

# Heterogeneous Photocatalysis in Wastewater Treatment-A Review

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## Abstract:

*Heterogeneous photocatalysis is a low-cost, sustainable and environment friendly advanced oxidation process. It is a process in which highly oxidative OH\* free radicals are produced due to the oxidation and reduction reactions on the semiconductor surface in the presence of ultraviolet light and oxygen. It aligns with the “zero” waste scheme in the wastewater industry and has the ability for the removal of persistent organic compounds and microorganism, present in air and water. Semiconductor photocatalyst material and photoreactor design are two important areas involved in this method for remediation of polluted water stream falls. By far, titania is known as the best photocatalyst as compared to others due to its inert nature and photo stability, but the post-recovery of fine photocatalyst particles after the treatment of contaminated water, still remains the challenge for commercialization of this process at industrial scale. The appropriate design of the photoreactor provides the solution to this problem.*

*The present review paper seeks to offer a scientific and technical overview of the use of TiO<sub>2</sub> nanoparticles as semiconductor photocatalyst material and photoreactor design for the remediation and decontamination of wastewater.*

**Keywords:** Wastewater, Photocatalysis, TiO<sub>2</sub> nanoparticles, Photoreactors.

## 1. Introduction

Increasing demand and shortage of clean water sources, due to the population growth and rapid industrialization, are issues of concern worldwide. Wastewater generated from various industries, such as textile, paper and pulp, pharmaceutical and, laboratories, contains dyes and their intermediates which are toxic to micro-organism, aquatic life and

human beings [1]. It has also been reported that 1-20% of the dyes are lost in the dyeing process and these dyes and their intermediates are one of the largest group of the organic compound that represent an increasing environmental danger [2, 3]. The conventional effluent treatment methods are not readily able to degrade the compounds present in the effluent streams of the processing plants, most of them results in the concentrated or toxic residues. As a response, the research is progressed into more efficient and effective wastewater treatment technologies, to degrade the complex refractory organic compound into simpler molecules such as wcarbon-dioxide and water.

“Advanced oxidation processes (AOPs)” has emerged as an environmentally friendly and innovative water treatment technology. AOPs are ambient pressure and temperature processes, which involves the in situ generation of highly reactive species like hydroxyl free radicals (OH\*) and superoxide radicals. The OH\* radicals are known as one of the powerful oxidizing agents with an oxidation potential of 2.8 V and it can act as the precursor for degradation of any organic and inorganic compound. Among AOPs, heterogeneous photocatalysis using semiconductor catalysts such as TiO<sub>2</sub>, ZnO, Fe<sub>2</sub>O<sub>3</sub>, CdS, etc. has proved to be of real research interest as an efficient method for degrading organic contaminants [4-7]. Among the different semiconductor catalysts known, titanium dioxide (TiO<sub>2</sub>) has received the immense interest in photocatalytic technology for wastewater treatment. The use of titania, was first unfolded by the pioneering research of Fujishima and Honda in 1972 [8], in which it was revealed the possibility of water splitting by photo-electrochemical cell, using a rutile titania anode. This opened the doors for application of titania for environmental frontiers. In 1977, Frank and Bard [9] firstly reported the photocatalytic oxidation of cyanide using TiO<sub>2</sub> powder and later in 1980,

degradation of many harmful chemical compounds present in the air and water was reported by many research groups [10].

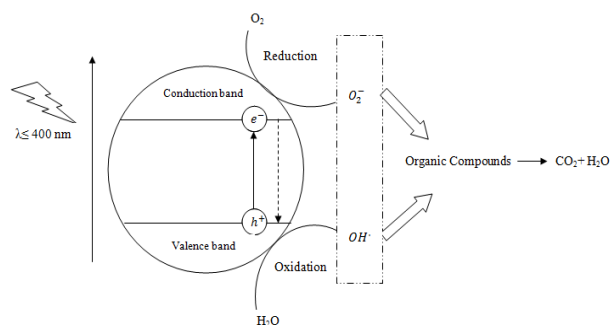
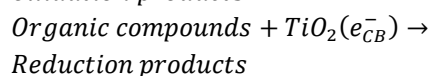
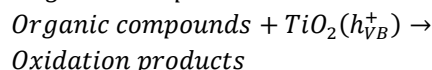
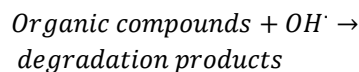
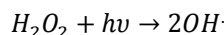
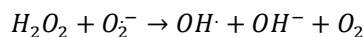
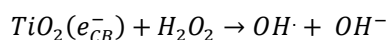
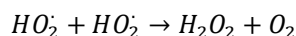
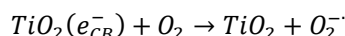
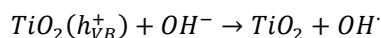
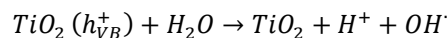
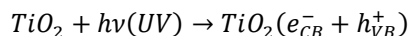
Heterogeneous photocatalysis uses ultraviolet light ( $\lambda \leq 400$  nm), photocatalyst ( $\text{TiO}_2$ ) and oxygen for complete mineralization and degradation of the parent and their intermediate compound. This method has a feasible application in water treatment because it is: i). Low cost method ii). No generation of secondary waste and iii). Ambient operating temperature and pressure. It was also observed that maximum quantum yield and best photocatalytic performance is always achieved using titanium dioxide nanoparticles. Degussa P-25 commercial  $\text{TiO}_2$  photocatalyst with a mixture of anatase and rutile in an approximate ratio of 80:20 is the most active form of catalyst and is found to give very good degradation efficiencies. These particles are approximately 21 nm in size with the approximate surface area of  $50\text{m}^2/\text{g}$ .

Another general agreement is about the development of highly efficient photocatalytic reactors to realize the nanosized  $\text{TiO}_2$  intrinsic performance. It has been stressed that due to the additional presence of light, several aspects of design, optimization and operation should be taken into consideration while fabrication of photocatalytic reactors, that are not usually considered in the conventional reactors. Thus, it is important to design an efficient photocatalytic reactor to improve the overall degradation efficiency of the wastewater treatment unit. This review paper aims to give a brief overview of understanding on the photocatalytic water treatment technology, specially on titanium dioxide photocatalyst and photoreactor development.

## 2. Photocatalysis

Photocatalysis can be termed as the series of chemical reaction (oxidation/reduction) which is assisted by light in the presence of oxygen and suitable catalyst. This type of reaction is activated by the absorption of a photon which has the energy, which is equal or higher than the band gap energy of the catalyst. This absorption of light by a semiconductor catalyst, leads to the charge separation because of the excitation of an electron ( $e^-$ ) from valence band to the conduction band

of the semiconductor, generating a hole ( $h^+$ ) in the valence band [11]. The schematic diagram of the process is presented in figure 1. The series of chain oxidation-reduction reactions that occur at the photon activated surface is widely postulated as:

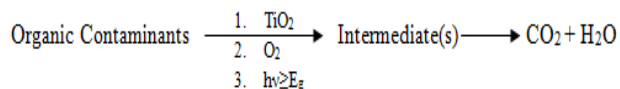


**Figure 1. Mechanism of formation of electron-hole on  $\text{TiO}_2$  surface.**

The series of reaction started with the absorption of a photon ( $\lambda < 400$  nm) as shown in Figure 1. The photo generated hole in the valence band must be sufficiently positive to carry out the oxidation of absorbed  $\text{OH}^-$  ions or  $\text{H}_2\text{O}$  molecules to produce highly oxidative in

nature OH\* radicals. Presence of oxygen prevents the recombination of electron and hole, thus acts as an electron scavenger. In the conduction band, due to the presence of e<sup>-</sup>, O<sub>2</sub> is reduced and superoxides (O<sub>2</sub><sup>-</sup>) ions are generated. These further reacts with protons and adsorbed water and produce hydroperoxide radicals (HO<sub>2</sub><sup>\*</sup>) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>), which are another source of OH\* radicals. More production hydroxyl radicals can effectively degrade the pollutants [12].

The overall photocatalytic reaction can be portrayed as the given equation, in which the organic compounds present in the liquid phase are degraded to their corresponding intermediates and then further degraded into water and carbon dioxide in the presence of sufficient photocatalyst, oxygen and UV light.



The design of photoreactors is an important factor which will decide the final overall efficiency of the process. Other than this, different operating parameters like catalyst loading, pH, oxygen content, initial reactant concentration, temperature, light intensity and wavelength are important factors affecting the photocatalytic process.

### 3. Photoreactors

Photoreactor is a device which can effectively transmit light in a highly scattering and absorbing medium, composed of reactant and photocatalyst. In a photocatalytic reactor, besides the complications of conventional reactors such as flow patterns, mixing, mass transfer, reaction kinetics, catalyst installation, temperature control, etc., an additional engineering factor related to the illumination of the catalyst is relevant. Besides the requirement for good contact between reactants and catalyst, it is also necessary that catalyst and UV light gets an efficient exposure time, as no photocatalytic activity will be shown by catalyst if the photons doesn't have the appropriate energy content [13]. The illumination factor is of utmost

importance as the water treatment capacity of water by the reactor will be determined by the activation of catalyst. Use of multiple light sources is also helpful for increasing the quantum yield of the photoreactor. Involvement of light in these reactors is the major obstacle in the development of photocatalytic reactor at the large scale [14, 15].

Photoreactor can be classified according to their design characteristics; like the type of illumination (ultraviolet lamps or solar light) or position of irradiation source (immersed, external or distributed light source, but mainly, the heterogeneous photoreactors are categorized according to the deployed state of photocatalyst i.e. either suspended in the reactant or immobilized on some surface. One of the main advantages of using photocatalyst in slurries is the presence of large surface area compared to the immobilized system. Whereas, in slurry photoreactors, post separation of semiconductor TiO<sub>2</sub> particles is a major step for regeneration and reuse the photocatalyst particles. In immobilized type photoreactor this problem is solved by immobilizing the photocatalyst on a support and thus it can be used for a longer period of time and can be removed easily after the reaction. Some of the main disadvantages of slurry photoreactors are: 1) Cost addition and more time requirement for the filtration or separation of photocatalyst after the process. 2) Because of the need of separation of photocatalyst these photoreactors are difficult to use in continuous process. 3) At higher catalyst loading problem of agglomeration and aggregation of nanosized photocatalysts also come into account.

Immobilized type photoreactors are used to overcome these disadvantages. Different types of supports such as glasses, tellerette-packings, silica, polymers, and clays are used for the purpose of immobilizing photocatalyst on a substrate. These reactors eliminates the problem of post-separation of catalyst particles from the reactor but then suffers the disadvantage of giving less photocatalytic activities while the reaction. Different reactor types of slurry and immobilized with the type of light source arrangement are listed in table 1.

**Table 1. Different configurations of heterogeneous photocatalytic reactors.**

Reactor group (on basis of catalyst)	Arrangement of light source	Reactor type	Reference
Slurry	Immersion	Annular reactor	[16]
		Thin falling film reactor	[17]
		Taylor vortex reactor	[18]
		Fountain reactor	[19]
		Air lift loop reactor	[20]
	Fluidized bed reactor	[21]	
External	Swirl flow reactor	[22]	
Immobilized	Immersion	Fixed bed reactor	[23]
		Rotating Drum Reactor	[24]
		Membrane reactor	[25]
	External	Spinning disc reactor	[26]
		Thin film reactor	[27]
	Swirl flow reactor	[28]	

Although, immobilized photocatalyst reactors can be used for continuous operations, but due to the less light utilization they show less photocatalytic activity compared to the slurry photoreactors.

#### 4. Conclusion

Heterogeneous photocatalysis has indeed been a very promising wastewater treatment technique, given the known photocatalyst and the perfect photoreactor with suitable operating parameters. The main technical issue is whether to consider photocatalysis as a pre-treatment step, or as a stand-alone system. As a pre-treatment step, prior to biological treatment, it will help in reducing the residence time and will therefore be advantageous for the overall efficiency of the process. As a stand-alone method, the residence time required may be much higher. Moreover to increase the degradation efficiency of the system, multiple light

sources will be desirable, increasing the overall cost of the process.

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