catalysts

MDPI

Review

Photocatalytic Applications in Wastewater and Air Treatment: A Patent Review (2010–2020)

Marica Muscetta and Danilo Russo *

Dipartimento di Ingegneria Chimica, dei Materiali e della Produzione Industriale, University of Naples "Federico II", Piazzale Vincenzo Tecchio 80, 80138 Napoli, NA, Italy; marica.muscetta@unina.it
* Correspondence: danilo.russo3@unina.it; Tel.: +39-081-768-2253

Abstract: In this work, we reviewed the most significant patents of the last decade (2010–2020) in the fields of water and air photocatalytic treatment. Patents were discussed by identifying the recurrent addressed issues and presenting the proposed solutions. Adoption of TiO_2 and/or modified-TiO_2-based material is still the most common choice of inventors, whereas many patents focus on the design of the plants/devices to improve efficiency of photocatalytic treatment by improving light utilization and contact between the phases. The review also highlights issues deriving from specific applications and outlines future trends in the field, such as the need for standardized testing and digitalization of monitoring and control.

Keywords: TiO_2; titanium dioxide; air treatment; water treatment; patents; photocatalysis; review; pollutants; micropollutants; efficiency

Citation: Muscetta, M.; Russo, D. Photocatalytic Applications in Wastewater and Air Treatment: A Patent Review (2010–2020). *Catalysts* **2021**, *11*, 834. https://doi.org/10.3390/catal11070834

Academic Editor: Gassan Hodaifa

Received: 18 June 2021
Accepted: 6 July 2021
Published: 9 July 2021

1. Introduction

Water and air pollution represents one of the most critical environmental problems of the 21st century [1,2]. In recent years, the discharge and disposal of toxic materials in water were regulated by stricter limits; as a result, the development of new technologies for wastewater treatment has become necessary [3]. On the other hand, outdoor air quality seems a more complex subject to regulate in many countries, and most directives up to date only refer to target pollutants such as PMs, ozone, and NOx [4]; more attention has been devoted to indoor air quality, also taking into account the increasing time that people spend in enclosed environments, and the ease of monitoring and controlling pollutants in such systems. The large and increasing number of pollutants and micropollutants in air and water poses a serious problem regarding the adoption of tertiary non-selective oxidative treatments, especially for those compounds particularly recalcitrant to traditional treatment. In particular, the possibility of using a renewable source and/or clean non-toxic oxidation catalysts has gained much attention in the last few decades [5]; among the renewable energies, solar radiation was studied by several authors, which reported the photocatalytic degradation of organics, as well as of bacteria and viruses, by using photocatalysts under UV and/or visible light radiation. In the last decade, an exponential growth in the research activities directed towards the utilization of this kind of technology may be recognized, thus indicating the growing interest in the photocatalytic application in wastewater and air treatment. However, despite the great number of promising aspects, such as the adoption of eco-friendly systems, the utilization of the solar source, and the non-toxic substances used as photocatalysts, several issues still need to be addressed, largely limiting the utilization of photocatalytic technologies on an industrial scale. Among them, the high installation and operating costs, the large dimensions of the plants depending on the application, the low efficiency of the process, and the recovery of the catalyst represent the most common problems to be solved. For these reasons, the number of patents for photocatalytic wastewater and air treatment is still limited. Despite this, an exponential growth was detected for the number of patents published in last 10 years: Figure 1a,b show the cumulative number of published patents per year since 2010, focusing the attention on the patents having "photocatalytic wastewater/air treatment" and "device"/"plant"/"reactor" as keywords; it is clear that these diagrams do not report all the published patents in the photocatalytic water/air treatment applications, but the identified trend clearly demonstrates the great interest of the inventors in this topic. Figure 2 shows the relative occurrence of the materials adopted in the patent literature of the last decade, demonstrating that TiO_2-based materials are still the most ubiquitous catalysts in the field.

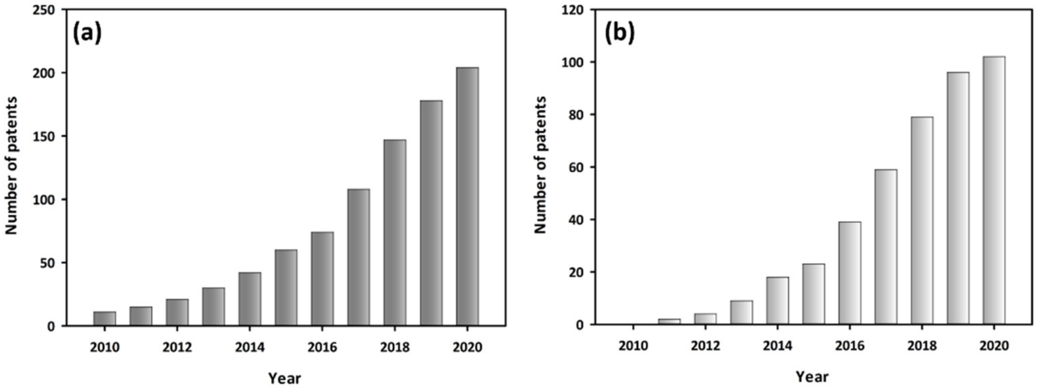

Figure 1. Cumulative number of published patents, for photocatalytic (**a**) wastewater and (**b**) air treatment (2010–2020) using "photocatalytic wastewater/air treatment" and "device/plant/reactor" as keywords.

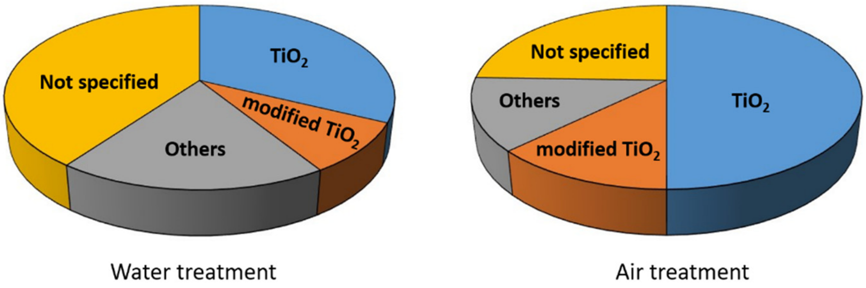

Figure 2. Occurrence of different photocatalytic material in patents published between 2010 and 2020 in the field of wastewater and air treatment.

As previous reported, the limited development of photocatalytic applications in wastewater/air treatment on an industrial scale may be ascribed to the several above-mentioned drawbacks, which also explain the gap existing between the large number of scientific papers published in the field and the actual applications adopting such technologies.

In the present work, we reviewed patents published in the last decade (2010–2020) on photocatalytic devices and plants for wastewater and air treatment. Based on this, we provide a critical overview of the main problems associated with real-world applications of academic studies, and the relevant practical solutions proposed. The detailed discussion about the theoretical principles behind the use of photocatalysts for these applications is out of the scope of the present review.

The structure of the paper is as follows: photocatalytic water and air treatment as reported in the patent literature, were discussed in Sections 2 and 3, respectively. In Section 2, problems related to wastewater treatment are discussed. In particular, in the Section 2.1, issues related to the materials—such as the low efficiency of the semiconductors and recovery of the photocatalysts—are presented; the challenges associated to the plants (expensive materials, reactors and lamps, large dimensions of the plants, etc.) are discussed in Section 2.2. The problems found with respect to air treatment were grouped into four sections—in particular, in Section 3.1, we discuss issues due to the proposed materials, their interaction with light, and the reactions occurring on their surface; in Section 3.2, we discuss the design of the devices to improve light utilization and contact between the phases; finally, in Sections 3.3 and 3.4, we discuss, respectively, the problems related to specific applications and the general needs and trends of photocatalytic air purifiers.

Tables S1 and S2 in the Supplementary Material summarize the most significant patents considered in this work for water and air treatment, respectively.

2. Water Treatment

From the analysis of the patent literature published in the last decade (since 2010), the most common issues related to photocatalytic wastewater treatment applications may be identified and divided in two different categories:

(i) Problems related to the materials (low efficiency of the semiconductors and recovery of the photocatalysts)—discussed in Section 2.1, and
(ii) Problems related to the plants (expensive materials, reactors and lamps, large dimensions of the plants, etc.)—discussed in Section 2.2.

For each of them, several authors have proposed possible solutions, and the most significant patents are summarized in Table S1, where the type of reactor and the photocatalyst recommended, a brief description of the inventions, and the main advantages claimed in each patent are reported; in the next section, focused on the above-identified problems, some of the most interesting patents will be discussed in detail.

2.1. Materials Efficiency and Catalyst Recovery

Despite the great number of semiconductors that can be used as photocatalyst [6–8], TiO_2 represents the most widely adopted and promising semiconductor in photocatalytic degradation, due to its low cost, high photocatalytic activity, and chemical stability [9–12]. The use of TiO_2 (or modified TiO_2) is actually proposed in about 40% of the reviewed patents, whereas only a few works recommend other photocatalysts, such as carbon-based materials [13–17] or ZnO [18]. Doping of TiO_2 photocatalyst with metals or other semiconductors, as well as the use of an external bias, are only a few examples of the possible solutions, reported in the reviewed patents, to the problems still associated to the most widely used semiconductor.

From a theoretical point of view, the photocatalytic process begins when the photocatalyst is irradiated through a UV or visible radiation (depending on the band gap energy of the semiconductor), generating electron-hole pairs (R1)

$$Cat \overset{radiation}{\rightarrow} h^{+} + e^{-} \tag{R1}$$

However, electron-hole pairs may rapidly recombine through radiative or non-radiative processes, producing heat and light, due to the presence of defects in the structures and the natural tendency of the charges to return at lower energy level (R2)

$$h^{+} + e^{-} \overset{k_r}{\rightarrow} Heat + light \tag{R2}$$

Reaction (R1) depends on the rate of photon absorption by the photocatalyst, whereas reaction (R2) depends on the electron/hole recombination rate constant. Organic compounds in the system, depending on the pH of the suspension, may be adsorbed on the catalyst surface (R3), thus forming complexes (monodentate, bidentate etc.).

$$Org + \theta \overset{K_{ads}}{\leftrightarrow} Org_{ads} \tag{R3}$$

The oxidative process may proceed with different steps, based on the hydroxyl radical attack, as described in the literature, and following the reported (R4–R10) [19]:

(i) Organic compounds adsorbed on the catalyst surface react with the free hydroxyl radicals

$$Org_{ads} + OH^{\bullet} \rightarrow P_{ads} \tag{R4}$$

(ii) Organic compounds adsorbed on the catalyst surface react with the adsorbed hydroxyl radicals

$$Org_{ads} + OH^{\bullet}_{ads} \rightarrow P_{ads} \tag{R5}$$

(iii) Organic compounds react with the free hydroxyl radicals

$$Org + OH^{\bullet} \rightarrow P \tag{R6}$$

(iv) Organic compounds react with the adsorbed hydroxyl radicals

$$Org + OH^{\bullet}_{ads} \rightarrow P \tag{R7}$$

(v) Organics can also be directly oxidized by photo-generated holes

$$Org + h^{+} \rightarrow P \tag{R8}$$

Photogenerated electrons can finally react with oxygen to form superoxide anions, which can further oxidize organics

$$O_2 + e^{-} \rightarrow O_2^{\bullet -} \tag{R9}$$

$$Org + h^{+} \rightarrow P \tag{R10}$$

The efficiency of the process strongly depends on the activity of the photocatalyst, and, in more detail: (i) on the surface area of the material, which influences the adsorption phenomena, and (ii) on the morphology of the material, on which the electron-hole recombination rate depends.

Therefore, in the literature, to increase the efficiency of photocatalytic processes for wastewater treatment (leaving aside the possible structural modification of a given photocatalyst), the coupling of the material (TiO_2, ZnO, etc.) with other semiconductors as well as with metals is reported as a possible solution [20–23]. Despite most of the reviewed patents reporting bare TiO_2 as a photocatalyst, some authors recommend the use of the doped material to improve the photocatalytic efficiency. In [24], for instance, the inventors proposed CdS/TiO_2 as a photocatalyst for the simultaneous electricity (or hydrogen) production and biomass degradation, whereas in [25], the photocatalyst recommended for the presented small-scale photocatalytic reactor consists of activated-carbon-fiber/TiO_2 composite material. The carbon fiber was also reported by Wang et al. [26] and Xinying et al. [18]: in the latter, the inventors proposed a purification device with a carbon fiber coated with ZnO as a photocatalyst. The metal doping of TiO_2 was instead proposed in [27], wherein a plate-type microreactor was described. An interesting invention was found in [28]: the authors proposed a photocatalytic emergency purification cup in which the photocatalyst was represented by microspheres and luminescent optical fibers; N- and W-doped TiO_2, WO_3, and C_3N_4 were recommended as photocatalytic materials.

Moreover, several authors have reported the suppression of the recombination between the photogenerated charge carriers through the application of an external anodic bias [29,30]. From a theoretical point of view, when an extra potential is applied, the photogenerated electrons migrate to the counter electrode, thus effectively preventing the recombination of electrons and holes [31]; therefore, the photogenerated holes may react more easily with organic compounds, enhancing the efficiency of the process [32]. The possibility of using bifunctional electrodes has been widely reported in the literature, and compared with traditional photocatalysts, the results demonstrate higher photodegradation efficiency [29,30,33]. Within the patent literature, some authors also proposed the utilization of bifunctional electrodes for the photodegradation of organics [34–37]. In particular, Chen et al. [37] proposed the application of bifunctional electrodes, comprising a photocatalyst on the first portion of the electrode, and an electrocatalyst applied to the second portion of the surface. A TiO_2 thin film was chosen as the photocatalyst, while a thin film of Ta_2O_5-IrO_2 composite was adopted as the electrocatalyst, both materials coated on the electrode. The electrode, inserted in wastewater, may be irradiated, generating the electron-hole pairs in the photocatalyst; at the same time, an anodic potential bias may be applied to the electrocatalyst, thus resulting in the band bending of the conduction and valence bands down into the depths of the photoconductor. That gives arise to the separation of the electron-holes pairs, resulting in the suppression of the recombination as well as in the oxidation of other organics, which then serves to separate the electron-hole pairs more efficiently. The use of a photoelectrochemical device was proposed by several authors [26,37–43]; among them, an interesting solution to improve the electron-hole pairs separation was proposed by Sheng and Wang [40]: their invention consists of a photoelectrochemical device for the reduction of heavy metals, comprised of (i) a TiO_2 nanotube array thin film as photoanode and (ii) a large-area titanium or platinum-based counter electrode, both placed in the reaction medium; the use of a TiO_2 nanotube array film improves the photocatalytic activity, due to the increased surface area with respect to the traditional TiO_2 films, and the applied bias voltage efficiently promoted the separation of electron-hole pairs; moreover, the large area of the counter electrode provides more adsorption and active sites for the reduction of the heavy metals (i.e., Cr(VI)), which take place on counter electrode.

Another problem related to the photocatalytic materials, which limits their application on an industrial scale, is associated to the recovery of the photocatalyst. Indeed, as previously reported, the surface area of the material and the contact between the photocatalyst and the organics in the wastewater, greatly influence the photocatalytic process; for this reason, most of the authors proposed the dispersion of the photocatalyst as suspension in the current to be treated, despite this approach involving a difficult recycle of the material, thus limiting the practical applications in wastewater treatment [44–46]. In order to overcome these drawbacks, some authors have proposed different solutions, with the use of thin films and photocatalyst immobilized on various materials [47–49] being the most widely suggested in literature, as well as in the patent survey [14,28,42,50–61]. Shuo et al. [53], for instance, carried out an efficient continuous disinfection technology in which the photocatalyst was supported on a plate-like structure placed in the UV disinfection device, with the lamp located in the cavity of the reactor, thus preventing the loss of the material. Another interesting solution was offered by Yuning et al. [56], who proposed a photocatalytic module for wastewater treatment able to improve the photocatalytic efficiency and to reduce the loss of the photocatalyst, thus extending the life of the device. In particular, the invention comprises a photocatalytic film layer, composed of a photocatalytic material, such as TiO_2, ZnO, or C_3N_4, placed on a stainless-steel bracket, and glass sheet; the presence of the photocatalytic material on the bracket reduced the loss of the material, while the presence of the glass sheet may be associated to the improved utilization of the light energy.

However, to combine the possibility of recovering the photocatalyst and a greater contact between the organics and the materials, in recent years, the coating of photocatalyst with magnetic particles has attracted much attention of scientists, due to the possibility of using a magnetic field to easily separate the material from the solution after the reaction. However, despite the great number of patents in which the use of photocatalytic thin films or coating of the photocatalyst on nets, wire, and sheets were proposed, only a few examples of photocatalytic materials coated with magnetic particles were found in the reviewed patents [60,62,63], probably due to the high costs and large area of the materials, the low efficiency, and the operating difficulties, which, at present, prevent the large-scale applications. As concerns the literature survey, the single-phase catalysts, composites, as well as binary or ternary core–shell catalysts are the most widely used classes of materials, prepared through different methods, such as dip coating and electrodeposition [64,65]. Among them, the combination of distinct oxides is the most largely adopted [66,67], due to the minimization of the recombination rate, the formation of p-n heterojunction as well as the easy recovery of the material [68]. Several authors proposed the utilization of the described materials, as core-shell composites, to maximize the surface area of the photocatalyst [69]. As concerns the materials forming the core, iron-based oxides represent the most popular magnetic materials, despite the photo-dissolution phenomenon occurring during the irradiation (due to the interaction with the photocatalyst), as well as the possible formation of an unfavourable junction [70]. In order to overcome these drawbacks, some authors have proposed the introduction of a barrier layer between the two species; Su et al. [70], for instance, have developed a magnetic photocatalyst, composed of a Fe_3O_4 core and a TiO_2/SiO_2 shell, able to be easily separated by the application of a magnetic field. In particular, they reported a recovery of more than 90% of the photocatalytic material, which may be redispersed and reused. The presence of silica has been demonstrated to be essential to reduce the dissolution of the ferrite core, despite some authors having proposed carbon as an alternative shell, able to effectively avoid the direct contact between the magnetic and photocatalytic materials [67]. As concerns the photocatalytic reactors used in the presence of magnetic photocatalyst, few reports have discussed the application of a magnetic reactor with solid–liquid systems; Sun et al. [71] have proposed a simple rectangular reactor in which $CoFe_2O_4$-Ag_2O composite material was used as a magnetic photocatalyst. The material was dispersed in the reactor, thus forming the magnetic aggregates due to the presence of magnets located outside the vessel (lateral or bottom configurations were analysed). A solution containing methyl orange was introduced in the reactor, and the prepared suspension was irradiated through a light source. In all cases, material loss was prevented, and the formed flower-like aggregates resulted in a high surface area, thus allowing an efficient photodegradation of the organic compound studied (i.e., methyl orange).

Despite the few reports concerning the photocatalytic magnetic reactors, also in the patent literature, some applications are reported [62,63,72]. For instance, Wei et al. [63] proposed a photocatalytic reactor (see the example in Figure 3), consisting of a reaction bed, inside of which they circulated a magnetic photocatalyst and wastewater to be treated. The suspension was irradiated with a light source (visible LED or natural light source), and the magnetic source (preventing the loss of the photocatalyst) was located at the outlet of the reactor. The photocatalyst proposed, used as a shell, was a magnetic composite material, such as Ag_2O, TiO_2, ZrO_2, CdS, C_3N_4, or $KBiO_3$, while a magnetic material such as $CoFe_2O_4$, $NiFe_2O_4$, $ZnFe_2O_4$, γ-Fe_2O_3, or Fe_3O_4 was proposed as the core.

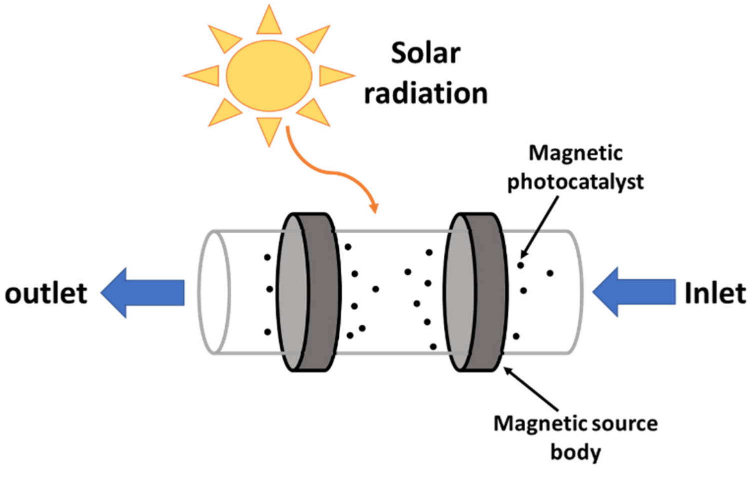

Figure 3. Photocatalytic magnetic reactor adapted from Wei et al. [63].

The described device is able to realize a continuous and simplified operation of the wastewater treatment method, and the results obtained seem to be an improvement with respect to the state-of-art of this technology, representing a promising aspect for its diffusion in the next years.

A different approach was proposed by Zhu Deshun [62], by using a dynamic photocatalytic device; the wastewater to be treated and the photocatalytic material were introduced in the reaction tank and mixed to give arise to the oxidative process in presence of the ultraviolet source (located inside the tank). After the reaction, a three-phase separator was used to recirculate the catalyst, separate the produced gas, and recover the liquid phase. This technology has the advantage of effectively solving the problems related to the loss and adhesion of the photocatalyst; moreover, the good contact between the sewage and the photocatalytic material improves the efficiency of the oxidative process with respect to other technologies.

2.2. Plants for Photocatalytic Water Treatment

The limitations of industrial-scale photocatalytic wastewater treatment can be ascribed, along with the limitations of the materials, to the problems related to the plants. The current technologies reveal serious shortcomings due to the large dimensions of the plants, high energy consumption, and low efficiency, negatively influencing the development of these methodologies. As one can see in Table S1, in about 50% of the reviewed patent, the authors proposed technical solutions with the aim to reduce, if not solve, the above-reported issues. In recent years, several authors described the key issues of these techniques; in particular, in a recent review [73], Gulyas reported the following limitations: (i) the short life of the UV source, which may represent up to 80% of the operation costs; (ii) low efficiency of the lamps; (iii) non-optimized reactor type, with respect to photon and mass transfer.

As concerns the reactors, open or closed vessel, static or rotating annular reactors, and multi-lamp or membrane reactors are only a few examples of the possible configurations reported in the literature [74–81], and proposed in the patent literature [14,55,59,82–89]. In particular, annular reactors were the most widely adopted reactors in the past decade, in the case of suspended photocatalysts; however, low conversion per pass, as well as the high axial flow rate to prevent loss of photocatalyst, made it necessary to develop different designs, such as the rotating disk (or cylinder) reactor configurations, in which the catalyst is immobilized on a rotating surface, resulting in improved efficiency [90]; a possible configuration was proposed by Shi et al. [91]: the described photocatalytic device is provided of a cylindrical rotating tank (disposed parallel or perpendicular to the ground) coated with the photocatalyst and one or more UV lamps fixed in the tank; the device can remove microbial bacteria and organic matter, with increased efficiency with respect to the prior state-of-art, while the coating of the photocatalyst prevents the loss of material and, as a result, the need for additional catalyst recovery units.

At present, despite the great number of research studies in the field of photocatalytic water treatment, the design optimization for the industrial applications is still far, and several mathematical models, based on the fundamentals of chemical engineering, were reported as a promising tool for the scale-up of the photocatalytic reactors [92].

From a theoretical point of view, the performance of the reactor is crucially dependent on the optimization of (i) the photon transfer, (ii) the mass transfer, and (iii) the catalyst load [75]; leaving aside the catalyst load, for which an in-depth evaluation of the costs and benefits should be necessary and is out of the scope of the present work, some inventions in the reviewed patents address the enhancement of photon and mass transfer, in order to obtain a more efficient and cost-effective photocatalytic process [63,86,93].

As concerns the photon transfer, some authors have considered the irradiated surfaces per unit of liquid reaction volume as the key parameter to describe the efficiency of the photon transfer [94]. However, this factor does not contemplate the possible distance between the lamp and the catalyst surface, as well as the presence of other absorbing species in the reaction medium. To overcome this drawback, Van Gerven et al. [95] proposed a new parameter, the illumination efficiency (η_{ill}), which takes into account: (i) the illuminated surface per unit liquid volume inside the reactor (κ, m^2/m^3), (ii) the radiant power incident on catalyst surface (P_{cat}, W) with respect to the power emitted from the lamp (P_{lamp}, W), (iii) surface area of the catalyst effectively irradiated (A_{min}, E) with respect to the total catalyst surface (A_{cat}).

Clearly, the optimization of the illumination efficiency is strictly dependent on the reactor geometry and the position of the light source in the photocatalytic device.

Along with the photon transfer, the efficiency of the mass transfer strongly influences photocatalytic wastewater treatment, and, as the photon transfer, may be associated with the reactor configuration. As reported in the previous sections, the photocatalytic oxidation process could take place (i) on the catalyst surface for the adsorbed species or (ii) close to the photocatalyst for the species in solution.

Sundar and Kanmani [77] have identified four important attributes to consider for the optimization of photocatalytic reactors, such as throughput, performance, energy efficiency, and cost. In particular, they observed the highest performance in terms of the apparent reaction rate constant and space time yield in microreactors, due to the efficient mass and photon transfer, despite the best performance in terms of throughput being observed for a translucent packed-bed reactor, in which several interconnected microchannel compartments between glass spheres are present.

Claes et al. [75] reported microreactors as a promising alternative reactor design: the mass and photon transfer may be optimized by using of a thin coating layer, while the high specific surface area allows the optimization of the catalyst load. Clearly, despite the good characteristics, the industrial-scale diffusion of this technology requires an in-depth analysis of its installation and operation costs, representing the key limitation of the process industrialization [96].

In the patent survey, possible solutions to overcome the shortcomings of the photocatalytic wastewater treatment plants are proposed; as previously reported, in Table S1, several of the most interesting patents published since 2010 to now are reported, focusing attention on the reactor type and the related advantages. On the basis of the considerations reported, several solutions are presented and discussed below, by dividing the sections considering the “light sources and configurations” and the “reactor types”.

2.2.1. Light Sources and Configurations

As previously discussed, UV sources represent a major contribution to the operational costs, and the utilization of more efficient and durable lamps as well as a more efficient way to use them, play a key role in the industrial diffusion of photocatalytic wastewater treatment.

In the reviewed patent literature, for instance, some authors reported the possibility of using UV LEDs, for which a reduced energy consumption and a longer life with respect to the traditional light sources is guaranteed [56,83,97]. For example, Lei et al. [97] have proposed a laminated double helix photocatalytic purifier (Figure 4a) for high-concentration wastewater, provided of several UV LED lamps and side-light fibers. Several purification discs, coated with TiO_2 film, are located horizontally in the photocatalytic reactor, while the lamps (along with the side-light fibers) are disposed between the rotating discs. The invention has numerous advantages, such as (i) an increased reaction area, due to the turbulence flow; (ii) an improved light utilization efficiency due to the presence of different lamps and side-light fibers in the reactor; (iii) the prevented material recovery due to the use of photocatalyst-coated rotating discs.

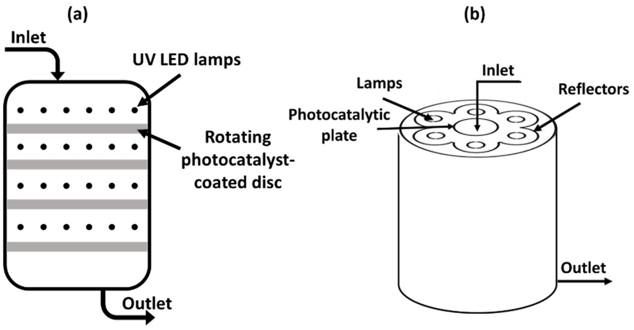

Figure 4. (**a**) Double helix photocatalytic reactor adapted from Lei et al. [97]. (**b**) Photocatalytic device adapted from Lianyong [88].

Along with Lei et al., in order to optimize the light utilization in the photocatalytic wastewater device, several authors proposed reactor configurations with a particular layout of the lamps, thus leading to an improvement of the process efficiency [15,28,88,89,98–101]. Lianyong, for instance [88], proposed a photocatalytic device wherein several UV lamp tubes are uniformly distributed along the vessel (Figure 4b), and as many curved reflectors are located close to the lamp tubes. The device is also provided with photocatalyst-coated plates, an adsorption column, and a turbulence generator. The invention is effective in the photodegradation, the presence of the reflectors strongly enhances the efficiency of the lamp utilization, and the coating of the photocatalyst prevents the loss of the material. The use of photocatalytic plates was also reported in [99], wherein a series of UV lamps fixed on the inner wall of the device can irradiate several photocatalytic plates located in different zones of the photocatalytic reactor. This very simple configuration allows the improvement of the photocatalytic efficiency due to the increase of the photon transfer. Similar solutions were presented in (i) [102], wherein a photocatalytic reaction chamber was provided of a series of glass plates with interlayer (disposed to form a serpentine flow channel) and several UV rays placed in the glass plate interlayer, in (ii) [103], where a number of light transmitting plates are located on a photocatalytic board, while the light source (not specified) is fixed on the outer wall of the reactor, as well as in (iii) [53]: the photocatalytic device was composed of a photocatalyst supported on a plate-like structure, and of a lamp located in the cavity of the reactor.

For a more efficient utilization of light irradiation, the investigation of the photocatalytic degradation rate at different light intensities may be of interest; an example is reported in the invention by Baoshan et al. [98]: they proposed a photocatalytic device, able to effectively treat black and odorous water, provided of a body frame wherein the light source is located, and the photocatalyst located on the inclined surface of the device. The device is also provided of a light source adjustment, to change the light intensity between 380 to 840 nm, in order to investigate the reaction time. The light source adjustment may be associated to the water quality control unit (inlet and outlet), thus (i) reducing the process time and (ii) increasing the light utilization efficiency. The need to adapt the photocatalytic process to various water qualities and quantities was also investigated and discussed by Jingchao et al. [104], which proposed a technology suitable for pre- and post-treatment of refractory wastewater; the deep treatment and reuse of municipal wastewater needs to develop new processes able to replace or assist the traditional wastewater treatment. The technical solution proposed by the authors includes a cylindrical reaction vessel arranged with UV light source arranged in a quartz jacket, thus avoiding the direct contact with wastewater, and a TiO_2-based photocatalytic powder coated on the surface of the reactor. Moreover, a microporous aeration tray is proposed for ozone or air bubbling to increase the reaction efficiency. A control unit is included in the invention to regulate the hydraulic retention time as well as the light intensity of the lamp, to adapt the process to various water quality and quantity. These features allow the adoption of the technology to a wide range of application, and a stable quality of the effluent is guaranteed. Finally, as in some previous discussed inventions the coating of the photocatalyst avoid the loss of the material, solving the needs of separation and recovery units. Due to the possibility of increasing photocatalytic efficiency and reducing costs, the adoption of control units is also reported in [14,53,104–109]: the adoption of pH, as well as water quality and quantity controllers, along with the flow regulating valves and the light intensity control, allow a high degree of automation, which improves efficiency, reduces the costs associated with the maintenance of the lamps, and enhances the simplicity of the treatment.

2.2.2. Reactor Types

Another key factor affecting photocatalytic wastewater processes is the reactor configuration. Clearly, the efficiency of the photocatalytic process is influenced not only by the photocatalytic reactor type, in which the reactions take place, but also by additional units such as membrane separators, atomization units, controllers, and turbulence generators, which can contribute to improving performance. The development of a photocatalytic wastewater treatment, suitable for implementation on an industrial scale, is strictly related to the optimization of the (i) reactor and plant configurations and (ii) costs, the latter strongly influencing the delay in dissemination of photocatalysis in wastewater treatment. In recent years, many efforts have been made in the design of photocatalytic plants that meet requirements such as cost-effectiveness, reduced volumetry, low energy consumption, and simplicity. Focusing attention on recent reactor designs, several patents were reported [16,25–27,39,53,61,86,91,93,102,107,110–113]; some of the most interesting will be discussed in the following paragraphs.

A relevant invention was proposed by Wang et al. [26]: in order to solve different problems such as (i) the recovery of the photocatalyst, (ii) the high energy consumption during the process, and (iii) the low efficiency of the treatment, the authors proposed a cylindrical photoelectric device (Figure 5) with a conical bottom, provided of a series of UV lamps located inside the reactor, parallel to the graphite electrodes (which inhibit the electro-hole recombination); the proposed photocatalyst is activated carbon loaded with TiO_2, suspended in the device, thus effectively using UV light; moreover, the outlet of the reactor is equipped with a nylon mesh, in order to efficiently separate the photocatalyst and the wastewater treated. Finally, an adjustment of the backflow ratio was provided to solve the problem of variability of the treatment effect according to the wastewater quality.

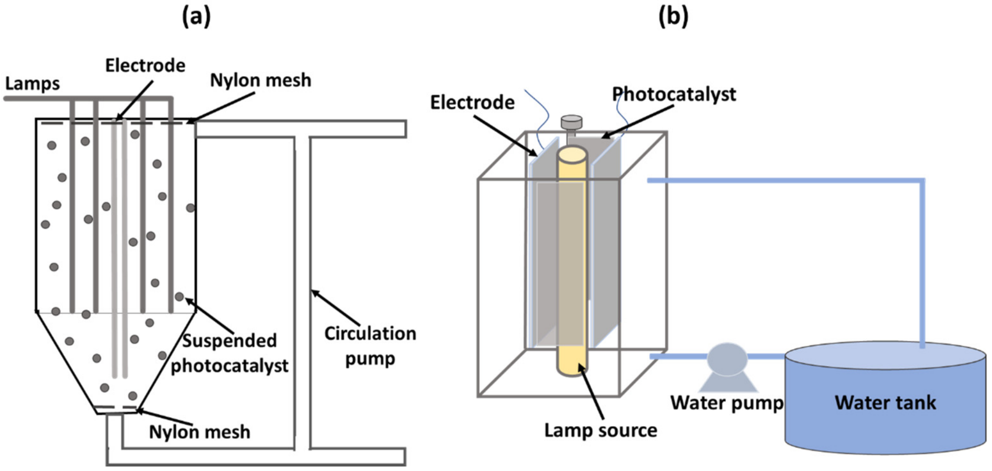

Figure 5. (**a**) Photoelectrocatalytic device adapted from Wang et al. [26]. (**b**) Photoelectrochemical device adapted from Feng et al. [39].

As part of the electrochemical devices, at present, the studies reported low efficiencies due to the poor conductivity in the solution, and some authors have proposed the addition of a high concentration of electrolyte to overcome this drawback [114], but the practical application of the method is still limited. As reported in Table S1 and Section 2.1, the combined action between the photolysis and electrolysis was adopted by different authors, but the low electrochemical efficiency and purification capacity seems to be difficult to solve. A possible solution is proposed by Feng et al. [39]: the photoelectrochemical reactor described (Figure 5b) is provided with a supported photocatalyst (TiO_2 film supported on a plate-shaped, filament-shaped, or net-shaped support formed of glass, ceramic, titanium plate, PVC or activated carbon fiber) and the electrochemical components (cathode—Ti, Pt, Fe, Al, Cu, or stainless steel; and anode—Pt, Ti, RuO_2, IrO_2, or RuO_2-Pt) in the same reactor; the light source ($\lambda < 365$ nm) is disposed in the middle of the reactor, the latter connected to a water supply tank, wherein a fixed amount ($0 \div 0.3$ g/L) of the chloride ions is added according to the chloride ion concentration of the water to be treated.

As discussed in Section 2, several authors have identified in microreactors a promising alternative to the traditional reactor design, and some of the most interesting technology reported in the reviewed patents will be discussed in the following. Wang et al. [93] for instance, proposed a photocatalytic microreactor (Figure 6a) composed of an optical fiber supported on a porous glass sand separator and connected with a light-transmitting sheet. The control of the temperature is carried out with a double-layer jacket filled with liquid medium and the recommended photocatalyst is TiO_2. With respect to the other inventions, the photocatalytic microreactor proposed allows the improvement of the exposed area to volume ratio, of the light utilization, and the life of the photocatalyst. Finally, the control of temperature allows the utilization of the system under normal or modified pressure. As a possible limitation, the weak interaction between the catalyst and the microchannel forming the reactor may be considered, which results in an increase in the operational costs due to the loss of photocatalyst.

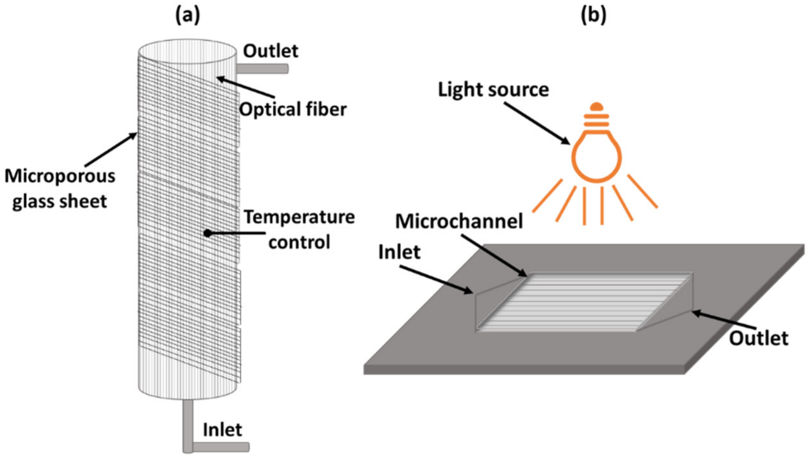

Figure 6. Photocatalytic microreactors adapted from (**a**) Wang et al. [93] and (**b**) Cheng et al. [27].

To overcome the drawback related to the loss or the difficult regeneration of the material, a different approach was adopted by Cong et al. [16], which proposed a photocatalytic device grafted with nanostructures in a microchannel (metal substrate), and a highly specific surface area supported catalyst grafted onto the microreactor by chemical bonding. The device is composed of a micro-feed pump, a microreactor, and a light source. The metal organic frameworks are recommended as a photocatalyst, due to the large specific surface area and porosity (easy introduction of additional active sites that enhance photocatalytic activity), easy functional modification, as well as the highly controllable structure. The proposed microreactor was able to improve the efficiency of photodegradation with respect to other inventions and to limit the costs. Another constraint of the industrial dissemination of the photocatalytic microreactors is clearly related to the limited throughput of each microchannel, as reported by Cheng et al. [27]. The small, irradiated area and the low processing capacity of a single microchannel are solved by the authors adopting a metal-ion-doped titanium-dioxide-plate-type photocatalytic microreactor (Figure 6b), wherein the stainless-steel plate substrate has a groove as a single channel reaction region (loaded with the photocatalyst). The use of a microchannel groove reaction zone increases the reaction volume and raw material processing capacity, and increases the light receiving area of the reactor, for continuous large-scale use of sunlight, while the stainless-steel plate (as a good light-reflecting material) enhances the efficiency of the light source; finally, as widely reported in the literature [115,116], the photocatalytic efficiency of the metal-doped TiO_2 is greatly improved with respect to the bare TiO_2.

2.3. Standardized Tests for Photocatalytic Water Treatment

One final remark in the field is the need for international standardized procedures for the evaluation of the performances of the proposed inventions. A very common practice in the patent literature is to claim improved performance with respect to the previous state-of-art on the basis of arbitrary tests. However, it is well known that the number of variables and target compounds that can affect water treatment by means of photocatalytic devices is very large; thus, results obtained under different conditions on different target molecules cannot be directly compared. At present, the available ISO tests only consider the intrinsic properties of the material under unrealistic conditions in real applications on a few target compounds—i.e., methylene blue and dimethyl sulfoxide (DMSO). It is desirable that in the future, standardized protocols will be provided to compare the performances of photocatalytic treatment units in more realistic conditions, taking into account the actual design of the devices. For a detailed discussion of available ISO tests, the reader can refer to [117]. In Section 3.4, an analogous discussion is provided for photocatalytic air treatment devices.

3. Air Treatment

Despite several similarities of the adopted devices, air treatment poses its own challenges compared to water treatment. In the case of air treatment, TiO_2 is also the most ubiquitous photocatalyst for VOCs (volatile organic compounds) removal and disinfection (Figure 2); it is adopted in 50% of the reviewed patents, whereas about 13% presents modified or doped TiO_2; these percentages cover almost the entire literature, considering that about 25% of the patents do not explicitly indicate a photocatalyst type and mainly focus on the device design. Specifically, most patents reviewed in this work in the field of photocatalytic air treatment deal with the design of devices for indoor air treatment, from homes to workplaces, livestock farms to cars cabins, and only a very few patents are adaptable to the field of industrial emissions; this demonstrates that photocatalytic devices are still far from being applied to emissions control and are mainly used to treat small volumes of gas in enclosed environments or for personal protection, e.g., for face-covering filters.

A scheme of a typical photocatalytic air treatment device is shown in Figure 7. It consists of: (i) a fan to induce convective flow of air through the device, that can be located at the inlet and/or the outlet of the device; (ii) an optional HEPA (high efficiency particulate air) filter to remove most of the particulate present in the gas flow that can negatively affect the next stages of treatment; (iii) an optional negative air ionizer (NAI) to further remove particles; (iv) a photocatalytic unit irradiated by one or more light sources; contrary to what shown for water treatment in the case of air treatment, the catalyst is almost always immobilized on a carrier; and (v) additional optional filters (activated carbon filter, etc.).

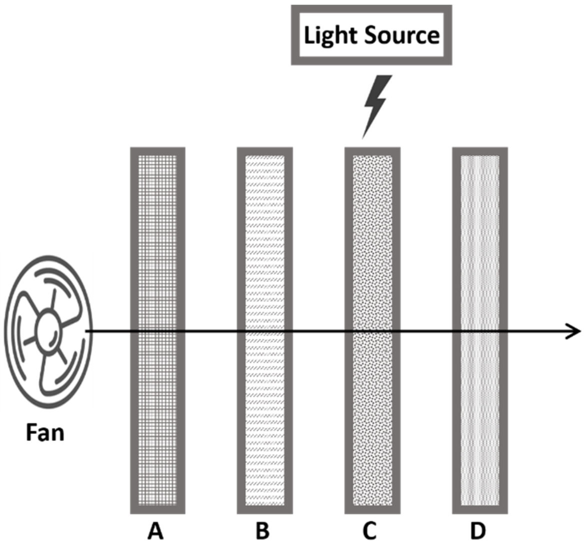

Figure 7. Scheme of the stages of a typical photocatalytic air treatment device. (**A**) HEPA filter; (**B**) negative air ionizer (NAI); (**C**) photocatalytic unit; (**D**) optional additional filters.

In the following, we discuss the main problems addressed by the reviewed patents. They can be grouped in four main categories:

- problems related to the chemical nature of the material, its interaction with light, and the photo-generated species (Section 3.1)
- problems related to the efficient utilization of the material and the device design (Section 3.2)
- problems related with some specific applications of the patented devices (Section 3.3)
- more general needs and trends in photocatalytic air purifiers (Section 3.4)

3.1. Materials, Light Interaction, and Photocatalytic Reactions

As outlined in the introduction of Section 3, TiO_2 is still the most adopted photocatalytic material for air treatment devices. However, it is well-known that TiO_2 can only efficiently work as a photocatalyst under UV irradiation [118]. Most of the considerations outlined in Section 2 for water treatment materials are still valid for air purification. In the patent literature of the last decade, authors still follow the traditional approaches outlined in the scientific literature and the previous patent publication: (i) adoption of UV sources; (ii) modification of TiO_2 or adoption of different materials that can photocatalyze VOCs and pathogens degradation under visible light irradiation. In this last case, this can be realized by either reducing the band gap of the material or by introducing impurities forming intra-band-gap energy levels [119]. It has been widely reported that the replacement of oxygen in $TiO_{2\text{-}x}A_x$ with A being N, C, S, F can activate TiO_2 for the decomposition of organics under visible irradiation [120–122]. Other common techniques are the doping with metals (Au, Ag, Cu, Co, Pt, Mn, Fe, etc. [120]) or coupling with other metal oxides such as Cu_2O, WO_3, and CeO_2 [123–126]. In particular, semiconductor coupling can create effective charge carrier separation and inhibit electron–hole recombination.

In the patent literature, common proposed alternatives to TiO_2 are: ZnO, SnO_2, ZrO_2, PbO_2, WO_3, $SrTiO_3$, Fe_2O_3, and CdS [127–129]. A more detailed list is provided in [130], also including co-doped materials such as $Na_2Ti_6O_{13}$, $BaTi_4O_3$, $K_2La_2Ti_3O_{10}$, $K_4Nb_6O_{17}$, $Sr_2Nb_2O_7$, $K_3Ta_3Si_2O_{13}$, $LiTaO_3$, $NaTaO_3$, $KTaO_3$, $BaTa_2O_6$, $CaTa_2O_6$, $RbNdTa_2O_7$, $SrTa_2O_6$, $Sr_2Ta_2O_7$, $RbNbWO_6$, $RbTaWO_6$, $CsNbWO_6$, $CsTaWO_6$, $ZnGa_2O_4$, $LiInO_2$, $NaInO_2$, $CaIn_2O_4$, $SrIn_2O_4$, Zn_2GeO_4, Sr_2SnO_4, $NaSbO_3$, $CaSb_2O_6$, $Ca_2Sb_2O_7$, $Sr_2Sb_2O_7$, $LaTiO_2N$, $CaNbO_2N$, TaON, Ta_3N_5, $CaTaO_2N$, $SrTaO_2N$, $BaTaO_2N$, $LaTaO_2N$, $TiON_x$, $Ti_{1\text{-}x}Ta_xO_{2\text{-}x}N_x$, $LaTaON_2$, and $TiO_{2\text{-}2x}N_xF_x$.

Doping with noble metals to increase the activity in the visible light spectrum has been proposed with Au, Ag, Ru, Pd, Os, Ir, and Pt [129].

Ag/TiO_2 was proposed with LED emitting between 100 and 400 nm in [131], demonstrating a formaldehyde removal of 90% and a sterilization capacity of 80% in 24 h. The same material is proposed by Su et al. [132], together with a detailed methodology for its preparation; in this patent, to obtain the photocatalytic modified material, a titanium mesh is used as anode in a 6 g/L Na_3PO_4 electrolytic solution and a steel plate cathode under a voltage of 270–310 V for 4 to 8 min. A total of 0.04 mol/L of $AgNO_3$ is then added and the voltage applied for other 3 to 6 min.

Another patented protocol for metal-doping is described by Lei et al. [133], consisting in the preparation of 1–2% wt. of the metal precursor solution ($Cu(Ac)_2$, $AgNO_3$, $FeCl_3$, $CoCl_2$, $Ni(NO_3)_2$, $Tb(NO_3)_3$, $Eu(NO_3)_3$) with respect to the weight of bare TiO_2, in 20% butyl titanate ethanol solution, followed by impregnation of the carrier, drying, and calcination.

Photodeposition of one or two metals on the surface of a porous metal oxide in water solution under UV irradiation, and in the presence of organics (e.g., methanol), is proposed by Jang et al. [134]. Metal oxides can be chosen among TiO_2, WO_3, ZnO, Nb_2O_5 or their combination, whereas photodeposited metals can be chosen among W, Cr, V, Mo, Cu, Fe, Co, Mn, Ni, Pt, Au, Ce, Cd, Zn, Mg, Ca, St, Ba, Ra, Pd, or their combination. In their patent, they stress that the metal wt. % with respect to the metal oxide must be in the range 0.1–10%. The prepared materials should be active in the range 380–500 nm. Lower content with respect to this range would lead to fast electron–hole recombination, whereas if the metal content is too high this would decrease exposed surface of the metal oxide, reducing the number of photo-generated electrons.

Zn- and Cu-modified TiO_2, and W- and Fe-modified TiO_2 are also used in their devices by Hersalek [135] and Cho et al. [136], respectively.

Coupling of different composites such as TiO_2/Ti and TiO_2/ACF (activated carbon fiber) have been proposed by Shuilin et al. [137], with a 90% removal of VOCs reported under UV irradiation. On the other hand, consecutive layers of TiO_2, Bi_2O_3, and a third non-metallic photocatalytic layer were reported as active materials under visible-light irradiation by Fu Lin et al. [138].

Other solutions proposed, include TiO_2-based materials treated with pigments, such as chlorophyll, carotene, and beet red pigments, to improve material absorption of visible light. With these modifications, Ping et al. [139] report the preparation of a photocatalytic coating that could remove 90% of tested formaldehyde in 60 h under simulated solar light.

Melamine-modified materials are claimed to be efficient under LED visible radiation. In particular, Duan et al. [140] proposed the use of melamine-modified TiO_2, whereas a more detailed protocol is provided by Siyu et al. [141], adopting graphitic carbon nitride (g-C_3N_4) under LED irradiation at 400–405 nm; in this case, the precursor of the active phase is prepared by treating melamine powder at high temperature (400–700 °C) under a nitrogen atmosphere.

Regarding the intrinsic material design discussed above, it is clear from the patent review that the main modification to bare TiO_2 targets the adoption of safer and cheaper visible light sources and the suppression of photo-generated electron–hole recombinant ion.

In the patent literature of the last 10 years, one can essentially find two main types of light source: (i) UV mercury lamps and (ii) UV and visible LEDs. Many patents stress the need to replace traditional UV mercury vapour lamps with LED strips, which are more efficient, cheaper, and easier to install/replace [127,131,140–148]. This is especially true for domestic systems, where the accidental exposition of users to UV light can be particularly hazardous; other concerns are related to the possibility of the accidental release of mercury vapours in confined spaces and the consequences on non-professional users' health. LED systems are also intrinsically smaller and allow for the optimization of the light irradiation, even for small devices such as the ones designed for vehicles cabins. It is worth stressing that many patents adopting UV LED systems for TiO_2 catalysts report that the best degradation performances were obtained with a peak wavelength between 360 and 370 nm [127,147,148], even though TiO_2 has an absorption peak at about 270 nm, and the absorption decreases almost linearly as the wavelength increases. The common indication is due to the light emission efficiency of LED strips, with the light intensity dramatically decreasing at lower wavelengths, which also explains the competitiveness of traditional UV lamps, despite their evident drawbacks. Some patents propose the combination of LEDs or light sources of different wavelengths for the simultaneous photocatalytic activation and sterilization of the material and the internal walls of the devices [127,130,144], also allowing for more flexibility when the device is not in use, or the pollutants levels are lower than threshold values, to save electrical power whilst keeping the device sterilized and clean.

Regarding the inhibition of the electron–hole recombination (reaction R2), together with the co-doping and coupling of different semiconductors, as discussed above, in the field of air purification a few photo-electrocatalytic devices also have been proposed, exploiting superimposed anodic bias to keep charges separated for a longer time and allowing for faster oxidation of the reactive species. This principle is adopted in [149], creating an electric connection between the adsorption module and the photocatalytic module of their device. Other photo-electrocatalytic devices have been proposed by [150,151], consisting of a photocatalytic anode and a cathode connected through an absorbent diaphragm, soaking up an electrolytic aqueous solution from a water tank that must be periodically filled by the user; the contact of the photocatalytic material with water also increases the presence of hydroxyl radicals that can oxidize VOCs.

To this merit, it is important to stress that, in the general mechanism reported for wastewater treatment (reactions R1–R10), in the case of air treatment, an important role can also be played by superoxide anions formed by the reaction of oxygen with photogenerated electrons, as reaction R9: $O_2 + e^- \rightarrow O_2^{\bullet -}$.

Superoxide anions are non-selective oxidizing species, such as hydroxyl radicals, but with a much longer lifetime [152]. For this reason, some patents proposed the deliberate introduction of water and/or oxygen in the system. In some cases, water curtains are used to absorb pollutants and particles than can then be treated using a photocatalyst [128]; Refs. [153,154] claim an improved device with an oxygen-enriched air system coupled with a trickle photocatalytic mesh covered by a water film resulting in 99.7% removal of PM2.5, 97% mortality of bacteria, and 99% removal of formaldehyde in 20 min. In [154], a spray chamber is included before the photocatalytic module with an atomizer dispersing water droplets in the air flow; the authors claim that this increases the photocatalytic activity by increasing the hydroxyl radical formation and also reflecting the light inside the photocatalytic module, thus increasing efficiency. In any case, these devices need to include a further post-treatment module to reduce water and oxygen concentrations in treated air to acceptable levels for the comfort of users.

3.2. Photocatalytic Module Design

In a previous patent review [155], it is clear that the main problems of air treatment photocatalytic devices are related to the low efficiency of such modules; specifically, these are mainly due to the (i) inefficient exploitation of light irradiation and (ii) the low contact time. A decade after, these are still the main difficulties that inventors try to address in their patents, suggesting that the scientific literature is mostly about the intrinsic nature of materials in relatively clean and controlled systems, with no clear indications on how to improve efficiency in practical use. The two problems of efficient light irradiation and contact time are highly interconnected in the case of photocatalytic devices, since an increase in the photocatalytic surface is a way to increase the contact time between the phases only if the surface is also efficiently irradiated by the light source; for this reason, the solutions provided in the reviewed patents will often be discussed simultaneously in the following. A simple solution is to increase the exposed surface by shaping the support appropriately. Many traditional devices propose one or more photocatalytic plates with holes to place tubular UV lamps through them (Figure 8a) [135,156,157], or with the light sources (either UV lamps or LEDs) placed in between the different plates (Figure 8b) [144,150,158,159].

Despite the fact that some level of porosity of the catalyst carrier is of course beneficial to VOCs degradation, it is important to take into account that light penetration in solid photocatalysts rapidly decreases with thickness [96] and, as also highlighted in the patent [160], the only effective way to increase the irradiation area is to increase the projected area of the light source on the photocatalytic material. Many patents address this issue by proposing different designs for the catalyst carrier. In [161], the ceramic support is folded in a W shape and placed around the tubular UV lamp, coaxial with the air flow (Figure 8c). In this symmetrical axial configuration, the lamp can easily irradiate the entire length of the carrier, but in the case of UV sources, it needs to be protected by a UV-transparent quartz sleeve; in this specific device, quartz glass is also covered with a layer of TiO_2 for self-cleaning, in order to avoid irradiation scavenging with time due to the deposition of particles. A conceptually similar solution is given in [149,162–164], where a corrugated surface or a mesh is placed around the light source. More complex axial geometries are represented by monolithic carriers, characterized by channels of different shapes and dimensions, internally covered with a layer of photocatalytic material (Figure 8d); in some patents, this configuration is replaced by a collection of tubings. In [165], a monolithic carrier is used surrounded by four tubular lamps; high removal efficiency is claimed, although it must be taken into account that activated carbon/TiO_2 composite filters are also provided at the inlet and outlet of the device. Another example of tubular structures with internal elements covered in TiO_2 is provided in [166]. These types of co-axial devices are usually preferred in those cases where higher pressure drops might be problematic, such as in the case of small and domestic devices, easily clogged and unpleasantly noisy when forced advection becomes difficult. In the patent [167], the number of tubular carriers inserted in the device and their diameter is decided based on pressure drop considerations; specifically, the approach suggested is to plot the experimentally measured permeability value provided by the Darcy law for different solutions vs. the exposed surface, choosing as optimal devices the ones located at the top right corner of the plot, combining large exposed areas with reasonable permeability; if such devices work under turbulent flow, most of the pressure drop is localized at the inlet of the tubing/channels so that if a higher exposed surface is needed, the best solution is to adopt longer channels, rather than decrease their hydraulic diameter in order to contain pressure drops; in any case, the best design will always be a compromise between degradation efficiency, contained pressure drops, and the maximum allowed dimensions of the device, depending on their specific final application.

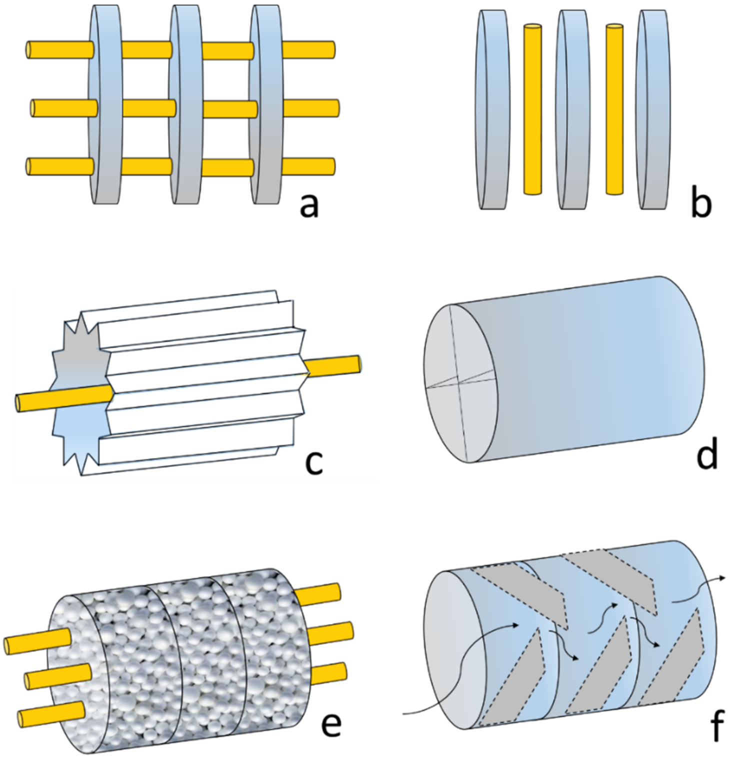

Figure 8. Scheme of recurrent device configurations to improve light exploitation and contact time. (**a**) Light sources passing through the catalytic support; (**b**) alternated light sources and catalytic support; (**c**) catalyst support shaped around the light source; (**d**) monolithic multichannel support; (**e**) packed bed or fibrous catalytic support; (**f**) baffles to enhance local turbulence.

Different solutions have been proposed when the authors did not explicitly try to contain pressure drops in the device. In [129], the porous support of the photocatalytic active phase is represented by porous silica or glass spheres with diameters of 1.5–2.5 mm and a pore size range of 1 nm–1000 μm, transparent to the chosen light source, with the lamps passing through the catalytic sphere bed (Figure 8e); interestingly, in this patent, the authors also took advantage of the beneficial effect of the increase in temperature caused by the adopted lamps to increase photocatalytic activity. Other ways to increase the contact surface have been proposed in [168], by adopting as a carrier a polymer in the shape of fine fibers, in [169,170], with complex networks and grid-like structures of the support. In some cases, the authors stressed the need to act on the flow patterns to increase the contact time and the efficiency of the devices: in [171], a system of baffles is deliberately inserted in the air flow in order to increase local turbulence, and thus, the contact between VOCs and the photocatalytic surface (Figure 8f); in [172], the inventors combine the principle of the local turbulence and transparent carriers, by depositing the photocatalytic material on the surface of transparent baffles. Inducing a more complex flow pattern is also the principle adopted in [173], wherein the device is internally shaped so that the air flow is deviated by moving deflectors and forced to pass through a more complex system of channels; in [141,146], air is forced through a spiral path: in the former, several photocatalytic units are placed along its length, whereas in the latter, the photocatalytic material is continuously dispersed along the channel; in this case, authors also claim that centripetal forces can be used to efficiently transport bacteria and pollutants towards the catalytic layer.

More unusual solutions to the problem of short contact time and reduced conversion per pass are represented by patents [174,175]. In the former, a fluidized bed reactor is used with particles of activated carbon loaded (0.1–0.3 mm) with nano-TiO_2; the fluidized state improves the mixing and the contact between the phases, which, combined with the adsorption capacity of activated carbon and the photocatalytic activity of TiO_2, results in good performance; however, it must be stressed that fluidized beds also introduce several other issues to address, such as the need of filters to avoid catalyst loss, the need for good mechanical properties of the catalytic material, and the possibility of formation of particle cakes at the outlet depending on the flow conditions, with a consequent increment in pressure drops. In the latter above-mentioned patent, the UV lamp is placed in the centre of the device and several support elements are attached to it, similarly to the blades of a mixer, and covered with the active phase; by rotating, these elements can also create turbulence and force the air flow. A similar but simpler static application of these principles is presented by Yuehua et al. [176].

As concerns irradiated light exploitation, reflective walls can be used to increase the photon flux on the catalytic surface, as shown in [177,178]. Very interestingly, when LEDs are adopted, different patents give a specific indication of the distance to adopt between the LED strips and the catalytic layer, usually between 2 and 40 mm, and preferably in the range 5–30 mm, so that the irradiation dose is in the range 12–18 mW/cm^2 [127,143,147,148,179], since UV doses higher than 18 mW/cm^2 do not give a significant increment in the photocatalytic activity and performance of the devices.

A final remark regarding the photocatalytic modules design is related to the problem of catalyst deactivation mainly due to (i) active phase losses and (ii) fouling.

Both problems are related to the long-term functionality of such devices. Despite the great importance of this aspect, this is rarely mentioned in the patent literature and most of the authors reporting the efficiency of removal/disinfection mostly operate a newly built device. The only patents we could find explicitly addressing the problem of active phase losses in the device are [135,180], both adopting a polymer-based carrier, in the form of fibres and a coating layer, respectively, to effectively keep the active phase nanoparticles on the support. More importance is given to active phase loss in [167], where adhesion of the photocatalyst to the support is discussed in detail, and two tests are used to assess it: (i) the adhesion tape test and (ii) a standard test at an air speed of 13 m/s to monitor the number of released TiO_2 nanoparticles using an ultrafine particle counter.

On the other hand, the problem of fouling is, in fact, almost always directly or indirectly mentioned in the patent literature. As shown in Figure 7, a photocatalytic air treatment device almost always includes one or more additional layers of filtration/purification, both to improve air quality but also to protect the photocatalyst and the light sources from dust, particles, and by-product deposition/adsorption. The most common operative solutions are represented by mechanical filters, HEPA (high efficiency particulate air) filters, activated carbon filters, and the use of electromagnetic fields, such as in the case of negative air ionizer, or more often, a combination of the above. The detailed discussion of the principles of operation of these well-established technologies is beyond the scope of the present work. However, in the following, we briefly discuss the main problems and most significant solutions proposed in the reviewed patents. Dust and solid particle removal is mostly tackled by using one or more gauzes and mechanical filters, often combined with an electrostatic precipitation filter, and HEPA filters in series [129,156]; however, this leads to relatively fast fouling of such filters, which then need to be cleaned or replaced [181]. Considering that dust removal is practically inevitable, different solutions have been proposed to improve the performance and durability of the devices. The most general principle is to use progressively finer filters in series [182], so that the more sophisticated ones can be replaced/washed less frequently. Whilst some patents stress the need for more practical and easy-to-disassemble devices for cleaning operations [183,184], others propose to use inclined devices as filters and photocatalytic carriers, in order to prevent dust and particles accumulation [177,185]; in some cases, these are coupled with vibrating motors to improve solids removal [177]. Some patents include dust chambers traps in their devices for the efficient collection and disposal of the collected particles [186,187]. Chemical filtration is often provided using activated carbon filters in series with the other elements of the device and at the inlet or the outlet of the device, depending on the specific situation. In one specific application [170], additional chemical filtration is provided by consecutive layers of alumina, sodium permanganate, potassium permanganate, and molecular sieves, due to the fact that the device is conceived for data-centre air purification, where the presence of several machines can release sulphides and NOx together with the usual VOCs found in closed environments. However, many authors stressed the fact that even though activated carbon can efficiently adsorb chemicals, they rapidly reach saturation, and if not properly replaced, they can release adsorbed species with time, worsening air quality [188]. For this reason, in many patents, activated carbon filters are combined with nano-TiO_2 deposited on the surface to combine the exceptional adsorption capacity of activated carbon with the photocatalytic regenerative action of titanium dioxide [142,165,170,174,189]. Even when TiO_2-modified activated carbon is not used, some authors have highlighted the need of also irradiating carbon activated filters and HEPA filters with UV light, which can otherwise become elements for the accumulation and growth of viruses and bacteria [188]. This was tackled by [190] by alternating HEPA filters and photocatalytic modules with UV lamps so that the UV light could conveniently irradiate both devices at the same time. Despite the adoption of filtration devices, and depending on their number and state, a certain amount of solid particles and/or volatile poisons can always reach the photocatalyst surface, decreasing its performance with time; to this merit, Jiwon et al. [191] proposed a method for the easy regeneration of photocatalytic filters: according to this patent, a photocatalytic material obtained by impregnation of a commercial P25 TiO_2 nanopowder in a solution of a silicon dispersant, calcinated at 400/500 °C, can be easily regenerated with boiling water; the so-prepared material was tested with target VOCs, demonstrating good performances after cycles of operation/regeneration.

Finally, it is important to mention that many patents include an NAI (negative air ionizer) or electromagnetic fields in their device [149,156,181,188,192]; an NAI uses high voltage to generate anionic species that are able to interact with solid particles and VOCs in the air to move them towards a collection point, a wall, a filter, or the photocatalytic surface. However, the corona discharge of air can generate ozone, representing a problem for closed environments, despite the beneficial effect that it can have in the photocatalytic module for the further oxidation of VOCs; as a result, ozone filters at the outlet of the device and/or absorption in water should be included in such devices.

3.3. *Specific Applications*

In this section, we highlight some peculiar aspects of the patent review related to specific applications of some inventions. One problem that a good number of patents claim to solve is the miniaturization of such air purifiers for portable applications or for the convenience of the users, in case, for example, the device is used for a car cabin. For these specific applications, the size of the photocatalytic unit is limited, and so is the number of units that can be included. Additionally, in this case, the use of filters (mechanical, electrostatic, HEPA, etc.) is difficult because they can be easily saturated, creating unpleasant noise and an increase in the pressure drop, often not compatible with the small dimensions of the fans. For this reason, many of these devices have no filters, take advantage of the LED technology and doping for visible light exploitation, and use porous catalyst carriers [138,143,148,193,194]. However, none of the authors patenting compact devices clearly explain how to overcome the problem of solid particle filtration; one possible solution would be to include such modules in the pre-existing air conditioning system. Modularity and the possibility of adapting the patented devices to pre-existing plants represents, in fact, an added value for many proposed photocatalytic purifiers. In this regard, the most common solutions consist of cylindrical photocatalytic modules that can be easily installed on tubing and pipes of pre-existing plants [161,192,195], or devices that can be integrated in pre-installed air conditioning systems [127,133,167,196,197].

Finally, it is worth mentioning some patents that addressed specific applications, representing completely original devices. Huang et al. [198] proposed a wallpaper consisting of paper covered with a layer of nano-TiO_2 and cyclodextrin, able to reduce VOC levels in closed rooms in the presence of natural light. The idea of including the photocatalytic device within one element of room decoration/furniture is also adopted in [135], proposing a bed frame with embedded photocatalytic elements and UV lamps to purify bedroom air. In [199], a miniaturized photocatalytic element was inserted in a face mask. In this case, the catalyst is in the form of a monolithic element consisting of consecutive layers of N-TiO_2, bismuth oxycarbonate, bismuth oxychloride, and/or carbon nitride, active under visible light irradiation.

3.4. General Observations and New Trends

Two final remarks suggested by the patent literature review concern the two emerging fields of (i) standardization of tests for the evaluation of the device activity and (ii) digitalization and autonomous control of the described devices.

The problem of standard tests to evaluate the performances of air purifiers is of crucial importance in order to easily assess and compare the devices and avoid claims not based on evidence or based on partial evidence. The problem is not trivial, since the disinfection and degradation efficiency are, in many cases, also a function of air parameters, such as temperature, humidity, solid particles content and distribution, time of operation, etc.

To this merit, it is important to mention, as highlighted in [167], that in the last decade, ISO standards were proposed to test photocatalytic materials for the removal of VOC removal (NO, acetaldehyde, and toluene), antibacterial action, and UV lamps [117]. The tests are based on the evaluation of the following fundamental quantities under controlled conditions:

$$percentage\ removal = \frac{q_{i0} - q_i}{q_{i0}} \cdot 100\% \tag{1}$$

$$moles\ removed = \left(\frac{60\,f}{22.4}\right) \cdot A \tag{2}$$

$$photocatalytic\ rate\ per\ unit\ area = \frac{q_{i0} \cdot f}{S} ln\left(\frac{1}{1 - \frac{q_i}{q_{i0}}}\right) \tag{3}$$

where q_{i0} is the initial concentration of target pollutant (ppm), q_i is the concentration at the end of the test (ppm), f is the flow rate of test gas (L/min), A is the amount of removed target pollutant (ppm/h), and S is the surface area of the catalytic material. However, these standards are designed to test the intrinsic properties of the material excluding mass transfer effects, and, in general, gradients of any quantities in the actual devices.

Different patents have proposed methods to test their own devices, also using mixtures of pollutants, such as ammonia, acetic acid, and acetaldehyde [136], or formaldehyde and/or bacterial colonies [137,153,200].

Patent [201] describes a device that is conceived to run standardized tests on photocatalytic air purifiers. In particular, this device can accurately adjust air parameters such as pressure, oxygen concentration, temperature, humidity, and flow rate, and force it through the device to be tested and then to GC-MS analysis, quantifying conversion per pass on target pollutants and the concentration levels of their degradation products; this last point is particularly relevant as many tests only focus on target molecules without considering that oxidized intermediated and by-products can in some cases be even more toxic than their parent compounds.

The concept of pollutant monitoring for testing, was extended in some patents to the continuous detection of target pollutants through embedded digital devices [145,192,202,203]. Very interestingly, the detectors shown in [192,202] are wireless and connected to internet or to internal updated databases to compare the actual concentrations with target levels. These applications pave the way for digitalized devices that can save energy when the air quality is acceptable, warn users when performances are decreasing, and be connected with other devices or centrally controlled databases for automatic updates and service, favouring their capillary diffusion.

4. Summary and Conclusions

The technologies proposed in the patents of the last decade and extensively discussed in this review clearly demonstrate the necessity to develop different materials able to improve the efficiency of photocatalytic wastewater and air treatment and, at the same time, to obtain a cost-effective process. Doping of the widely used TiO_2 with other semiconductors or metals were reported as possible solutions in the last 10 years. However, TiO_2 still remains the most ubiquitous material in several applications, together with its doping or combination with other oxides or active materials, both in water and air treatment. Combination of photocatalysis with anodic bias for photoelectrocatalytic applications is also still widely discussed.

Other common problems in the fields of water and air treatment are (i) the increase in the efficiency of the treatment devices by enhancing turbulence and thus contact between the phases, (ii) better utilization of light by including reflecting surfaces and transparent supports, and (iii) the adoption of safe and cheaper LED light sources.

Suspended solid catalyst is still the most common solution adopted for wastewater treatment, posing the problem of catalyst losses and recovery, tackled by immobilizing, filtrating, or magnetizing the catalyst. On the other hand, catalyst immobilization is the norm in air purifiers, with only a very few exceptions represented by fluidized bed reactors. Static and rotating annular reactors are the most adopted in water treatment, although improved solutions have been proposed in the last decade to conjugate efficiency, conversion per pass, and throughput. Air purifiers mostly rely on several stages of treatment coupling filters, ionisers, photocatalytic units, adsorbents, etc. Filtration can be crucial to avoid catalyst fouling. Where immobilized catalysts are adopted, corrugated surfaces or the radial disposition of several catalytic elements are the most common solutions to increase the exposed surface. Finally, in the patent literature about air treatment devices, many patents pose the challenge of increasing contacting between phases whilst at the same time containing pressure drops, which can dramatically affect performance, especially for small devices.

As concerns wastewater treatment, design optimization of reactors for industrial applications is still far from being fully developed. At present, microreactors are often proposed as a promising alternative to the traditional devices, despite some problems still being present, and their application seems likely only for the treatment of small volumes or specific studies. With the aim of a capillary diffusion of photocatalytic wastewater treatment on an industrial scale, a detailed cost analysis is necessary; for this purpose, in future works, an attempt to compare the technologies from an economic point of view should be carried out.

In the field of air treatment, the patents of the last decade mostly address indoor VOC and pathogen removal. Despite the great number of proposed solutions, the main issues seem to still be connected to the design of such purifiers, with particular interest in light utilization and contact between the phases to improve efficiency. User-friendly and energy-saving LEDs are increasingly adopted, also allowing the miniaturization of the devices for specific applications. The problem of solid particle removal in such photocatalytic air purifiers is still an open issue, considering that a good removal efficiency is often associated with high maintenance and frequent replacement of the filtering elements.

For both water and air treatment, the increasing adoption of digital control units for monitoring water/air quality and pollutant levels allows to (i) extend the life of light sources, (ii) reduce the operation costs, and (iii) guarantee a constant quality level of treated volumes.

Finally, the need for standardized testing procedure is emerging, considering the large number of patents claiming to improve efficiency with respect to previously reported devices based on arbitrary tests under a variety of different conditions.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/catal11070834/s1: Table S1: summary of the most significant patent reviewed in the field of photocatalytic water treatment (2010–2020); Table S2: summary of the most significant patent reviewed in the field of photocatalytic air treatment (2010–2020).

Author Contributions: Conceptualization, D.R.; investigation, M.M. and D.R.; writing—original draft preparation, M.M. and D.R.; writing—review and editing, M.M. and D.R.; visualization, M.M. and D.R.; supervision, D.R. Both authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Data Availability Statement: Data sharing not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Evans, A.E.; Mateo-Sagasta, J.; Qadir, M.; Boelee, E.; Ippolito, A. Agricultural Water Pollution: Key Knowledge Gaps and Research Needs. *Curr. Opin. Environ. Sustain.* **2019**, *36*, 20–27. [CrossRef]
2. Ahmed, S.; Ismail, S. Water Pollution and its Sources, Effects & Management: A Case Study of Dehli. *Int. J. Curr. Adv. Res.* **2018**, *7*, 10436–10442. [CrossRef]
3. Crini, G.; Lichtfouse, E. Advantages and Disadvantages of Techniques Used for Wastewater Treatment. *Environ. Chem. Lett.* **2019**, *17*, 145–155. [CrossRef]
4. World Health Organisation (WHO). Air Quality Standards under the Air Quality Directive, and WHO Air Quality Guidelines. Available online: https://www.eea.europa.eu/themes/data-and-maps/figures/air-quality-standards-under-the (accessed on 7 July 2021).
5. Loeb, S.K.; Alvarez, P.J.J.; Brame, J.A.; Cates, E.L.; Choi, W.; Crittenden, J.; Dionysiou, D.D.; Li, Q.; Li-Puma, G.; Quan, X.; et al. The Technology Horizon for Photocatalytic Water Treatment: Sunrise or Sunset? *Environ. Sci. Technol.* **2019**, *53*, 2937–2947. [CrossRef]
6. Hernández-Ramírez, A.; Medina-Ramírez, I. *Photocatalytic Semiconductors Synthesis, Characterization, and Environmental Applications*; Hernández-Ramírez, A., Medina-Ramírez, I., Eds.; Springer: Cham, Switzerland, 2015; ISBN 9783319109985.
7. Wang, H.; Zhang, L.; Chen, Z.; Hu, J.; Li, S.; Wang, Z.; Liu, J.; Wang, X. Semiconductor Heterojunction Photocatalysts: Design, Construction, and Photocatalytic Performances. *Chem. Soc. Rev.* **2014**, *43*, 5234–5244. [CrossRef] [PubMed]
8. Souza, R.P.; Freitas, T.K.F.S.; Domingues, F.S.; Pezoti, O.; Ambrosio, E.; Ferrari-Lima, A.M.; Garcia, J.C. Photocatalytic Activity of TiO_2, ZnO and Nb_2O_5 Applied to Degradation of Textile Wastewater. *J. Photochem. Photobiol. A Chem.* **2016**, *329*, 9–17. [CrossRef]
9. Monteagudo, J.M.; Durán, A.; San Martín, I.; Carrillo, P. Effect of Sodium Persulfate as Electron Acceptor on Antipyrine Degradation by Solar TiO_2 or TiO_2/RGO Photocatalysis. *Chem. Eng. J.* **2019**, *364*, 257–268. [CrossRef]
10. Mathew, S.; Ganguly, P.; Rhatigan, S.; Kumaravel, V.; Byrne, C.; Hinder, S.J.; Bartlett, J.; Nolan, M.; Pillai, S.C. Cu-Doped TiO_2: Visible Light Assisted Photocatalytic Antimicrobial Activity. *Appl. Sci.* **2018**, *8*, 2067. [CrossRef]
11. Krýsa, J.; Waldner, G.; Měšt'ánková, H.; Jirkovský, J.; Grabner, G. Photocatalytic Degradation of Model Organic Pollutants on an Immobilized Particulate TiO_2 Layer. Roles of Adsorption Processes and Mechanistic Complexity. *Appl. Catal. B Environ.* **2006**, *64*, 290–301. [CrossRef]
12. Gaya, U.I.; Abdullah, A.H. Heterogeneous Photocatalytic Degradation of Organic Contaminants over Titanium Dioxide: A Review of Fundamentals, Progress and Problems. *J. Photochem. Photobiol. C Photochem. Rev.* **2008**, *9*, 1–12. [CrossRef]
13. Chen, H.; Huang, K.; Xu, W. Sewage Treatment Composite Artificial Wetland System. CN209957604U, 17 January 2020.
14. Fu, T.; Ji, D.; Xu, D.; Zhu, J. Photocatalytic Water Purification Device Based on G-C3N4. CN107986385A, 5 May 2018.
15. Zhai, A. Photocatalytic Water Treating Device. CN106430401A, 22 February 2017.
16. Li, C.; Liu, Y.; Sun, Z.; Wang, A.; Wang, Y.; Yu, Z. Photocatalysis Device with Nanostructure Grafted in Micro-Channel. CN211988550U, 24 November 2020.

17. Feng, G.; Yan, W. Cyclone Type Photo-Catalytic Reaction Apparatus. CN102976533A, 20 March 2013.
18. Chen, X.; Chu, X.; Fang, F.; Fang, X.; Li, J.; Sun, S.; Wang, F.; Wang, X.; Wei, Z.; Xu, Y. Photo-Catalytic Reactor for Degrading Organic Substance. CN103159288A, 10 June 2013.
19. Turchi, C.S.; Ollis, D.F. Photocatalytic Degradation of Organic Water Contaminants: Mechanisms Involving Hydroxyl Radical Attack. *J. Catal.* **1990**, *122*, 178–192. [CrossRef]
20. Milnes, A.G.; Feucht, D.L. Fabrication of Heterojunctions. *Heterojunctions Met. Semicond. Junctions* **1972**, 226–305. [CrossRef]
21. Huang, L.; Peng, F.; Wang, H.; Yu, H.; Li, Z. Preparation and Characterization of Cu_2O/TiO_2 Nano–Nano Heterostructure Photocatalysts. *Catal. Commun.* **2009**, *10*, 1839–1843. [CrossRef]
22. Sakthivel, S.; Geissen, S.U.; Bahnemann, D.W.; Murugesan, V.; Vogelpohl, A. Enhancement of Photocatalytic Activity by Semiconductor Heterojunctions: α-Fe_2O_3, WO_3 and CdS Deposited on ZnO. *J. Photochem. Photobiol. A Chem.* **2002**, *148*, 283–293. [CrossRef]
23. Bessekhouad, Y.; Robert, D.; Weber, J.V. Photocatalytic Activity of Cu_2O/TiO_2, Bi_2O_3/TiO_2 and $ZnMn_2O_4/TiO_2$ Heterojunctions. *Catal. Today* **2005**, *101*, 315–321. [CrossRef]
24. Kalamaras, E.; Lianos, P.; Sfaelou, S.; Tantis, I. Photocatalytic Fuel Cell System for Producing Electric Energy or Hydrogen by Means of Electromagnetic Radiation. GR1008900B, 5 December 2016.
25. Gong, Y.; Li, Y.; Liu, B.; Peng, Y.; Wang, Y.; Xiao, S. Organic Wastewater Photocatalytic Treatment Device. CN110921890A, 27 March 2020.
26. Hu, X.; Li, Y.; Wang, Q.; Zhang, W. Photoelectrocatalysis Device Used for Treating Refractory Organics. CN102358635B, 22 February 2012.
27. Lin, C.; Liu, M.; Yang, Z. Metal Ion-Doped Titanium Dioxide Plate-Type Photocatalytic Microreactor and Preparation Method for Catalyst Thin Films in Reactor. CN104147994A, 19 November 2014.
28. Cao, X.; Kuang, J.; Liu, W.; Sun, P.; Zhuang, S. All-Weather Visible Photocatalytic Emergent Water Purifying Cup. CN109160649A, 8 January 2019.
29. Thind, S.S.; Rozic, K.; Amano, F.; Chen, A. Fabrication and Photoelectrochemical Study of WO_3-Based Bifunctional Electrodes for Environmental Applications. *Appl. Catal. B Environ.* **2015**, *176–177*, 464–471. [CrossRef]
30. Wang, N.; Li, X.; Wang, Y.; Quan, X.; Chen, G. Evaluation of Bias Potential Enhanced Photocatalytic Degradation of 4-Chlorophenol with TiO_2 Nanotube Fabricated by Anodic Oxidation Method. *Chem. Eng. J.* **2009**, *146*, 30–35. [CrossRef]
31. Shen, Y.; Li, F.; Li, S.; Liu, D.; Fan, L.; Zhang, Y. Electrochemically Enhanced Photocatalytic Degradation of Organic Pollutant on β-PbO_2-TNT/Ti/TNT Bifuctional Electrode. *Int. J. Electrochem. Sci.* **2012**, *7*, 8702–8712.
32. Garcia-Segura, S.; Brillas, E. Applied Photoelectrocatalysis on the Degradation of Organic Pollutants in Wastewaters. *J. Photochem. Photobiol. C Photochem. Rev.* **2017**, *31*, 1–35. [CrossRef]
33. Asmussen, R.M.; Tian, M.; Chen, A. A New Approach to Wastewater Remediation Based on Bifunctional Electrodes. *Environ. Sci. Technol.* **2009**, *43*, 5100–5105. [CrossRef]
34. Fan, L.; Li, F.; Li, S.; Liu, D.; Ning, Z.; Shen, Y. Method for Preparing PbO2-Modified TiO2 Nanotube Electrode. CN102534718A, 4 July 2012.
35. Cao, Y.; Deng, W.; Fang, J.; He, X.; Jiang, J.; Mao, D.; Zou, J. Double-Functional Beta-FeOOH/Eg-C3N4 Composite Nanomaterial and Preparation Method and Application Thereof. CN109317184A, 12 February 2019.
36. Cao, S.; Li, F.; Liu, Y.; Shi, J.; Xu, S.; Zhang, L. Symmetric Difunctional Photocatalyst, Double-Chamber Photoreactor and Method for Photocatalytic Reduction of Carbon Dioxide. CN105749914A, 13 July 2016.
37. Asmussen, R.M.; Chen, A.; Tian, M. Method and System for Combined Photocatalytic and Electrochemical Wastewater Remediation. CA2762209A1, 25 November 2010.
38. Lefebvre, O.P.; Mousset, E.; Wang, Z. A Photoelectrochemical Cell for Wastewater Treatment and Method of Fabricating the Photoelectrochemical Cell. U.S. Patent No. 2019194041A1, 27 June 2019.
39. Feng, C.; Li, W.; Wang, S.; Wu, L.; Zhang, F. Device and Method for Removing Organics from Water. CN101863548A, 20 October 2010.
40. Shang, J.; Wang, Q. Photoelectrocatalytic Device and Method for Reducing Heavy Metal Ions Using Same. CN101913678B, 15 December 2010.
41. Nagasawa, A.; Sugawara, H.; Takahashi, K. Apparatus and Method for Decomposing Organic Substance in Pure Water. JP2011120967A, 23 June 2011.
42. Hou, J.; Huang, B.; Hui, Z.; Li, M.; Liu, Y.; Pi, J.; Song, Q.; Wang, Y.; Zhang, Z.; Zhou, J. Photoelectric Combined Catalytic Water Purification Device. CN212076499U, 24 December 2020.
43. Lu, Z.; Ni, M.; Su, X.; Lu, Z.; Ni, M.; Su, X. Photodegradation Purification Device for Sewage Treatment. CN210193481U, 27 March 2020.
44. Mascolo, G.; Comparelli, R.; Curri, M.L.; Lovecchio, G.; Lopez, A.; Agostiano, A. Photocatalytic Degradation of Methyl Red by TiO_2: Comparison of the Efficiency of Immobilized Nanoparticles versus Conventional Suspended Catalyst. *J. Hazard. Mater.* **2007**, *142*, 130–137. [CrossRef] [PubMed]
45. Dong, H.; Zeng, G.; Tang, L.; Fan, C.; Zhang, C.; He, X.; He, Y. An Overview on Limitations of TiO_2-Based Particles for Photocatalytic Degradation of Organic Pollutants and the Corresponding Countermeasures. *Water Res.* **2015**, *79*, 128–146. [CrossRef]

46. Ahmad, R.; Ahmad, Z.; Khan, A.U.; Mastoi, N.R.; Aslam, M.; Kim, J. Photocatalytic Systems as an Advanced Environmental Remediation: Recent Developments, Limitations and New Avenues for Applications. *J. Environ. Chem. Eng.* **2016**, *4*, 4143–4164. [CrossRef]
47. Pichat, P. *Photocatalytic Coatings*; Elsevier: Amsterdam, The Netherlands, 2014; Volume 4, ISBN 9780080965338.
48. Kemmitt, T.; Al-Salim, N.I.; Waterland, M.; Kennedy, V.J.; Markwitz, A. Photocatalytic Titania Coatings. *Curr. Appl. Phys.* **2004**, *4*, 189–192. [CrossRef]
49. Jiang, X.; Li, D.; Li, P.; Li, S.; Li, Z.; Wan, D.; Zhang, Y. Visible-Light Photocatalytic Nano Titanium Dioxide Floating Type Water Purification Material. CN103816883A, 28 May 2014.
50. Singh, J.; Khan, S.A.; Shah, J.; Kotnala, R.K.; Mohapatra, S. Nanostructured TiO_2 Thin Films Prepared by RF Magnetron Sputtering for Photocatalytic Applications. *Appl. Surf. Sci.* **2017**, *422*, 953–961. [CrossRef]
51. Pala, A.; Politi, R.R.; Kurşun, G.; Erol, M.; Bakal, F.; Öner, G.; Çelik, E. Photocatalytic Degradation of Cyanide in Wastewater Using New Generated Nano-Thin Film Photocatalyst. *Surf. Coat. Technol.* **2015**, *271*, 207–216. [CrossRef]
52. Herring, R. Photoreactor and Formulations for Environmental Remediation and Methods of Use Thereof. WO2020160638A1, 13 August 2020.
53. Chen, S.; Quan, X.; Song, L.; Yu, H. Photocatalytic Water-Treatment Sterilizing Equipment. CN103754982A, 30 April 2014.
54. GUAN, F. Photocatalytic Sterilizing Device for Water Treatment. CN106082391A, 9 November 2016.
55. Hou, H.; Liu, C.; Ji, M.; Zhu, Y.; Yang, Q.; Wang, C.; Xu, F. Photocatalytic Device for High-Salt Wastewater and System. CN106745475B, 15 October 2019.
56. An, Y.; Li, L.; Liu, W.; Sun, P.; Wang, F.; Zhuang, S. Water Treatment Module. CN108002481A, 8 May 2018.
57. Mendelow, A.S.; Modak, A.; Osumi, Y.T.C.; Pomeranz, S.F. Potable Water Producing Device. WO2020014218A2, 16 January 2020.
58. Guo, D.; He, Y.; Wang, D.; Zhang, J. Efficient Photocatalysis Water Treatment Method and Device. CN103086469A, 8 May 2013.
59. Tang, S. High-Efficiency Device for Treating Sewage and Waste Water COD by Photocatalysis. CN101780996A, 21 July 2010.
60. Zhang, J. Horizontal Photocatalytic Water Treatment Device. CN203333426U, 11 December 2013.
61. He, Z.; Huang, J.; Xiong, Z.; Zhang, G.; Zhang, W. Ultrasound-Assisted Photocatalysis Water Processing Device. CN103232090A, 7 August 2013.
62. Zhu, D. Dynamic and Photocatalytic Waste-Water Treating Device. CN104671330A, 3 June 2015.
63. Jiang, W.; Liang, B.; Sun, F.; Tian, W. Magnetic Coagulation Photocatalysis Reactor and Photocatalytic Wastewater Processing Facility and Method. CN108928881A, 4 December 2018.
64. Jacinto, M.J.; Ferreira, L.F.; Silva, V.C. Magnetic Materials for Photocatalytic Applications—A Review. *J. Sol Gel Sci. Technol.* **2020**, *96*, 1–14. [CrossRef]
65. Sun, D.; Wang, J.; Yuan, X.; Zhang, X. Preparation Method of Magnetic Separation Titanium Dioxide Visible Light Catalyst. CN101850251A, 6 October 2010.
66. Iervolino, G.; Vaiano, V.; Sannino, D.; Rizzo, L.; Galluzzi, A.; Polichetti, M.; Pepe, G.; Campiglia, P. Hydrogen Production from Glucose Degradation in Water and Wastewater Treated by Ru-$LaFeO_3/Fe_2O_3$ Magnetic Particles Photocatalysis and Heterogeneous Photo-Fenton. *Int. J. Hydrog. Energy* **2018**, *43*, 2184–2196. [CrossRef]
67. Shi, F.; Li, Y.; Zhang, Q.; Wang, H. Synthesis of $Fe_3O_4/C/TiO_2$ Magnetic Photocatalyst via Vapor Phase Hydrolysis. *Int. J. Photoenergy* **2012**, *2012*, 365401. [CrossRef]
68. Zhang, L.; Wang, W.; Zhou, L.; Shang, M.; Sun, S. Fe_3O_4 Coupled BiOCl: A Highly Efficient Magnetic Photocatalyst. *Appl. Catal. B Environ.* **2009**, *90*, 458–462. [CrossRef]
69. Bielan, Z.; Sulowska, A.; Dudziak, S.; Siuzdak, K.; Ryl, J.; Zielińska-Jurek, A. Defective TiO2 Core-Shell Magnetic Photocatalyst Modified with Plasmonic Nanoparticles for Visible Light-Induced Photocatalytic Activity. *Catalysts* **2020**, *10*, 672. [CrossRef]
70. Su, T.L.; Chiou, C.S.; Chen, H.W. Preparation, Photocatalytic Activity, and Recovery of Magnetic Photocatalyst for Decomposition of Benzoic Acid. *Int. J. Photoenergy* **2012**, *2012*, 909678. [CrossRef]
71. Sun, F.; He, J.; Wu, P.; Zeng, Q.; Liu, C.; Jiang, W. Magnetic Photocatalyst $CoFe_2O_4$-Ag_2O with Magnetic Aggregation Bed Photocatalytic Reactor for Continuous Photodegradation of Methyl Orange. *Chem. Eng. J.* **2020**, *397*, 125397. [CrossRef]
72. Huang, X.; Jiang, Z.; Wu, C.; Xie, Q.; Yao, Y. Magneto-Optical Sewage Treatment Apparatus. CN102942283A, 27 February 2013.
73. Gulyas, H. Solar Heterogeneous Photocatalytic Oxidation for Water and Wastewater Treatment: Problems and Challenges. *J. Adv. Chem. Eng.* **2016**, *4*, 1–11. [CrossRef]
74. Sacco, O.; Vaiano, V.; Sannino, D. Main Parameters Influencing the Design of Photocatalytic Reactors for Wastewater Treatment: A Mini Review. *J. Chem. Technol. Biotechnol.* **2020**, *95*, 2608–2618. [CrossRef]
75. Claes, T.; Fransen, S.; Degrève, J.; van Gerven, T.; Enis Leblebici, M. Kinetic Optimization of Multilayered Photocatalytic Reactors. *Chem. Eng. J.* **2020**, *421*, 127794. [CrossRef]
76. McCullagh, C.; Skillen, N.; Adams, M.; Robertson, P.K.J. Photocatalytic Reactors for Environmental Remediation: A Review. *J. Chem. Technol. Biotechnol.* **2011**, *86*, 1002–1017. [CrossRef]
77. Sundar, K.P.; Kanmani, S. Progression of Photocatalytic Reactors and It's Comparison: A Review. *Chem. Eng. Res. Des.* **2020**, *154*, 135–150. [CrossRef]
78. Braham, R.J.; Harris, A.T. Review of Major Design and Scale-up Considerations for Solar Photocatalytic Reactors. *Ind. Eng. Chem. Res.* **2009**, *48*, 8890–8905. [CrossRef]

79. Enesca, A. The Influence of Photocatalytic Reactors Design and Operating Parameters on the Wastewater Organic Pollutants Removal—A Mini-review. *Catalysts* **2021**, *11*, 556. [CrossRef]
80. Xing, Z.; Zong, X.; Pan, J.; Wang, L. On the Engineering Part of Solar Hydrogen Production from Water Splitting: Photoreactor Design. *Chem. Eng. Sci.* **2013**, *104*, 125–146. [CrossRef]
81. Kuvarega, A.T.; Mamba, B.B. Chapter 19. Photocatalytic Membranes for Efficient Water Treatment. In *Semiconductor Photocatalysis—Materials, Mechanisms and Applications*; Cao, W., Ed.; IntechOpen: London, UK, 2016. [CrossRef]
82. Feiying, W. Continuous Selenomethionine Wastewater Photocatalytic Treatment Device. CN209668815U, 22 November 2019.
83. Gong, Y.; Li, X.; Liu, H.; Mu, M. Photocatalytic Degradation Treatment Device of Wastewater with Organic Pollutants. CN206705734U, 5 December 2017.
84. The Inventor Has Waived the Right to be Mentioned. Photocatalytic Water Purification Device. CN110950401A, 3 April 2020.
85. Da, I.H. Swimming Pool Water Treatment System with Photocatalytic Module. CN109502844A, 22 March 2019.
86. Liu, Y.; Xie, L. Photocatalytic Oxidation-Membrane Separation Circulating Fluid Bed Reaction Device. CN101875001B, 3 November 2010.
87. Wang, J.; Zhang, Y.; Zhong, K. Photocatalytic Water Storage Tank for Sewage Treatment. CN110723805A, 24 January 2020.
88. Niu, L. Adsorption and Photocatalysis Water Treatment Device. CN210559840U, 19 May 2020.
89. Huang, Z.; Situ, W.; Wei, C.; Zhang, G. Photocatalytic Water Purifier Based on Solar Energy Driving. CN106396212A, 15 February 2017.
90. Subramanian, M.; Kannan, A. Photocatalytic Degradation of Phenol in a Rotating Annular Reactor. *Chem. Eng. Sci.* **2010**, *65*, 2727–2740. [CrossRef]
91. Huihui, S.; Huili, W.; Qinglu, W.; Song, Z.; Zhongfu, Z. Equipment for Novel Photocatalysis Water Treatment. CN204550132U, 12 August 2015.
92. Janczarek, M.; Kowalska, E. Computer Simulations of Photocatalytic Reactors. *Catalysts* **2021**, *11*, 198. [CrossRef]
93. Ma, X.; Wang, C.; Xu, L. Titanium Dioxide Photo-Catalytic Micro-Reactor. CN102580651A, 18 July 2012.
94. Ray, A.K.; Beenackers, A.A.C.M. Development of a New Photocatalytic Reactor for Water Purification. *Catal. Today* **1998**, *40*, 73–83. [CrossRef]
95. van Gerven, T.; Mul, G.; Moulijn, J.; Stankiewicz, A. A Review of Intensification of Photocatalytic Processes. *Chem. Eng. Process. Process. Intensif.* **2007**, *46*, 781–789. [CrossRef]
96. Russo, D. Kinetic Modeling of Advanced Oxidation Processes Using Microreactors: Challenges and Opportunities for Scale-Up. *Appl. Sci.* **2021**, *11*, 1042. [CrossRef]
97. Rao, L.; Shi, Z.; Wang, P. Stacked Double-Helix Photocatalytic Purifier Suitable for High-Concentration Wastewater. CN111943312A, 17 November 2020.
98. Gu, B.; Mou, M.; Yang, P.; Zhao, H. Water Treatment Device for Promoting Photocatalytic Reaction. CN210656249U, 2 June 2020.
99. Niu, L. UV Photocatalysis Sewage Treatment Device. CN210340579U, 17 April 2020.
100. He, Y.; LI, F. Photocatalytic Water Treatment Equipment. CN211521900U, 18 September 2020.
101. Chen, W.; Chen, Y.; Lyu, W. Photocatalytic-Biological Degradation Water Treatment Device and Method. CN108751332A, 6 November 2018.
102. Niu, L. Novel Photocatalytic Water Treatment Device. CN210974241U, 10 July 2020.
103. Liu, Q.; Liu, Y.; Tong, D.; Wang, D.; Zeng, Q.; Zhou, X. Photocatalytic Sewage Treatment Device. CN211619995U, 2 October 2020.
104. Han, J.; Song, C.; Xu, W.; Zhu, J.; Zhu, Y. Photocatalytic Water Treatment Equipment for Light Guide Medium Supporting Catalysts. CN204265477U, 15 April 2015.
105. Chen, L.; Zhao, X. Photocatalytic Reaction Purifying Device. CN106745486A, 31 May 2017.
106. Lee, S.H.; Lee, T.J.; Lee, Y.H. Method and Apparatus for Enhanced Photocatalytic Oxidative Decolorization of Wastewater Containing Reactive Anthraquinone Dye. U.S. Patent No. 2012118833A1, 17 May 2012.
107. Dai, X.; Liu, G.; Sun, Y.; Wang, L.; Wang, S. Method for Treating Dry Distillation Sewage of Oil Shale. CN101857284A, 13 October 2010.
108. Chen, S.; Quan, X.; Wang, S.; Yu, H. Continuous Flow Photocatalytic Water Treatment Device. CN106006921A, 12 October 2016.
109. Du, G.; Liu, M.; Liu, W.; Shen, X.; Yang, X. Photocatalysis Water Treatment Disinfecting Equipment Who Possesses Photovoltaic Power Generation Control. CN205275256U, 1 June 2016.
110. Jiang, L.; Li, Y.; Wang, J.; Wang, W. Skid Mounted Equipment of Upper Spreading In-Diffusion Vertical-Push Photocatalytic Waste Water Treatment. CN107055895A, 18 August 2017.
111. Liang, B.; Shi, W.; Wei, Y.; Zuo, X.; Liang, B.; Shi, W.; Wei, Y.; Zuo, X. Photocatalytic Reactor and Wastewater Treatment System Comprising Same. CN210193463U, 27 March 2020.
112. Guo, H.; Hong, Y.; Liang, R.; Lin, A.; Lin, J.; Ye, X. Spiral Photocatalytic Water Purifier. CN210974267U, 10 July 2020.
113. Bi, J.; Shan, L. Photocatalytic Treatment Waste Water Device. CN208200444U, 7 December 2018.
114. Li, M.; Feng, C.; Hu, W.; Zhang, Z.; Sugiura, N. Electrochemical Degradation of Phenol Using Electrodes of Ti/RuO_2-Pt and Ti/IrO_2-Pt. *J. Hazard. Mater.* **2009**, *162*, 455–462. [CrossRef]
115. Wilke, K.; Breuer, H.D. Transition Metal Doped Titania:Physical Properties and Photocatalytic Behaviour. *Z. Phys. Chem.* **1998**, *1*, 333–338. [CrossRef]
116. Basavarajappa, P.S.; Patil, S.B.; Ganganagappa, N.; Reddy, K.R.; Raghu, A.V.; Reddy, C.V. Recent Progress in Metal-Doped TiO_2, Non-Metal Doped/Codoped TiO2 and TiO2 Nanostructured Hybrids for Enhanced Photocatalysis. *Int. J. Hydrog. Energy* **2020**, *45*, 7764–7778. [CrossRef]

117. Mills, A.; Hill, C.; Robertson, P.K.J. Overview of the Current ISO Tests for Photocatalytic Materials. *J. Photochem. Photobiol. A Chem.* **2012**, *237*, 7–23. [CrossRef]
118. Clarizia, L.; Russo, D.; di Somma, I.; Andreozzi, R.; Marotta, R. *Metal-Based Semiconductor Nanomaterials for Photocatalysis*; Elsevier Ltd.: Amsterdam, The Netherlands, 2018; ISBN 9780081019788.
119. Tryba, B.; Rychtowski, P.; Markowska-Szczupak, A.; Przepiórski, J. Photocatalytic Decomposition of Acetaldehyde on Different TiO_2-Based Materials: A Review. *Catalysts* **2020**, *10*, 1464. [CrossRef]
120. el Saliby, I.; McDonagh, A.; Erdei, L.; Shon, H.K. Water Reclamation by Heterogeneous Photocatalysis over Titanium Dioxide. *Green Technol. Sustain. Water Manag.* **2016**, 679–704. [CrossRef]
121. Abdullah, A.M.; Garcia-Pinilla, M.Á.; Pillai, S.C.; O'Shea, K. UV and Visible Light-Driven Production of Hydroxyl Radicals by Reduced Forms of N, F, and P Codoped Titanium Dioxide. *Molecules* **2019**, *24*, 2147. [CrossRef] [PubMed]
122. Peng, X.; Fu, J.; Zhang, X.; Li, Y.; Huang, M.; Huo, K.; Chu, P.K. Carbon-Doped Tio_2 Nanotube Array Platform for Visible Photocatalysis. *Nanosci. Nanotechnol. Lett.* **2013**, *5*, 1251–1257. [CrossRef]
123. Muscetta, M.; Andreozzi, R.; Clarizia, L.; di Somma, I.; Marotta, R. Hydrogen Production through Photoreforming Processes over Cu_2O/TiO_2 Composite Materials: A Mini-Review. *Int. J. Hydrog. Energy* **2020**, *45*, 28531–28552. [CrossRef]
124. Han, J.; Li, Y.; Yang, L.; Li, T.; Luo, Y.; Yang, L.; Luo, S. Mesoporous TiO_2 with WO_3 Functioning as Dopant and Light-Sensitizer: A Highly Efficient Photocatalyst for Degradation of Organic Compound. *J. Hazard. Mater.* **2018**, *358*, 44–52. [CrossRef] [PubMed]
125. Lu, B.; Li, X.; Wang, T.; Xie, E.; Xu, Z. WO_3 Nanoparticles Decorated on Both Sidewalls of Highly Porous TiO_2 Nanotubes to Improve UV and Visible-Light Photocatalysis. *J. Mater. Chem. A* **2013**, *1*, 3900–3906. [CrossRef]
126. Contreras-García, M.E.; García-Benjume, M.L.; Macías-Andrés, V.I.; Barajas-Ledesma, E.; Medina-Flores, A.; Espitia-Cabrera, M.I. Synergic Effect of the TiO_2-CeO_2 Nanoconjugate System on the Band-Gap for Visible Light Photocatalysis. *Mater. Sci. Eng. B Solid State Mater. Adv. Technol.* **2014**, *183*, 78–85. [CrossRef]
127. Jeong, J.H.; Jeong, W.K.; Kim, J.W.; Shin, S.C. Photocatalytic Module for Automobile Air Conditioner and Automobile Air Conditioner Having the Same. U.S. Patent No. 10737556B2, 11 August 2020.
128. Chen, J.; Yao, Y. High-Energy Ultrasonic Coupling Photocatalytic Air Purification System. CN102506468B, 19 February 2014.
129. Han, J.; Lu, H.; Yao, S. Photocatalytic Air Purifier. CN106512722A, 22 March 2017.
130. Beckers, L.J.A.M.; Ronda, C.R.; Valster, S.M. An air Purification Device, a Lighting Device and a Luminaire. WO2016020115A1, 11 February 2016.
131. Zeng, Q. Photocatalysis Air Purification Device and Air Conditioner. CN204902056U, 23 December 2015.
132. Su, H.; Sun, R.; Sun, Z.; Zhang, H.; Zhang, S. Silver-Loaded Photocatalytic Air Purifier. CN104930614A, 23 September 2015.
133. Lei, Y. Special Nano-Crystalline Photocatalytic Air Purifier Mechanism for Air Conditioner. CN204084616U, 7 January 2015.
134. Jang, H.-Y.; Jung, S.-M.; Kim, H.-N.; Lee, D.-I.; Seo, J.-H. Visible Light-Activated Photocatalytic Coating Composition and Air Purification Filter. U.S. Patent No. 10449519B2, 22 October 2019.
135. Hersálek, M. Photocatalytic Filter Device for Air Purification, Based on Titanium Oxide Combined with Colloidal Copper and Zinc. EP3095516A1, 23 November 2016.
136. Cho, G.; Jeong, J.; Kim, J.; Ku, H.K.; Lee, D.Y.; Suh, D.; Yi, J.; Yoon, K.S. Photocatalytic Filter for Degrading Mixed Gas and Manufacturing Method Thereof. U.S. Patent No. 2018029017A1, 1 February 2018.
137. Li, S.; Shi, J.; Wang, Y.; Zheng, Q. Utilize Composite Material's Photocatalysis Air Purification Device. CN204710107U, 21 October 2015.
138. Zhou, Y.; Li, W.; Li, H.; Fu, L. On—Vehicle Air Purification Device of Integral Photocatalysis. CN206446410U, 29 August 2017.
139. Wang, P.; Xing, Z.; Zhu, Q. Novel Photocatalytic Coating for Purifying Indoor Air and Preparation Method of Novel Photocatalytic Coating. CN109370280A, 22 February 2019.
140. Duan, Q.; Fu, M.; Guo, H.; Huang, Y.; Li, J.; Liao, J.; Luo, Q.; Zuo, X. Indoor Air Purifier. CN203469810U, 12 March 2014.
141. Chen, S.; Cheng, W.; Fei, Z.; Sun, Z.; Wang, H.; Wang, K.; Wu, Z.; Yu, Z. Photocatalytic Air Purification Device. CN203540331U, 16 April 2014.
142. Wei, W.; Yang, R.; Yu, Q.; Zhang, Z. Photocatalytic Air Purifier. CN104841270A, 19 August 2015.
143. Kim, J.-W.; Shin, S.-C.; Yi, J.-S. Compact Air Cleaner Using UV Led and Photocatalytic Filter. CN105987443A, 5 October 2016.
144. Chen, Y.; Huang, Z.; Li, Y.; Liu, J.; Wei, Y.; Zhang-Wen, Q.; Zhao, W.Z.Y. High Efficiency Nanometer Photocatalytic Indoor Air Purifier. CN108278691A, 13 July 2018.
145. Ge, Y.; Song, W.; Wang, K.; Wang, K.; Wang, L.; Wang, Y.; Zhou, J. Photocatalytic Air Purifier. CN110743360A, 4 February 2020.
146. Polunin, G.A.; Zajnishev, A.V. Photo Catalytic Air Cleaner. RU2497584C1, 10 November 2013.
147. Jeong, J.H.; Koo, J.H.; Song, H.S. Multifunctional Photocatalytic Module. U.S. Patent No. 2019083674A1, 21 March 2019.
148. Byun, S.-H.; Jeong, J.-H.; Kim, J.-W.; Kim, J.-R.; Ko, I.-H.; Lee, S.-M.; Shin, S.-C.; Yi, J.-S. Compact Air Cleaner Using UV Led and Photocatalytic Filter. WO2016072774A1, 12 May 2016.
149. The Inventor has Waived the Right to be Mentioned. Novel Air Purification System. CN110748997A, 4 February 2020.
150. Wu, Y.; Zhu, J. Photoelectrocatalytic Coordinated Air Purification Device and Using Method Thereof. CN108905616A, 30 November 2018.
151. Wu, Y.; Zhu, J. Photoelectrocatalysis Synergistic Air Purification Device. CN208927931U, 4 June 2019.
152. Nosaka, Y.; Nakamura, M.; Hirakawa, T. Behavior of Superoxide Radicals Formed on Tio_2 Powder Photocatalysts Studied by a Chemiluminescent Probe Method. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1088–1092. [CrossRef]
153. Zeng, Q. Photocatalytic Water Curtain Oxygen-Enriched Air Conditioning System. CN111023338A, 17 April 2020.

154. Yang, B. Photocatalytic Structure of Air Treatment Equipment. CN208998226U, 18 June 2019.
155. Paz, Y. Application of TiO2 Photocatalysis for Air Treatment: Patents' Overview. *Appl. Catal. B Environ.* **2010**, *99*, 448–460. [CrossRef]
156. Jin, Y. Photocatalytic Air Purifier. CN107084451A, 22 August 2017.
157. Zheng, J. Nanometer Photocatalysis Air Purifier. CN108050601A, 18 May 2018.
158. Li, W.; Meng, J.; Sun, Y.; Zhong, Y. Photocatalytic Deodorization Device. CN203437034U, 19 February 2014.
159. Ayinqi. Photocatalysis Air Sterilization Purifier. CN206755403U, 15 December 2017.
160. Huang, Y.; Qin, X.; Yuan, Z.; Zhang, L. Photocatalytic Purification Subassembly for Air Purifier. CN206730182U, 12 December 2017.
161. Gao, X.; Liu, P.; Lu, J.; Song, X.; Zheng, J. Air Flue Type Photocatalysis Air Purifier. CN104089348A, 8 October 2014.
162. Kong, X. Detachable Photocatalytic Air Purifier Having Humidifying Function. CN105333518A, 17 February 2016.
163. Ayinqi. Photocatalysis Air Sterilization Purifier. CN206755402U, 15 December 2017.
164. Wang, X. Photocatalytic Waste Gas Treatment Device. CN209576310U, 5 November 2019.
165. Jia, L.; Shang, Q.; Tan, X.; Yu, T.; Zhang, Z. Box-Type Photocatalytic Air Purification Device. CN105289290A, 3 February 2016.
166. Bian, Y.; Dong, X.; Zhang, J. Air Purifier with Photocatalysis Function. CN110425658A, 8 November 2019.
167. Denys, S.; Lenaerts, S.; Modde, B.; Roegiers, J.; Van Walsem, J. Photocatalytic Reactor for Ventilation Systems. WO2019002430A2, 3 January 2019.
168. Tang, Y.; Zhang, G.; Zhang, X.; Zhao, T. Photocatalytic Fiber Air Purification Device and Using Method Thereof. CN111229029A, 5 June 2020.
169. Chen, H.; Wang, Y.; Yin, W.; Zhang, D.; Zhang, Q. Photocatalysis Air Cleaning Device. CN205815478U, 21 December 2016.
170. Gu, L.; Li, K.; Li, Y.; Liu, P.; Song, C.; Yang, H.; Yang, Z.; Zhang, Y. Improved Photocatalytic Deodorization Equipment. CN210278798U, 10 April 2020.
171. Lin, X. Photocatalytic Air Treatment Pipe. CN107261834A, 20 October 2017.
172. Liu, Y.; Zhang, X. Air Purification Device and Air Purification System. CN110056996A, 26 July 2019.
173. Cai, C. Photocatalytic Purification Device. CN107638799A, 30 January 2018.
174. Deng, C.; Liu, Y.; Tang, M.; Xian, P.; Xu, Y. Photocatalytic Fluidized Bed Air Purifier. CN103453591A, 18 December 2013.
175. Xu, W. Novel Tubular Photocatalytic Air Purification Device. CN204159209U, 18 February 2015.
176. Liu, Y.; Zhao, B. Medicine or Factor Controlled Release Film Bracket. CN206730183U, 12 December 2017.
177. Liu, G.; Sun, Y.; Xu, J.; Zhang, Y.; Zhou, Y.; Zhu, R. Photocatalytic Air Purification Device. CN110410893A, 5 November 2019.
178. Zupin, E. Photocatalytic Purifying Chamber for Air Purifier. WO2011135601A1, 3 November 2011.
179. Kim, J.H.; Kwon, B.K. High Efficiency Air Cleaning Module by Maximizing Photocatalyst Decomposition Time. KR20190072162A, 25 June 2019.
180. Tang, Y.; Zhang, G.; Zhang, X.; Zhao, T. Photocatalytic Fiber Air Purifier and Using Method Thereof. CN111229028A, 5 June 2020.
181. Cheng, M.; Ge, H.; Guo, Z.; Zhang, L. Photocatalytic High-Activity Air Pollution Treatment Device. CN104315612A, 28 January 2015.
182. Shi, W. Photocatalysis Room Air Purifier. CN208635242U, 22 March 2019.
183. Lin, H.; Mu, J.; Xu, J.; Zhao, J. Photocatalytic Air Processor. CN208927171U, 4 June 2019.
184. Chen, X.; Shen, W.; Zhang, Z. Photocatalysis Oxidation Air Purifier Structure. CN204365141U, 3 June 2015.
185. Duan, S.; Huang, C.; Li, D.; Li, S.; Liu, H.; Liu, R.; Xu, C.; Zhang, B.; Zhang, M. Photocatalytic Air Purifier for Livestock and Poultry Breeding Greenhouse. CN110425677A, 8 November 2019.
186. Sun, J.; Xie, X. Home Use Photocatalytic Deodorizing and Sterilizing Air Purifying Device. CN108844134A, 20 November 2018.
187. Lee, S.H. Air Purifier. WO2016163598A1, 13 October 2016.
188. Cheng, M.; Ge, H.; Gou, Z.; Zhang, L. Photocatalytic High-Activity Air Pollution Processing Device. CN204214056U, 18 March 2015.
189. Ai, M.; Wu, C. Photocatalytic Air Purifier. CN104990150A, 21 October 2015.
190. Jung, S.W. AIR CLEANER. KR20180079766A, 11 July 2018.
191. Kim, J.; Suh, D.; YI, J. Photocatalytic Filter. CN205019962U, 10 February 2016.
192. Du, G. Photocatalytic Air Sterilization Device. CN209864753U, 31 December 2019.
193. Byun, S.-H.; Kim, J.-R.; Ko, I.-H. Air Purifier. WO2016085171A1, 2 June 2016.
194. Gong, W. Automotive Glass Photocatalytic Air Purification Membrane. CN108771765A, 9 November 2018.
195. Wang, X.; Wang, X.; Wu, R.; Zhou, J. Photocatalytic Oxidization Device. CN105964139A, 28 September 2016.
196. Zhao, Y. Photocatalytic Air Purification Device. CN103736375A, 23 April 2014.
197. Kim, H.J.; Kim, J.H.; Lee, S.J. Air Conditioner for Vehicle with Photocatalytic Module. U.S. Patent No. 2017036516A1, 9 February 2017.
198. Gao, Y.; Huang, J.; Liu, Z. Inclusion Enriching-Photocatalytic Type Air Purification Paper. CN101649587A, 17 February 2010.
199. Zhou, Y.; Li, H.; Fu, L.; Li, W. Integral Photocatalytic Air Purification Gauze Mask. CN206641408U, 17 November 2017.
200. AYINQI. Photocatalysis Air Sterilization Purifier. CN206755426U, 15 December 2017.
201. Cao, W.; Liu, W.; Sun, P.; Wang, F.; Zhang, J. Testing Method for Performance of Photocatalytic Air-Purifying Material. CN105929048A, 7 September 2016.
202. Guo, Y.; Li, J.; Li, J.; Li, S.; Lin, L.; Luo, F.; Ou, Z.; Sun, Y.; Yu, Z.; Zhang, H. Harmful Gas Intelligent Monitoring Photocatalytic Purifying System Based on Internet of Things. CN108954510A, 7 December 2018.
203. Cao, G. Air Purifier. CN210320418U, 14 April 2020.