

Review

Improvement in photocatalysts and photocatalytic reactors for water and wastewater treatment: A review

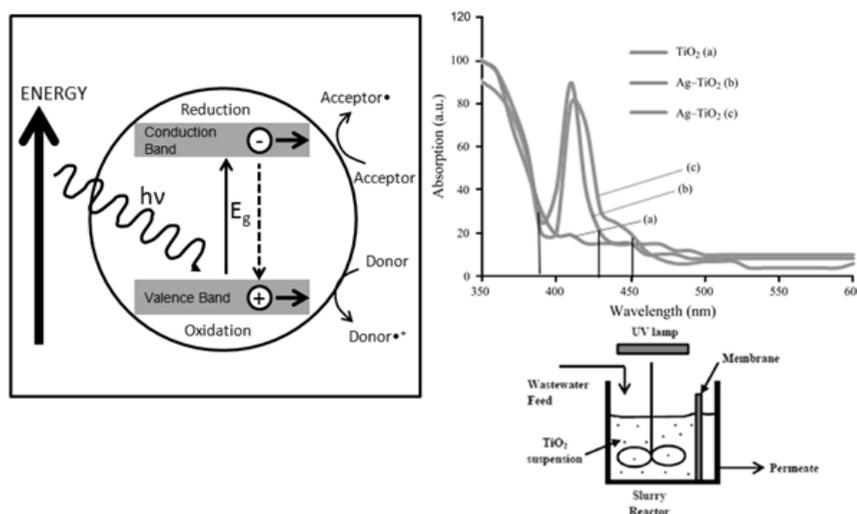
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HIGHLIGHTS

- Principles of semiconductors and photocatalysts were investigated due to their applications in the advanced oxidation processes.
- Various improvement strategies in photocatalysts were discussed.
- Recent developments in photocatalytic reactors in wastewater treatment were investigated.

GRAPHICAL ABSTRACT



ABSTRACT

During recent years, many advanced oxidation techniques have been investigated for water and wastewater treatment to overcome the shortage of clean water. This review summarizes the background and principles of photocatalysis applied as an advanced oxidation technology. In particular, this paper focuses on modification of photocatalysts with various dopants as well as the novel photocatalytic reactors to improve the oxidation efficiency of the pollutants in water and wastewater.

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1. Introduction

Shortage and availability of clean and healthy water is one of the universal problems of our century. Enormous amount of researches have been conducted to overcome these problems with the approach of minimizing the chemicals, energy, cost and environmental damage. In both developing and industrialized countries, a growing number of contaminants are entering water supplies from human activity: from traditional compounds such as heavy metals to emerging micro-pollutants such as endocrine disrupters and nitrosamines [1-3]. Conventional methods of water purification and disinfection can remove contaminants from water, but these methods are often chemically, energy consuming and operationally intensive. Thus, severe chemical treatments (such as those using ammonia, chlorine compounds, ozone...) and waste from treatment (sludge, brines, toxic material) can add to the problems of contamination and polluting water sources. Advanced Oxidation Processes (AOPs) can be used for treating of water polluted by organic matters and for disinfection of pathogens. These methods are based on highly reactive chemicals formation which degrades even most refractory molecules into biodegradable compounds. The Methods that are using UV, H_2O_2/UV , O_3/UV and $H_2O_2/O_3/UV$ combinations use photolysis of H_2O_2 and ozone to generate the OH^\bullet radicals which are able to oxidize organic molecule. Heterogeneous photocatalysis, are based on the use of a wide band gap semiconductor and irradiation with UV-vis light [4, 5]. Among various treatment methods, chemical oxidative treatments, and especially, AOPs, are suitable for their capability of oxidizing and mineralizing almost any organic contaminant [6].

Compared to the typical chemical treatments AOP is a method that uses a range of technologies to the increase oxidation power. For effective water treatments, a range of pollutants need to be removed economically at room temperature and under atmospheric pressure [7-9]. As shown in Table 1, AOP produces OH^\bullet , which has stronger oxidation power than ordinary oxidants [10].

Technology that uses the catalytic activity of semiconducting metal oxides, such as TiO_2 , ZnO , Bi_2WO_6 , $Bi_{20}Ti_{20}$, Fe_2O_3 , Nb_2O_5 , $BiTiO_3$, $SrTiO_3$, $ZnWO_4$, CuS/ZnS , WO_3 , Ag_2CO_3 , ZnS , etc. [11, 12], has been researched actively with particular focus on TiO_2 photocatalytic technology [13]. The advanced technology that uses TiO_2 photocatalysis use only photo energy without additional chemicals [14]. In

Table 1.

Redox potential of major oxidizing agents that are used in water treatment [10].

Oxidizing agent	Oxidation potential (V)	Relative oxidation power*
OH radical	2.80	2.06
Ozone	2.07	1.52
Hydrogen peroxide	1.77	1.30
Perhydroxyl radical	1.70	1.25
Permanganate	1.68	1.24
Chlorine dioxide	1.57	1.15
Chlorine	1.36	1
Oxygen	1.20	0.88

*Relative oxidizing power when chlorine oxidation power is 1

semiconductor photocatalysis, electrons from the valence band of a semiconductor are excited to the conduction band by wavelength of higher energy than the respective band gap [15], resulting in the formation of e^-_{CB}/h^+_{VB} pairs. The lack of a continuum of inter-band states in semiconductors assures an adequately extended lifetime for photo generated e^-_{CB}/h^+_{VB} pairs to initiate redox reactions on the catalyst surface. Electrons in the conduction band can reduce O_2 to form superoxide radicals ($O_2^{\bullet-}$). Additional reaction of $O_2^{\bullet-}$ with holes on the valence band produce single oxygen ($1O_2$) [16, 17].

Subsequent reactions of valence band holes with surface adsorbed H_2O or HO^- result in the formation of hydroxyl radical, H_2O_2 and protonated superoxide radicals (HOO^\bullet). H_2O_2 is resulting from the combination of two HOO^\bullet [18, 19]. Further reaction of H_2O_2 with HO^\bullet results in the formation of HOO^\bullet [19, 20]. During the photocatalytic process, free electrons/holes, and reactive oxidizing species such as HO_2^\bullet , HO^\bullet and $O_2^{\bullet-}$ react with the surface adsorbed impurities such as inorganic/organic compounds, and biological species leading to their decomposition. Photocatalytic treatment of polluted water has some advantages over other methods such as low operational and installation cost, simple pre-processing, less area and decomposition possibility of non-biodegradable matters. Limited lamp life (when UV-Lamp is used) and photocatalyst recovery (when using powder) are disadvantages of photocatalytic water treatment [19]. Photocatalytic research is basically related to the development of solar energy use [21, 22].

Conventional wastewater treatment consists of a combination of physical, chemical, and biological processes and operations to remove solids, organic

matter and, sometimes, nutrients from wastewater that are almost energy and cost consuming processes [23]. The water treatment process may vary slightly at different locations, depending on the technology of the plant and the water it needs to process [24]. Although many excellent review articles have been published until now discussing the importance of photocatalysts in water and wastewater treatment, but the few reviews have been published on photocatalytic reactor configuration conjugated with membrane processes. So the the purposes of the present article is to review the improving strategies of photocatalytic activity, and various types of reactor configuration and combination of photocatalysts with membranes for water and wastewater treatment. A summary of advanced oxidation processes, principles and mechanism of photocatalysis, improvement strategies of photocatalytic water treatment, and photocatalytic reactors in water and wastewater treatment have been discussed in this review.

2. Advanced Oxidation Process

The wide area of water pollution, variety and non-biodegradable problems has become a problem that cannot be solved by the conventional treatments like Coagulation / Flocculation, sedimentation, filtration, Disinfection, sludge drying, Fluoridation and pH correction [24-27]. Moreover, in the case of water treatment technology, it is very difficult to remove pollutants completely with existing biological treatment technology. Compared to the typical chemical treatments, AOP is a method that uses a range of technologies to increase oxidation power. Generated OH[•] radicals strongly oxidize organic compounds, toxic pesticide and manure emissions to minerals in AOP (Fig.1).

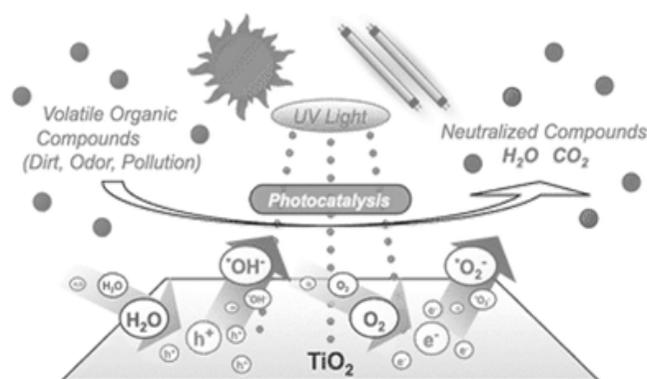


Fig. 1. Degradation of pollutants by OH radicals generated from photocatalysis process [25].

The formation of OH radicals can occur through several processes that are discussed below. AOPs are divided into two categories according to the presence or absence of light (UV) as reaction promoter [28].

2.1. Dark oxidative process

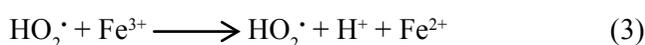
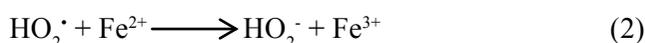
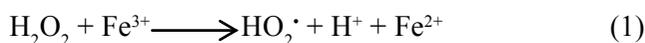
Advanced oxidation processes based on presence or absence of light, are divided into dark oxidative process and UV conjugated process. In the dark oxidative processes, the light is not effective in the reaction. These processes are consisting of using ozone, Fenton's reagent, electro-magnetic beam, ultrasound, microwave, and cavitation. In the following sections, these processes are discussed.

2.1.1. Ozone (O₃)

This technology injects ozone gas directly into polluted water [29]. In one mechanism the organic contaminants react directly with ozone, and in another effectively oxidation decomposition occur through an indirect reaction with OH[•] radical, which is generated by decomposed ozone. The mechanism of ozone decomposition depends on the properties of the organic pollutants in polluted water. Hence, the organic pollutants in contaminated water can either promote or inhibit ozone decomposition and can interact with contaminants decomposition [9, 30].

2.1.2. Fenton's reagent

Fenton oxidation technology that uses the Fenton reaction is a method to generate OH[•] in a Fe²⁺ and H₂O₂ mixture [31, 32]. This can decompose H₂O₂ by Fe²⁺ in the liquid phase without light irradiation, and generate OH[•] radical. In the case light irradiation can promote decomposition of H₂O₂ due to ferrous or ferric ions and rapid hydroxyl radical generation is possible. The Fenton oxidation reaction is only applicable under the acidic conditions, i.e., pH < 4. Therefore, the process has disadvantages of high cost of operation due to the additional cost of the acid/base for pH adjustments [33, 34]. Fenton reaction can be express as:



2.1.3. *Electro-magnetic beam, Ultrasound, and microwave*

OH[•] radical can be generated by directly decomposing water using an external energy source, such as an electromagnetic beam, ultrasound and [35]. When water is irradiated with gamma rays (as electromagnetic beam), water molecules are decomposed to OH[•], H⁺, and aqueous electrons. also high-voltage discharge in water can decompose water molecules. When high voltage pulses of approximately 10 kV, are added between two electrodes located with a few centimeter gap between them, a flame is generated as water discharge is caused. This generates high concentrations of OH[•] radical. OH[•] can also be produced by ultrasound or microwaves [36]. When these energy sources pass through water, localized pressure differences with time generate micro bubbles, which acquire vibration energy and become unstable. These bubbles generate strong energy at high temperatures and high pressures, and the water molecule is broken down to OH[•] and H⁺.

2.1.4. *Cavitation (sonication and hydrodynamic)*

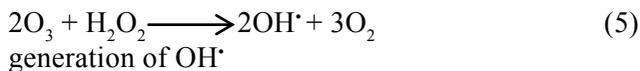
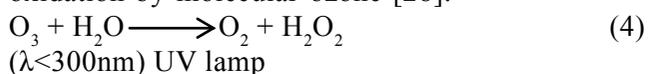
Sonication or hydrodynamic processes include the formation of cavitation micro bubbles. These bubbles collapse severely after reaching a critical resonance size and generate high temperature and highly reactive OH[•] radicals. Removal of organics occurs by thermal decomposition at the bubble-water interface and by reaction with the radicals. Oxidation by cavitation is enhanced by addition of O₃ or H₂O₂ [28].

2.2. *UV conjugated process*

The second category of advanced oxidative processes is UV conjugated processes. These processes occur in the presence of light especially in the range of ultra-violet wavelength and are consisting of UV/O₃, UV/H₂O₂, UV/Fenton, and UV/photocatalyst processes.

2.2.1. *UV/O₃ (Ozonation)*

Hydroxyl radicals are generated when low pressure UV light is applied to ozonated water. Destruction of organic compounds occurs by hydroxyl radical reactions, coupled with direct photolysis and oxidation by molecular ozone [28].



2.2.2. *UV/H₂O₂*

The OH[•] radical route is the predominant removal mechanism in the destruction of organics [28].



2.2.3. *UV/Fenton*

UV/Fenton processes are like Fenton reaction. UV light can accelerate generation of OH[•] radicals.

2.2.4. *UV/semiconductors (photocatalysis)*

Photocatalysis refers to the speed-up of the chemical reaction in the presence of substances called photocatalysts, which can absorb special wavelengths depending on the band structure [37-40]. Usually, semiconductors including TiO₂, Fe₂O₃, WO₃, ZnO, CeO₂, CdS, Fe₂O₃, ZnS, MoO₃, ZrO₂, and SnO₂ are selected as photocatalysts due to their narrow band gap and distinct electronic structure (unoccupied conduction band and occupied valence band) [20, 41-59]. In the following principles and mechanism of photocatalysis have been discussed.

3. Principles and mechanism of photocatalysis

3.1. *Structural and electronic properties*

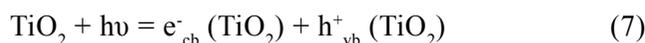
The initial work of water decomposition using electrodes composed of TiO₂ was done by Fujishima and Honda [47]. The quantum efficiencies of TiO₂ in solar energy conversions are rather poor due to the usually faster recombination of electron-holes [60, 61]. Other noteworthy advances include the invention of dye sensitized solar cells by Grätzel *et al.*, which are composed of TiO₂ anodes and the discovery of anti-fogging abilities of TiO₂ surfaces by Wang *et al.* [13, 62]. TiO₂ is widely used because of its non-toxicity, abundance (inexpensiveness), thermal/chemical stability, and high redox potential [47, 63, 64]. Due to superior mobility of electron-hole pairs, and improved surface hydroxyl density, anatase TiO₂ considered as the photocatalytically most active polymorph of TiO₂ [65, 66]. Factors, such as surface area, particle size, ratio of poly-morphs, type of dopants, defect concentration, synthesis method, and phase purity, affect the

photocatalytic activity of semiconductors [67-69].

3.2. Principles of photocatalysts

A photocatalyst receives UV radiation from sunlight and uses the energy to decompose different substances including organic matters, organic acids, estrogens, pesticides, dyes, hydrocarbons, microbes and chlorine resistant organisms, inorganic molecules such as nitrous oxides (NO_x) [70-72]. For preventing free nanoparticles in water, photocatalysts nanoparticles are usually immobilized on a substrate [73] or integrated into thin-films and other materials. For the activation of TiO_2 , UV irradiation is needed. To allow activation by visible light, TiO_2 can be modified with a second semiconductor, dyes, nitrogen, carbon or sulphur. For example, TiO_2 doped with nitrogen has better photocatalytic performance than pure TiO_2 nanoparticles [74].

Photocatalytic reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the semiconductor. This produces electron-hole (e^-/h^+) pairs as in Equation (7), Fig. 2:



Where cb is the conduction band and vb is the valence band. Thus, as a result of irradiation, the TiO_2 particle can behave either as an electron donor or acceptor for molecules in contact with the semiconductor. The electron and hole can recombine, releasing the absorbed light energy as heat, with no chemical reaction. On the semiconductor surface, the excited electron and the hole can participate in redox reactions with water, hydroxide ion (OH^-), organic compounds or oxygen leading to mineralization of the pollutant.

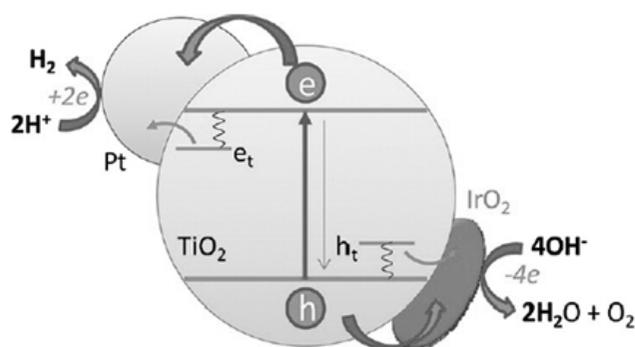


Fig. 2. Schematic of the charge transfer across semiconductor interface [75].

Oxidation of water or OH^- by the hole generates the hydroxyl radical. OH^- radicals are able to rapidly attack pollutants on the semiconductor surface [76, 77].

Pervious work indicate that heterogeneous photocatalytic process involves five separate steps [78] and include (1) diffusion of reactants to the surface of photocatalyst, (2) adsorption of reactants onto the surface of semiconductor, (3) reaction on the surface of semiconductor, (4) desorption of products from the semiconductor and (5) diffusion of products from the surface of the semiconductor. There are two routes through which OH^- radicals can be formed the reaction of the valence-band holes with either adsorbed H_2O or with the surface OH groups on the photocatalyst particle [79].

3.3. Limitation of semiconductors

One of the main disadvantages of TiO_2 photocatalyst is the recombination of photo-generated charge carriers, which decreases the efficiency of the reaction [80]. The photo-excited electrons come back to the valence band during the recombination processes [81-83]. Methods such as hetero junction formation, doping with ions, and nano sized crystals have been demonstrated to reduce recombination [84-90]. For example, TiO_2 partially loaded with Ag and Au noble metal nanoparticles exhibited better photocatalytic activities [91], because metal nanoparticles act as electron traps during the photocatalytic reaction, and thus decreasing the rate of electron-hole recombination [92]. Notably, higher visible-light photocatalytic activities of N-doped, and S, N-codoped anatase-rutile nano hetero junctions have been reported by Etacheri *et al.* [93]. In conclusion, increasing the life-time of electron-hole pairs resulted in increasing the photocatalytic performance of photocatalysts. Both rutile and anatase have tetragonal crystal structure and previous reports proved that the kinetic stability of anatase is higher than that of rutile under ambient conditions. A thermodynamic phase stability calculation by Banfield and co-workers show that a critical particle size of 14 nm is required to initiate anatase to rutile transformation. Another disadvantage of the TiO_2 photocatalyst is the large band gap of TiO_2 , that limits its use to UV light with wavelength lower than 390 nm. therefore only 5% of the solar radiations can be used by undoped TiO_2 photocatalysis, which significantly decreases Economic justification [94]. Studies have been done to synthesize small band

gap photocatalysts that can utilize both UV and visible light. Various methods conducted for the visible light activation are explained in the following sections [94].

4. Strategies to improve photo degradation efficiency

In principle, photocatalytic activity will be enhanced if the absorption of light is increased or if the recombination losses for photogenerated charge carriers are decreased. Different strategies for enhancing the photocatalytic activity of photocatalysts under visible and UV have been conducted include sensitization with different sensitizers (spatially dyes), addition of noble metals, doping with transient metal ions, addition of inert elements, and using compound materials [95]. In the following section, these strategies have been discussed.

4.1. Photoexcited treatment on the surface of photocatalysts

Addition of photo excited sensitizers (e.g., ruthenium-II) on the surface of photocatalysts can widen the wavelength range and enlarge the utilization range of sun light. The principle of photosensitization of photocatalyst is showed in Fig. 3. The visible light excites the sensitizer molecules adsorbed on TiO_2 and hence inject electrons to conduction band of TiO_2 . While the conduction band acts as a mediator for transferring electrons from the sensitizer to substrate electron acceptors on TiO_2 surface, the valence band remains unaffected in a common photosensitization [95]. Various inorganic/organic dyes [96-103] as a sensitizer in relation to photo electrochemical cells and water splitting systems have been used. The studies of photosensitization used to degradation of pollutants using visible light are few.

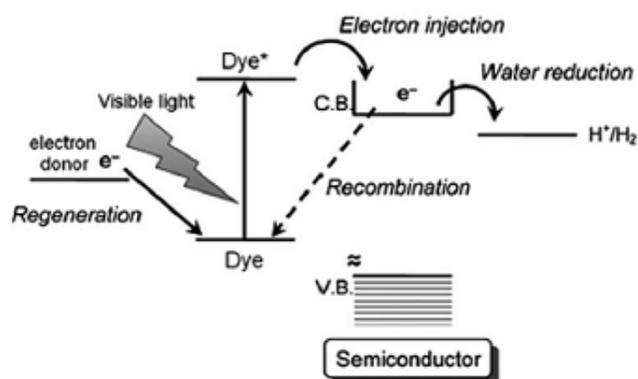
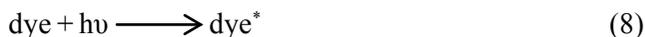


Fig. 3: Photosensitized TiO_2 Particles [104].

Some dyes having redox property and visible light sensitivity can be used in photocatalytic [105, 106]. The process is similar to composite semiconductors (are discussed in section 4.5), The photo-excitation, electron injection and dye regeneration can be proposed as follows:



To achieve higher efficiency in oxidation reactions, fast electron injection and slow backward reaction are needed. The recombination times were found to be mostly in the order of nanoseconds to microseconds on electron/hole recombination of dyes [107], while the duration of electron injection is in the order of femtoseconds [108]. The quick electron injection and slow recombination reaction make dye sensitized semiconductors suitable. Frequently used dyes are listed in Table 2.

Sensitized photocatalysis usually leads to a rapid destruction of chromophore structure to form smaller organic species, resulting in final mineralization of the dye [110-113].

4.2. Addition of noble metal

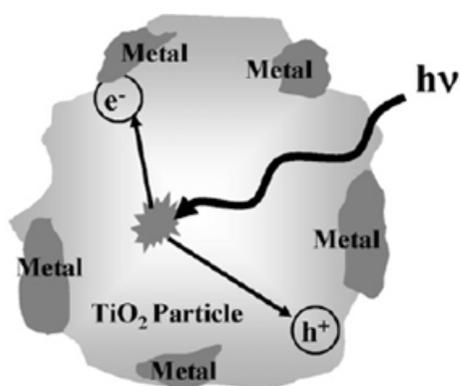
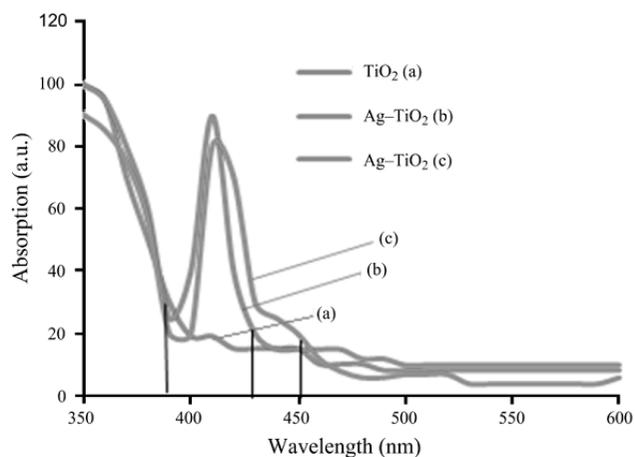
Noble metals, such as Ag, Pt, Rh, Pd, Au have been investigated and showed to be very effective for promotion of TiO_2 photocatalyst. Photo-excited electrons can be transferred from conduction band to noble metal particles located on the surface of TiO_2 (Fig.4). These metals reduce the recombination, resulting efficient charge separation and higher photocatalytic activity [114]. Because of high cost of Au and Pt, more research is needed to find low-cost metals with suitable improvement of photocatalytic activity [115].

The atomic radiuses of noble metal (e.g., Pt, Ag, Au) are bigger, so they are unable to enter the crystal lattice of photocatalysts. But, they can improve the surface characteristics of photocatalysts, and restrain the recombine of electron-hole [116].

It has been shown that noble metals such as platinum, palladium, silver, and gold ions allow to wide light absorption of TiO_2 to the visible light [118]. The surface of noble metal acts as visible light absorbing agent [119]. The photocatalyt-

Table 2.
Frequently used dyes [109].

Dye	Type	λ_{\max} (nm)
Thionine (TH ⁺)	Thiazines	596
Toluidine blue (Tb ⁺)	Thiazines	630
Methylene blue (MB)	Thiazines	665
New methylene blue	Thiazines	650
Azure A	Thiazines	635
Azure B	Thiazines	647
Azure C	Thiazines	620
Phenosafranin (PSF)	Phenazines	520
Safranin-O (Saf-O/SO)	Phenazines	520
Safranin-T (Saf-T/ST)	Phenazines	520
Neutral red (NR)	Phenazines	534
Fluorescein	Xanthenes	490
Erythrosin	Xanthenes	530
Erythrosin B	Xanthenes	525
Rhodamin B (Rh. B)	Xanthenes	551
Rose Bengal	Xanthenes	550
Pyronine Y (PY)	Xanthenes	545
Eosin	Xanthenes	514
Rhodamin 6G	Xanthenes	524
Acridine orange (AO)	Acridines	492
Proflavin (PF)	Acridines	444
Acridine yellow (AY)	Acridines	442
Fusion	Triphenyl methane derivatives	545
Crystal violet	Triphenyl methane derivatives	578
Malachite green	Triphenyl methane derivatives	625
Methyl violet	Triphenyl methane derivatives	580

**Fig. 4.** Electrons capture by a metal in contact with a semiconductor surface [114].**Fig. 5.** UV-vis absorption spectra of the annealed (a) TiO₂ and (b) 3% and (c) 7% Ag-doped TiO₂ nanoparticles [117].

activity improvement of silver doped TiO_2 was mainly belong to the increase of surface area, which promotes more reactive sites available to take part in photoreactions. On the other hand, doping TiO_2 with Ag (Fig.5) retards the recombination rate of electron-hole pair by enhancing the charge carrier separation and hence improves the photocatalytic activity [120, 121]. Sobana [122] and Xin [123] show that Ag deposited on TiO_2 act as electron traps, enhance the electron-hole separation and lowering recombination.

4.3. Addition of transition metal ion

One of the most effective methods to create visible-light sensitive photocatalysts is adding impurity in the forbidden band through metal ion doping [124, 125].

Common metal ion dopants are V, Ni, Cr, Mo, Fe, Sn, Mn, Co, Cu. A trace quantity of transition metal ion is deposited on TiO_2 , extended the available wavelength range, and increase the utilization rate of visible light. Fe^{3+} , Mo^{5+} , Ru^{2+} , V^{5+} and Rh^{2+} can

improve the activity of photocatalysts. Among them the effect of Fe^{3+} is the most prominent. But Cr^{3+} is harmful to the activity of photocatalysts (Fig. 6). The doping Fe^{3+} induces the narrowing of the band gap of TiO_2 . The dopant Fe^{3+} ion causes the formation of new states near the conduction band. Therefore the doping by iron ions significantly promotes the photocatalytic activity in the visible light region [126]. Also, it inhibits the recombination of the photo-generated electron and hole. The Fe ions with a suitable concentration can trap the photo-generated electron, which enhances the utilization efficiency of the photo-generated electron and hole.

Fig.7 shows mechanism of Fe ion narrowing the band gap. According to figure various structures of iron can change the energy levels of TiO_2 . Metal ion cause creation of impurity energy levels in the band gap of TiO_2 as below:

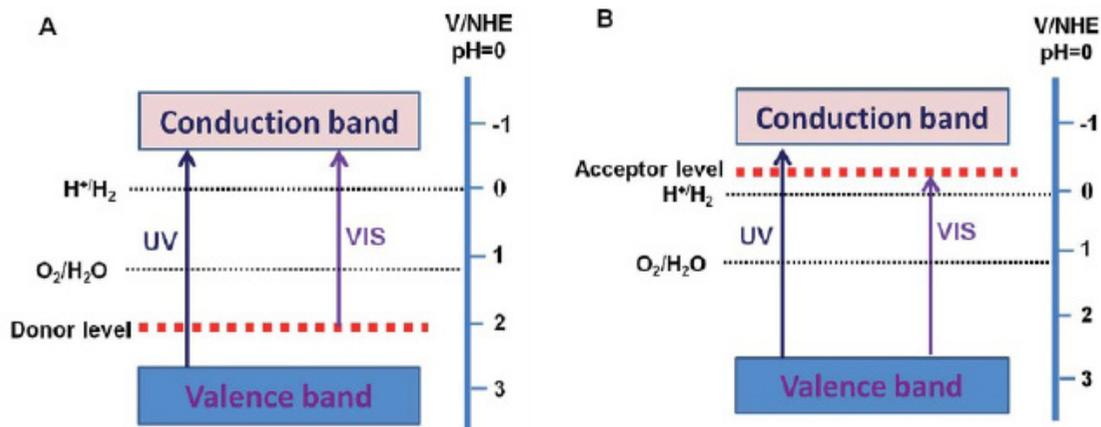
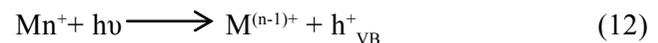
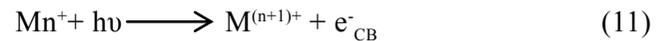


Fig. 6. Donor level (A) and acceptor level (B) formed by metal ion doping [124]

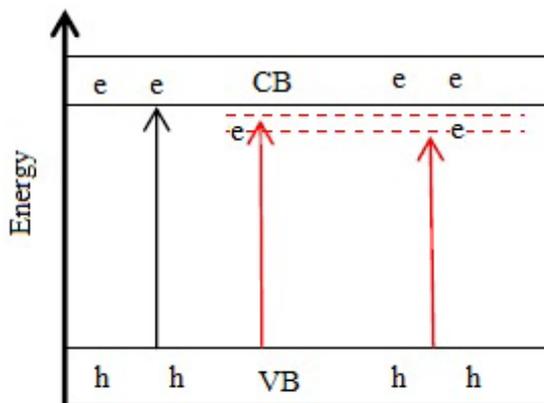


Fig. 7. Schematic diagram of the mechanism of Fe^{3+} doping on TiO_2 [125].

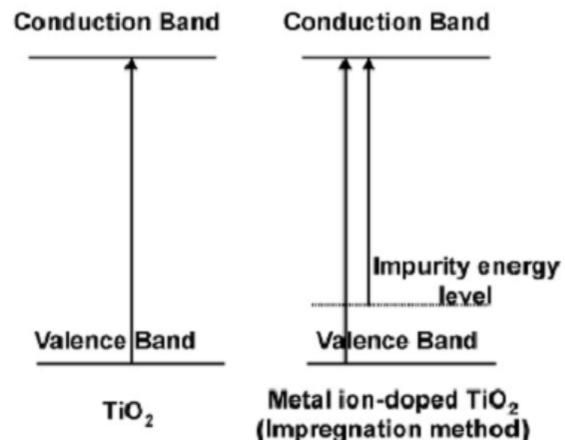


Fig. 8. Scheme of TiO_2 band structures, chemically ion-doped TiO_2 [114].

M is metal and Mn^{+} is metal ion dopant. Electron (hole) transfer between metal ions and TiO_2 can modify electron/hole recombination (Fig.8):



Photocatalytic reaction only takes place when the trapped electron and hole are transferred to the surface of particle. Therefore, metal ions should be deposited near the surface of TiO_2 particles for a suitable charge transfer. There is an optimum of metal ion concentration, above which the photocatalytic activity decreases because of the increase in recombination [114].

Fe, Rh, Mo, V, Ru, Re, and Os ions can enhance photocatalytic activity, while Al and Co ions cause detrimental effects. Fe and Cu ions can trap electrons and holes, and the impurity energy levels generated are near to conduction band as well as the valence band edge of TiO_2 . Therefore, doping of either Fe or Cu ions is suitable for enhancement of photocatalytic activity. In the same way, the effects of doping transition metal ions (Cr, Mn, Fe, Co, Ni and Cu) on photocatalytic efficiency of TiO_2 also have been investigated. As, Cu, Mn, and Fe ions can trap both electrons and holes, doping of these metal ions may be better than doping with Cr, Co and Ni ions, as the latter metal ions can only trap one type of charge carrier. Enhanced photocatalytic activities were observed at certain doping concentration of different rare earth metal ions (La, Ce, Er, Pr, Gd, Nd and Sm) doped into TiO_2 . Gd ions were found to be most effective in increasing the photocatalytic activity due to their higher ability to transfer charge carriers to the interface of photocatalyst [125].

4.4. Addition of inert elements

The utilization of visible light could be increased significantly when the oxygen of TiO_2 was partially substituted with nitrogen. TiO_2 improved with carbon contains more pores, and its degradation capability is two times greater than that pure TiO_2 . Doping of anions (N, F, C, S, etc.) in TiO_2 could increase its photoactivity into the visible wavelength.

Zhao and Liu [127] investigated N- TiO_2 and found that TiO_2 doped with substitutional N has shallow acceptor states above the valence band. In other hand, TiO_2 doped with interstitial nitrogen has isolated impurity states in the middle of the band gap

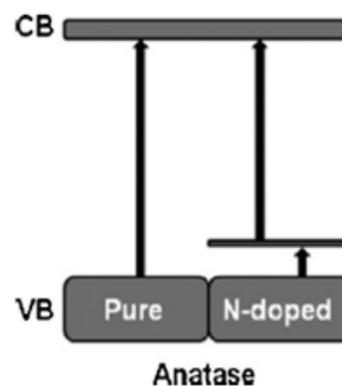


Fig. 9. Doping TiO_2 with N [114].

(Fig.9). The N-doped TiO_2 was determined to be effective for methylene blue decomposition, disinfection and for phenol degradation under visible light. S doping is leading to similar band gap narrowing. C and P are less effective as the introduced states were so deep that photo-generated charge carriers cannot be transferred to the surface of the photocatalyst. S-doped TiO_2 is more efficient than pure TiO_2 under visible light radiation. Although the valence band was shifted upwards, the oxidation ability was found to be still high. Similar to S-doping, N-doping also causes a valence band shift upward, led to narrow band gap and less oxidizing holes [128].

4.5. Compound materials

Compound materials extend the specific surface area, improve the reaction conditions, and widen the range of absorption light. The band-gap energy of $ZnFe_2O_4$ is lower, and it can absorb visible light. When the mass ratio of Zn to Ti in the compound materials of $ZnFe_2O_4/TiO_2$ is 0.05, it possesses the highest photocatalytic activity [128].

Mixing different semiconductors with different energy levels is another method, which has received great interest recently [130-134]. In photocatalytic systems, combining TiO_2 with other semiconductors was done to widen the absorption wavelength range into the visible light region and to mitigate the charge carrier recombination in individual photoelectrodes (Fig.10) [131]. Zhang [131] showed that the good matching of the conduction band and valence band of the two semiconductors could ensure an efficient transfer of the charge carriers from one to another. When the large band gap of TiO_2 is coupled with a small band gap semiconductor having more negative conduction band level, the electron can

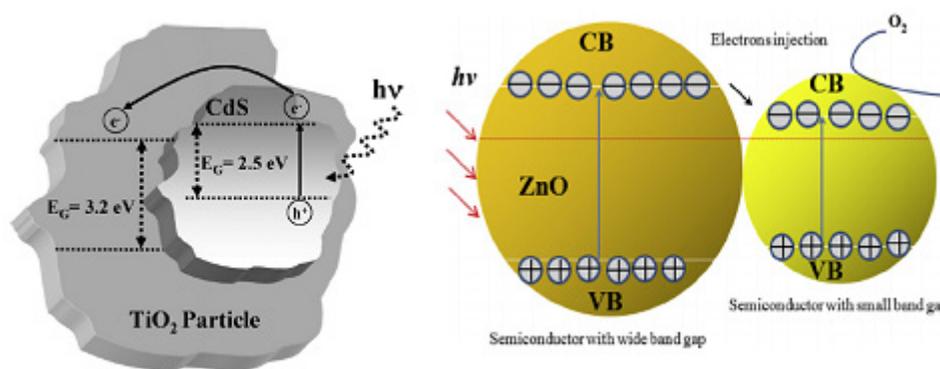


Fig. 10. The excitation process in a semiconductor–semiconductor photocatalyst [114, 129].

be injected from the small band gap of the semiconductor used as a sensitizer to the TiO_2 [138]. According to Robert [132] the efficient transfer of electron between TiO_2 and the sensitizer was occurred when the conduction band of TiO_2 is more anodic than the corresponding band of the sensitizer. Under visible irradiation, only the sensitizer is excited and the electrons photogenerated will flow into the conduction band of the adjacent TiO_2 . As mentioned in certain number of studies, the photocatalytic activity of TiO_2 combined with metal oxides such as CdS, [134] SnO_2 , [135] WO_3 , [136] and FeO_3 [137]. Bi_2S_3 , [138] among others, has been largely used for improving the process under visible irradiation. For photocatalytic application intended for water and wastewater treatment, the systems $\text{M}_x\text{O}_y/\text{TiO}_2$ and $\text{M}_x\text{S}_y/\text{TiO}_2$ are the most widely used catalyst. By comparison, $\text{SnO}_2/\text{TiO}_2$ and ZnO/TiO_2 are examples of a $\text{TiO}_2/\text{M}_x\text{O}_y$ system, which have been used by Zhang [139] and Ge [140], respectively.

5. Photocatalytic reactors in water and wastewater treatment

Hybrid photocatalysis-membrane processes are used in the installations called “photocatalytic membrane reactors”. In the literature, other names such as “membrane chemical reactor” (MCR) [9], “membrane reactor” [56], “membrane photoreactor” [56], or more specific, “submerged membrane photocatalysis reactor” [5] and “photocatalysis-ultrafiltration reactor” (PUR) [35] are used for these configurations. Because all these names mean the hybridization of photocatalysis with membrane process, it will be useful to use a general term of the “photocatalytic membrane reactor”. Photocatalytic membrane reactors are divided commonly into two main groups: (I) reactors with catalyst suspended in feed solution and (II) reactors with catalyst supported in/on the

membrane. In case of the reactors with photocatalyst in suspension a membrane filtration may be needed as a single step for the proper recovery of catalyst particles from the solution [56]. The main drawback of such configuration are decay of the permeate flux and membrane fouling, which are especially observed in case of pressure drive membrane methods. One solution for this problem can be application of photocatalytic membranes reactors. In this configuration, oxidation by hydroxyl radicals occurs on the outer surface and within the pores of the membrane, at a same time reactants are permeating in a one-pass flow. However, fixation of the photocatalyst often results in a loss of photoactivity of photocatalyst [82]. Moreover, selection of a proper membrane, refractory to UV irradiation and hydroxyl radicals is necessary. In both configurations, i.e. utilizing photocatalyst in suspension or fixed on/in a membrane, the membrane might act as a barrier for the molecules which are decomposed and products and by-products of their decomposition. However, this role significantly depends on the separation characteristics of the membrane used and the membrane process applied. The products and by-products of photo degradation of organics are often low molecular weight compounds. Therefore, in case of pressure driven membrane processes, NF and RO only might be considered as processes able to separate these substances. In case of membrane methods in which the mechanism of separation is other than the sieve one, other properties of substances, for example volatility, should be taken into consideration. Based on these considerations, the photocatalytic reactors for water and wastewater treatment are divided into three main groups, including slurry reactors, wall and fixed bed reactors, and fluidized bed reactors.

5.1. Slurry reactors

Figures 11-14 show different configuration of slurry

photocatalytic reactors. In this reactors, micrometric particles of photocatalyst are suspended in liquid system. Light irradiated to feed tank and membrane separate micrometric particles of photocatalyst. Degradation of pollutants occurs by suspended micrometric photocatalyst radiated with UV, separa

tion take place by microfiltration or nanofiltration. Reactions take place on the surface of photocatalysts. Reactants diffuse from bulk of liquid to surface of particles, reaction take place and then degraded products defuse to the bulk.

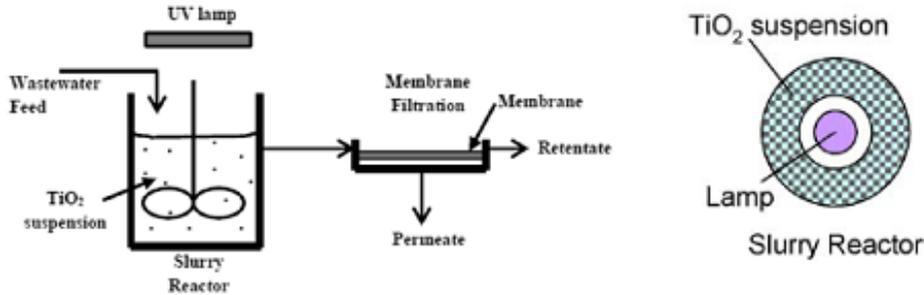


Fig.11. schematic of slurry reactors [137].

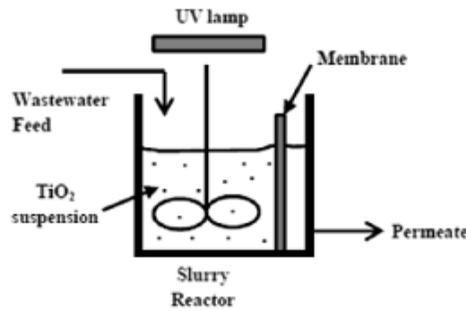


Fig. 12. schematic of slurry reactor [137].

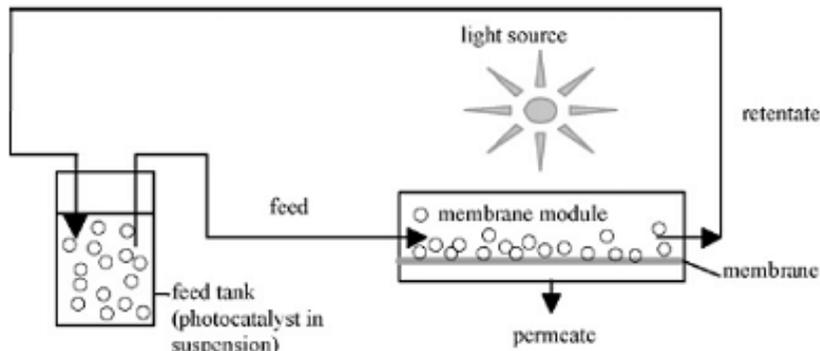


Fig. 13. Schematic of slurry reactor [138].

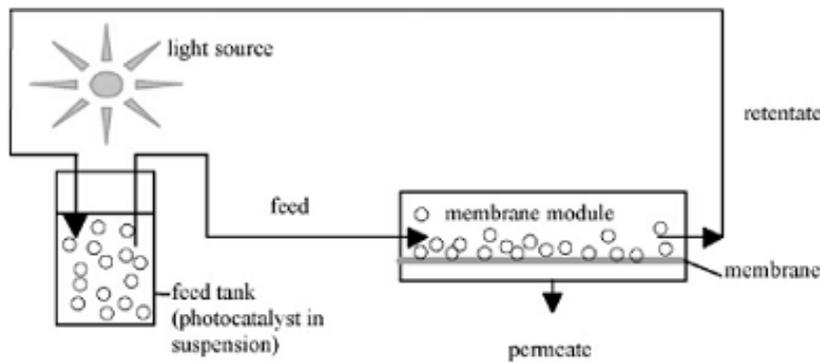


Fig. 14. Schematic of slurry reactor [138].

The fine particles of the Degussa P-25 TiO₂ have always been applied in a slurry form.

Light is irradiated to membrane vessel or feed tank, Fig. 13 and Fig. 14.

Another type of slurry photocatalytic reactor is thin film slurry (TFS) [139]. This configuration benefits from a very large illuminated catalyst surface area per unit volume of reactor and minimal mass transfer limitations. Two feasible configurations of TFS photocatalytic reactors are shown in Table 3.

In TFSFW the water is flowing along a flat wall (FW), as a falling film or between parallel plates and the reactor is irradiated by lamps that are distributed equally. In TFSIW the liquid film is flowing along the internal wall (IW), of a cylindrical reactor as a falling film or in an annulus with the lamp that are located along the central axis. Between these two options, the TFSIW is better configuration for commercial design when using UV lamps. The advantages of this reactor geometry are:

(1) The cylindrical symmetry of the system allows all parts of the photoreactor to be uniformly illumi-

nated with little loss of efficiency providing that the lengths of the reactor and lamp are comparable;

(2) There is improved photon utilization as back-scattered photons have a low probability of escaping from the reactor and can be recaptured by the liquid film;

(3) There is no need for a light reflector which inevitably introduces a loss in photon utilization and adds to the overall cost of the unit;

(4) Improved safety aspects such as the containment of the lamp inside the reactor in case of fire or explosions;

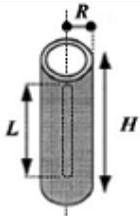
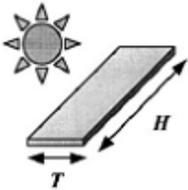
(5) Simple design that require the use of a single lamp and occupies minimum floor space.

The comparison of ideal flow systems has shown that falling film laminar flow and plug flow systems have high performance depending on the degree of conversion obtained in the photocatalytic reactors [139].

5.2. Wall and fixed bed reactors

There is another type of photocatalytic systems that photocatalyst fixed on the surface of membrane, the wall of reactor or fixed granular beads. Fig. 15-

Table 3.
TFS photocatalytic reactors [139].

Reactor configuration		
	TFSIW (UV lamps)	TFSFW (solar radiation or UV lamps)

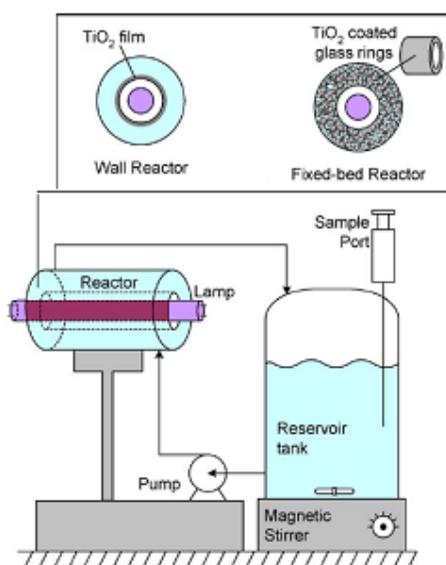


Fig. 15. Schematic representation of the fixed photocatalyst without membrane [140].

20 show various configurations of these reactors. In this configuration catalysts has been fixed on wall of the reactor or has been fixed on surface of the membrane or fixed on fixed millimetric granular beads. Reaction is only limited to the surface of wall or membrane.

Fig. 15 show a fixed photocatalytic system consists of an annular reactor 15 cm long, 3 cm inner tube diameter and 5 cm external tube diameter operating in a closed recirculation system. A centrifugal pump is used for circulating water and reactor equipped with a stirred reservoir tank of 2L volume with a device for withdrawal of samples [140]. Van Grieken *et al.* showed disinfection of *E. coli* bacteria suspensions in slurry, wall and fixed-bed reactors and concluded that immobilized systems have shown that they are stable and do not present deactivation after several cycles of reuse, being readily applicable for continuous water treatment systems.

Photocatalyst can be fixed on the wall of glassy reactor in to configuration (Fig. 16).

Fig. 17-19 show different configuration of catalyst that fixed on wall reactor.

In Fig. 20 the hybrid photo-catalytic/UF experimental set-up is reported. It consists of three concentric tubes placed in the vertical direction. The inner tube is the photocatalytic UF membrane. The intermediate and external tubes are made of Plexiglas, and define an outer flow channel the annular space between the tubes) where polluted water is fed in the lumen of the transparent Ca alginate/TiO₂ polymer fibers.

Membranes with catalyst coating (Fig. 21) have fouling problems. For long time processes, because of membrane fouling, pressure drop increases significantly at constant flux mode, while flux reduces greatly at constant pressure drop mode. In PMRs, fouling mechanisms can be mainly divided into two

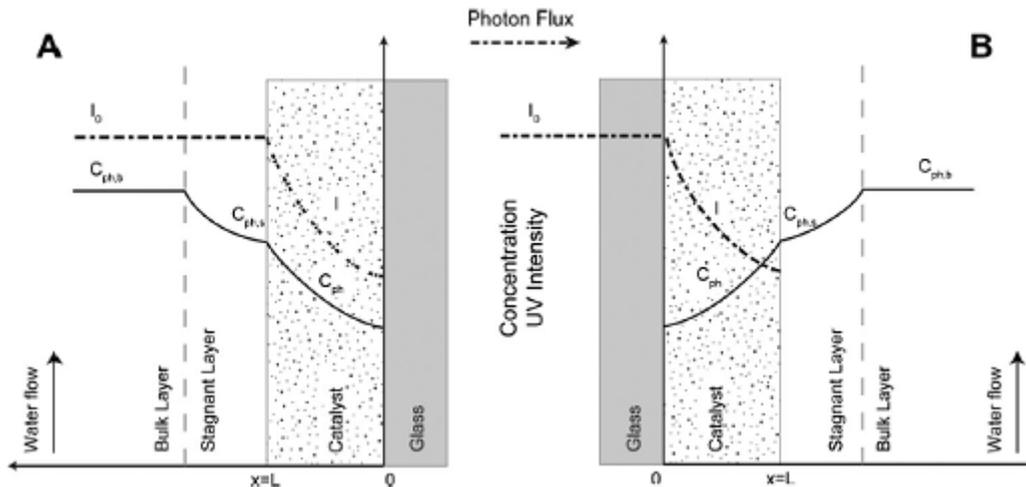


Fig. 16. (A) Schematic of the liquid side illumination system where pollutant and photon flux come from the same direction. (B) Schematic of the support side illumination where pollutant and photon flux come from opposite directions [141].

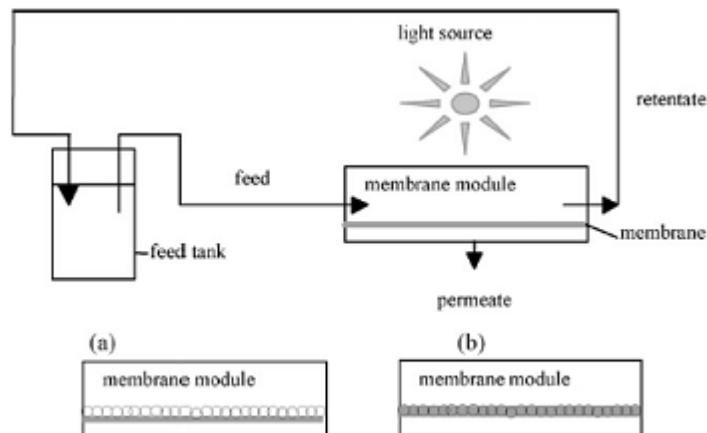


Fig. 17. Schematic of fixed on wall reactor [138].

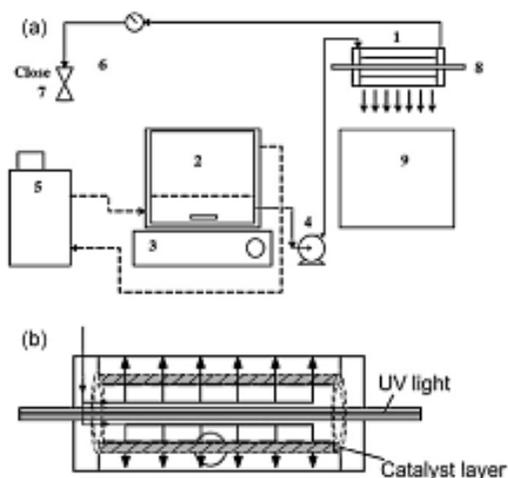


Fig. 18. Schematic of fixed on wall reactor [138].

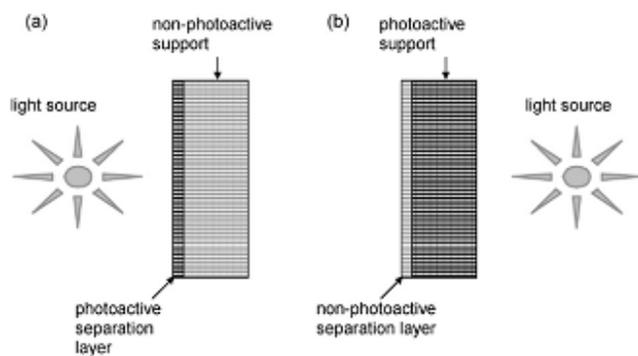


Fig. 19. Schematic of fixed on wall reactor [138].

steps: pore blocking and cake layer steps, which are shown in Fig. 22.

Both suspension and fixed catalyst reactors have their advantages and disadvantages. These properties are listed in Table 4.

Javier Marugan *et al.* [145] used fixed bed photocatalytic reactor for inactivation of *Escherichia coli* bacteria. P25 industrial titanium dioxide immobilized onto glass Raschig rings was used [Fig.23].

5.3. Fluidized bed reactors

Suspension catalytic reactors are more efficient than fixed bed reactors because mass transfer is easier and there is possibility to add desired amount of catalyst to the reactor. At the other side fixed catalyst on wall reactors do not have separation problem of photocatalyst from water. Therefore the third type of reactor configuration has been formed. This reactor is

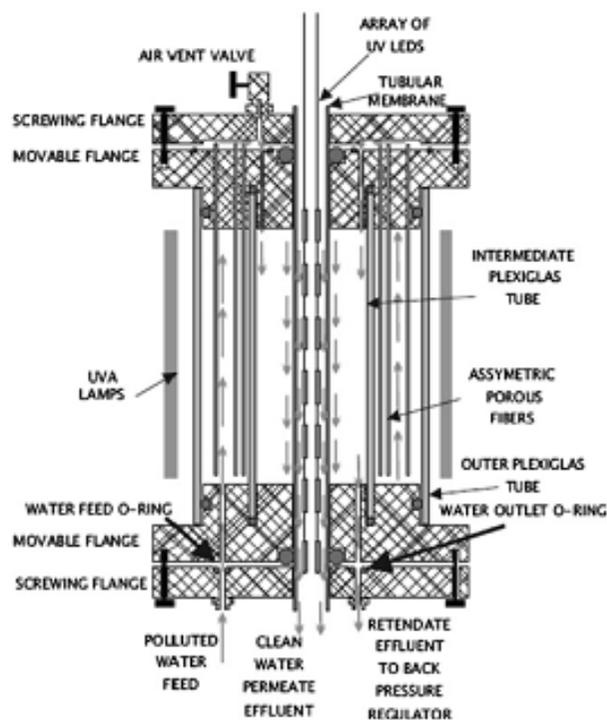


Fig. 20. Photocatalytic membrane system used in the hybrid-photocatalytic/ultrafiltration with catalyst fixed on wall of reactor [142].

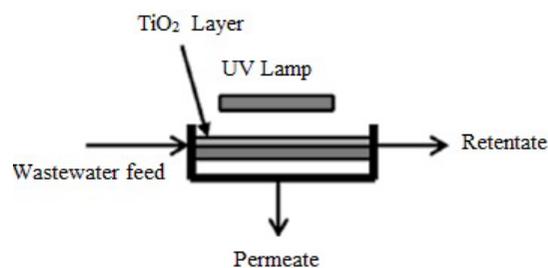


Fig. 21. Schematic of fixed on membrane wall [143].

something between slurry and fixed on wall catalyst reactors. Photo catalysts fixed on millimetric balls and these balls fluidized by air force or water flow. There for by this way advantages of two previous model is accessible and overcome to their limitations. Fig. 24 show configuration that air fluidized millimetric balls and reaction take place on surface of balls.

Photocatalytic degradation of organic contaminants in wastewater by TiO_2 introduced in immobilized state on supporting material [137]. Soo *et al.* 2005 synthesized hollow ceramic ball (Fig. 25) with a novel method, 1.5 mm in diameter, and coated TiO_2 on wall and photocatalytic activity of fluidized bed process (Fig. 26) was investigated for RhB degradation. Results show that this process effectively photocatalyzed the degradation of RhB.

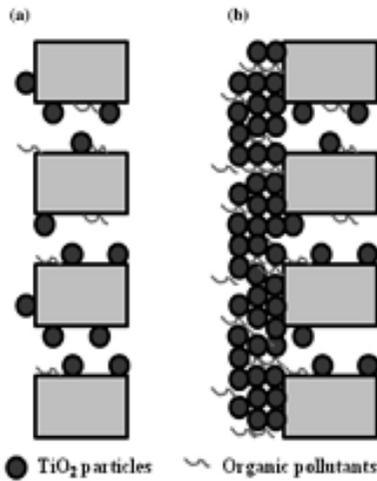


Fig. 22. Schematic illustration of membrane fouling mechanisms: (a) pore blocking and (b) cake layer [144].

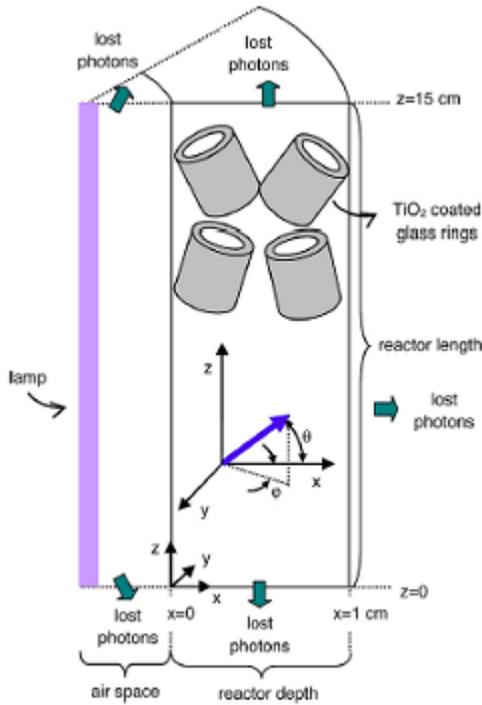


Fig. 23. schematic representation of fixed bed reactor [145].

In another work Wang *et al.* used granular activated carbon as support of photocatalyst [146]. The photocatalytic oxidation of acid dye under visible light irradiation was done in a recycle fluidized bed reactor. $ZnFe_2O_4/TiO_2$ -immobilized granular activated carbon ($ZnFe_2O_4/TiO_2$ -GAC) was used as the photocatalyst, and the lamp (CDM-T, 150 W) was used as the light source. Granular activated carbons with an average diameter of 2.172 mm (8–9 mesh), 1.189 mm (12–16 mesh), and 0.542 mm (28–32 mesh) were hired as the supports of $ZnFe_2O_4/TiO_2$ photocatalysts. Zulfakar

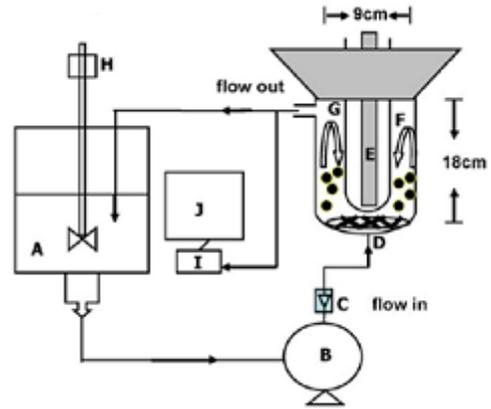


Fig. 24. Schematic of fluidized bed reactor [137].

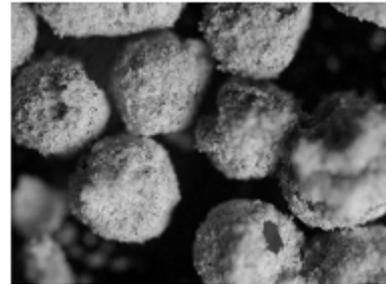


Fig. 25. The SEM photograph of Photomedia ($\times 40$) [146].

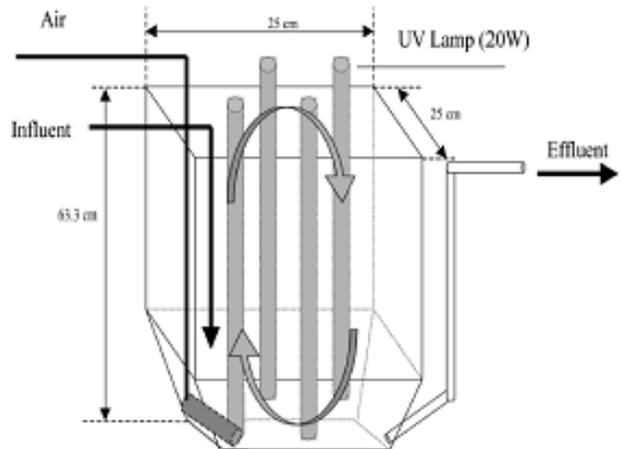


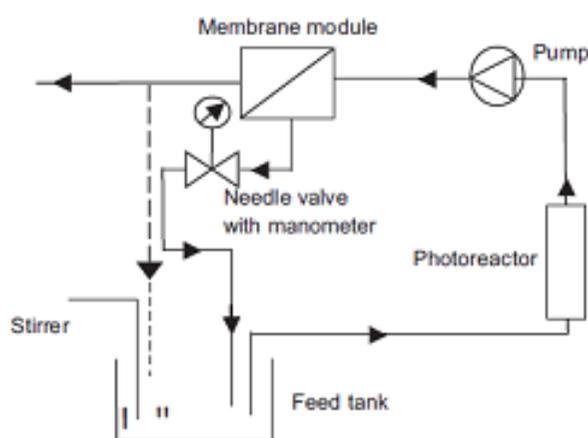
Fig. 26. The schematic diagram of photocatalytic fluidized bed reactor [146].

et al. used immobilized TiO_2 on quartz sand with 0.3 mm in diameter [147]. The performance of the supported photocatalyst was evaluated in different operating parameters such as photocatalyst loading and initial phenol concentration in a fluidized bed reactor (Fig.27).

Fluidized bed photocatalytic reactor systems have several benefits over common immobilized (coated on wall) or slurry-type photocatalytic reactors. The unique reactor configuration provides both exposure of photocatalyst to UV/sun light and good

Table 4.Advantages and disadvantages of suspended reactors with TiO₂ immobilized in/on the membrane [137].

Advantages	Disadvantages
- No need to separate and recycle the catalyst—the membrane can be used as long as the activity of TiO ₂ remains high	- The effectiveness of degradation lower than in case of catalyst in suspension
- No membrane fouling due to presence of TiO ₂ particles	- Adjustment of catalyst loading to the composition of the treated solution is impossible (fixed amount of the catalyst immobilized in/on the membrane)
- Possibility of fouling mitigation due to enhanced hydrophilicity of the TiO ₂ -modified membrane	- Risk of damage of polymer membranes by the UV light or hydroxyl radicals
- Possibility of fouling mitigation due to decomposition of organic contaminants forming the gel layer or filtration cake	- Necessity of the membrane exchange when the catalyst loses its activity
- Contaminants could be decomposed either in feed or in permeate	

**Fig. 27.** Fluidized bed reactor set-up [148].

penetration of the light into the photocatalyst bed that allow more contact of photocatalyst and reactant fluid. Also, UV light can be more evenly distributed within the given catalyst bed. Separation problem of catalysts from treated water is very easy in fluidized bed reactor systems.

6. Conclusions

This article reviews the principles and methods of photocatalysts preparation, promoting photocatalyst activity and improving performance, mainly for TiO₂. In addition to destruction of viruses and bacteria, heterogeneous photocatalysis has been used to decompose natural organic matters, volatile organic compounds in water, air and soil. Widening the wavelength for semiconductor application by doping is an area of increasing interest. Various configurations of photocatalytic reactors were investigated and their advantages and disadvantages were reported. The photocatalysts can be modified and used in

an appropriate reactor configuration for destruction of specific pollutants.

References

- [1] S. Suárez, M. Carballa, F. Omil, J.M. Lema, How are pharmaceutical and personal care products (PPCPs) removed from urban wastewaters?, *Reviews in Environmental Science and Bio/Technology*, 7 (2008) 125-138.
- [2] C. Zwiener, S.D. Richardson, Analysis of disinfection by-products in drinking water by LC-MS and related MS techniques, *TrAC Trends in Analytical Chemistry*, 24 (2005) 613-621.
- [3] T. Wintgens, F. Salehi, R. Hochstrat, T. Melin, Emerging contaminants and treatment options in water recycling for indirect potable use, *Water Science and Technology*, 57 (2008) 99-107.
- [4] P.R. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: oxidation technologies at ambient conditions, *Advances in Environmental Research*, 8 (2004) 501-551.

- [5] M. Pera-Titus, V. Garcia-Molina, M.A. Baños, J. Giménez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, *Applied Catalysis B: Environmental*, 47 (2004) 219-256.
- [6] C. Comninellis, A. Kapalka, S. Malato, S.A. Parsons, I. Poullos, D. Mantzavinos, Advanced oxidation processes for water treatment: advances and trends for R&D, *Journal of Chemical Technology and Biotechnology*, 83 (2008) 769-776.
- [7] R. Ameta, S. Benjamin, A. Ameta, S.C. Ameta, Photocatalytic degradation of organic Pollutants: A Review, in: *Materials Science Forum*, Trans Tech Publ, 2013, pp. 247-272.
- [8] R.C. Martins, R.M. Quinta-Ferreira, Remediation of phenolic wastewaters by advanced oxidation processes (AOPs) at ambient conditions: comparative studies, *Chemical engineering science*, 66 (2011) 3243-3250.
- [9] S.-Y. Lee, S.-J. Park, TiO₂ photocatalyst for water treatment applications, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 1761-1769.
- [10] L.G. Devi, R. Kavitha, A review on non metal ion doped titania for the photocatalytic degradation of organic pollutants under UV/solar light: Role of photogenerated charge carrier dynamics in enhancing the activity, *Applied Catalysis B: Environmental*, 140 (2013) 559-587.
- [11] J. Yu, X. Yu, Hydrothermal synthesis and photocatalytic activity of zinc oxide hollow spheres, *Environmental science & technology*, 42 (2008) 4902-4907.
- [12] A. Mehdizadeh Dehkordi, An Experimental Investigation Towards Improvement of Thermoelectric Properties of Strontium Titanate Ceramics, (2014).
- [13] R. Wang, K. Hashimoto, A. Fujishima, M. Chikuni, E. Kojima, A. Kitamura, M. Shimohigoshi, T. Watanabe, Light-induced amphiphilic surfaces, *Nature*, 388 (1997) 431-432.
- [14] A. Sonune, R. Ghate, Developments in wastewater treatment methods, *Desalination*, 167 (2004) 55-63.
- [15] T. Daimon, T. Hirakawa, M. Kitazawa, J. Suetake, Y. Nosaka, Formation of singlet molecular oxygen associated with the formation of superoxide radicals in aqueous suspensions of TiO₂ photocatalysts, *Applied Catalysis A: General*, 340 (2008) 169-175.
- [16] Y. Nosaka, T. Daimon, A.Y. Nosaka, Y. Murakami, Singlet oxygen formation in photocatalytic TiO₂ aqueous suspension, *Physical Chemistry Chemical Physics*, 6 (2004) 2917-2918.
- [17] H. Sakai, R. Baba, K. Hashimoto, A. Fujishima, A. Heller, Local Detection of Photoelectrochemically Produced H₂O₂ with a "Wired" Horseradish Peroxidase Microsensor, *The Journal of Physical Chemistry*, 99 (1995) 11896-11900.
- [18] K. Ranjit, I. Willner, S. Bossmann, A. Braun, Lanthanide oxide-doped titanium dioxide photocatalysts: novel photocatalysts for the enhanced degradation of p-chlorophenoxyacetic acid, *Environmental science & technology*, 35 (2001) 1544-1549.
- [19] J.R. Harbour, M.L. Hair, Radical intermediates in the photosynthetic generation of hydrogen peroxide with aqueous zinc oxide dispersions, *Journal of Physical Chemistry*, 83 (1979) 652-656.
- [20] A. Mills, S.-K. Lee, A web-based overview of semiconductor photochemistry-based current commercial applications, *Journal of Photochemistry and Photobiology A: Chemistry*, 152 (2002) 233-247.
- [21] N.S. Lewis, Toward cost-effective solar energy use, *science*, 315 (2007) 798-801.
- [22] S. Bouadila, S. Kooli, M. Lazaar, S. Skouri, A. Farhat, Performance of a new solar air heater with packed-bed latent storage energy for nocturnal use, *Applied Energy*, 110 (2013) 267-275.
- [23] <http://www.lenntech.com/composition-seawater.htm>, in.
- [24] M. Heikkinen, H. Poutiainen, M. Liukkonen, T. Heikkinen, Y. Hiltunen, Subtraction analysis based on self-organizing maps for an industrial wastewater treatment process, *Mathematics and computers in simulation*, 82 (2011) 450-459.
- [25] A. Biati, F. Moattar, A. Karbassi, A. Hassani, Role of saline water in removal of heavy elements from industrial wastewaters, (2010).
- [26] L. Tajeddine, M. Nemmaoui, H. Mountacer, A. Dahchour, M. Sarakha, Photodegradation of fenamiphos on the surface of clays and soils, *Environmental Chemistry Letters*, 8 (2010) 123-128.
- [27] S. Kommineni, J. Zoeckler, A. Stocking, P.S. Liang, A. Flores, R. Rodriguez, T. Browne, P.R. Roberts, A. Brown, 3.0 Advanced Oxidation Processes, _____ Treatment Technologies for removal of Methyl Tertiary Butyl Ether (MTBE) from drinking water: air stripping, Advanced Oxidation Process, Granular Activated carbon, Synthetic resin sorbents, 2 (2000) 109-208.
- [28] J. Zhang, K.-H. Lee, L. Cui, T.-s. Jeong, Degradation of methylene blue in aqueous solution by ozone-based processes, *Journal of Industrial and Engineering Chemistry*, 15 (2009) 185-189.
- [29] S.C. Kwon, J.Y. Kim, S.M. Yoon, W. Bae, K.S. Kang, Y.W. Rhee, Treatment characteristic of 1, 4-dioxane by ozone-based advanced oxidation processes, *Journal of Industrial and Engineering Chemistry*, 18 (2012) 1951-1955.
- [30] Z. Li, S. Yuan, C. Qiu, Y. Wang, X. Pan, J. Wang, C. Wang, J. Zuo, Effective degradation of refractory organic pollutants in landfill leachate by electro-peroxone treatment, *Electrochimica Acta*, 102 (2013)

- 174-182.
- [31] S. Sabhi, J. Kiwi, Degradation of 2, 4-dichlorophenol by immobilized iron catalysts, *Water Research*, 35 (2001) 1994-2002.
- [32] D. Tabet, M. Saidi, M. Houari, P. Pichat, H. Khalaf, Fe-pillared clay as a Fenton-type heterogeneous catalyst for cinnamic acid degradation, *Journal of environmental management*, 80 (2006) 342-346.
- [33] H.-J. Jung, J.-S. Hong, J.-K. Suh, A comparison of fenton oxidation and photocatalyst reaction efficiency for humic acid degradation, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 1325-1330.
- [34] S. Şahinkaya, COD and color removal from synthetic textile wastewater by ultrasound assisted electro-Fenton oxidation process, *Journal of Industrial and Engineering Chemistry*, 19 (2013) 601-605.
- [35] G. Muthuraman, I.-S. Moon, A review on an electrochemically assisted-scrubbing process for environmental harmful pollutant's destruction, *Journal of Industrial and Engineering Chemistry*, 18 (2012) 1540-1550.
- [36] S. Banerjee, S.C. Pillai, P. Falaras, K.E. O'shea, J.A. Byrne, D.D. Dionysiou, New insights into the mechanism of visible light photocatalysis, *The journal of physical chemistry letters*, 5 (2014) 2543-2554.
- [37] M. Pelaez, N.T. Nolan, S.C. Pillai, M.K. Seery, P. Falaras, A.G. Kontos, P.S. Dunlop, J.W. Hamilton, J.A. Byrne, K. O. shea, A review on the visible light active titanium dioxide photocatalysts for environmental applications, *Applied Catalysis B: Environmental*, 125 (2012) 331-349.
- [38] J. Schneider, M. Matsuoka, M. Takeuchi, J. Zhang, Y. Horiuchi, M. Anpo, D.W. Bahnemann, Understanding TiO₂ photocatalysis: mechanisms and materials, *Chemical reviews*, 114 (2014) 9919-9986.
- [39] S. Banerjee, D.D. Dionysiou, S.C. Pillai, Self-cleaning applications of TiO₂ by photo-induced hydrophilicity and photocatalysis, *Applied Catalysis B: Environmental*, 176 (2015) 396-428.
- [40] A. Fujishima, Electrochemical photolysis of water at a semiconductor electrode, *nature*, 238 (1972) 37-38.
- [41] P.V. Kamat, K. Tvrđy, D.R. Baker, J.G. Radich, Beyond photovoltaics: semiconductor nanoarchitectures for liquid-junction solar cells, *Chemical reviews*, 110 (2010) 6664-6688.
- [42] V. Etacheri, M.K. Seery, S.J. Hinder, S.C. Pillai, Oxygen Rich Titania: A Dopant Free, High Temperature Stable, and Visible-Light Active Anatase Photocatalyst, *Advanced Functional Materials*, 21 (2011) 3744-3752.
- [43] D.A. Keane, K.G. McGuigan, P.F. Ibáñez, M.I. Polo-López, J.A. Byrne, P.S. Dunlop, K. O'Shea, D.D. Dionysiou, S.C. Pillai, Solar photocatalysis for water disinfection: materials and reactor design, *Catalysis Science & Technology*, 4 (2014) 1211-1226.
- [44] S.C. Pillai, P. Periyat, R. George, D.E. McCormack, M.K. Seery, H. Hayden, J. Colreavy, D. Corr, S.J. Hinder, Synthesis of high-temperature stable anatase TiO₂ photocatalyst, *The Journal of Physical Chemistry C*, 111 (2007) 1605-1611.
- [45] V. Etacheri, M.K. Seery, S.J. Hinder, S.C. Pillai, Highly Visible Light Active TiO₂-x N x Heterojunction Photocatalysts†, *Chemistry of Materials*, 22 (2010) 3843-3853.
- [46] L. Vayssieres, Growth of arrayed nanorods and nanowires of ZnO from aqueous solutions, *Advanced Materials*, 15 (2003) 464-466.
- [47] V. Etacheri, R. Roshan, V. Kumar, Mg-doped ZnO nanoparticles for efficient sunlight-driven photocatalysis, *ACS applied materials & interfaces*, 4 (2012) 2717-2725.
- [48] G.-S. Li, D.-Q. Zhang, J.C. Yu, A new visible-light photocatalyst: CdS quantum dots embedded mesoporous TiO₂, *Environmental science & technology*, 43 (2009) 7079-7085.
- [49] A. Kudo, M. Sekizawa, Photocatalytic H₂ evolution under visible light irradiation on Ni-doped ZnS photocatalyst, *Chemical Communications*, (2000) 1371-1372.
- [50] F. Kong, L. Huang, L. Luo, S. Chu, Y. Wang, Z. Zou, Synthesis and characterization of visible light driven mesoporous nano-photocatalyst MoO₃/TiO₂, *Journal of nanoscience and nanotechnology*, 12 (2012) 1931-1937.
- [51] V. Etacheri, M.K. Seery, S.J. Hinder, S.C. Pillai, Nanostructured Ti_{1-x} S_x O_{2-y} N_y Heterojunctions for Efficient Visible-Light-Induced Photocatalysis, *Inorganic chemistry*, 51 (2012) 7164-7173.
- [52] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahnemann, Environmental applications of semiconductor photocatalysis, *Chemical reviews*, 95 (1995) 69-96.
- [53] V. Etacheri, G. Michlits, M.K. Seery, S.J. Hinder, S.C. Pillai, A Highly Efficient TiO₂-x C x Nano-heterojunction Photocatalyst for Visible Light Induced Antibacterial Applications, *ACS applied materials & interfaces*, 5 (2013) 1663-1672.
- [54] N. Wetchakun, S. Chaiwichain, B. Inceesungvorn, K. Pingmuang, S. Phanichphant, A.I. Minett, J. Chen, BiVO₄/CeO₂ nanocomposites with high visible-light-induced photocatalytic activity, *ACS applied materials & interfaces*, 4 (2012) 3718-3723.
- [55] S. Poliseti, P.A. Deshpande, G. Madras, Photocatalytic activity of combustion synthesized ZrO₂ and ZrO₂-TiO₂ mixed oxides, *Industrial & Engineering Chemistry Research*, 50 (2011) 12915-12924.
- [56] L. Li, M. Krissanasaeranee, S.W. Pattinson, M.

- Stefik, U. Wiesner, U. Steiner, D. Eder, Enhanced photocatalytic properties in well-ordered mesoporous WO_3 , *Chemical Communications*, 46 (2010) 7620-7622.
- [57] Y. Liu, L. Yu, Y. Hu, C. Guo, F. Zhang, X.W.D. Lou, A magnetically separable photocatalyst based on nest-like $\gamma\text{-Fe}_2\text{O}_3/\text{ZnO}$ double-shelled hollow structures with enhanced photocatalytic activity, *Nanoscale*, 4 (2012) 183-187.
- [58] D. Chu, J. Mo, Q. Peng, Y. Zhang, Y. Wei, Z. Zhuang, Y. Li, Enhanced Photocatalytic Properties of SnO_2 Nanocrystals with Decreased Size for ppb-level Acetaldehyde Decomposition, *ChemCatChem*, 3 (2011) 371-377.
- [59] M. Grätzel, *Heterogeneous photochemical electron transfer*, CRC Press Boca Raton, FL, 1989.
- [60] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, *Journal of hazardous materials*, 112 (2004) 269-278.
- [61] S.N. Frank, A.J. Bard, Heterogeneous photocatalytic oxidation of cyanide and sulfite in aqueous solutions at semiconductor powders, *The journal of physical chemistry*, 81 (1977) 1484-1488.
- [62] Y. Wang, Y. Huang, W. Ho, L. Zhang, Z. Zou, S. Lee, Biomolecule-controlled hydrothermal synthesis of C-N-S-tridoped TiO_2 nanocrystalline photocatalysts for NO removal under simulated solar light irradiation, *Journal of Hazardous materials*, 169 (2009) 77-87.
- [63] C. Su, C.-M. Tseng, L.-F. Chen, B.-H. You, B.-C. Hsu, S.-S. Chen, Sol-hydrothermal preparation and photocatalysis of titanium dioxide, *Thin Solid Films*, 498 (2006) 259-265.
- [64] R. Asahi, Y. Taga, W. Mannstadt, A.J. Freeman, Electronic and optical properties of anatase TiO_2 , *Physical Review B*, 61 (2000) 7459.
- [65] M. Muruganandham, M. Swaminathan, Solar photocatalytic degradation of a reactive azo dye in TiO_2 -suspension, *Solar Energy Materials and Solar Cells*, 81 (2004) 439-457.
- [66] T. Miyagi, M. Kamei, T. Mitsuhashi, T. Ishigaki, A. Yamazaki, Charge separation at the rutile/anatase interface: a dominant factor of photocatalytic activity, *Chemical Physics Letters*, 390 (2004) 399-402.
- [67] M. Toyoda, Y. Nanbu, Y. Nakazawa, M. Hirano, M. Inagaki, Effect of crystallinity of anatase on photoactivity for methyleneblue decomposition in water, *Applied Catalysis B: Environmental*, 49 (2004) 227-232.
- [68] E. Beyers, P. Cool, E.F. Vansant, Anatase formation during the synthesis of mesoporous titania and its photocatalytic effect, *The Journal of Physical Chemistry B*, 109 (2005) 10081-10086.
- [69] A.O. Ibadon, P. Fitzpatrick, Heterogeneous photocatalysis: recent advances and applications, *Catalysts*, 3 (2013) 189-218.
- [70] P. Schmitt-Kopplin, N. Hertkorn, H.-R. Schulten, A. Kettrup, Structural changes in a dissolved soil humic acid during photochemical degradation processes under O_2 and N_2 atmosphere, *Environmental science & technology*, 32 (1998) 2531-2541.
- [71] A. Paleologou, H. Marakas, N.P. Xekoukoulotakis, A. Moya, Y. Vergara, N. Kalogerakis, P. Gikas, D. Mantzavinos, Disinfection of water and wastewater by TiO_2 photocatalysis, sonolysis and UV-C irradiation, *Catalysis Today*, 129 (2007) 136-142.
- [72] K. Sunada, T. Watanabe, K. Hashimoto, Studies on photokilling of bacteria on TiO_2 thin film, *Journal of Photochemistry and Photobiology A: Chemistry*, 156 (2003) 227-233.
- [73] N. Daneshvar, A. Niaei, S. Akbari, S. Aber, N. Kazemian, Photocatalytic disinfection of water polluted by *Pseudomonas aeruginosa*, *Global Nest J*, 9 (2007) 1-5.
- [74] P.V. Kamat, Graphene-based nanoarchitectures. Anchoring semiconductor and metal nanoparticles on a two-dimensional carbon support, *The Journal of Physical Chemistry Letters*, 1 (2009) 520-527.
- [75] D.S. Bhatkhande, V.G. Pangarkar, A.A. Beenackers, Photocatalytic degradation for environmental applications—a review, *Journal of Chemical Technology and Biotechnology*, 77 (2002) 102-116.
- [76] K. Pirkanniemi, M. Sillanpää, Heterogeneous water phase catalysis as an environmental application: a review, *Chemosphere*, 48 (2002) 1047-1060.
- [77] A. Huang, L. Cao, J. Chen, F.-J. Spiess, S.L. Suib, T.N. Obee, S.O. Hay, J.D. Freihaut, Photocatalytic degradation of triethylamine on titanium oxide thin films, *Journal of catalysis*, 188 (1999) 40-47.
- [78] I. Arabatzis, S. Antonaraki, T. Stergiopoulos, A. Hiskia, E. Papaconstantinou, M. Bernard, P. Falaras, Preparation, characterization and photocatalytic activity of nanocrystalline thin film TiO_2 catalysts towards 3, 5-dichlorophenol degradation, *Journal of Photochemistry and Photobiology A: Chemistry*, 149 (2002) 237-245.
- [79] W. Choi, A. Termin, M.R. Hoffmann, The role of metal ion dopants in quantum-sized TiO_2 : correlation between photoreactivity and charge carrier recombination dynamics, *The Journal of Physical Chemistry*, 98 (1994) 13669-13679.
- [80] X. Chen, S.S. Mao, Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications, *Chem. Rev.*, 107 (2007) 2891-2959.
- [81] A. Sclafani, J. Herrmann, Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions, *The Journal of Physical Chemistry*, 100 (1996) 13655-13661.

- [82] J. Liqiang, Q. Yichun, W. Baiqi, L. Shudan, J. Bao-jiang, Y. Libin, F. Wei, F. Honggang, S. Jiazhong, Review of photoluminescence performance of nano-sized semiconductor materials and its relationships with photocatalytic activity, *Solar Energy Materials and Solar Cells*, 90 (2006) 1773-1787.
- [83] N. Serpone, Relative photonic efficiencies and quantum yields in heterogeneous photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, 104 (1997) 1-12.
- [84] J.C. Yu, L. Zhang, J. Yu, Direct sonochemical preparation and characterization of highly active mesoporous TiO₂ with a bicrystalline framework, *Chemistry of Materials*, 14 (2002) 4647-4653.
- [85] Y. Do, W. Lee, K. Dwight, A. Wold, The effect of WO₃ on the photocatalytic activity of TiO₂, *Journal of Solid State Chemistry*, 108 (1994) 198-201.
- [86] J. Engweiler, J. Harf, A. Baiker, WO_x/TiO₂ catalysts prepared by grafting of tungsten alkoxides: morphological properties and catalytic behavior in the selective reduction of NO by NH₃, *Journal of Catalysis*, 159 (1996) 259-269.
- [87] K. Vinodgopal, P.V. Kamat, Enhanced rates of photocatalytic degradation of an azo dye using SnO₂/TiO₂ coupled semiconductor thin films, *Environmental science & technology*, 29 (1995) 841-845.
- [88] A. Maira, K.L. Yeung, C. Lee, P.L. Yue, C.K. Chan, Size effects in gas-phase photo-oxidation of trichloroethylene using nanometer-sized TiO₂ catalysts, *Journal of Catalysis*, 192 (2000) 185-196.
- [89] Y. Li, D.-S. Hwang, N.H. Lee, S.-J. Kim, Synthesis and characterization of carbon-doped titania as an artificial solar light sensitive photocatalyst, *Chemical Physics Letters*, 404 (2005) 25-29.
- [90] R. Georgekutty, M.K. Seery, S.C. Pillai, A highly efficient Ag-ZnO photocatalyst: synthesis, properties, and mechanism, *The Journal of Physical Chemistry C*, 112 (2008) 13563-13570.
- [91] G. Balasubramanian, D.D. Dionysiou, M.T. Suidan, I. Baudin, J.-M. Lané, Evaluating the activities of immobilized TiO₂ powder films for the photocatalytic degradation of organic contaminants in water, *Applied Catalysis B: Environmental*, 47 (2004) 73-84.
- [92] P. Periyat, S.C. Pillai, D.E. McCormack, J. Colreavy, S.J. Hinder, Improved high-temperature stability and sun-light-driven photocatalytic activity of sulfur-doped anatase TiO₂, *The Journal of Physical Chemistry C*, 112 (2008) 7644-7652.
- [93] J.A. Gamboa, D.M. Pasquevich, Effect of Chlorine Atmosphere on the Anatase-Rutile Transformation, *Journal of the American Ceramic Society*, 75 (1992) 2934-2938.
- [94] A. Hagfeldt, M. Graetzel, Light-induced redox reactions in nanocrystalline systems, *Chemical Reviews*, 95 (1995) 49-68.
- [95] N.J. Cherepy, G.P. Smestad, M. Grätzel, J.Z. Zhang, Ultrafast electron injection: implications for a photoelectrochemical cell utilizing an anthocyanin dye-sensitized TiO₂ nanocrystalline electrode, *The Journal of Physical Chemistry B*, 101 (1997) 9342-9351.
- [96] A. Kay, R. Humphry-Baker, M. Graetzel, Artificial photosynthesis. 2. Investigations on the mechanism of photosensitization of nanocrystalline TiO₂ solar cells by chlorophyll derivatives, *The Journal of Physical Chemistry*, 98 (1994) 952-959.
- [97] B. Patrick, P. Kamat, Photosensitization of large-bandgap semiconductors. Charge injection from triplet excited thionine into ZnO colloids, *Journal of Physical Chemistry*, 96 (1992).
- [98] P.V. Kamat, Picosecond charge-transfer events in the photosensitization of colloidal titania, *Langmuir*, 6 (1990) 512-513.
- [99] P.V. Kamat, K. Gopidas, D. Weir, Photoelectrochemistry in particulate systems. Photosensitized charge injection into opaque TiO₂ semiconductor powder as probed by time-resolved diffuse reflectance laser flash photolysis, *Chemical physics letters*, 149 (1988) 491-496.
- [100] K. Kalyanasundaram, N. Vlachopoulos, V. Krishnan, A. Monnier, M. Grätzel, Sensitization of titanium dioxide in the visible light region using zinc porphyrins, *Journal of Physical Chemistry*, 91 (1987) 2342-2347.
- [101] R. Eichberger, F. Willig, Ultrafast electron injection from excited dye molecules into semiconductor electrodes, *Chemical physics*, 141 (1990) 159-173.
- [102] Y. Cho, W. Choi, C.-H. Lee, T. Hyeon, H.-I. Lee, Visible light-induced degradation of carbon tetrachloride on dye-sensitized TiO₂, *Environmental science & technology*, 35 (2001) 966-970.
- [103] S. Malato, P. Fernández-Ibáñez, M. Maldonado, J. Blanco, W. Gernjak, Decontamination and disinfection of water by solar photocatalysis: recent overview and trends, *Catalysis Today*, 147 (2009) 1-59.
- [104] X. Zhang, T. Peng, S. Song, Recent advances in dye-sensitized semiconductor systems for photocatalytic hydrogen production, *Journal of Materials Chemistry A*, 4 (2016) 2365-2402.
- [105] R. Argazzi, N.Y.M. Iha, H. Zabri, F. Odobel, C.A. Bignozzi, Design of molecular dyes for application in photoelectrochemical and electrochromic devices based on nanocrystalline metal oxide semiconductors, *Coordination Chemistry Reviews*, 248 (2004) 1299-1316.
- [106] A.S. Polo, M.K. Itokazu, N.Y.M. Iha, Metal complex sensitizers in dye-sensitized solar cells, *Coordination Chemistry Reviews*, 248 (2004) 1343-1361.
- [107] I. Martini, J.H. Hodak, G.V. Hartland, Effect of

- water on the electron transfer dynamics of 9-anthracenecarboxylic acid bound to TiO₂ nanoparticles: demonstration of the Marcus inverted region, *The Journal of Physical Chemistry B*, 102 (1998) 607-614.
- [108] J.M. Rehm, G.L. McLendon, Y. Nagasawa, K. Yoshihara, J. Moser, M. Grätzel, Femtosecond electron-transfer dynamics at a sensitizing dye-semiconductor (TiO₂) interface, *The Journal of Physical Chemistry*, 100 (1996) 9577-9578.
- [109] A.K. Jana, Solar cells based on dyes, *Journal of Photochemistry and Photobiology A: Chemistry*, 132 (2000) 1-17.
- [110] G. Liu, J. Zhao, Photocatalytic degradation of dye sulforhodamine B: a comparative study of photocatalysis with photosensitization, *New Journal of Chemistry*, 24 (2000) 411-417.
- [111] F. Zhang, J. Zhao, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, TiO₂-assisted photodegradation of dye pollutants II. Adsorption and degradation kinetics of eosin in TiO₂ dispersions under visible light irradiation, *Applied Catalysis B: Environmental*, 15 (1998) 147-156.
- [112] F. Zhang, J. Zhao, L. Zang, T. Shen, H. Hidaka, E. Pelizzetti, N. Serpone, Photoassisted degradation of dye pollutants in aqueous TiO₂ dispersions under irradiation by visible light, *Journal of Molecular Catalysis A: Chemical*, 120 (1997) 173-178.
- [113] J. Zhao, T. Wu, K. Wu, K. Oikawa, H. Hidaka, N. Serpone, Photoassisted degradation of dye pollutants. 3. Degradation of the cationic dye rhodamine B in aqueous anionic surfactant/TiO₂ dispersions under visible light irradiation: evidence for the need of substrate adsorption on TiO₂ particles, *Environmental science & technology*, 32 (1998) 2394-2400.
- [114] M. Ni, M.K. Leung, D.Y. Leung, K. Sumathy, A review and recent developments in photocatalytic water-splitting using TiO₂ for hydrogen production, *Renewable and Sustainable Energy Reviews*, 11 (2007) 401-425.
- [115] K. Gupta, R. Singh, A. Pandey, A. Pandey, Photocatalytic antibacterial performance of TiO₂ and Ag-doped TiO₂ against *S. aureus*, *P. aeruginosa* and *E. coli*, *Beilstein journal of nanotechnology*, 4 (2013) 345-351.
- [116] V.N. Nguyen, N.K.T. Nguyen, P.H. Nguyen, Hydrothermal synthesis of Fe-doped TiO₂ nanostructure photocatalyst, *Advances in Natural Sciences: Nanoscience and Nanotechnology*, 2 (2011) 035014.
- [117] E. Kowalska, S. Rau, Photoreactors for wastewater treatment: a review, *Recent Patents on Engineering*, 4 (2010) 242-266.
- [118] M.V. Dozzi, A. Saccomanni, E. Selli, Cr (VI) photocatalytic reduction: effects of simultaneous organics oxidation and of gold nanoparticles photo-deposition on TiO₂, *Journal of hazardous materials*, 211 (2012) 188-195.
- [119] J.-W. Yoon, T. Sasaki, N. Koshizaki, Dispersion of nanosized noble metals in TiO₂ matrix and their photoelectrode properties, *Thin Solid Films*, 483 (2005) 276-282.
- [120] M.K. Seery, R. George, P. Floris, S.C. Pillai, Silver doped titanium dioxide nanomaterials for enhanced visible light photocatalysis, *Journal of Photochemistry and Photobiology A: Chemistry*, 189 (2007) 258-263.
- [121] S. Tomás, A. Luna-Resendis, L. Cortés-Cuautli, D. Jacinto, Optical and morphological characterization of photocatalytic TiO₂ thin films doped with silver, *Thin Solid Films*, 518 (2009) 1337-1340.
- [122] N. Sobana, M. Muruganadham, M. Swaminathan, Nano-Ag particles doped TiO₂ for efficient photodegradation of direct azo dyes, *Journal of Molecular Catalysis A: Chemical*, 258 (2006) 124-132.
- [123] B. Xin, Z. Ren, H. Hu, X. Zhang, C. Dong, K. Shi, L. Jing, H. Fu, Photocatalytic activity and interfacial carrier transfer of Ag-TiO₂ nanoparticle films, *Applied Surface Science*, 252 (2005) 2050-2055.
- [124] A.J. Nozik, M.C. Beard, J.M. Luther, M. Law, R.J. Ellingson, J.C. Johnson, Semiconductor quantum dots and quantum dot arrays and applications of multiple exciton generation to third-generation photovoltaic solar cells, *Chemical reviews*, 110 (2010) 6873-6890.
- [125] B. Yu, Z. Hu, M. Liu, H. Yang, Q. Kong, Y. Liu, Review of research on air-conditioning systems and indoor air quality control for human health, *International journal of refrigeration*, 32 (2009) 3-20.
- [126] S. Kment, H. Kmentova, P. Kluson, J. Krysa, Z. Hubicka, V. Cirkva, I. Gregora, O. Solcova, L. Jastrabik, Notes on the photo-induced characteristics of transition metal-doped and undoped titanium dioxide thin films, *Journal of colloid and interface science*, 348 (2010) 198-205.
- [127] D. Robert, Photosensitization of TiO₂ by M_xO_y and M_xS_y nanoparticles for heterogeneous photocatalysis applications, *Catalysis Today*, 122 (2007) 20-26.
- [128] H. Zhang, G. Chen, D.W. Bahnemann, Photoelectrocatalytic materials for environmental applications, *Journal of Materials Chemistry*, 19 (2009) 5089-5121.
- [129] K.M. Lee, C.W. Lai, K.S. Ngai, J.C. Juan, Recent developments of zinc oxide based photocatalyst in water treatment technology: a review, *Water research*, 88 (2016) 428-448.
- [130] M.D. Hernández-Alonso, F. Fresno, S. Suárez, J.M. Coronado, Development of alternative

- photocatalysts to TiO₂: challenges and opportunities, *Energy & Environmental Science*, 2 (2009) 1231-1257.
- [131] M. Ilieva, A. Nakova, V. Tsakova, TiO₂/WO₃ hybrid structures produced through a sacrificial polymer layer technique for pollutant photo- and photoelectrooxidation under ultraviolet and visible light illumination, *Journal of Applied Electrochemistry*, 42 (2012) 121-129.
- [132] Y. Bessekhoud, D. Robert, J. Weber, Bi₂S₃/TiO₂ and CdS/TiO₂ heterojunctions as an available configuration for photocatalytic degradation of organic pollutant, *Journal of Photochemistry and Photobiology A: Chemistry*, 163 (2004) 569-580.
- [133] G. Ren, Y. Gao, J. Yin, A. Xing, H. Liu, Synthesis of High Activity TiO₂/WO₃ Photocatalyst via Environmentally Friendly and Microwave Assisted Hydrothermal Process, *Journal of Chemical Society Pakistan*, 33 (2011) 666-670.
- [134] S. Kuang, L. Yang, S. Luo, Q. Cai, Fabrication, characterization and photoelectrochemical properties of Fe₂O₃ modified TiO₂ nanotube arrays, *Applied Surface Science*, 255 (2009) 7385-7388.
- [135] A.H. Zyoud, N. Zaatar, I. Saadeddin, C. Ali, D. Park, G. Campet, H.S. Hilal, CdS-sensitized TiO₂ in phenazopyridine photo-degradation: Catalyst efficiency, stability and feasibility assessment, *Journal of Hazardous Materials*, 173 (2010) 318-325.
- [136] M. Ge, C. Guo, X. Zhu, L. Ma, Z. Han, W. Hu, Y. Wang, Photocatalytic degradation of methyl orange using ZnO/TiO₂ composites, *Frontiers of Environmental Science & Engineering in China*, 3 (2009) 271-280.
- [137] S. Leong, A. Razmjou, K. Wang, K. Hapgood, X. Zhang, H. Wang, TiO₂ based photocatalytic membranes: a review, *Journal of Membrane Science*, 472 (2014) 167-184.
- [138] S. Mozia, Photocatalytic membrane reactors (PMRs) in water and wastewater treatment. A review, *Separation and Purification Technology*, 73 (2010) 71-91.
- [139] G.L. Puma, P.L. Yue, Modelling and design of thin-film slurry photocatalytic reactors for water purification, *Chemical engineering science*, 58 (2003) 2269-2281.
- [140] R. van Grieken, J. Marugán, C. Sordo, C. Pablos, Comparison of the photocatalytic disinfection of *E. coli* suspensions in slurry, wall and fixed-bed reactors, *Catalysis Today*, 144 (2009) 48-54.
- [141] M. Vezzoli, T. Farrell, A. Baker, S. Psaltis, W.N. Martens, J.M. Bell, Optimal catalyst thickness in titanium dioxide fixed film reactors: Mathematical modelling and experimental validation, *Chemical engineering journal*, 234 (2013) 57-65.
- [142] R. Molinari, C. Lavorato, P. Argurio, Recent progress of photocatalytic membrane reactors in water treatment and in synthesis of organic compounds. A review, *Catalysis Today*, (2016).
- [143] S. Mozia, D. Darowna, K. Szymański, S. Grondzewska, K. Borchert, R. Wróbel, A.W. Morawski, Performance of two photocatalytic membrane reactors for treatment of primary and secondary effluents, *Catalysis Today*, 236 (2014) 135-145.
- [144] W. Zhang, L. Ding, J. Luo, M.Y. Jaffrin, B. Tang, Membrane fouling in photocatalytic membrane reactors (PMRs) for water and wastewater treatment: A critical review, *Chemical Engineering Journal*, 302 (2016) 446-458.
- [145] J. Marugán, R. van Grieken, C. Pablos, M.L. Satuf, A.E. Cassano, O.M. Alfano, Photocatalytic inactivation of *Escherichia coli* aqueous suspensions in a fixed-bed reactor, *Catalysis Today*, 252 (2015) 143-149.
- [146] Y.-S. Na, D.-H. Kim, C.-H. Lee, S.-W. Lee, Y.-S. Park, Y.-K. Oh, S.-H. Park, S.-K. Song, Photocatalytic decolorization of rhodamine B by fluidized bed reactor with hollow ceramic ball photocatalyst, *Korean Journal of Chemical Engineering*, 21 (2004) 430-435.
- [147] R.-C. Wang, K.-S. Fan, J.-S. Chang, Removal of acid dye by ZnFe₂O₄/TiO₂-immobilized granular activated carbon under visible light irradiation in a recycle liquid-solid fluidized bed, *Journal of the Taiwan Institute of Chemical Engineers*, 40 (2009) 533-540.
- [148] M. Zulfakar, A.H. Hairul Nazirah, A. Hadi, A. Rahman, Photocatalytic degradation of phenol in a fluidized bed reactor utilizing immobilized TiO₂ photocatalyst: Characterization and process studies, (2011).

