

Chapter 2

Basic Principles, Mechanism, and Challenges of Photocatalysis

R. Saravanan, Francisco Gracia and A. Stephen

Abstract Photocatalyst is a gifted method which can be used for various purposes like degradation of various organic pollutants in wastewater, production of hydrogen, purification of air, and antibacterial activity. When compared with other methods, photocatalysis is rapidly growing and gaining more attention from the researchers due to its several advantages such as low cost and attractive efficiency. Photocatalysis is a unique process for rectifying energy and environmental issues. In this connection, this chapter deals with basic principles, classification, mechanism, limitations, and operating parameters of photocatalytic processes. Furthermore, the most efficient photocatalytic materials, its mechanism, its challenges, and their solution of rectification were discussed in detail.

Keywords Photocatalyst • Mechanism • Semiconductors • Oxidation • Reduction

Introduction

Removal of pollution is of worldwide importance as such it goes beyond the national borders of each and every nation. In recent times, the essentiality to maintain a good eco-friendly nature has come up with the destruction of various pollutions in the atmosphere due to environmental contamination which occurs in any form of untreated hazards disposal or discharge of material into water, land, or air that causes or may cause acute (short-term) or chronic (long-term) detriment to the Earth's ecological balance or that lowers the quality of life (Chong et al. 2010; Pelaez et al. 2012; Schwarzenbach et al. 2010). The spectrum of pollutants present

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in the environment happens as a result of excessive human needs due to overpopulation, and so the skills related to the technologies have been developed for the researchers being necessary to carry out the pollution rectification processes (Pelaez et al. 2012; Schwarzenbach et al. 2010). A wide range of chemical contaminants flowing freely from industries and agricultural activities have become an important issue that is affecting the ecological safety (Jegannathan and Nielsen 2013; Freeman et al. 1992; Chong et al. 2010).

Water is one of the essential enablers of life on earth. Worldwide, 3.2 million people die per year because of unsafe water, poor sanitation, and inadequate hygiene (Liu et al. 2012). Thus, the quality of water directly affects the life standard of human beings and animals. The main water contamination sources are from industrial discharge of chemicals, agricultural movements, and other environmental changes. In spite of fresh water being a renewable source of energy, the requirement of good water quality is essential and the same is needed for healthy life. Water pollutants may exist in different hazardous wastes like pharmaceutical wastes, pesticides, herbicides, textile dyes, resins, and phenolic compounds (Chong et al. 2010; Konstantinou and Albanis 2004; Zhang and Fang 2010).

In the modern era, water pollution turns out to be the finest topic to discuss because of the depletion of underground water resources and the lack of managing wastewater, which ensures an unsustainable life with safe water. Even, very lesser amounts of water effluents create adverse health effects in humans and other ecosystems. Hence, industrial discharge of wastewater requires proper sewage treatment plants for the essential wastewater management (Akpan and Hameed 2009; Gupta et al. 2012; Konstantinou and Albanis 2004). Wastewater treatment technologies have come up with various efficient methods, but cheaper and less time-consuming method is a major tool to access safe water (Gupta et al. 2012). Initially, this chapter deals with the main source of water pollution and their rectifying methods with merits and demerits. When compared with other methods, photocatalysis is one of the distinctive methods for remedying energy and environmental issues due to several advantages. The main core of this chapter presents the description of the more attractive photocatalytic method and their basic principles, mechanism, limitations, and operating parameters in photocatalytic processes and the challenges of photocatalysis in detail.

Main Source of Water Pollution

Water as an environmental resource is regenerative in the sense that it could absorb the pollution loads up to certain levels without affecting its quality. In fact, there could be a problem of water pollution only if the pollution loads exceed the natural regenerative capacity of a water resource (Schwarzenbach et al. 2010). In the last decades, water pollution has moved to the top of the international political agenda due to its undesirable health and environmental effects. The contaminants released from industries and agricultural activities have become the main source, which

affects most of the water bodies in the ecological system (Chong et al. 2010; Gupta et al. 2012). It has already been reported that the major organic compounds responsible for increasing environmental threat are the industrial dyes and textile dyes. About 10–20% of total dye products in the world is lost in textile wastes during the manufacturing process and released as effluents into the green environment (Konstantinou and Albanis 2004; Akpan and Hameed 2009). Organic dyes are one of the leading groups of pollutants released into wastewaters from textile and other industrial processes (Gupta et al. 2012; Chong et al. 2010). On a global scale, over 0.7 million tons of organic synthetic dyes are manufactured every year mainly for use in the textile, leather goods, industrial painting, food, plastics, cosmetics, and consumer electronic sectors (Rajeshwar et al. 2008). There are at least million colored chemical substances that were produced during the last century, out of these about 10,000 were industrially produced (Akpan and Hameed 2009; Konstantinou and Albanis 2004). Major pollutants in textile wastewaters are highly suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances (Gupta et al. 2012; Freeman et al. 1992). Out of which, textile industries discharge a large quantity of dyes into water bodies which pose serious ecological problems (Schwarzenbach et al. 2010). Many industries use dyes extensively for various operations such as textile, paper, plastic, leather, tanning, etc. These industries discharge mixing of pollutants in a different process (Gupta et al. 2012). The main pollution in textile wastewater came from dyeing and finishing processes. The textile industry uses approximately 21–377 m³ of water per ton of textile produced and thus generates large quantities of wastewater from different steps of dyeing and finishing process (Gupta et al. 2012).

Colorants or additive substances causing variation in color or visible light absorption can be divided into two categories: dyes and pigments (Rajeshwar et al. 2008; Pagga and Brown 1986). The distinct delineation between dyes and pigments is as follows: Dyes are soluble or partly soluble organic (carbon-based plant and animal extracted) colored compounds suspended in a medium that represents one type of colorant (Pagga and Brown 1986). The process of dyeing can be loosely defined as imparting color to the textile fiber or leather. On the other hand, typically pigments are complete insoluble substances that have no chemical affinity for the substrate to be colored (Pagga and Brown 1986).

Industrial wastewater is becoming more and more contaminated with the increasing number of industrial chemical products. The wastewater generated by the textile industry is rated as the most polluting source among all industrial sectors. The textile industry utilizes about 10,000 different dyes and pigments and more than 50% of which are azo dyes. Dyes can be classified on the basis of structure, function, or both. Dyes can also be classified as acid, basic, direct, disperse, reactive, anionic, cationic, etc., and indeed this notation is often simultaneously used with the dye chemical structure type (for example Basic Blue 41 and Acid Yellow 23 are both mono azo dyes) of the synthetic dyes manufactured today; azo compounds are considered dominant (~50–70%) with anthraquinone dyes being a distant second (Akpan and Hameed 2009; Konstantinou and Albanis 2004; Pagga and Brown 1986).

On the other hand, pigments are categorized into two main groups—the organic and other one is inorganic pigments (Rajeshwar et al. 2008; Pagga and Brown 1986). The organic pigments are established by carbon chains and carbon rings. Which are classified into following classes such as azo pigments, polycyclic pigments, anthraquinone pigments, dioxazine pigments, triaryl carbonium pigments, and quinophthalone pigments

Examples:

Artificial—Prussian blue, verdigris.

Animal—Indian yellow, carmine, sepia.

Vegetable—gamboge, sap green, indigo.

For inorganic pigments basically, chemical compounds not based on carbon, are usually metallic salts precipitated from solutions. Inorganic pigments are classified into following: white pigments, black pigments, special pigments, and color pigments

Examples:

Artificial Pigments: aureolin, viridian, cobalt blue

Natural Pigments: ochre, terre verte, ultramarine.

The textile wastewater treatment is a very serious problem due to several reasons which are listed as follows:

- High total dissolved solids (TDS) content of the wastewater,
- Presence of toxic heavy metals such as Cr, As, Cu, Cd, etc.
- Nonbiodegradable nature of organic dyestuffs present in the effluent, and
- The presence of free chlorine and dissolved silica. Most dyes used in the textile industries are stable to light and not biologically degradable. Because dyes usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to biodegrade (Jegannathan and Nielsen 2013; Gupta et al. 2012). Pagga et al. reported that out of 87% dyestuffs, only 47% are biodegradable. It was estimated that about 12–15% of these dyes are released as effluents during the making processes which cause unfavorable environmental pollution (Pagga and Brown 1986).

Wastewater Treatment Methods

Wastewater treatment and recycling is an essential component and the researchers are coming forward to carry out with convenient economical technologies. The wastewater has been treated by different physical, chemical, and biological processes (Gupta et al. 2012). The major environmental aspect is the removal of color from textile and dyestuff manufacturing wastewater. A large number of conservative

treatment processes have been employed in various industrial wastewaters such as chemical, biological, food, pharmaceutical, pulp and paper, dye processing, and textile wastes (Esplugas et al. 2007; Gupta et al. 2012; Moo-Young 2007; Gogate and Pandit 2004). Conventional biological treatment processes are not successful because of the recalcitrant nature of synthetic dyes and the high salinity of wastewater containing dyes (Johnson and Mehrvar 2008; Rajeshwar et al. 2008; Gupta et al. 2012). Chlorination and ozonation are also quite incapable owing to their high operating costs (Rajeshwar et al. 2008; Coleman et al. 2000). The traditional physical techniques such as adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc., have been used for the removal of dye pollutants (Coleman et al. 2000; Esplugas et al. 2007; Gogate and Pandit 2004; Gupta et al. 2012; Johnson and Mehrvar 2008; Moo-Young 2007). These methods are successful only in transferring organic compounds from water to another phase, thus creating secondary pollution which requires further treatment of solid wastes and regeneration of the adsorbent which makes the process costlier.

The following essential factors must be considered in the wastewater treatment technologies (Gogate and Pandit 2004; Oller et al. 2011; Serpone et al. 2010):

- Treatment flexibility.
- Mineralization of parent and intermediate contaminants.
- The final efficiency of wastewater treatment.
- Recycling capacity and potential use of treated water.
- Cost-effectiveness and eco-friendliness.

Therefore, substantial attention has been focused on complete oxidation of organic compounds to harmless products such as CO_2 and H_2O by the advanced oxidation process (AOP) and appears as one of the most confidential technologies.

AOPs can be classified into two groups:

- (1) Non-photochemical AOPs; Non-photochemical AOPs include cavitations, Fenton and Fenton-like processes, ozonation, ozone/hydrogen peroxide, wet air oxidation (Fujishima et al. 2000; Malato et al. 2009; Nakata and Fujishima 2012), etc.,
- (2) Photochemical AOPs and photochemical oxidation processes include homogeneous (UV/hydrogen peroxide, UV/ozone, UV/ozone/hydrogen peroxide, photo-Fenton, homo and heterogeneous (photocatalysis) processes) (Parida and Parija 2006; Rehman et al. 2009; Gupta et al. 2012). The intention of any AOPs design is to produce and use hydroxyl free radical (OH^\bullet) as a strong oxidant to destroy compounds that cannot be oxidized by the conventional oxidant. Hydroxyl radicals are nonselective in nature and they can react without any other additives with a series of contaminants whose rate constants are usually in the order of 10^6 – $10^9 \text{ mol L}^{-1} \text{ s}^{-1}$ (Rehman et al. 2009).

The main and short mechanism of AOPs can be explained as follows:

- Initially, the light energy fall on the surface of a catalyst, the valence band electrons are agitated and move to the conduction band. Holes would be left in the valence band of the catalyst. These holes in the valence band can oxidize donor molecules and react with water molecules to generate hydroxyl radicals (The hydroxyl radicals have strong oxidizing power responsible for the degradation of pollutants).
- The oxidative reaction of these radicals with organic compounds in the water producing biodegradable intermediates.
- The reaction of biodegradable intermediates with oxidants is referred to as mineralization (i.e., production of water, carbon dioxide, and inorganic ions).

Discovery of Photocatalysis

In 1972, *Fujishima* and *Honda* discovered the phenomenon of a photocatalytic splitting of water on a TiO_2 electrode under ultraviolet (UV) light (Fujishima and Honda 1972). This event becomes noticeable as the beginning of a new era in heterogeneous photocatalysis. However, this discovery was not accepted at first by electrochemists because at that time, the idea that light could also be used as an energy source had not yet taken hold among electrochemists who maintained that oxygen could not be generated at such a low voltage, because water electrolysis takes place at 1.5–2 V or even higher. Since then, for understanding the fundamental processes and enhancing the photocatalytic efficiency of TiO_2 , extensive research was performed by chemists, physicists, and chemical engineers. Such studies are frequently related to energy renewal and energy storage (Fujishima and Honda 1972; Fujishima et al. 2000). TiO_2 -based photocatalysts are considered as an attractive approach growing rapidly for the total destruction of organic compounds in polluted air and wastewater (Fujishima et al. 2000; Fujishima and Honda 1972; Rajeshwar et al. 2008).

Prof. Fujishima stresses that benefits of science and technology should be shared by everyone. He says “*The primary objective of science and technology is to create a society where people can have healthy, comfortable and long lives. The crucial thing in science and technology is to develop a new concept that can be applied to actual products and services, and these new products and services will eventually make people happy*”. By making use of his discovery of photocatalyst, he came forward to create such a society (Fujishima et al. 2000).

Definition of Photocatalysis

Photocatalysis is the amalgamation of photochemistry and catalysis. The word “*photocatalysis*” is derived from the Greek language and composed of two parts:

- The prefix photo means *light*
- *Catalysis* is the process where a substance involves in altering the rate of a chemical transformation of the reactants without being altered in the end. The substance which is known to be a catalyst increases the rate of the reaction by reducing the activation energy.

Hence, photocatalysis is a process where light and catalysts are concurrently used to support or speed up a chemical reaction. So, photocatalysis can be defined as “*catalysis driven acceleration of a light-induced reaction.*”

Photocatalyst is classified into two categories: homo- and heterogeneous process (Rajeshwar et al. 2008; Rehman et al. 2009; Fujishima et al. 2000).

Homogeneous photocatalytic processes mostly are used with metal complexes as catalysts (transition metals complexes like iron, copper, chromium, etc.). In this process, under the photon and thermal condition, the higher oxidation state of metal ion complexes generated hydroxyl radicals. Then, these hydroxyl radicals react with organic matter which leads destruction of toxic matters. While the comparing homogeneous and heterogeneous; heterogeneous photocatalysis is a technically gifted method which can be used for the degradation of various organic pollutants in wastewater (Rajeshwar et al. 2008; Rehman et al. 2009; Fujishima et al. 2000). This process has several advantages over the competing processes (Fujishima and Honda 1972; Fujishima et al. 2000; Rajeshwar et al. 2008). They are (i) complete mineralization, (ii) no waste disposal problem, (iii) low cost, and (iv) necessity of mild temperature and pressure conditions only.

For example, semiconducting materials (TiO_2 , ZnO , SnO_2 , and CeO_2) mainly act as heterogeneous photocatalysts, because of its favorable combination of electronic structures which is characterized by a filled valence band and an empty conduction band, light absorption properties, charge transport characteristics and excited states lifetime (Khan et al. 2015b; Rehman et al. 2009; Konstantinou and Albanis 2004; Fujishima et al. 2000; Nakata and Fujishima 2012). An excellent semiconductor photocatalyst should be (i) photoactive, (ii) able to utilize visible and/or near-UV light, (iii) biologically and chemically inert, (iv) photostable (i.e., stability toward photo corrosion), (v) inexpensive, and (vi) nontoxic. Semiconductor photocatalysis emerges to be a promising technology that has a number of applications in environmental systems (Khan et al. 2015b; Rehman et al. 2009; Konstantinou and Albanis 2004; Fujishima et al. 2000; Nakata and Fujishima 2012).

The photocatalyst is an extraordinary method which can be used for various purposes like degradation of various organic pollutants in wastewater, production of hydrogen, purification of air, and antibacterial activity. Recently, the photocatalytic process is attaining more concentration in the field of wastewater treatment to

obtain complete mineralization of the pollutant achieved under mild conditions of temperature and pressure. The noteworthy features of these processes include undisposed of waste and cost-effectiveness when sunlight or near-UV light can be used as a source of irradiation. Photocatalyst is a term which means photon assisted generation of catalytically active species. In general, Photocatalysis can be defined as “a change in the rate of chemical reactions or their generation under the action of light in the presence of substances called photocatalyst that absorbs light quanta and is involved in the chemical transformations of the reactants” (Hagen 2006).

Photocatalytic Mechanism

Photocatalytic reaction primarily depends on wavelength or light (photon) energy and the catalyst. In general, semiconducting materials are used as a catalyst which performs as sensitizers for the irradiation of light stimulated redox process due to their electronic structure, which is characterized by a filled valence band and a vacant conduction band (Hagen 2006; Khan et al. 2015b). Figure 2.1 shows the schematic representation of semiconductor photocatalytic mechanism.

The fundamental steps in the process of semiconductor photocatalysis are as follows (Khan et al. 2015b; Rajeshwar et al. 2008; Rehman et al. 2009; Fujishima et al. 2000; Hagen 2006):

- When the light energy in terms of photons fall on the surface of a semiconductor and if the energy of incident ray is equivalent or more than the bandgap energy

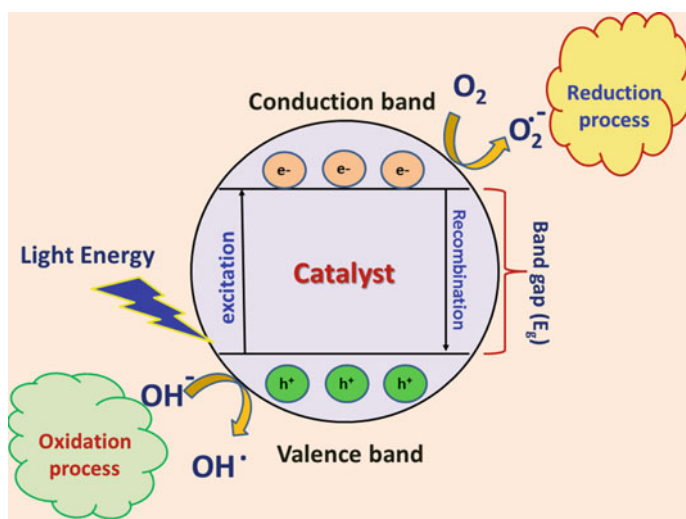


Fig. 2.1 Schematic representation of semiconductor photocatalytic mechanism

of the semiconductor, the valence band electrons are agitated and move to the conduction band of the semiconductor.

- Holes would be left in the valence band of the semiconductor. These holes in the valence band can oxidize donor molecules and react with water molecules to generate hydroxyl radicals (The hydroxyl radicals have strong oxidizing power responsible for the degradation of pollutants).
- The conduction band electrons react with dissolved oxygen species to form superoxide ions. These electrons induce the redox reactions.

These holes and electrons could undergo successive oxidation and reduction reactions with any species, which might be adsorbed on the surface of the semiconductor to give the necessary products.

Description of Oxidation Mechanism

The photocatalyst surface contains water, which is mentioned as “absorbed water.” This water is oxidized by positive holes created in the valence band due to the electrons shift to the conduction band as a result of light irradiation, thus making way for the formation of hydroxyl (OH^\bullet) radicals (agents which have strong oxidative decomposing power). Afterward, these hydroxyl radicals react with organic matter present in the dyes. If oxygen is present when this process happens, the intermediate radicals in the organic compounds along with the oxygen mole-

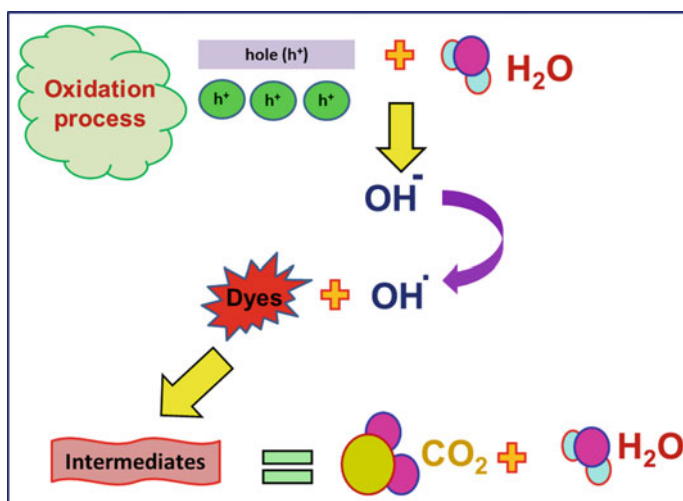


Fig. 2.2 Schematic representation of oxidation mechanism

cules can experience radical chain reactions and consume oxygen in some cases. In such a case, the organic matter finally decomposes ultimately becoming carbon dioxide and water (Khan et al. 2015b; Fujishima and Honda 1972; Rajeshwar et al. 2008). Under such circumstances, organic compounds can react straightly with the positive holes, resulting in oxidative decomposition. The complete oxidation processes were shown in Fig. 2.2.

Description of Reduction Mechanism

Figure 2.3 represents the reduction process, the reduction of oxygen contained in the air occurs as a pairing reaction (Rajeshwar et al. 2008; Rehman et al. 2009). Reduction of oxygen takes place as an alternative to hydrogen generation due to the fact that oxygen is an easily reducible substance. The conduction band electrons react with dissolved oxygen species to form superoxide anions. These superoxide anions attach to the intermediate products in the oxidative reaction, forming peroxide or changing to hydrogen peroxide and then to water. The reduction is likely to occur more easily in organic matter than in water. Therefore, the higher concentration of organic matter tends to increase the number of positive holes. This reduces the carrier recombination and enhances the photocatalytic activity (Nakata and Fujishima 2012; Rajeshwar et al. 2008; Khan et al. 2015b).

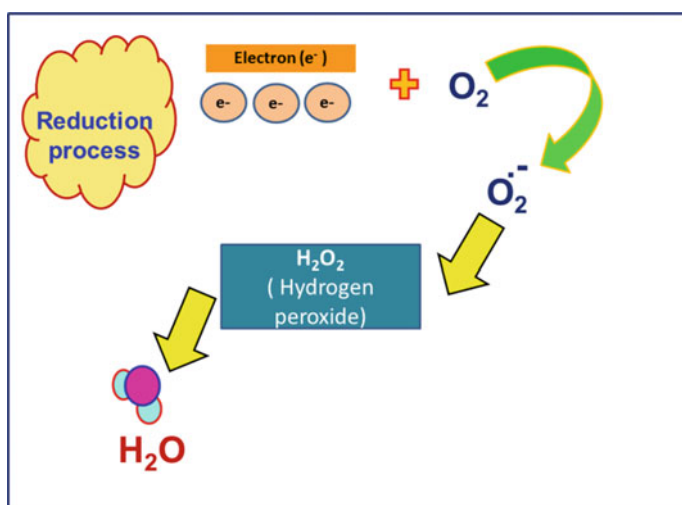


Fig. 2.3 Schematic representation of reduction mechanism

Operating and Affecting Parameters of Photocatalysis

The rate of photo mineralization of an organic compound by photocatalysis method primarily depends on the following parameters: structure, shape, size, and surface area of the catalyst, reaction temperature, pH, light intensity, amount of catalyst, and concentration of wastewater (Saravanan et al. 2011b; Rajeshwar et al. 2008; Rehman et al. 2009; Fujishima et al. 2000; Wang et al. 2007, 2008).

Crystal Structure, Shape, Size, and Surface Area of Catalyst

The structure of catalyst plays a key role in achieving superior photocatalytic activity. For example, TiO_2 material has three phases such as anatase, rutile, and brookite. But the most sensitive and attractive phase is the anatase phase having a notable photocatalytic activity due to its stability, the position of the conduction band, the higher degree of hydroxylation, and adsorption power (Khan et al. 2014b; Gnanasekaran et al. 2015). On the other hand, morphology also acts as a potential factor that influences the final degradation efficiency which was reported earlier (Saravanan et al. 2011b; Wang et al. 2007, 2008). Saravanan et al. reported that spherical-shaped ZnO samples show higher efficiency compared with the spindle-and rod-shaped ZnO samples due to its large surface area (Saravanan et al. 2013a). Nanomaterials having large surface area and smaller size are compared with bulk materials so that it can effectively show higher efficiency in the photocatalytic reaction. When compared with bulk TiO_2 , the nanosized TiO_2 material shows more efficient for water purification and recycling ability due to their smaller size (Han et al. 2014; Cernuto et al. 2011). When the size of the catalyst is smaller, a huge number of atoms are accumulated on the surface of a catalyst which leads to increase in surface to volume ratio. This property enhances number of active sites and interfacial charge carrier transfer rates thereby achieving higher catalytic activities (Cernuto et al. 2011). And also it is well known that the photocatalytic redox reaction mainly takes place on the surface of the photocatalysts and so the surface properties significantly influence the efficiency of catalyst (Saravanan et al. 2013a; Khan et al. 2015b).

Effect of Reaction Temperature

A number of researchers have been demonstrated to study the dependence of photocatalytic activity on reaction temperature (Malato et al. 2009; Rajeshwar et al. 2008; Rehman et al. 2009). During the photocatalytic reaction of TiO_2 material, when the temperature is raised above 80°C , it will enhance the electron-hole recombination and desorption process of adsorbed reactant species, resulting in the

decrease of photocatalytic activity. The degradation rate dependency on temperature is reflected by the low activation energy ($5\text{--}20\text{ kJ mol}^{-1}$) compared with ordinary thermal reactions. Due to photonic activation, heat is not required for photocatalytic systems and can operate at room temperature. The optimum reaction temperature for photocatalytic activity of TiO_2 material is reported to be in the range of $20\text{--}80\text{ }^\circ\text{C}$. When the temperature is at $0\text{ }^\circ\text{C}$, there is an increase in the apparent activation energy (Chatterjee and Dasgupta 2005). This optimum range mainly depends on the activation energy of the material in the photocatalytic reaction (Chatterjee and Dasgupta 2005).

Effect of pH

In the photocatalytic reactions, the pH of the solution is a vital factor, since it makes a clear explanation on the surface charge properties of the photocatalyst. Shourong et al. reported that the change in pH affects the efficiency of degradation of organic pollutants (Castillo-Ledezma et al. 2011; Kazeminezhad and Sadollahkhani 2016; Reza et al. 2015). The photocatalytic degradation of TiO_2 material for Reactive Blue 4 was done under different pH conditions (Neppolian et al. 2002). The results were clearly explained that the lower degradation efficiency in the acidic solutions ($\text{pH} < 5$) due to the degradation of the dye is lagging by the high concentration of proton. However, in alkaline medium ($\text{pH} > 10$), the existence of hydroxyl ions defuses the acidic end products that are produced by the photodegradation reaction. Furthermore, an unexpected drop of degradation has been detected in the alkaline range ($\text{pH } 11\text{--}13$) because of hydroxyl radicals (OH^\bullet) are rapidly scavenged and does not react with dyes (Neppolian et al. 2002; Reza et al. 2015). The effect of pH on the rate of reaction can be interpreted in terms of electrostatic interactions between charged particles and the contaminants. These influence the adsorption and subsequently the surface properties.

Effect of Light Intensity

The degradation rate of photocatalytic reaction mostly depends upon the light intensity. The quanta of light absorbed by any photocatalyst or reactant are given by the quantum yield which is the ratio of the rate of reaction to the rate of absorption of radiation. The result of photocatalytic reaction responses varied under different wavelengths of the light source (Malato et al. 2009; Reza et al. 2015; Chatterjee and Dasgupta 2005; Akpan and Hameed 2009). The catalyst TiO_2 having a large bandgap (3.2 eV) which absorb mostly in the UV region (Reza et al. 2015). The degradation reaction rate of TiO_2 varies for different intensities of light as follows; the reaction rate increases with increasing light intensity in the range of $0\text{--}20\text{ mW/cm}^2$. Certainly, the reaction rate depends on the square root of the light

intensity (half order) above the certain value ($\sim 25 \text{ mW/cm}^2$) of intermediate light intensity. The reaction rate decreases at high-intensity light irradiation due to the favoring of more electron–hole recombination. The excessive light intensity promotes more electron–hole recombination thereby causing decrease in the reaction rate (Malato et al. 2009; Reza et al. 2015; Chatterjee and Dasgupta 2005; Akpan and Hameed 2009).

Effect of Amount of Catalyst

The amount of catalyst (sample) also influences the efficiency of photocatalytic degradation. If there is an increase in the quantity of catalyst, the number of active sites on the semiconductor surface increases moreover, which in turn produces number of OH^\bullet and $\text{O}_2^{\bullet-}$ radicals (Malato et al. 2009; Rajeshwar et al. 2008). As a result, the photocatalytic degradation rate is increased. Konstantinou et al. elucidated that the degradation rate is directly proportional to the catalyst concentration in any reactor system (Konstantinou and Albanis 2004). However, as the catalyst loading is improved beyond an optimum concentration, the degradation rate is unfavorable because there will be decrease in the light penetration depth into the solution and consequently diminishing of light scattering occurs.

Concentration of Pollutants in Wastewater

Another main factor to find out the degradation rate is the pollutant type and their concentration (Rajeshwar et al. 2008; Rehman et al. 2009; Malato et al. 2009; Chatterjee and Dasgupta 2005). Many researchers have accounted for the photocatalytic activity under similar operating conditions and using similar catalyst, but the variation in the preliminary concentration of water contaminants results with different irradiation time necessary to attain complete mineralization (Chong et al. 2010; Rajeshwar et al. 2008; Rehman et al. 2009; Malato et al. 2009; Chatterjee and Dasgupta 2005). Kiriakidou et al. reported that the TiO_2 material shows different efficiency under similar operating conditions with use of different concentrations of Acid Orange 7 (25–600 mg/L) and the results indicated that complete degradation rate was achieved (25–100 mg/L). After that, the degradation rate diminishes at higher concentration of dye (200–600 mg/L) (Kiriakidou et al. 1999). The above observation has been completely agreed with similar type of several previous reports (Malato et al. 2009; Reza et al. 2015; Chatterjee and Dasgupta 2005; Akpan and Hameed 2009).

Major Advantages of Photocatalysis

The advantages of this photocatalytic technology are as follows (Nakata and Fujishima 2012; Konstantinou and Albanis 2004; Fujishima et al. 2000; Rajeshwar et al. 2008; Rehman et al. 2009):

- (i) Photocatalysis offers a good replacement for the energy-intensive conventional treatment methods (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins) with the capacity for using renewable and pollution-free solar energy.
- (ii) Photocatalysis leads to the formation of harmless products, unlike conventional treatment measures which transfer pollutants from one phase to another.
- (iii) The photocatalytic process can be used in the destruction of a variety of hazardous compounds in different wastewater streams.
- (iv) The reaction conditions for photocatalysis are mild, the reaction time is modest and a lesser chemical input is required.
- (v) Minimal of secondary waste generation and
- (vi) It can be applied to hydrogen generation, gaseous phase, and aqueous treatments as well for solid (soil) phase treatments to some extent.

Limitations of Photocatalysis

The photocatalytic activity depends on the following limitations. (Rehman et al. 2009; Rajeshwar et al. 2008; Fujishima et al. 2000):

- interfacial charge transfer
- improve the charge separation and
- inhibition of charge carrier recombination.

These are essential for enhancing the efficiency of the photocatalytic process.

Semiconductor Photocatalyst and Its Challenges

During the last three decades, the researchers have much focusing attention on the reactions that take place on the illuminated surface of semiconductor metal oxides, sulfides, and selenides (Fig. 2.4), which have a modest bandgap energy of 1.1–3.8 eV between their valence and conduction bands (Khan et al. 2015b). The most efficient photocatalytic materials found in the literature are metal oxides such as TiO_2 , ZnO , and CeO_2 because metal sulfides and metal selenides are not stable,

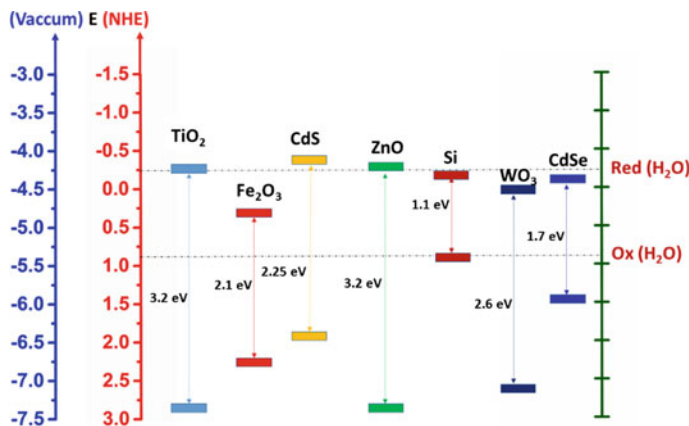
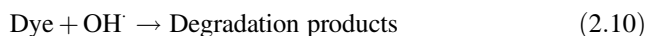
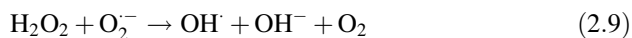
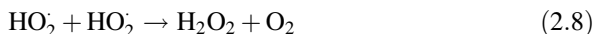
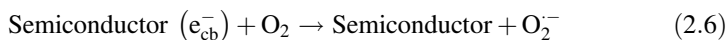
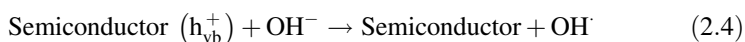
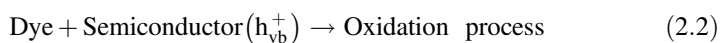
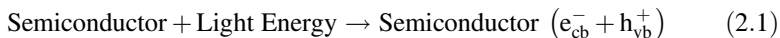


Fig. 2.4 Bandgaps and redox potentials, using the normal hydrogen electrode (NHE) as a reference for several semiconductors

photo anodic corrosive and also toxic (Zhou et al. 2012; Saravanan et al. 2013a; Khan et al. 2014b, c, 2015b).

In general, the photocatalytic reaction mechanism of semiconductors is explained by the following equation based on the earlier reports (Konstantinou and Albanis 2004; Saravanan et al. 2013a).



When compared with other metal oxides, titanium dioxide (3.32 eV) is considered better and also a hopeful candidate for the photocatalytic devastation of organic

pollutants due to its high quantum efficiency, high stability in aqueous media and nontoxic in nature (Nakata and Fujishima 2012; Konstantinou and Albanis 2004; Khan et al. 2015b; Schneider et al. 2014). ZnO and CeO₂ which have a similar bandgap of about 3.32 eV are sometimes preferred over TiO₂ for the degradation of organic pollutants due to its high adsorption properties (Saravanan et al. 2013c; Zhang et al. 2009; Choi et al. 2016). Unfortunately, both TiO₂ and ZnO which are highly evaluated for UV photocatalysis are inactive under visible light due to their wide bandgaps. On the other hand, hematite is also a preferred photocatalytic material, because its absorption is in the visible region. While compared with ZnO or TiO₂, hematite shows lower photocatalytic efficiency because of corrosion property or the formation of short-lived metal-to-ligand or ligand-to-metal charge transfer states (Fox and Dulay 1993). Worldwide efforts are in progress to make use of sunlight for energy production, environmental protection, and water purification. Sunlight contributes about 5–7% ultraviolet light, 46% visible light, and 47% infrared radiation (Saravanan et al. 2011a; Rehman et al. 2009; Khan et al. 2015b). Hence, inherent are the TiO₂ and ZnO semiconductors which have the inability to make use of the vast potential solar photocatalysis (Rehman et al. 2009). Various technical methods have been employed to make them absorb photons of lower energy as well (Rehman et al. 2009; Nakata and Fujishima 2012). Researchers have been focusing on achieving higher degradation efficiency with these materials, particularly under visible light. In the next section, a brief of explanation about the methods of improving photocatalytic activity is presented.

Methods of Improving Photocatalytic Activity

In order to improve the photocatalytic activity, the way of modifying the surface of the particles is an essential step to prevent the electron–hole recombination via metal and nonmetal doping, coupling with various metal and metal oxides and surface sensitization by the polymer.

Composite System

A mixture of different oxides can diminish the bandgap, expanding the absorbance range to visible light region accordingly to achieve a higher photocatalytic activity (Saravanan et al. 2011a, 2013a, b; Khan et al. 2014d; Khoa et al. 2015). The composite system is based on the principle of dye sensitization due to their smaller (narrow) bandgap that can be used as sensitizer rather than organic dyes. The coupled materials have two different energy level systems which play an important role in accomplishing charge separation (Rehman et al. 2009). Some of the coupled systems such as semiconductor/metal, semiconductor/semiconductor, or semiconductor/polymer were successfully synthesized (Khan et al. 2013, 2015a;

Ansari et al. 2015). Many researchers have prepared the coupled systems that contain Au/TiO₂ (Khan et al. 2014d), ZnO/CdO (Saravanan et al. 2015) and CeO₂/Au (Khan et al. 2014a) PANI/ZnO (Saravanan et al. 2016). The conjugated polymer acts as a sensitizer and this conjugated polymer [poly-fluorine-co-thiophene (PFT)] shows more stability in water when compared with organic dyes, and the reductive potential of PFT is weaker than that of semiconductors (TiO₂ and ZnO) and support injection of its excited electrons to the conduction band of these semiconductors (Qiu et al. 2008; Song et al. 2007). Cun et al. explained that the ZnO/SnO₂ system shows greater photocatalytic activity, because the conduction band of SnO₂ is lower than that of ZnO so that the former can act as a sink for the photogenerated electrons. Since the holes move in the opposite direction from the electrons, photogenerated holes might be caught within the ZnO particle, making charge separation resulting in more degradation rates (Cun et al. 2002).

Metal Ion Dopants

The doping of an appropriate material into a catalyst can enhance the photocatalytic performance. Kanade et al. explained that the synthetic strategy for doping of transition metal ions in semiconductor nanostructures would be useful for the improvement of visible light photocatalysts and photovoltaic devices (Kanade et al. 2007). The transition metal ions (Cu, Co, Mn, and Fe) substitute for Zn ions with tetrahedral O coordination in ZnO lattice and the result gives the narrow bandgap (visible region) due to the spin exchange interactions which leads the enhancement of photocatalytic activity under visible light (Milenova et al. 2014). The co-doped ZnO sample having maximum surface oxygen defects proves degrading more methylene blue under visible light (Xiao et al. 2007). When transition metal incorporated in the particles, the d-electronic configuration of the dopant and its energy level within the TiO₂ lattice also seem to significantly influence the photoactivity (Ekambaram et al. 2007). When vanadium ion is implanted on TiO₂ surface, the absorption edge of the sample is in the visible region and consequently, the enhanced photocatalytic activity is examined at a lower concentration. At higher concentration, the excess vanadium ion wraps up the TiO₂ surface and acts as recombination centers leading to lower visible light activity (Yamashita et al. 2002).

Nonmetal Doping

Doping with nonmetals [B, C, N, and S] in TiO₂ promote the photocatalytic activity in visible light due to the synergetic effect (In et al. 2007; Sakthivel and Kisch 2003). Shifu et al. explained that the photocatalytic activity of N doped ZnO sample is higher than that of pure ZnO because conductivity conversion of the samples from zinc oxide to nitrogen leads red shift and subsequently improves the

photocatalytic activity under visible light (Shifu et al. 2009). The degradation of methyl orange using N–S co-doped TiO₂ catalyst shows improved visible light activity due to excess of oxygen vacancies (Wei et al. 2008). The B and N co-doping with TiO₂ samples shows visible light absorption since the synergetic effect modifying the electronic structure of TiO₂ was reported (Ling et al. 2008).

Dye Sensitization

Different dyes such as acid red 44, eosin-Y, merbromine, rhodamine B, and rhodamine 6G, 8-hydroxyquinoline have been used to sensitize TiO₂ particles under visible light (Moon et al. 2003; Abe et al. 2000; Rehman et al. 2009). When there is visible light illumination, the dye molecules are excited and assist in promoting electrons, these excited electrons shift into the conduction band of the semiconductor. These reactions make number of holes and electrons which are capable of the efficient decomposition of organic pollutants through oxidation and reduction reactions (Rehman et al. 2009).

Summary

In this chapter, we concluded that the basic theory of photocatalysis, mechanism, and its advantages clearly indicated that photocatalysis is the simply powerful emerging and promising technology that holds a number of applications in environmental systems which are effectively utilized for the industrial applications including wastewater treatment, hydrogen generation, air purification, antibacterial activity, and so on. Photocatalysts have several advantages, but however an ideal photocatalyst should be inexpensive, nontoxic, long-term stability, easily reproducible on separation, and also has a highly effective photocatalytic activity.

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