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Photocatalytic Degradation of Organic Pollutants in Water

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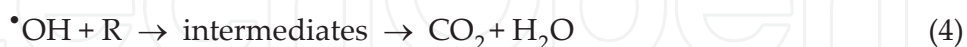
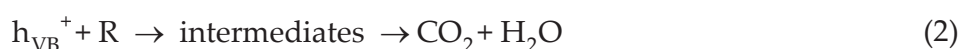
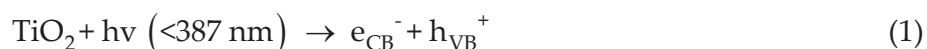
1. Introduction

A photocatalyst is defined as a substance which is activated by adsorbing a photon and is capable of accelerating a reaction without being consumed [1]. These substances are invariably semiconductors. Semiconducting oxide photocatalysts have been increasingly focused in recent years due to their potential applications in solar energy conversion and environmental purification. Semiconductor heterogeneous photocatalysis has enormous potential to treat organic contaminants in water and air. This process is known as advanced oxidation process (AOP) and is suitable for the oxidation of a wide range of organic compounds. Among AOPs, heterogeneous photocatalysis have been proven to be of interest due to its efficiency in degrading recalcitrant organic compounds. Developed in the 1970s, heterogeneous photocatalytic oxidation has been given considerable attention and in the past two decades numerous studies have been carried out on the application of heterogeneous photocatalytic oxidation process with a view to decompose and mineralize recalcitrant organic compounds. It involves the acceleration of photoreaction in the presence of a semiconductor catalyst [2]. Several semiconductors (TiO_2 , ZnO , Fe_2O_3 , CdS , ZnS) can act as photocatalysts but TiO_2 has been most commonly studied due to its ability to break down organic pollutants and even achieve complete mineralization. Photocatalytic and hydrophilic properties of TiO_2 makes it close to an ideal catalyst due to its high reactivity, reduced toxicity, chemical stability and lower costs [3]. Fujishima and Honda [4] pioneered the concept of titania photocatalysis (also known as "Honda-Fujishima effect"). Their work showed the possibility of water splitting in a photoelectrochemical cell containing an inert cathode and rutile titania anode. The applications of titania photoelectrolysis has since been greatly focused in environmental applications including water and wastewater treatment. This chapter provides insight into the fundamentals of the TiO_2 photocatalysis, discusses the effect of variables af-

fecting the performance of degradation of organic pollutants in water with a view to current state of knowledge and future needs.

2. Mechanism and fundamentals of photocatalytic reactions

Heterogeneous photocatalysis using UV/TiO₂ is one of the most common photocatalytic process and is based on adsorption of photons with energy higher than 3.2 eV (wavelengths lower than ~390 nm) resulting in initiating excitation related to charge separation event (gap band) [5]. Generation of excited high-energy states of electron and hole pairs occurs when wide bandgap semiconductors are irradiated higher than their bandgap energy. It results in the promotion of an electron in the conductive band (e_{CB}^-) and formation of a positive hole in the valence band (h_{VB}^+) [5] (Eq. 1). The h_{VB}^+ and e_{CB}^- are powerful oxidizing and reducing agents, respectively. The h_{VB}^+ reacts with organic compounds resulting in their oxidation producing CO₂ and H₂O as end products (Eq. 2). The h_{VB}^+ can also oxidize organic compounds by reacting with water to generate \bullet OH (Eq. 3). Hydroxyl radical (\bullet OH) produced by has the second highest oxidation potential (2.80 V), which is only slightly lower than the strongest oxidant – fluorine. Due to its electrophilic nature (electron preferring), the \bullet OH can non-selectively oxidize almost all electron rich organic molecules, eventually converting them to CO₂ and water (Eq. 4).



where R represents the organic compound.

The conductive band can react with O₂ forming an anion radical superoxide as shown in Eq. 5. Further reaction can lead to the formation of hydrogen peroxide which lead to the formation of \bullet OH [6]. The mechanism of the electron hole-pair formation when the TiO₂ is irradiated is given in Figure 1 [7].



The presence of dissolved oxygen is extremely important during photocatalytic degradation as it can make the recombination process on TiO_2 ($e_{\text{CB}}^-/h_{\text{VB}}^+$) difficult which results in maintaining the electroneutrality of the TiO_2 particles [5]. In other words, it is important for effective photocatalytic degradation of organic pollutants that the reduction process of oxygen and the oxidation of pollutants proceed simultaneously to avoid the accumulation of electron in the conduction band and thus reduce the rate of recombination of e_{CB}^- and h_{VB}^+ [8, 9].

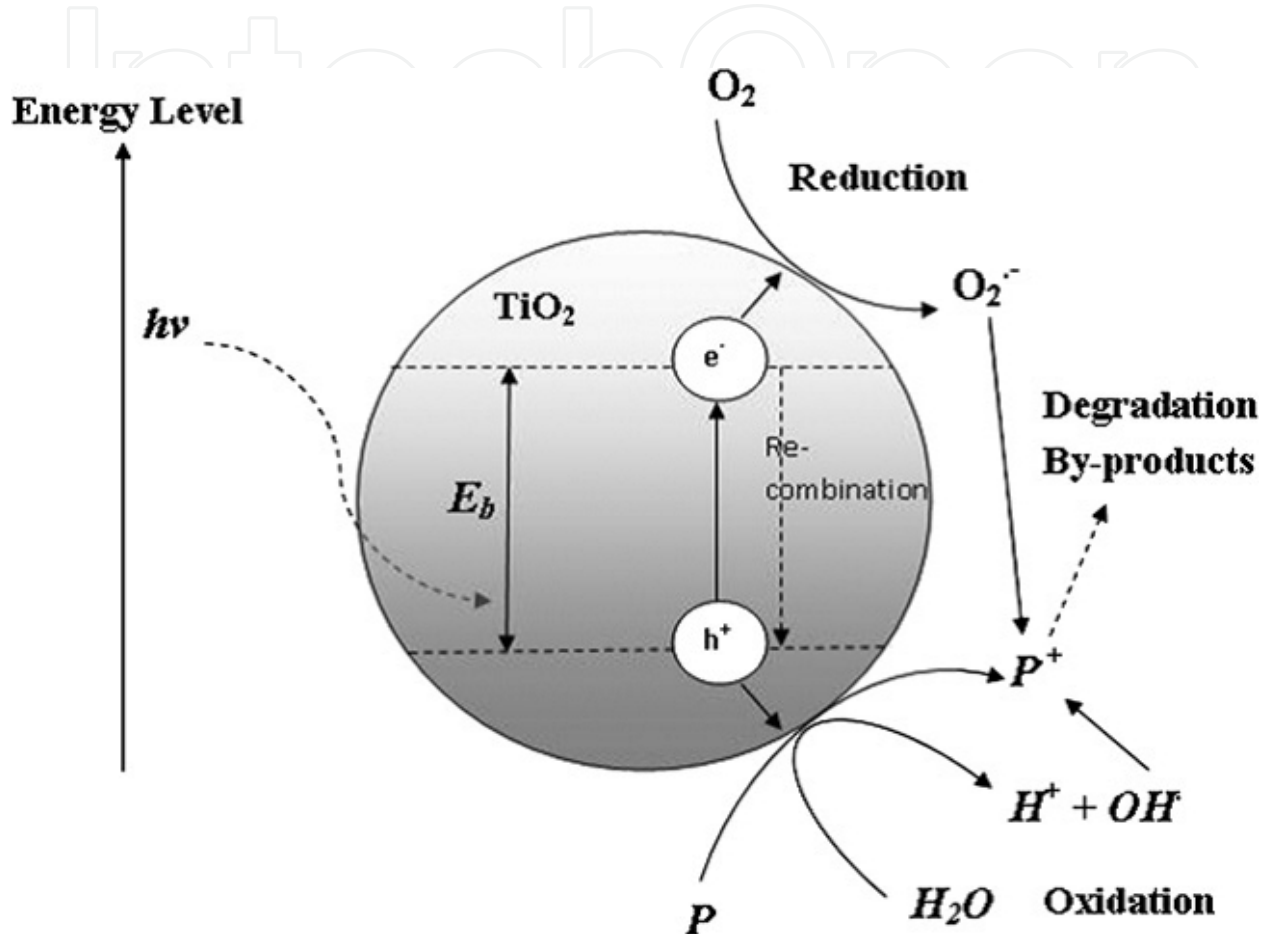


Figure 1. Mechanism of electron-hole pair formation in a TiO_2 particle in the presence of pollutant in water [7].

3. Types of photocatalysts and their characteristics

A number of solids can be referred to as photocatalysts and as mentioned earlier, metal oxide semiconductors are considered to be the most suitable photocatalysts due to their photo-corrosion resistance and wide band gap energies [10]. Table 1 provides the band gap energies at corresponding wavelength for well known semiconductors. TiO_2 stands out as the most effective photocatalyst and has been extensively used in water and wastewater treatment studies because it is cost effective, thermally stable, non-toxic, chemically and biologically inert and is capable of promoting oxidation of organic compounds [11]. The photocatalytic activity of TiO_2 is dependent on surface and structural properties which include

crystal composition, surface area, particle size distribution, porosity and band gap energy [12]. TiO_2 is also known as titania, titanic oxide, titanium white, titanic anhydride, or titanic acid anhydride. It is prepared using ilmenite and rutile in crystalline forms called anatase and rutile. The anatase form is achieved by processing of titanium sulphate, which is achieved when ilmenite is treated with sulphuric acid. Rutile crystalline form is obtained when raw rutile is chlorinated and the resulting titanium tetrachloride is subjected to vapor phase oxidation [13]. When photon energy ($h\nu$) of higher than or equal to the bandgap energy of TiO_2 is illuminated onto its surface, typically 3.2 eV (anatase) or 3.0 eV (rutile), the lone electron is photoexcited to the empty conduction band in femtoseconds [7]. Degussa P25 which is the most widely used form of TiO_2 is composed of 75% anatase and 25% rutile and has a specific BET surface area of $50 \text{ m}^2/\text{g}$. The high effectiveness of D25 is related to the inhibition of recombination process on TiO_2 ($e_{\text{CB}}^-/h_{\text{VB}}^+$) due to the smaller band gap of rutile that absorbs photons and generates electron-hole pairs and the electron transfer from the rutile conductive band to the electron traps occurs in the anatase phase [14].

Semiconductor	Band gas energy (eV)	Wavelength
TiO_2 (rutile)	3.0	413
TiO_2 (anatase)	3.2	388
ZnO	3.2	388
ZnS	3.6	335
CdS	2.4	516
Fe_2O_3	2.3	539

Table 1. Band gap energies of various semiconductors at relevant wavelengths [15]

4. Radiation sources for photocatalysis

Both artificial UV lamps and sunlight can be used as the radiation source for photocatalytic process. Artificial UV lamps containing mercury are the most commonly used source of UV irradiation. These can be divided into low pressure mercury lamp, medium pressure mercury lamp and high pressure mercury lamp. Sunlight has also been used in the photocatalytic process as nearly 4-5% of the sunlight that reaches the earth's surface is in the 300-400 nm near UV light range. Furthermore solar energy has limitations due to the graphical variations when compared with the artificial UV lamps. However ongoing interests and developments in harnessing solar energy are expected to increase its use in photocatalytic degradation applications.

5. Photocatalytic reactors

Photocatalytic reactors can be classified based on the deployed state of the photocatalyst, i.e., suspended or attached. Photocatalytic reactors can use either UV or solar radiation. Solar photocatalytic reactors have been of great interest for the photooxidation of organic contaminants in water. Such kind of reactors can be divided into concentrating or non-concentrating reactors [16]. Both the reactor types extend certain advantages and disadvantages. For example, non-concentrating reactors have negligible optical losses and therefore can use direct and diffuse sun irradiation but are larger in size compared with the concentrating reactors and have high frictional pressure losses [16]. However, the use of solar radiated photoreactors is limited due to the intrinsic nature of the TiO₂ particles. Following section provides details on the type of reactors used in various studies for the degradation of organic pollutants in water.

5.1. Slurry reactors

Until recently, TiO₂ slurry reactors are most commonly type used in water treatment. These show largest photocatalytic activity compared with the immobilized photocatalyst and provide a high total surface area of photocatalyst per unit volume which is one of the most important factor configuring a photocatalytic reactor [7]. However, these reactors require separation of the sub-micron TiO₂ particles from the treated water which complicates the treatment process. Several techniques were proposed to achieve post-treatment separation such as the use of settling tanks (overnight particle settling) or external cross-flow filtration system [7]. However the use of filtrations systems increases the cost of the treatment process.

5.2. Immobilized TiO₂ reactors

Photocatalytic reactors with immobilized TiO₂ are those in which catalyst is fixed to support via physical surface forces or chemical bonds. These reactors extend the benefit of not requiring catalyst recovery and permit the continuous use of the photocatalyst [16]. Hybrid photocatalytic membrane reactors have been developed to achieve the purpose of downstream separation of photocatalyst. The photocatalytic membrane reactors can be generalized in two categories (1) irradiation of the membrane module and (2) irradiation of feed tank containing photocatalyst in suspension [17]. Various membranes such as microfiltration, ultrafiltration, and nanofiltration membranes may be used for this purpose depending on the requirements of the treated water quality [7]. Photocatalytic membrane reactors have been successfully used for the degradation of trichloroethylene and 4-nitrophenol [18, 19]. However, these reactors possess drawbacks such as low surface area to volume ratios, catalyst fouling and significant pressure drop [16]. Another problem associated with the membrane photocatalytic reactors is the diffusion of organic compounds to the catalyst surface which is slow particularly when the organic compounds concentration is low [20]. One possible solution to the slow diffusion is using pores of nano size to enable photocatalyst to perform selective permeation and to produce an oxidized permeate stream [21].

It can be observed that the photocatalytic reactors can be either slurry or immobilized systems and each possess certain advantages and disadvantages related to their design and efficiency. Further research on the design and energy efficiency of photocatalytic reactors could make photocatalytic degradation process more feasible for future applications in water treatment. Membrane photoreactors appear to be a promising alternative to conventional photoreactors and more research in this area can assist overcome some of the problems faced with the use of conventional reactors.

6. Factors affecting the degradation performance

6.1. Catalyst loading

The amount of TiO_2 being directly proportional to the overall photocatalytic reaction rate, the concentration of the TiO_2 particles affects the overall photocatalysis reaction rate in a true heterogeneous catalytic regime [2]. However, when the amount of TiO_2 is above certain level (saturation stage), the light photon adsorption co-efficient decreases radially and the excess photocatalyst can create a light screening effect that leads to the reduction in the surface area exposed to irradiation and thus reduces the photocatalytic efficiency of the process [7]. A number of studies have reported the effect of TiO_2 loadings on the treatment efficiency of the photocatalytic reactor [2, 22-24]. Although a direct comparison between these studies is difficult to be made due to the differences in the working geometry, radiation fluxes and wavelengths used, it was evident that the optimum dosages of photocatalyst loading were dependent on the dimension of the reactor. The importance of the determination of the reactor diameter has been emphasized to achieve effective photon absorption [25]. The optimum dosage of TiO_2 used by various authors either alone or in combination with other catalysts is given in Table 2.

6.2. pH of the solution

The effect of pH on the photocatalytic reaction has been extensively studied [26, 27] due to the fact that photocatalytic water treatment is highly dependent on the pH as it affects the charge on the catalyst particles, size of aggregates and the position of conductance and valance bands [7]. Furthermore the surface of the TiO_2 can be protonated or deprotonated under acidic or alkaline conditions [2], respectively according to the reaction given below.



The point of zero discharge for P25 Degussa, the most commonly used form of TiO_2 is 6.9 [28]. Therefore the surface of the TiO_2 is positively charged under acidic conditions and negatively

charged under alkaline conditions. The maximum oxidizing capacity of the titania is at lower pH however the reaction rate is known to decrease at low pH due to excess H^+ [29]. The selection of pH is thus need to be appropriate in order to achieve maximum degradation efficiency.

Target compound	Photocatalyst	Optimum dosage (g/L)	References
Erioglauicine	TiO ₂	0.3	[23]
Tebuthionon	TiO ₂	5	[33]
Propham	TiO ₂	5	[33]
Triclopyr	TiO ₂	2	[34]
Phorate	TiO ₂	0.5	[54]
Turbophos	TiO ₂	0.5	[55]
Trichlorfon	TiO ₂	8	[56]
Methamodiphos	Re- TiO ₂	1	[57]
Methylene blue	La-Y/TiO ₂	4	[58]
Carbendazim	TiO ₂	0.07	[59]
Direct red 23	Ag-TiO ₂	3	[60]
Phenol	Pr- TiO ₂	1	[61]
Carbofuran	TiO ₂	0.1	[62]
Beta-cypermethrin	RuO ₂ -TiO ₂	5	[63]
Aniline	Pt-TiO ₂	2.5	[64]
Benzylamine	Pt-TiO ₂	2.5	[64]
Glyphosate	TiO ₂	6	[65]
Picloram	TiO ₂	2	[66]
Floumeturon	TiO ₂	3	[67]
Imazapyr	TiO ₂	2.5	[68]

Table 2. Optimum dosage of photocatalyst for degradation of organic compounds

6.3. Size and structure of the photocatalyst

Surface morphology such as particle size and agglomerate size, is an important factor to be considered in photocatalytic degradation process because there is a direct relationship between organic compounds and surface coverage of the photocatalyst [30]. The number of photon striking the photocatalyst controls the rate of reaction which signifies that the reaction takes place only in the absorbed phase of the photocatalyst [2, 31]. A number of different forms of TiO₂ have been synthesized to achieve the desired characteristics of the photocatalyst [32]. Some of the examples include UV100, PC500 and TTP. For the degradation of various organic compound such as pesticides and dyes, the efficacy of these

photocatalysts has generally been reported in the order of Degussa P25 > UV100 > PC500 > TTP [33-36].

6.4. Reaction temperature

An increase in reaction temperature generally results in increased photocatalytic activity however reaction temperature >80°C promotes the recombination of charge carriers and disfavor the adsorption of organic compounds on the titania surface [2]. A reaction temperature below 80°C favours the adsorption whereas further reduction of reaction temperature to 0°C results in an increase in the apparent activation energy [7]. Therefore temperature range between 20-80°C has been regarded as the desired temperature for effective photomineralization of organic content.

6.5. Concentration and nature of pollutants

The rate of photocatalytic degradation of certain pollutant depends on its nature, concentration and other existing compounds in water matrix. A number of studies have reported the dependency of the TiO₂ reaction rate on the concentration of contaminants in water [37]. High concentration of pollutants in water saturates the TiO₂ surface and hence reduces the photonic efficiency and deactivation of the photocatalyst [38]. In addition to the concentration of pollutants, the chemical structure of the target compound also influences the degradation performance of the photocatalytic reactor. For example, 4-chlorophenol requires prolonged irradiation time due to its transformation to intermediates compared with oxalic acid that transforms directly to carbon dioxide and water, i.e., complete mineralization [39]. Furthermore if the nature of the target water contaminants is such that they adhere effectively to the photocatalyst surface the process would be more effective in removing such compounds from the solution. Therefore the photocatalytic degradation of aromatics is highly dependent on the substituent group [2]. The organic substrates with electron withdrawing nature (benzoic acid, nitrobenzene) strongly adhere to the photocatalyst and therefore are more susceptible to direct oxidation compared with the electron donating groups [40].

6.6. Inorganic ions

Various inorganic ions such as magnesium, iron, zinc, copper, bicarbonate, phosphate, nitrate, sulfate and chloride present in wastewater can affect the photocatalytic degradation rate of the organic pollutants because they can be adsorbed onto the surface of TiO₂ [41-43]. Photocatalytic deactivation has been reported whether photocatalyst is used in slurry or fixed-bed configuration which is related to the strong inhibition from the inorganic ions on the surface of the TiO₂ [44]. A number of studies have been conducted on the effect of inorganic ions (anions and cations) on TiO₂ photocatalytic degradation [30, 45-51]. Some of the cations such as copper, iron and phosphate have been reported to decrease the photodegradation efficiency if they are present at certain concentrations whereas calcium, magnesium and zinc have little effect on the photodegradation of organic compounds which is associated to the fact that these cations have are at their maximum oxidation states that results in their inability to have any inhibitory effect on the degradation process [7].

The inorganic anions such as nitrate, chlorides, carbonates and sulphates are also known to inhibit the surface activity of the photocatalyst. The presence of salts diminishes the colloidal stability, increases mass transfer and reduces the surface contact between the pollutant and the photocatalyst [7]. Other than fouling of the TiO₂ surface certain anions such as chlorides, carbonates, phosphate and sulphates also scavenge both the hole and the hydroxyl radicals [52]. The mechanism of hole and radical scavenging by chloride has been proposed by Matthews and McEnvoy [53] as follows.



The inhibitory effect of chloride ions occurs through preferential adsorption displacement mechanism which results in reducing the number of OH⁻ available on the photocatalyst surface [7].

The fouling of photocatalytic surface can be reduced by pre-treatment of water such as with ion exchange resins which have been reported to reduce the fouling and so the cost of treatment (Burns et al., 1999). Similarly the fouling induced by sulphates and phosphates has been reported to be displaced by NaOH, KOH and NaHCO₃ [41]. However, most of studies conducted on the effect of inorganic ions are based on the model compounds and therefore do not necessarily represent their effect in real water matrix where several ions exist. More work concentrating on the effect of complex mixtures of inorganic ions is thus required.

7. Conclusions

Photocatalytic degradation of organic pollutants is promising technology due to its advantage of degradation on pollutants instead of their transformation under ambient conditions. The process is capable of removing a wide range of organic pollutants such as pesticides, herbicides, and micropollutants such as endocrine disrupting compounds. Although significant amount of research has been conducted on TiO₂ photocatalysis at laboratory scale, its application on industrial scale requires certain limitations to be addressed. However the application of this treatment is constrained by several factors such as wide band gap (3.2eV), lack and inability of efficient and cost-effective catalyst for high photon-efficiency to utilize wider solar spectra. The effect of variables is required to be further studied in real water matrix to achieve representative results. The results achieved can be used to optimize the process and design appropriate reactor for potential large scale applications. The use of solar radiation has to be improved by virtue of the design of the photoreactor in order to reduce the cost of treatment. Further research to investigate the degradation of the real water constituents is required to better comprehend the process applications.

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