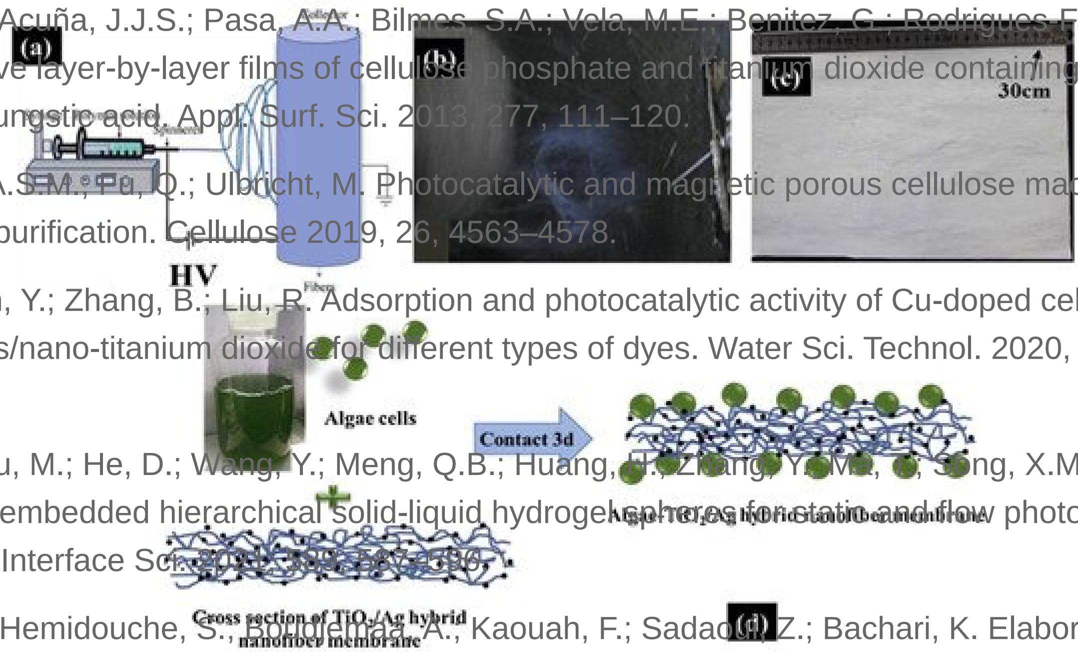

Figure 2. (**a**) Schematic illustration of electrospinning system; (**b**) nanofibers generation by single needle electrospinning; (**c**) demonstration of large-scale nanofibers mat and (**d**) scheme modeling the preparation of algae decorated TiO2/Ag hybrid nanofiber membrane. Reprinted with permission from [9].

Photocatalytic Performance

Chitosan based composites achieved a wide range of degradation efficiency reaching 90% in most of the cases, while UV radiation was most frequently employed for the degradation of pollutants. Different structures of chitosan-based materials were used in photocatalytic experiments, such as films, bilayers, 3D printed scaffolds and fibers. Another important factor is the reusability of polymeric materials used in photocatalysis. Chitosan based catalysts were applied for 3-5 cycles in the majority of studies with sufficient results. However, a decrease in the photocatalytic activity was recorded after the second cycle in most of studies. Nevertheless, Bahrudin et al. investigated the photodegradation of methyl orange (MO), in which the reusability of TiO2/CS-Mt composite was tested for 10 cycles. According to this study, two chitosan bilayers were manufactured with or without the addition of Mt. The insertion of Mt showed a favorable effect in charge separation of TiO2. Thus, these bilayers performed a higher photocatalytic performance in degradation of MO dye.

2.1.2. Cellulose

Synthetic and Characterization Routes

Cellulose is another non-toxic, biocompatible as well as biodegradable polysaccharide found in great abundance in nature. It comprises a linear chain with multiple hydroxyl groups able to form hydrogen bonds with other oxygen atoms on the nearby polymeric chain. Biodegradation of cellulose is achieved either by enzymatic oxidation, with peroxidase emitted by fungi, or by bacteria. Cellulose and its derivatives, such as carboxymethyl cellulose, cellulose phosphate, and acetate, have been used primarily as reinforcement materials owing to its excellent

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mechanical, chemical, and biological properties for dyes and metal binding for environmental remediation purposes.

Concerning the upper layer comprising of TiO2-nanoparticles, it was clearly that it acted as a photocatalytic surface for the degradation of various contaminants (**Figure 3**).

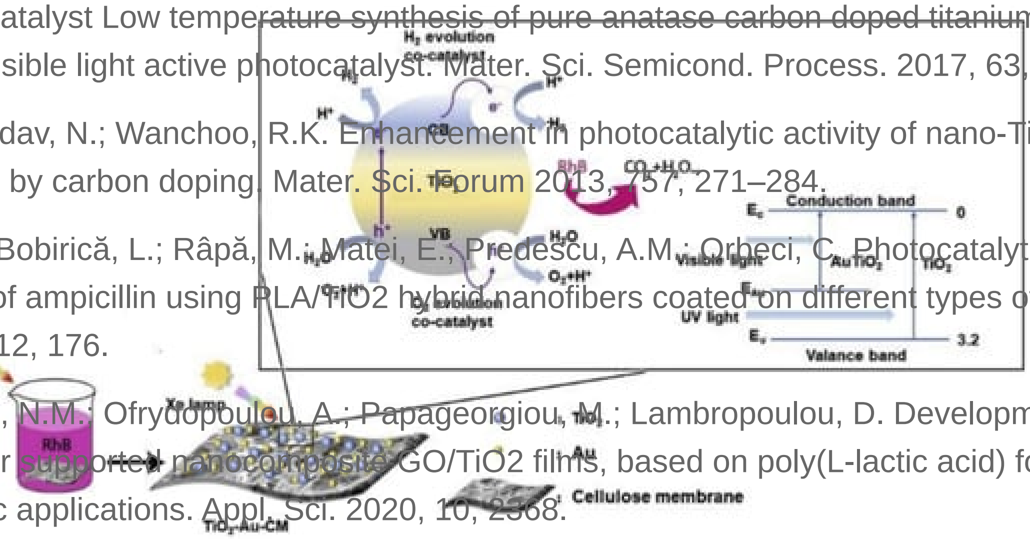

Figure 3. Schematic image for the mechanism of photoinduced charge carrier transfers in TiO2-Au cellulose membranes under solar irradiation. Reprinted with permission of Reference [11].

Photocatalytic Performance

Getting an insight into bibliography about the use of cellulose destined for the fabrication of photocatalytic membranes, it was shown that various pollutants were targeted for the examination of their possible removal. The majority of studies investigated the removal of dyes such as MB, RhB, MO, crystal violet, reactive brilliant red K-2BR and cationic red X-GRL. Their degradation was more than 90% in most of the cases and the experiments were carried out under UV light, sunlight, and visible light while the irradiation time ranged from 10 to 180 min [12][13][14][11][15][16][17][18][19][20]. Furthermore, other organic pollutants were explored with worth noticing results. Phenol, benzene, toluene, ethylbenzene, and xylene were studied under UV and visible light irradiation, while their degradation efficiency ranged between 70% and 90% [16], [15] after 180–360 min of treatment. Moreover, other toxic pollutants were examined such as stearic acid, Cr(VI), and cyanotoxins microcystin-LR or cylindrospermopsin with remarkable photocatalytic results [13][14][18]. Concerning the photocatalytic substrates, various matrices of cellulose material were tested such as membranes, films, fibers, and magnetic macrospheres. Regarding the reusability of cellulose material in photocatalysis, the synthesized composites were tested for three to six repetition cycles, and as a result, the photocatalytic materials showed exhibiting good stability.

2.1.3. Alginate (Alg)

Synthetic and Characterization Routes

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Alginate is a natural anionic polysaccharide, mainly derived from the cell walls of algae. In recent years, the low price and abundance in nature, have rendered the alginate as a polymer of much attention. Due to the presence of hydroxyl and carboxyl groups on its molecule, alginate has been as well explored for the effective removal of metal ions.

Gelation techniques are commonly chosen for the preparation of alginate-based photocatalysts. Within an innovative effort, Kalpoçe et al. [21] reported on the synthesis of a buoyant alginate photocatalyst with immobilized TiO2 nanoparticles for accomplishing both superior photocatalytic behavior and more feasible separation after treatment processes. The ionotropic gelation technique was employed, with CaCO3 or NaHCO3 gas-forming agents added firstly to a TiO2 dispersion with the addition of a sodium alginate solution (**Figure 4**).

Figure 4. **(a)** Scheme from ionotropic gelation and CO2 generation from both gas forming agents (CaCO3 and NaHCO3); **(b)** bubbles held within the gel beads with CaCO3 in its formulation, and **(c)** floating TiO2/CaAlg beads with 1:1 ratio of NaHCO3/alginate and 1:1 ratio of CaCO3/alginate [21].

Photocatalytic Performance

Getting an insight into bibliography of alginate-based materials with combination of TiO2 nanoparticles, it is observed that they were used for various applications, such as the photo-degradation of common dyes (MO, basic blue 41, tartrazine, RhB), removal of pharmaceuticals (ibuprofen, and sulfamethoxazole), and other organic compounds (2-naphthol). Moreover, alginate-TiO2 nanocomposites were used in different morphologies including fibers, membranes, hydrogel spheres, and papers. The irradiation was carried out under two main sources, UV light or sunlight for a time range between 45–340 min. Photocatalytic materials based on alginate showed a high recyclability with a range of 3–7 cycles [22][21][23][24][25][26][27].

2.1.4. Starch

Synthetic and Characterization Routes

Starch is a renewable material with biocompatible and biodegradable nature, low cost and high abundance, and due to this positive profile, it has been widely explored in food, textile, packaging as well as pharmaceutical industries. It mainly consists of amylose and amylopectin, while one of the most challenging chapters concerning its use is its dissolution since the strong inter- and intra-molecular hydrogen bonds and its semicrystalline nature

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with double helices, require strong polar systems. Biodegradation of starch can mainly proceed via hydrolysis at the acetal bonds by enzymes.

Photocatalytic Performance

Regarding the literature of starch-based TiO2 materials for the removal of different pollutants from wastewater through photocatalytic process, it was noticed that researchers mainly focused on MB and rhodamine B (RhB) dyes removal, widely used in textile industry. In most studies UV light and/or sunlight radiation was employed for the degradation of different initial concentration of dyes, ranging from 4 to 50 ppm [28][29][30][31][32]. The removal of contaminants ranged within 94–100% in most of the cases, and treated solutions were exposed to irradiation for 90 to 360 min.

2.2. Synthetic Polymers with Biodegradable Nature

2.2.1. Poly(Lactic Acid) (PLA)

Synthetic and Characterization Routes

PLA is one of the most dynamic and promising biodegradable synthetic polymers derived from renewable resources, such as corns, sugar beets, wheat and other starch-based products. It can be synthesized mainly by the polycondensation of lactic acid or by ring opening polymerization of lactide with the aid of a catalyst. PLA is totally degraded under compost conditions. Except its wide use in pharmaceutical technology, the fabrication of PLA for the synthesis of TiO2-immobilized photocatalytic materials has limited literature, which is presented below, in brief. The synthetic pathways for these photocatalysts include mainly casting, electrospinning and spin-coating methods.

Photocatalytic Performance

In the field of bio-based polymers, PLA has also been used for the fabrication of TiO2 composite materials with photocatalytic activity. Three interesting studies used the synthesized composites for the degradation of pharmaceuticals (mainly antibiotics) [33][34][35], while another group of studies examined the degradation of common dyes such as MB and methylene orange [36][37][38]. The polymeric materials, acting as supports for the photocatalysts, were mainly manufactured in two morphologies: films and nanofibers. The degradation efficiency of pollutants ranged within different levels. The degradation of pharmaceuticals was near to 90% in most of cases, while the photocatalytic degradation of the azo dyes varied mostly between 70% and 90%. The photocatalytic experiments were carried out under UV and sunlight irradiation, while an adsorption step was priorly applied. A wide range of irradiation times was applied starting from 2 to 10 h.

2.2.2. Polycaprolactone (PCL)

Synthetic and Characterization Routes

PCL (polycaprolactone) is a semi-crystalline aliphatic polyester produced by a ring-opening polymerization of ε-caprolactone, mainly in the presence of tin octanoate as catalyst. It is soluble in many organic solvents, while it possesses a semi-rigid nature in room temperature conditions. Enzymes and fungi simply degrade PCL, while for the enhancement of its biodegradation several copolymers with lactide or glycolide are proposed. Due to its low melting point, advanced rheological and viscoelastic characteristics, PCL has been extensively explored in the manufacture of electrospun porous fibers. Only recently PCL was reported as a template to prepare PCL/TiO2 fibrous mats as dynamic candidates for efficient photocatalysts and thus further exploration in this field should be investigated.

Photocatalytic Performance

According to the available bibliography, PCL-TiO2 composites were applied for the degradation of organic dyes including MB, RhB, and Reactive Black 5 or even for disinfection from bacteria often found in wastewater effluent, such as E. Coli, C. albicans, and Staphylococcus aureus. The PCL composites were manufactured in different structures for photocatalytic purposes, including nanofibers and membranes. Most experiments were carried out under UV light radiation with treatment time ranging from 80–300 min according to the targeted pollutants and the photocatalytic material used. Moreover, the reusability of materials was monitored up to three cycles exhibiting satisfactory results [39][40][41][42][43][44].

2.2.3. Other Synthetic Polymers

There are also few biodegradable polymers which have been explored to prepare photocatalysts for TiO2 immobilization, but the relative reports are limited (**Table 2**).

Table 2. Summary of other synthetic polymer-supported TiO2 photocatalysts enclosed in the presented literature.

	Biodegradable Polymeric Matrix					Photocatalysis Parameters			Ref.
No.	Polymer Substrate	TiO2 Precursor	Dopant	Immobilization technique	Morphology of the Photocatalyst	Type of (Target) Pollutant	Light Source	Degradation Efficiency (Time Required)	
1	PLA + PBAT + PBS	Titanium isopropoxide (97 wt%)	-	- Sol-gel method for theTiO2 nanoparticles - blown film technique	Composite films	Toluene	Photocatalytic oxidation reactor with UV-C lamp 6 W and λ = 254 nm	52% (270 min)	[45]
2	PLGA	TiO2 nanopowder	-	Air-liquid foaming technique	Porous 3D-PCL scaffolds	Methylene blue E. Coli	UV lamp light with wavelength 365 nm	90% (180 min) ~99% (24 h)	[46]
3	PHB & CS	Titanium (IV) oxide (nano-	-	Electrospinning/Electrospraying & Impregnation techniques	Hybrid fibrous	Methylene Blue	UV light (UVASPOT	>92% (180 min)	[47]

Biodegradable Polymeric Matrix						Photocatalysis Parameters			Ref.
No.	Polymer Substrate	TiO2 Precursor	Dopant	Immobilization technique	Morphology of the Photocatalyst	Type of (Target) Pollutant	Light Source	Degradation Efficiency (Time Required)	
	oligomers	TiO2) (99.7% anatase nanopowder)			materials	Escherichia Coli	400/T, Dr. Honle AG; UV lamp 400 F/2; 400 W)	100% (30–60 min)	

Abbreviations: CS, chitosan; PBAT, polybutylene adipate-co-terephthalate; PBS, poly(butylene succinate); PLA, poly(lactic acid); PLGA, poly(lactide-co-glycolide); PHB, poly(3-hydroxybutyrate).

One of them is poly(lactide-co-glycolide) (PLGA), which is a copolymer of poly(lactic acid) (PLA) and poly(glycolic acid) (PGA). It is a biodegradable and biocompatible polyester with tunable mechanical properties; merits that led Pelaseyed et al. [46] to utilize it for the fabrication of 3D porous PLGA/TiO2 nanocomposite scaffolds. Air-liquid foaming technique was employed to manufacture the very porous nanocomposite scaffolds with the PLGA/10 wt% TiO2 being the optimal product, whereas a high photocatalytic efficiency against methylene blue dye was also confirmed, amongst the other beneficial properties of the final composite scaffolds.

Poly(3-hydroxybutyrate) (PHB) is another interesting biodegradable polymer which is easily degraded by numerous microorganisms (bacteria, fungi, algae) under several conditions. With an innovative concept, PHBcombined with CS oligomers were utilized for the fabrication of fibrous photocatalysts with TiO2 nanoparticles incorporated. Researchers used a grouping of electrospinning, electrospraying and impregnation methods, which potentially ensure the desired architecture of the fibrous scaffolds [47].

3. Conclusions

TiO2-induced photocatalysis considerably remains as the most efficient and feasible option for the photo-degradation of persistent organic pollutants, including mainly pharmaceuticals, azo dyes, toxic metals and pathogenic microorganisms present in water and wastewater. Constant efforts are performing to modify the TiO2 photocatalyst and provide materials highly effective in visible light in accordance with their ease post-treatment recovery. Several research articles have been published in which biodegradable polymers were facilitated to manufacture eco-friendly and sufficient photocatalytic materials against several target pollutants, especially from wastewater. Several methods were applied like sol-gel, film casting, electrospinning, spin coating and 3D printing, transfusing photocatalytic efficiency, mechanical strength and reusability to the fabricated composites. Fibers, membranes and aerogels fabricated from biodegradable polymers, presented different advantages in their overall performance. In fact, the pollutants' removal can be fulfilled by the synergistic effects of the biodegradable polymer-based adsorption and the redox reactions induced by the photo-generated charge carriers, created on the surface of TiO2.

Future studies should be focusing on new methodologies and combined techniques for the application of biodegradable polymers, as to prepare chemical and thermal resistant polymer-supported/TiO_2 composite materials, with advanced architecture and superior reusability, recyclability and photocatalytic performance. Moreover, the facilitation of green practices for the preparation of the photocatalysts should also be taken into consideration. More research and work are still needed for the categorization of the appropriate manufacturing and TiO_2 anchoring techniques for each biodegradable polymer, since each of them possesses a special character with specific chemical and physical properties.

Despite the fact that exceptional studies are found in the literature including the preparation and photocatalytic activity of several polymer-based/TiO_2 materials for remediation of wastewater, these works are performed in the laboratory environment and not at large scale. Biodegradable polymer-supported TiO_2 materials should be further researched and advanced, exceptionally in the visible light region. Thus, a lot of effort should also be extended for the commercialization of the prepared photocatalysts, under real conditions.