Photocatalytic Reactor as a Bridge to Link the Commercialization of Photocatalyst in Water and Air Purification

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Abstract: The development of clean and sustainable teleology is vital to treat the critical environmental pollutants. In the last decade, the use of photocatalytic reactors has been widely reported for organic pollutants degradation. From photocatalysis’s application in environmental remediation, the primary technical issue to scientists is always the efficiency. The enhanced photocatalytic efficiency is mainly depended on the materials improvement. However, the design of photoreactors lags behind the development of photocatalysts, which strongly limit the widespread use of photocatalysis technology in environmental remediation. The nanoparticles separation, mass transfer limitation, and photonic efficiency have always been problematic and restrict the high photocatalytic efficiency of photoreactors. To overcome these bottleneck problems, the most popular or newfangled designs of photoreactors employed in air and water treatment has been reviewed. The purpose of this review is to systematize designs and synthesis of innovative TiO$_2$-based photoreactors and provides detailed survey and discussion on the enhanced mechanism of photocatalytic performance in different TiO$_2$-based photoreactors. The most studied photoreactors are the following: packed bed reactor, film reactor and membrane reactor, which have some limitations and advantages. A comprehensive comparison between the different photocatalytic performance of TiO$_2$-based photoreactors is presented. This work aims to summarize the progress of TiO$_2$-based photoreactors and provides useful information for the further research and development of photocatalysis for water and air purification.

Keywords: TiO$_2$; photocatalytic reactors; organic contaminants; water and air purification

1. Introduction

The unabated release of industrial organic pollutants into the air and waterways has caused severe environmental pollution and destruction, which is one of the global and national problems [1–6]. With the development of clean energy and pursuit of green development, exploring clean and sustainable way for environmental remediation is overwhelming [7–10]. Since ‘Honda-Fujishima Effect’ was found in 1972, scientists have shown great concerned to develop semiconductor photocatalysis for sustainable environmental modification and energy generation [11–13]. This inspired potential application of photocatalysis for the removal of organic compounds [11,14–17].

Photocatalysis as a “green” remediation technology is one of the most sustainable methods to removal organic pollutants, which uses sunlight as the source of energy. Because of the ability to attain complete mineralization and zero end wastes, photocatalysis is one of the environmentally friendly treatment methods known so far [18]. Recently, photocatalysis by the use of light irradiations, a sustainable and favorable technology, has attracted much considerations because it is carried out at low temperature, normal pressure and without the requirement of high input energy [19]. Substantial development in the strategies to enhance
the efficiency of semiconductor materials has been accomplished [19]. Photocatalysis has great potential to alleviate the energy and environmental issues [13,20,21]. Recently, numerous photocatalysts have been developed for environmental remediation due to their effective, powerful, clean, and environment friendly [22–26]. The implementation of most photocatalysts at industrially feasible applications requires the photoreactor, a device which brings photons, photocatalysts and reactants into contact [27–31]. However, the progress of the photoreactor lags behind in development of semiconductor, which severely limit the widespread application of photocatalysis technology in environmental remediation. Several efforts have been devoted to the design and developments of photo-catalysts, however very little focus had been done before the development of the photocatalyst technology, especially in photocatalyst reactor development [32]. It is well known that organic pollution is commonly found in water bodies and the atmosphere. The concentration of pollutants in the atmosphere are strict limited for the reactor. The high concentrations tend to deactivate the catalyst and low reaction kinetics at low concentrations. Many researchers solve such problems by reactor design in recent years [33].

Photocatalysis is gaining recognition as an efficient wastewater remediation technique [34]. Photocatalytic reactor is one of the important factors affecting photocatalytic efficiency. Moreover, the efficient use of light and effective mass transfer in the water column have been the main factors limiting the reactor, and a better generalization of existing reactors and the construction of more efficient reactors is very meaningful [34,35]. Therefore, more effective reactor designs are desired to promote photocatalysis technology to practical applications.

In recent years, significant advances have been witnessed on the synthesis and application of photocatalyst in the air purification, wastewater treatment, and so on [36]. Moreover, the photocatalysis technology has been thought as an environment-friendly wastewater treatment approach since it utilizes light source as the energy. Photocatalysis have been a promising candidate to solve environmental problems due to its low-cost, non-toxic and efficient [34]. It requires minimum moderate-state chemicals at a reasonable time, and is effective in removing a wide range of pollutants from various media. It involves the more effective use of resources, the less of the total amount of outputs and the improvement of returns in monetary terms through the reduction of energy and material consumption.

Photocatalysis technology has attracted enormous research interest recently in solving water contamination problems, especially the degradation of organic pollutants due to its merits of high efficiency, high reaction rate, low toxicity, etc. [37–40]. Ren et al. reviewed that photocatalysis is suitable for treating with radioactive pollutants because of its high efficiency, no secondary pollution and wide application range [41]. Liang et al. reported that plasma/photocatalysis system which combines the advantage of non-thermal plasma with that of photocatalysts with synergetic effect is a high effective technology for decomposition of VOCs with low energy consumption [42]. Xu et al. concluded that the combined usage of plasma and photocatalysis, keeping a fit distance and setting a net of special material, may produce a considerable synergistic effect in air purification [43]. Lin et al. claimed that photocatalysis is proposed to be combined with other treatment processes, such as biological treatments, to partially reduce total organic carbon, break down macromolecular organic compounds, increase biodegradability, and reduce the toxicity of produced water [44]. Akinori et al. have studied on the decomposition of dye by photocatalysis, and considered that the photocatalysis with sonication is most effective for the decomposition of dye in this study [45]. The photocatalytic method is effective for the degradation of oxalic acid in suspension of TiO$_2$ irradiated with near-UV light [46]. Moreover, the photocatalysis technology has been thought as an environment-friendly wastewater treatment approach since it utilizes light source as the energy [47]. However, there is not sufficient information for practical applications of photocatalysis.

In order to compare the performance of different reactor configurations, it is vital to use and define fundamentally based efficiency parameters, which mainly contain the photonic efficiency ($\eta$) and the quantum efficiency ($\eta_{\text{Rxn}}$) [48]. The photonic efficiency
relates the rates of reactant molecules transformed or product molecules formed to the rate of incident photons \[49\] as follows:

\[
\eta = \frac{\text{Rate of reactant molecules transformed}}{\text{Rates of incident photons}} \tag{1}
\]

On this basis a more adequate photocatalytic efficiency should be established using the quantum efficiency parameter, which relates the photocatalytic reaction rate with the radiation absorption rate:

\[
\eta_{\text{Rxn}} = \frac{\text{observed reaction rate}}{\text{rate of photon absorption}} \tag{2}
\]

The analysis of rate of reactant molecules transformed, the photon absorption rate and the quantum efficiency are essential to developed photocatalytic reactors with high removal efficiency.

Regarding photocatalysts, TiO\(_2\) has become one of the ripest and most commercialized photocatalysts due to its physicochemical characteristics and high photocatalytic activity \[12,28,50–52\]. Besides, TiO\(_2\) is a material of wide interest for clean production and renewable energy. Many methods can be used to produce TiO\(_2\) particles, such as flame aerosol synthesis \[53\], hydrothermal synthesis \[54\], and sol–gel synthesis \[55\]. The main advantage of Flame aerosol synthesis is easily scalable to produce, but shows all the disadvantages of high temperature synthesis. The TiO\(_2\) crystalline powder are directly produced by Hydrothermal synthesis. However, it is difficult to control the overall process due to the lack of knowledge of the chemical equilibria, nucleation kinetics and growth of the different phases, which have a great influence on photocatalytic performance. The sol–gel chemistry synthesis plays a vital role in producing the porous structure of the TiO\(_2\) materials, which reduces the hydraulic resistance of TiO\(_2\) films and improves their photocatalytic activity. In 1985, Tadashi Matsunaga et al. firstly found that TiO\(_2\) had a bactericidal effect under ultraviolet light \[56\]. In recent years, several studies have investigated the behavior of sterilization on the photoexcited TiO\(_2\) surface and the sterilization effect of photoexcited TiO\(_2\) \[57–59\]. Kim et.al reported the investigation of the sterilization performance for the G. lamblia using a TiO\(_2\) photocatalytic system \[58\]. The TiO\(_2\) film was prepared by a modified hydrothermal method and attached to the UV-lamp. Under TiO\(_2\)/UV-irradiation system, the G. lamblia was rapidly sterilized and the sterilization performance increased at lower pH in initial step. J.C. Tello et al. designed a CPC reactor for solar photocatalytic disinfection to sterilize with F. solani spores \[59\]. The efficiency of solar photocatalysis was experimentally demonstrated in 14 L of distilled and natural well water in 5 h of treatment time. Hence, a review of TiO\(_2\)-based photoreactors designs focused on separation of photocatalyst, mass transfer, reaction kinetics, and irradiation characteristics were reported. We revealed the enhanced photocatalytic performance of these TiO\(_2\)-based photoreactors. This study aims to gain insights into the future progress of TiO\(_2\)-based photoreactors for environmental remediation.

2. Photocatalysis Mechanism of TiO\(_2\)

TiO\(_2\) has been commercially manufactured and shown to be the promising materials for energy and environmental applications \[26,60–63\]. TiO\(_2\) has three crystal types of rutile, anatase, and brookite. All these forms are described by distorted TiO\(_6\) octahedra with different symmetries or arrangements \[51,64,65\]. The anatase framework is composed of TiO\(_5\) octahedra with shared edge and the rutile and brookite structures show both corner and edge shared structure (Figure 1). The band gap of TiO\(_2\) 3.2 eV, which is the distance between the electronically filled valence band and empty conduction band. TiO\(_2\) exhibits an excellent photocatalytic activity and photostability for organic pollutants degradation and the detailed photocatalysis mechanism was shown in Figure 2 \[66\]. The electrons (e\(^-\)) and holes (h\(^+\)) are generated under the UV irradiation and the interfacial redox reactions
determine the photocatalytic activity [67,68]. In particular, the generation of H+, •OH, and active oxygen species via path 1,5 and 6 are useful for organic pollutants mineralization (path 7). Therefore, TiO2 as a clean energy has been widely used in fields of polluted water and air purification.

![Representations of the TiO2 anatase, rutile, and brookite forms](image)

**Figure 1.** Representations of the TiO2 anatase, rutile, and brookite forms [51]. Copyright 2014, American Chemical Society.

![Primary steps in the mechanism of TiO2 photocatalysis](image)

**Figure 2.** Primary steps in the mechanism of TiO2 photocatalysis [66]. Copyright 1995, American Chemical Society.

### 3. Types of TiO2-Based Photoreactors in Environmental Remediation

Recently, a wide variety of TiO2-based photoreactors have been investigated for organic contaminant degradation in polluted air and water [69–71]. This section summarizes the recent development of photoreactor designs and presents some advances on toxic organic pollutants removal processes.

#### 3.1. Application of TiO2-Based Photoreactors for Air Purification

Volatile organic compounds (VOCs) as the common air pollutants are mainly generated from industrial effluents, vehicle emissions and indoor ambient [25,72–76]. These organic molecules such as trichloroethylene, formaldehyde, benzene, and toluene can induce several respiratory diseases and then endanger public health [77–79]. Researches have demonstrated the immobilized TiO2 photoreactors of packed bed reactors and film reactors, which are effective for gas phase photocatalysis.

##### 3.1.1. Packed Bed Reactor

The packed bed reactor is consisted by catalysts, the support/carrier for immobilizing catalyst, the light source and the different/unique configuration [80–83]. Such reactors
used various supports or carriers exhibit the different properties for VOC degradation. Glass beads is a traditional support for TiO$_2$ immobilization. The packed bed with coated TiO$_2$ glass beads was applied for removing trichloroethylene (TCE) under 365 nm UV light irradiation [84]. The same model with supported TiO$_2$ based catalysts was also used for 1-butanol and 1-butylamine’s photo degradation, which can remove these model pollutants effectively [53]. Recently, a LED-illuminated packed bed reactor with coated TiO$_2$ glass beads fluidization builds an efficient system for VOCs (n-hexane, benzene, and toluene) abatement (Figure 3a) [85]. The bubbling regime creates the internal recirculation in the reactor, which can update the catalyst continuously in the strong artificial light areas and lead to a high photonic collection efficiency of the catalyst. Scattered TiO$_2$ immobilized on the clear glass spheres surface can promote light to permeate the bed (Figure 3b).

![Figure 3](image-url) Scheme describing the different parts of the fluidized bed photoreactor (a) and the schematic of VOCs removal mechanism (b) [85]. Copyright 2019, Elsevier.

Generally, the above packed reactors with zero-order kinetics shows low performance for the high concentrations VOCs removal. Then some other glass-based supports with different shapes are selected for TiO$_2$ immobilization. For example, nanofibers, nanowires, and nanorods with a protruded rod structure have been employed in photochemistry to intensify both mass and photon transfer, which can remove the mass transfer limitation, thereby exhibiting excellent photocatalytic properties for high concentrations VOC removal [86–88]. The annular photocatalytic reactor with four inlets and four outlets was studied (Figure 4a,b) [89–91]. The fiber glass support was consisting of randomly oriented fiber bundles with TiO$_2$ photocatalyst (Figure 4c,d). This support was inserted into two 1.8 mm glass tubes, which afford an optimal contact between TiO$_2$ and VOCs (1-propanol, TCE, and methanol) [89]. The removal efficiency of VOCs was 62%, which was attributed to the negligible mass transfer limitations in this reactor. The mechanism of the photocatalytic degradation of 1-propanol is also presented. Adsorbed 1-propanol can react with a hydroxyl radical (OH$^-$) to produce the 1-propanol radical as below (3):

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{OH}^- \rightarrow \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{H}_2\text{O} \quad (3)$$

The 1-propanol radical can react with oxygen to form propionaldehyde via the following Equation (4):

$$\text{CH}_3\text{CH}_2\text{CH}_2\text{OH} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{CHO} + \text{HO}_2^- \quad (4)$$
Then propionaldehyde can be directly oxidized by OH· to form a carbonyl radical (5) which can react with oxygen through the following series of reactions (6) and (7):

\[
\text{CH}_3\text{CH}_2\text{CHO} + \text{OH} \cdot \rightarrow \text{CH}_3\text{CH}_2\text{C} \cdot \text{O} + \text{H}_2\text{O} \quad (5)
\]

\[
\text{CH}_3\text{CH}_2\text{C} \cdot \text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{CH}_2\text{C} (\text{O})\text{OO} \cdot \quad (6)
\]

\[
2\text{CH}_3\text{CH}_2\text{C} (\text{O})\text{OO} \cdot \rightarrow 2\text{CH}_3\text{CH}_2\text{C} (\text{O})\text{O} \cdot + \text{O}_2 \quad (7)
\]

The carboxylate radical (CH₃CH₂C(O)O·) can be decomposed by β scission with a cleavage of C-C bond in order to produce an ethyl radical and carbon dioxide:

\[
\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{O} \cdot \rightarrow \text{CH}_3\text{CH}_2\cdot + \text{CO}_2 \quad (8)
\]

The formation of carbon dioxide has been highlighted by a homemade microreactor of methanation during the photocatalytic degradation of 1-propanol.

Carbon-based supporters can provide more active sites for adsorbing VOCs, which can enhance removal efficiency of the low-concentration VOCs [61,92–95]. Xi et al. investigated that low-concentration toluene (1–2 mg m⁻³) was rapidly decomposed in a plasma-driven photocatalyst reactor with TiO₂/activated carbon fiber as photocatalyst [92]. Another research reported a filter reactor using TiO₂/activated carbon as photocatalyst. Both TiO₂ and activated carbon were coated on non-woven fabric filter and toluene with low concentration (200–600 ppb) were used to test the photocatalytic performance [96]. As shown in Figure 5a,b, the toluene removal efficiency (93%) in the prepared filter reactor is higher than that of TiO₂ filter reactor (62%). This type reactor shows high stability for low-concentration VOCs removal. Based on the identified intermediates, a reaction mechanism for toluene degradation was proposed. The first step is the formation of benzyl alcohol from H-abstraction from the methyl group of toluene and OH· radical inclusion in the aromatic ring. In the subsequent reactions, benzyl alcohol was oxidized to produce benzaldehyde benzoic acid and then to CH containing intermediates and CO₂ through photo-Kolbe reaction.
The photocatalytic performance of packed bed reactor can be enhanced via the fluidization of coated TiO$_2$ glass beads, which was ascribed to the high photonic collection efficiency. The glass-based supporters with large surface areas can eliminate the mass transfer limitation and are very suitable for treating the high concentrations VOCs. The packed bed reactor with TiO$_2$ immobilization on carbon-based supporters can solve the pollution of VOCs at a low-concentration owing to the high adsorption capacity. Therefore, packing conditions such as supporter material and geometry of packed bed photoreactor has great effect on VOCs adsorption and light distribution, which play a great role for low-concentration VOCs removal.

3.1.2. Film Reactor

Although packed bed reactors can achieve a high utilization of catalyst, light intensity loss through the filler still present, which reduce the photocatalytic performance [97,98]. Film photoreactors with TiO$_2$ immobilized on the ‘wall’ of the support have been designed to overcome this drawback. Different film reactor designs such as flat glass plate reactor, tube reactors, spiral reactor, and annular reactor were reported [99–103]. These film reactors for VOCs removal were compared as follows.

The flat plate reactor with geometric dimension was investigated (Figure 6) [100]. Previous work demonstrated that the flat plate reactors are not suitable for high air throughput. Zhang et al. found that the number of mass transfer units is one of the main parameters influencing the photooxidation performance of the reactor [104]. To overcome this barrier, several types of reactors have been proposed towards process intensification. A plate film photoreactor with a network of static mixing chambers interconnected by transport channels was developed by Vítor et al. [102]. The degree of mixing inside the photoreactor can enhance the interface mass transfer, increasing the mobility of the photogenerated radicals from the catalyst surface to the boundary layer and promoting the oxidation reaction. Figure 6b indicated the structure of the experimental facility. The mixing device photoreactor (Figure 6c) was put into a solar radiation reactor. The results demonstrated that the network with micro chambers and channels can reduce VOCs diffusion distances and enlarge interfacial contact region, which can effectively enhance the contact between photocatalyst and pollutants [105–109]. Additionally, these networks sealed by borosilicate glass can facilitate penetration of light into the entire reactor. The photocatalytic
sheet was prepared by immobilizing TiO$_2$ on cellulose acetate and then placed between two borosilicate glass. This structure allowed a high uniform irradiation on the catalyst surface. As a result, this micro-meso-structured photoreactor exhibits an efficient photocatalytic oxidation performance for n-decane gas-phase, which is 1.4 times higher than that of the packed photoreactor of cellulose acetate support coupling with TiO$_2$.

![Figure 6](image1.png)

**Figure 6.** The geometric dimension of the plate-type reactor (a) [100]. Copyright 2007, Elsevier. Schematic representation of the microreactor facility: air stream generation unit; solar simulator with photoreactor; master gas chromatography analytic system (b) and Schematic representation of the photoreactor (c) [102]. Copyright 2017, Elsevier.

For further improving the illumination efficiency, effects of illumination mechanism (irradiated vis backside (BSI) or front side (FSI), Figure 7a) and light intensity on VOCs oxidation were studied [27]. Under the 9 LEDs system irradiation, the maximum reaction rate for FSI show a 1.1-fold increase in contrast with the BSI system (Figure 7b). A ∼3.6 folds increase on the maximum reaction rate was obtained when using the LED plate with 18LEDs (Figure 7c). Then under the condition of FSI illuminated by LED18, the micro-meso-structured photoreactor with higher photonic flux to the catalyst, generate a high density of charge carriers on the surface, react with the VOC pollutant.

![Figure 7](image2.png)

**Figure 7.** Schematic representation of back-side illumination or front-side illumination mechanisms (a). Photoreactor with LED 9 illumination system and LED 18 illumination system (b,c) [27]. Copyright 2019, Elsevier.
Therefore, the above plate film photoreactor with microchannels structure has a higher surface-to-volume ratio than conventional plate type photoreactors. This microstructure in plate film photoreactors can provide the remarkable mass transfer rates, short molecular diffusion distance, and better spatial illumination homogeneity, which makes the plate type reactor commercially.

Other plate film reactors have also been investigated. For example, Pumac et al. reported a multi-plate photocatalytic reactor (MPPR). This reactor is consisted by parallel TiO$_2$-coated plates and cylindrical UV lamps, which can provide a large irradiated surface area and high photonic efficiency (Figure 8a) [99]. Effective toluene oxidation in MPPR indicated that reactor geometry design is a promising approach to lower mass transfer resistance. Besides, the plate film reactors, tubular and annular film photoreactors are also the most common for VOCs degradation [101,103,110]. Shiraishi et al. indicated that proper arrangement of light source can enhance the photocatalytic decomposition of VOCs (acetone, isopropanol (IPA), and toluene) [101]. As shown in Figure 8b, circular arrangement shows a higher reactor performance than that of parallel arrangements. The surface of plate film can be fully irradiated by the intensity UV light when the glass tube reactor exhibits a circular arrangement. Vilar et al. reported an annular photoreactor for perchloroethylene (PCE) and n-decane oxidation. The commercially available TiO$_2$ was deposited onto the cellulose acetate, which was applied into the annular reactor (Figure 8c) [110]. The high photonic efficiency was obtained because the light illumination can radiate the entire reactor perimeter. The coating TiO$_2$ catalyst with large surface areas has more active sites, which further enhance the photocatalytic oxidation of VOCs. Therefore, specific attention should be given to the distribution of light energy and TiO$_2$ film coating for optimizing the photocatalytic reactor.

Verbruggen et al. developed a continuous flow spiral tube reactor. The silver-modified TiO$_2$ was coated on the inside of a glass tube, which was spiraled around a UVA lamp. This continuous contact reactor between silver-modified TiO$_2$ and light illumination pro-
vide a better illumination homogeneity, which contributed to a high photonic utilization (Figure 8d) [103]. The acetaldehyde is fully degraded when the residence time was 60 s in spiral reactor, which is 16.7 times than that of annular reactor. For providing more active sits of TiO$_2$, Hugode et al. immobilized TiO$_2$ on stainless steel mesh via an spray method [111]. The prepared uniform TiO$_2$ coating can avoid leaching and agglomeration of catalyst effectively. The quantum yields of the TiO$_2$ coating can reached up to 55–60% and such TiO$_2$ coated mesh exhibits an excellent photocatalytic degradation of 55.1 L acetone wastewater.

Although the light intensity quickly declines through the monolith type reactors, an efficient strategy for better illumination homogeneity was achieved by using the new reactor geometry and design, such as multi-plate photocatalytic reactor, annular/tubular photoreactors, and spiral tube photocatalytic reactor. According to the above results, reactor optimization should be conducted from those aspects of compact design, large throughput, optimal incident radiation, and reduced catalyst losses. Moreover, the comparison of above photoreactors as shown in Table 1.

Table 1. Various photoreactors parameters for pollutant degradation.

| Photoreactor                  | Radiation Parameters | Photocatalysis       | Ref. |
|------------------------------|----------------------|----------------------|------|
| Type                         | Volume (L)           | Flow Rate (L/min)    | Light Source | Intensity (W m$^{-2}$) | Period (min) | Materials and Dosage (g) | Pollutant | Concentration (mg/L) | Efficiency (%) |      |
| Packed bed reactor           | 0.1                  | -                    | UV-Vis       | 10           | 100          | FSP $^a$-made TiO$_2$ 0.000040 TiO$_2$ 0.000075 | RhB | 4.8 | 70 | [53] |
| Fluidized bed reactor        | 0.0025               | 0.1                  | UV LED       | 0.22         | 30           | TiO$_2$ 0.0057 | n-hexane | 200 | 80 | [85] |
| DBD$^b$ reactor              | 0.23                 | 5.0                 | UV lamp      | 41.1         | -            | Isovaleraldehyde 50 | n-decane | 1.86 | 83 | [102] |
| Film reactor                 | 5.57                 | 2000                | UV           | 15           | 480          | TiO$_2$-PET | toluene | 1.0 | 99 | [103] |
| Annular reactor              | 0.22                 | 0.22                | Sunlight     | 18.9         | 4320         | TiO$_2$-P25 0.0075 TiO$_2$ 0.0066 | n-decane | 200 | 100 | [103] |
| glass spiral reactor         | 0.033                | 1.6                 | UVA lamp     | 42           | 16.7         | TiO$_2$ 0.0053 | acetaldehyde | 71 | 100 | [110] |
| Film reactor                 | 0.22                 | 0.075               | UV           | 38.4         | -            | PC500 0.0523 | n-decane | 71 | 100 | [110] |

$^a$ flame spray pyrolysis, $^b$ dielectric barrier discharge.

3.2. Application of TiO$_2$-Based Photoreactors for Water Purification

Photocatalytic water treatment offers the dominant advantage of organic pollutants mineralization rather than transfer them from the water [87,112–114]. There has been significant research on the development of TiO$_2$-based photoreactors and examples of these various reactors have been reviewed.

3.2.1. Membrane Reactor

Some research works showed that TiO$_2$-based slurry photoreactor has a high mass transfer, which facilitated the organic pollutants degradation [115–117]. To overcome the problem of liquid-solid separation in this reactor, the membrane module combining with TiO$_2$ has been studied (Figure 9a,b) [118]. Zhang et al. indicated a ultrafiltration (UF) membrane (polyacrylonitrile 700), which was not only effective to separate the TiO$_2$ photocatalyst, but also showed a high permeate flux and stabilization [119]. A submerged ceramic membrane photocatalytic reactor was designed by Li et al. (Figure 9c), which inherits both advantages of TiO$_2$ photocatalysis and ceramic flat membrane separation technology [120]. This slurry photocatalytic membrane reactors exhibits an excellent mineralization ability and stability for textile and antibiotic wastewater treatment.
3.2. Application of TiO2-Based Photoreactors for Water Purification

The photocatalytic performance of suspension or immobilization system was compared by Espíndola, J.C. et al. (Figure 9d,e) [28]. TiO2-based slurry system showed a higher oxytetracycline (OTC) degradation ability than that of TiO2 immobilization system owing to the higher mass transfer efficiency. However, the formation of TiO2-based compact layer in the slurry system leads to a higher permeate flux decrease. TiO2 assembled on the membrane in immobilization system can improve its fouling resistance, thereby contributing to a lower decline on the permeate flux. Then TiO2 immobilized on the membrane make the immobilization system more suitable for continuous removal of organic pollutants.

3.2.2. Film Reactor

Some other researchers have fabricated the photocatalytic membrane reactors with TiO2 immobilized onto membrane [118,121]. For example, the prepared membrane photoreactor with TiO2 assembled on the porous ceramic filter tube exhibited an efficient mineralization for organic pollutants [122]. The photocatalytic performance of suspension or immobilization system was compared by Espíndola, J.C. et al. (Figure 9d,e) [28]. TiO2-based slurry system showed a higher oxytetracycline (OTC) degradation ability than that of TiO2 immobilization system owing to the higher mass transfer efficiency. However, the formation of TiO2-based compact layer in the slurry system leads to a higher permeate flux decrease. TiO2 assembled on the membrane in immobilization system can improve its fouling resistance, thereby contributing to a lower decline on the permeate flux. Then TiO2 immobilized on the membrane make the immobilization system more suitable for continuous removal of organic pollutants.

Figure 9. Configurations of photocatalytic membrane reactors: submerged membrane in a slurry reactor (a) and TiO2 coated reactor (b) [118]. Copyright 2014, Elsevier. Schematic of the submerged ceramic membrane photocatalytic reactor (SCMPR) (c) [120]. Copyright 2019, Elsevier. Schematic representation of reactor movable polypropylene flanges and membrane module with TiO2 in suspension (d) and with TiO2 immobilized on the membrane shell-side (e) [28]. Copyright 2019, Elsevier.
coating TiO₂ on tubular glass tubes (Figure 10c) [126]. This structure can improve the contact possibility of pollutants with catalyst, and then break the mass transfer limitation. Then the photocatalytic performance is comparable to the slurry system. Natarajan et al. also confirmed that the tubular photoreactor with coating TiO₂ on the quartz tube and LEDs irradiation has a high turbulent kinetic energy and long average residence time, thereby enhancing the efficiency degradation of dyes [127].

Figure 10. Light transport mechanism through the optical fiber and light delivery to the photocatalyst (a) and schematic of the optical fibers/LED reactor design (b) [124]. Copyright 2018, Elsevier. TiO₂ coated glass tubes in the tubular photoreactor chamber (c) [126]. Copyright 2004, Elsevier.

The film reactor with the step geometry structure have been investigated [128–131]. Because the presence of several breaks of the flow slope in the step geometry reactor can generate the backflow and turbulence, then improving mass transfer efficiency (Figure 11a) [128]. The mixed liquid flow can enhance the O₂ adsorption and accelerate transport of photocatalytic e⁻ from the TiO₂ surface to the O₂. This process can enhance the generation of active oxygen species (path 6, Figure 2) and this step geometry film reactor can mineralize organic pollutants such as pesticides efficiently. For the maximum mass transfer rate, Boiarkina et al. designed a rotating disc reactor and thin TiO₂ film was fabricated via the spin coating method (Figure 11b) [130]. This process can facilitate oxygen mass transfer from air to TiO₂ surface and then improve the separation efficiency of photogenerated carrier during the photocatalysis. The high the oxygen transfer rate contributed to the increase of reaction kinetics. The photonic efficiency of the photocatalytic spinning disc reactor is larger one order than that of the conventional annular reactor.

Figure 11. Falling film closed loop step photoreactor. Insert: detail of the steps with associated notation (a) [128]. Copyright 2011, Elsevier. Schematic diagrams of spinning disc reactor and annular reactor (b) [131]. Copyright 2013, Elsevier. Schematic diagrams of light utilization in different photocatalytic water treatment processes (c) and schematic diagram of the TiO₂/Ti wedge rotating disk photocatalytic reactor (d) [132]. Copyright 2015, Elsevier.
Although the photocatalytic spinning disc reactor exhibits an excellent performance for methylene blue degradation, plane structure with a high reflection causes an energy loss by irradiation. Li et al. designed the TiO$_2$/Ti wedge rotating disk photocatalytic reactor (Figure 11c,d) [132]. This wedge-shaped structure can increase the illumination area and provide the multiple light reflections. Therefore, the wedge disk exhibits a higher photonic utilization than that of the planar disk. Meanwhile, rotating speed of the treatment disk is critical for mass transfer, that of both pollutants and oxygen on the surface of the wedge disk enhanced with the increase of rotating speed up to 20 rpm. The optimized geometry of film reactor and the design of film structure are effective to improve the light utilization and mass transfer, thus promoting the degradation efficiency of organic pollutants.

3.2.3. Packed-Bed Reactor

The implementation of the packed-bed reactor with TiO$_2$ immobilization onto solid support shows great potential in wastewater treatment and have been developed [133–137]. The degradation reaction was mainly limited by external mass transfer under our investigated conditions. It appeared that the reaction was in photon limited regime with high flow rate for the residence time <20 s, and was limited by mass transfer for the residence time >20 s. As shown in Figure 12a,b, the developed packed-bed reactor can shorten the light path and increase the photonic collection efficiency [138]. The packing structure can introduce the perturbation to the laminar flow, which minimize the transfer route of organic pollutant and then improve the mass transfer efficiency. The photocatalytic performance of packed-bed reactor is more than two orders of magnitude larger than that in wall-coated microphotoreactor under the same operating condition. The organic pollutants in the packed-bed reactor can be degraded completely within 20 s, which has a good development prospect in the rapid treatment of pollution incidents. To prevent catalysts loss, the current research group has deposited TiO$_2$ on supporting materials such as clay, calcium alginate beads, and glass raschig rings [139–141]. They developed the fixed-bed photoreactor packed with these above packing materials for the organic wastewater treatment. The refractory organic pollutants such as persistent pesticides and antibiotic drugs are removed and large amount of wastewater can be treated using these systems. These reactors also showed good durability in the continuous reactor. Orlando et al. compared the photocatalytic activity of the fixed-bed photoreactor with that of slurry and fixed film photoreactor (Figure 12c,d) [48]. As the lower interfacial area available for photocatalysis, immobilized systems (fixed-film and fixed-bed photoreactor) showed a reduction of the efficiency in contrast with the slurry reactor. However, the fixed bed reactor still achieved a satisfactory quantum efficiency ($\eta = 2.96\%$). Considering the advantages of the immobilization systems, the fixed bed photoreactor is promising for organic wastewater purification.

![Figure 12. Schematic representation of packed-bed reactor with TiO$_2$ coated on glass beads (a,b) [138]. Copyright 2018, Elsevier. Experimental installation and photocatalytic performance of fixed bed reactor, slurry reactor and fixed film reactor (c,d) [48]. Copyright 2017, Elsevier.](image-url)
Fluidization in packed-bed reactor is a good way for further improving the removal efficiency. The packed-fluidized bed can provide a larger interfacial area and more irradiation available for photocatalytic reaction [142–145]. Han et al. immobilized TiO$_2$ on a porous SiO$_2$ support and studied the photocatalytic performance of fluidized bed reactor (FBR) and draft tube fluidized bed (DTFBR) [146]. The DTFBR showed a better photocatalytic performance than that of FBR. The draft tube using air as the conveying media make the fluidization of packing materials easier, which can improve the light utilization and mass transfer effectively. Another moving bed reactor immobilized TiO$_2$ on the polymeric support was studied by Surenjan et al. [147]. The complete removal of carbamazepine, diclofenac and ibuprofen was achieved after 4 h. This high photocatalytic efficiency was attributed to the high contact possibility of micropollutants with catalyst in the LED based fluidized bed photocatalytic reactor, which provide a way for clean energy development.

Therefore, these packed bed photoreactors are of simple construction and efficient for organic pollutant degradation and catalysts recycling. The shortcoming of radial radiation gradients can be removed by coating TiO$_2$ on glass beads. The designed geometry and packing structure can overcome the mass transfer limitation and photogenerated carrier recombination. Additionally, fluidization system in packed bed reactors can further promote efficient mass transfer for surface reactions.

4. Conclusions and Future Perspectives

This article is viewed on the design of TiO$_2$-based photocatalytic reactor for environmental applications. The TiO$_2$ photocatalysis mechanism demonstrated that the generation of H$^+$, •OH, and active oxygen species are useful for the organic pollutant mineralization. TiO$_2$ coupling with developed photocatalytic reactors is one of the most promising approaches for the polluted water and air purification. Although many literatures on photocatalytic reactors have been published, this field show fragmentation with no detailed classification, which make comparisons difficult. The review summarized the different types of TiO$_2$-based photocatalytic reactor and their application for water bodies and the atmosphere.

An application of TiO$_2$-based photocatalytic reactor is purification for the polluted air. The packed bed photoreactor with suitable supporters, geometry and packing conditions can treat the pollution of VOCs at low- and high- concentration. To overcome the light intensity declines, the configuration of film reactors were designed. The plate film photoreactors with small channels structure provide the remarkable mass transfer rates, short molecular diffusion distance, and better spatial illumination homogeneity, which can increase photon transfer capability compared to conventional plate film photoreactors. The film photoreactors with the new geometry structure, such as multi-plate, annular/tubular, and spiral tube, can also offer the optimal conditions for photocatalytic reactions.

Another application of TiO$_2$-based photocatalytic reactor is treating the wastewater. The TiO$_2$-based membrane reactors are effective for wastewater treatment owing to its high separation efficiency and easy maintenance. The slurry type of membrane photoreactors shows high removal efficiency for organic pollutants and the immobilization type of membrane photoreactors can reduce membrane fouling and showed to be suitable for continuous wastewater treatment. To avoid the decline of light intensity in photocatalytic reactors, film photoreactors are developed. The optimized geometry of film reactor and the design of film structure are promising methods to improve the light utilization and mass transfer. The packed bed photoreactors with excellent photocatalytic performance is also found to be effective for catalysts separation and recycling. The designed geometry, packing materials and structure can overcome the radial radiation gradients, mass transfer limitation and photogenerated carrier recombination, respectively.

However, several issues and challenges need to be further researched in the practical application. Despite successes in the laboratory of the TiO$_2$-based photocatalytic reactors design, commercially implement in the industry needs to be better developed. The industrialization is hindered by the factors of a costly investment requirement and complex
operating procedures. The TiO$_2$-based photocatalytic reactors with simple construction, low operating cost and high removal efficiency still need to be studied. Developing the novel types of photoreactors for combining two or more previous photoreactors to convert organic pollutants to clean energy. Moreover, numerous kinetic parameters and models should be constructed, which are necessary for the scale-up design. This review article presents an overview of TiO$_2$-based photocatalytic reactors on the application of polluted air purification and water remediation. TiO$_2$-based photocatalytic reactors will remain among the most cost-efficient and useful technology in the field of environmental modification.

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