

# Chapter 15

## Mechanistic Understanding of Heterogeneous Photocatalysis for the Dye Degradation in Wastewater



Sahil Thareja

**Abstract** Water is one of the fundamental needs for the life on earth. However, the wastewater released from the industries consists of dyes and other organic molecules, which become the serious issue for the water pollution. Among all water remediation techniques, heterogeneous photocatalysis has gained scientific attention for the water purification in terms of degradation of dyes and other organic pollutants. Heterogeneous photocatalysis is a very robust, low cost method and can provide complete mineralization of the pollutants. In this context, this chapter deals with the basic principle and mechanism of heterogeneous photocatalysis; and the parameters affecting the degradation kinetics. Furthermore, the different functional photocatalyst material, their limitation and the modification in the structure of semiconductor catalyst to absorb visible light are discussed in this chapter.

**Keywords** Dye degradation · Heterogeneous photocatalysis · Semiconductor · Visible light · Wastewater

### 15.1 Introduction

The rapid population growth and global warming are comprehensively affecting our ecosystem, which reducing its capability to provide with sufficient quantity of food, drinkable water and good environment to live a healthy life (Pimental 1991). Water is one of the essence requirements for the human kind to survive on earth. To feed large population, there is exponential increase in the industrialization, agricultural activities from which many hazardous chemicals as pollutants are flowing through the wastewater without any pre-treatment, which is adversely affecting the water resources. As per World Health Organization (WHO) report, more than five million

---

S. Thareja (✉)

Department of Chemistry, Indian Institute of Technology, Roorkee, Roorkee, Uttarakhand, India

e-mail: [sthareja@cy.iitr.ac.in](mailto:sthareja@cy.iitr.ac.in)

© Springer Nature Singapore Pte Ltd. 2021

P. K. Gupta, R. N. Bharagava (eds.), *Fate and Transport of Subsurface Pollutants*, Microorganisms for Sustainability 24,

[https://doi.org/10.1007/978-981-15-6564-9\\_15](https://doi.org/10.1007/978-981-15-6564-9_15)

283

peoples die annually due to diseases associated with unsafe drinking water and inadequate sanitation (Gleick 2015). The major sources of water adulteration are industrial and agricultural waste which deprive the quality of water sources by contaminating it with the hazardous wastes like textile dyes, paints, pesticides, herbicides, heavy metals (such as mercury (Hg), lead (Pb), etc.), benzene, and phenolic compounds (Singh et al. 2019). By keeping in mind about the steady decrease in the clean and safe ground water level, there is an urgent requirement for developing a low cost and high competent water treatment technology to manage the wastewater efficiently and to mitigate its harsh effects on the environment.

To save the clean water for drinkable and other important purposes, the recycling of wastewater effluent is one of the possible solutions by treating it to reuse in the agricultural and industrial consumption (Chong et al. 2010). As mentioned earlier, wastewater effluent contains hazardous chemicals like heavy metals and organic compounds; the efficient treatment of these is a challenging task. There are different wastewater treatment processes, which can be combined together in three types: primary, secondary and tertiary treatment process (Gupta et al. 2012). Primary treatment processes include filtration, centrifugation, sedimentation, coagulation and flotation method. Filtration and centrifugation are generally used to remove the suspended solid particles in wastewater physically; coagulation and flotation methods are used to remove the suspended solids, oil and grease by adding certain chemicals like activated silica (Gupta et al. 2012). However, these methods do not mineralize the pollutants completely. Furthermore, these methods have some working difficulties such as sludge generation and phase change of the pollutants (Saggiaro et al. 2016). Secondary water treatment process includes the removal of pollutants by using biological route in which certain microbes like bacteria are used to degrade the pollutants in simple molecules like water, carbon dioxide and ammonia gas (Gupta et al. 2012; Goswami et al. 2017; Kushwaha et al. 2017). However, most of the dyes effluent in wastewater are obstinate towards the biological degradation, which ultimately decrease the efficiency of degradation through this treatment method (Saggiaro et al. 2016). Tertiary wastewater treatment processes are mainly responsible to provide clean and safe water for consumption purposes by treating the wastewater upto 99% which include the processes like distillation, crystallization, oxidation, solvent extraction and electro-dialysis (Gupta et al. 2012). By considering the essential factors for adopting a technology like cost effectiveness, eco-friendliness, recyclability and overall efficiency of wastewater remediation, the complete oxidation of harmful compounds of wastewater effluent into non-hazardous products such as  $H_2O$  and  $CO_2$  is attracting as a most reliable technology (Serpone et al. 2010; Oller et al. 2011).

Among all the available wastewater treatment techniques, the advanced oxidative processes (AOP) are the most attractive, which can be highly efficient for the degradation of dyes and other organic pollutants. These processes involve the in-situ generation of highly reactive and non-selective hydroxide radical ( $OH^\cdot$ ) oxidant that promote the complete mineralization or endorse the production of biodegradable by-products like water ( $H_2O$ ) and carbon dioxide ( $CO_2$ ) (Yoon et al. 2001). Advanced oxidation processes (AOP) include a variety of methods

**Table 15.1** Comparison of different chemical and biological methods with heterogeneous photocatalysis

Method	Comment
Physical/chemical methods—precipitation, adsorption, flocculation, coagulation, chemical oxidation, reverse osmosis, membrane filtration and electrochemical (Gupta et al. 2012)	These methods can purify wastewater but with the production of secondary sludge. The disposal of this secondary sludge is a costly process. Moreover, the transformation of hazardous materials from one form to another is not a long-term solution to save the environment from the toxic waste
Biological—Using bacteria for the removal of toxic material in the wastewater (Saggiaro et al. 2016)	Due to the high chemical stability of synthetic dyes, biological treatment using bacteria is not able to remove dyes efficiently
Heterogeneous photocatalysis (Serpone et al. 2012; Saravanan et al. 2017)	Heterogeneous photocatalysis has the advantage of complete mineralization of the pollutant especially dyes. Moreover, through this method, it is easy to separate the catalyst after degradation process as the phase of catalyst is generally solid which is dispersed in the liquid solution of wastewater

like Fenton process, ozonation, ozone with peroxide are chemical based methods to degrade the organic pollutants (Balciolu and Otker 2003; Khataee et al. 2009), whereas UV/fenton process, UV/ozone, UV/peroxide, homo and heterogeneous photocatalysis use photon to induce the degradation processes, thus called as photochemical processes. (Fujishima et al. 2000; Ghaly et al. 2001; Gernjak et al. 2003). Light induced methods increase the efficiency of the degradation process.

Among all light induced processes, the heterogeneous photocatalysis is the most attractive and efficient method for the degradation of wide range of hazardous organic pollutants into biodegradable compounds and ultimately complete mineralization by producing water (H<sub>2</sub>O) and carbon dioxide (CO<sub>2</sub>) gas. In the heterogeneous photocatalysis, light is incident on the surface of catalyst, which further induces the charge separation between the valence band and conduction band of the catalyst. This charge separation is the key of the photocatalysis for the organic/dyes pollutants mineralization without producing any secondary pollutants. This chapter presents the mechanistic understanding of photocatalytic degradation, operating parameters, photocatalytic materials and modification in the semiconductor photocatalyst to absorb visible light in detail (Table 15.1).

## 15.2 Mechanism of Heterogeneous Photocatalysis

Heterogeneous photocatalysis can be defined as the process in which light is used to increase the efficiency of the reaction in the presence of catalyst. In 1972, Fujishima and Honda were the first to describe the process of heterogeneous photocatalysis by

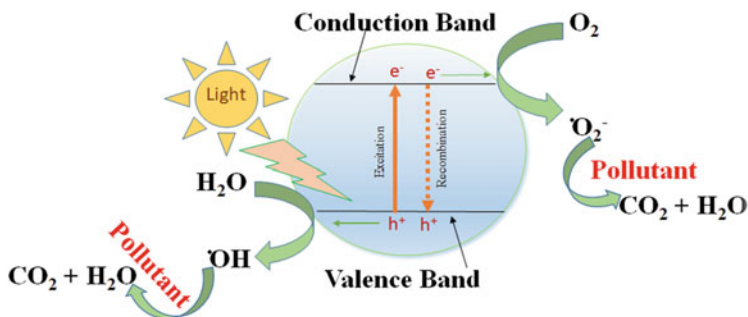


Fig. 15.1 Schematic representation of photocatalytic mechanism on semiconductor

demonstrating the photochemical splitting of water into hydrogen and oxygen under UV light by using  $\text{TiO}_2$  as the catalyst (Fujishima and Honda 1972). By considering the importance of this viable process, many researchers have carried out extensive research for different application like water splitting into hydrogen and oxygen, degradation of organic and inorganic effluent in water and air, dehalogenation and many others related to energy and environment (Ollis 1985; Teoh et al. 2012; Serpone et al. 2012).

The fundamental processes involved in the heterogeneous photocatalysis are as follows (Saravanan et al. 2017; Ahmed et al. 2011):

- When the light (photon) incident on the surface of semiconductor having incident energy equal or greater than the bandgap energy of semiconductor, the electrons of the valence band adsorbs the energy and gets excited to the conduction band.
- This excitation process of electron into conduction band leaves a hole in the valence band. This charge separation is the fundamental of photocatalysis, which induces the degradation of harmful chemicals at the surface of semiconductor.
- The hole in the valence band can either oxidize the adsorbed harmful organic pollutants on the surface of semiconductor directly or react with the water ( $\text{H}_2\text{O}$ ) to produce hydroxide radical. The reaction with water is the predominant process as generally the concentration of water molecules would be more abundant relative to pollutant(s). The generated hydroxide radical has high oxidizing character, which is mainly responsible for the degradation of the organic compounds.
- The electron in the conduction band further reacts with the adsorbed oxygen to reduce it into superoxide radical, which can further degrade the adsorbed pollutants.

This synergetic effect of charge separation into hole in valence band and electron in conduction band is responsible for the complete mineralization of harmful organic pollutants. A schematic representation of the photocatalytic mechanism of dye degradation on semiconductor photocatalyst is shown in Fig. 15.1. An important point for consideration is that the presence of oxygen or air is favourable to the

heterogeneous photocatalysis as it prevents the electron–hole recombination process by reacting with electron in conduction band.

### 15.3 Operation and Influence of Parameters on Heterogeneous Photocatalysis

The degradation of organic compounds by using heterogeneous photocatalysis process mainly depends upon the factors such as catalyst physical parameters (structure, size, shape and surface area), pH of solution, light intensity, impurity concentration in wastewater, catalyst concentration and oxidizing agent (Bahnemann et al. 2007; Cassano and Alfano 2000; Rajeshwar et al. 2008).

#### 15.3.1 Effect of Catalyst Physical Parameters

The photocatalytic activity of the photocatalyst is dependent upon the catalyst physical properties such as its crystal size, composition, surface area, porosity, bandgap and hydroxyl functionalities on catalyst surface. Crystal size can be the most important parameter since its direct relation with the surface area of catalyst. In general, the catalyst particles with relatively high surface area shows better photocatalytic activity due to availability of large number of sites for the dye adsorption. Lu et al. (2007) use natural rutile (rutile ~90%) and P25 (80% anatase and 20% rutile) type of TiO<sub>2</sub> as catalytic surface to compare its efficiency for the photocatalytic degradation of methyl orange (MO). After 2 h illumination, the photocatalytic efficiency of the above two catalyst was found to be 82.3% and 94.8%, respectively. A possible reason was the particle size of P25 (~30 nm) which is significantly smaller compared with the natural rutile sample (70–80 μm). Another possible reason for the higher photocatalytic activity of P25 would be due to the slow electron–hole recombination process as compared to the case of natural rutile. As mentioned, P25 is composed of 80% anatase and 20% rutile phase in which nano-crystals of rutile are dispersed in the matrix of anatase. Due to lower bandgap of rutile (3.0 eV) compared to anatase (3.2 eV), rutile absorbs the energy of illuminated light, which separates the electron–hole pair. Then, the electron transfer from the conduction band of rutile to anatase inhibits the electron–hole recombination process, which can further move to the surface of the catalyst and increase the degradation process of dyes (Bahnemann et al. 2007). While in the case of natural rutile, the photocatalytic efficiency is low due to having more defects in its crystal structure, which serves as the electron–hole recombination centre (Lu et al. 2007). Besides these, other commercially available TiO<sub>2</sub> powders, namely Hombikat UV100 and PC500 have also been used for the photocatalytic degradation of organic dyes (Bahnemann et al. 2007; Saquib et al. 2008). Hombikat UV100 is composed of

100% anatase with a high specific BET surface area of  $>250 \text{ m}^2/\text{g}$  and primary particle size of 5 nm. The photocatalyst PC 500 is also composed of 100% anatase having a specific BET surface area of  $287 \text{ m}^2/\text{g}$  and primary particle size of 5–10 nm, while Degussa P25 have a specific BET-surface area of  $50 \text{ m}^2/\text{g}$  and primary particle size of 20 nm. It has been found that the activity of these photocatalysts is not only depend upon their physical properties such as BET surface area, defects and density of surface hydroxyl groups but also depend on the type of the model pollutant for the degradation. Saquib et al. (2008) have reported that the Hombikat UV100 have high photocatalytic activity for the degradation of Fast Green FCF, whereas Degussa P25 have shown relatively higher activity for the Patent Blue VF. As discussed earlier, Degussa P25 shows the higher activity due to slow electron–hole recombination process, whereas Hombikat UV100 exhibit high photocatalytic activity due to fast interfacial electron transfer process (Martin et al. 1994; Saquib et al. 2008). Lindner et al. (1995) have reported that the UV100 have almost four times more photocatalytic activity as compared to P25 for the degradation of dichloroacetic acid. It is observed that Hombikat UV100 can be a better catalyst for the degradation of benzidine and 1,2-diphenylhydrazine (Muneer et al. 2002). Recently, Flores et al. (2014) have synthesized ZnO nanostructures with different morphology such as hexagonal disks, dumb bell shaped, rice and rod like structures for the photocatalytic degradation of methylene blue (MB) in aqueous solution. This study reported that the activity of these nanostructures is directly related with the surface area and defect content in the nanostructure. It has been suggested that the ZnO nanostructure might be a low cost alternative to the  $\text{TiO}_2$  for the degradation of organic pollutants due to similar electronic bandgap (3.2 eV) and relatively higher photocatalytic activity especially for azo dyes (Flores et al. 2014). Akyol et al. (2004) have carried out photocatalytic decolourization of an azo dye Remazol red (RR), which shows that ZnO catalyst has much higher activity as compared to  $\text{TiO}_2$  for the degradation process. Lee et al. (2009) have carried out the study using ZnO and  $\text{TiO}_2$  for the photocatalytic degradation of total organic carbon (TOC) from aqueous solution of phenol which establishes that the ZnO nanopowder has 1.6 fold higher photocatalytic activity as compared to Degussa P-25 that is known as a standard photocatalyst.

### 15.3.2 Effect of pH of Solution

The photocatalytic degradation of organic dyes is strongly influenced by the pH of the solution as the charge on the surface of catalyst alters with the change in the pH of the solution. In addition, the physio-chemical properties of organic compound in the wastewater can also change with the change in the pH. As a result, the electrostatic interaction between the catalyst surface and organic dye is effected with the change in pH of the solution which will change the adsorption affinity of the organic pollutant on the surface of the catalyst thus would alter the degradation rate (Reza et al. 2017; Kazeminezhad and Sadollahkhani 2016).  $\text{TiO}_2$  as a photocatalyst has an

amphoteric character, i.e. the surface of  $\text{TiO}_2$  can be charged positive or negative in acidic and basic pH, respectively, which will affect the degradation kinetics of the dyes on the surface of  $\text{TiO}_2$  (Poulios et al. 2000; Reza et al. 2017). Moreover, it has been found that the pH of the solution affects the formation of hydroxide radical by the reaction between light induced holes on the surface of catalyst and hydroxide ions. At low pH, the holes are considered as the major participant during the oxidation step in photocatalytic degradation, whereas at neutral and high pH, the hydroxide radicals are considered to be the predominant species for the degradation of organic dyes (Shifu and Gengyu 2005). As the presence of hydroxide ions are high on the surface of  $\text{TiO}_2$ , which would increase the generation of hydroxide radical at high pH. Thus, the degradation efficiency would be high at higher pH in the case of  $\text{TiO}_2$ , which have been indicated through the literature. Bubacz et al. (2010) have reported an increase in the rate of the photocatalytic degradation of methylene blue on the surface of  $\text{TiO}_2$  with the increase in pH. Su et al. (2009) have reported the degradation of acid blue 80 dye at different pH (2–10) on the surface of  $\text{TiO}_2$  and found the highest activity at pH 10, which can be attributed to the high adsorption of cationic acid blue 80 dye on the anionic  $\text{TiO}_2$  surface at pH 10. Ling et al. (2004) have reported the degradation of methylene blue at the surface of  $\text{TiO}_2$  at different pH and found highest activity at pH 12. Aly and Abd-Elhamid (2018) have reported the degradation of methylene blue on the surface of  $\text{SiO}_2$  nanoparticles at different pH and found that discolouration increases at very low pH of 1 and high pH of 11. As stated above, these results can be attributed to the fact that the positive holes are predominant oxidation species at low pH. On the contrary, at high pH,  $\text{OH}^\cdot$  radical is more easily generated by oxidizing more hydroxide ions present on the surface of  $\text{SiO}_2$ , which increase the efficiency of degradation (Goncalves et al. 1999). Chen et al. (2017) reported the degradation of azo dyes such as methyl orange (MO), direct black 38(DB38) and Congo red (CR) on the surface of ZnO at different pH condition. They found that the degradation of these dyes is more efficient at low pH (acidic) in contrast to high basic pH. This can be understood in terms of the charge on the surface of ZnO and the properties of dyes at different pH condition. The ZnO surface becomes positively at acidic pH and the above dyes are anionic in nature. Thus, at lower pH, the high degradation of these dyes was attained due to the high electrostatic attraction between anionic dyes and positively charged ZnO catalytic surface, which results in the increase in the adsorption of dyes. On the contrary, at higher pH, there would be electrostatic repulsion between the anionic dyes and negatively charged ZnO surface, which results in negligible adsorption.

### 15.3.3 *Effect of Light Intensity*

The wavelength and the intensity of the incident light affect the amount of light absorption by the semiconductor photocatalyst. The electron–hole separation in photochemical reaction is initiated by the incident light with a particular wavelength and intensity on the surface of photocatalyst, which eventually monitor the

degradation rate of the pollutant on the catalyst surface. It has been reported that the rate of photocatalytic degradation is better when the artificial UV-Vis light source is used as compared to solar irradiation (Viswanathan 2018). Ollis et al. (1992) have reported that the kinetics of the photocatalytic degradation is dependent on the intensity of incident light.

Accordingly,

1. At low intensity of light (0–20 mW/cm<sup>2</sup>), the kinetics of photodegradation would follow first order, i.e. the rate would increase linearly with increasing intensity of light;
2. At the intermediate light intensities, the kinetics follow half order, i.e. the rate of the photochemical reaction would depend on the square root of the intensity of incident light.
3. At high intensities of incident light, the kinetics follow zero order w.r.t light intensity, i.e. the rate of photochemical reaction is independent of the intensity of light.

With the increase in light intensity, there would be more photons per unit time and unit area. Which increase the electron–hole separation on semiconductor catalytic surface, which eventually enhance the photocatalytic activity. However, at high light intensity, the number of activation sites on catalytic surface remains the same beside the increase in photon concentration. Thereby, the photochemical reaction rate would become independent of the light intensity.

### ***15.3.4 Effect of Pollutant Concentration***

The pollutant type and its concentration in the solution also affect the photocatalytic degradation process. In the solution containing pollutant and the catalyst, the pollutant molecules get adsorb on the surface of the catalyst. When there is increase in the concentration of the pollutant substrate, there will be subsequently more demand of the catalyst surface to adsorb the large number of pollutant molecules, however with the same amount of catalyst, the pollutant molecules would cover all active sites. Therefore, the demand of reactive radicals (OH<sup>·</sup> and <sup>·</sup>O<sub>2</sub>) for the degradation of pollutant would increase; however, the formation of these radicals on the catalyst surface would remain constant for a given catalyst amount, light intensity and irradiation time. Therefore, the available reactive radicals (OH<sup>·</sup> and <sup>·</sup>O<sub>2</sub>) would not be sufficient for the degradation of pollutant at its higher concentration (Bahnemann et al. 2007). Consequently, degradation rate of pollutant decreases with the increase in its concentration. Qamar and Muneer (2009) have reported that with the increase in concentration of the vanillin from 0.35 mM to 0.5 mM, the degradation rate increases, but with further increase in concentration from 0.5 mM to 1 mM, the rate of degradation decreases.



### 15.3.5 *Effect of Catalyst Concentration*

The amount of the photocatalyst also influences the kinetics of photocatalytic degradation. In general, with the increase in the quantity of semiconductor catalyst in photochemical reactor, the number of active sites on the semiconductor photocatalyst increases, which in turn would produce more number of reactive radicals ( $\text{OH}^\cdot$  and  $\cdot\text{O}_2$ ) (Ahmed et al. 2011). Hence, there will be increase in the degradation rate of pollutants. However, after an optimum concentration, the further increment in catalyst loading may adversely affect the kinetics of degradation. With the further increase in catalyst concentration, there will be decrease in the penetration depth of light into the solution, which would diminish the light scattering. In addition, the agglomeration of catalyst particles could increase with the increment in catalyst concentration, which decreases the overall surface area for light absorption. Due to these combined effect, the degradation rate decreases with the increase in catalyst concentration beyond optimum limit. However, optimum limit could be different with different type of catalyst and design of photochemical reactor. Sharma et al. (2008) reported the degradation of isoproturon on  $\text{TiO}_2/\text{SBA-15}$  substrate with different loading of  $\text{TiO}_2$  catalyst from 0.5 to 2 g/L. They found that there is increase in the degradation rate when catalyst concentration increases from 0.5 to 1 g/L and thereafter, the degradation rate decreases slightly.

### 15.3.6 *Effect of Oxidizing Agent*

In the photocatalysis process using conventional catalyst like  $\text{TiO}_2$ , electron-hole recombination process is the major drawback, which decreases the efficiency of photochemical degradation of dyes. The presence of molecular oxygen traps the excited electron of conduction band, thus inhibit the electron-hole recombination process to some extent. However, the presence of oxidizing agent(s) such as ozone ( $\text{O}_3$ ), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), bromate ( $\text{BrO}_3^-$ ) and peroxodisulphate ( $\text{S}_2\text{O}_8^{2-}$ ) can further increase the kinetics of photochemical degradation of dyes (Wang et al. 2002; Saquib et al. 2008; Chen et al. 2018; Rehman et al. 2018; Feilizadeh et al. 2019). This is primarily due to their role in trapping more numbers of electrons from conduction band and thus further preventing the electron-hole recombination process, which may generate more oxidizing radicals ( $\text{OH}^\cdot$ ) and thus leads to increase in the photochemical degradation of dyes. It has been found that the  $\text{H}_2\text{O}_2$  influences the kinetics of photochemical degradation by producing more hydroxide radical ( $\text{OH}^\cdot$ ) in two ways either by reduction of  $\text{H}_2\text{O}_2$  by trapping electron at the conduction band or by self-decomposition of  $\text{H}_2\text{O}_2$  into  $\text{OH}^\cdot$  when light falls on it, thereby increase the rate of dye degradation. Mahmoodi et al. (2006) have reported the effect of  $\text{H}_2\text{O}_2$  on the photochemical degradation of the Reactive Blue 8 (RB 8) and Reactive Blue 220 (RB 220) and found increase in the degradation rate when

concentration of  $\text{H}_2\text{O}_2$  increases from 0 to its optimal concentration (300 mg/L for RB8 and 450 mg/L for RB220).

The effect of various parameters on the photocatalytic degradation of pollutants shown in literature has been summarized in Table 15.2.

## 15.4 Photocatalyst Material(S)

In recent times, several semiconducting material such as metal oxide(s) like  $\text{TiO}_2$ ,  $\text{ZnO}$ ,  $\text{ZrO}_2$ ,  $\text{WO}_3$ ,  $\text{CeO}_2$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$  and metal sulphide(s) like  $\text{CdS}$  and  $\text{ZnS}$  are used as catalyst surface in heterogeneous photocatalysis (Saravanan et al. 2017; Viswanathan 2018). Among all these,  $\text{TiO}_2$  has received the great attention in the photocatalysis industry due to its low cost and toxicity, chemical inertness, high photochemical activity, and non-specific oxidizing character (Akpan and Hameed 2009).  $\text{TiO}_2$  comprises three phases: anatase (3.2 eV), rutile (3.0 eV) and brookite (3–3.6 eV). Among these, anatase is the most effective phase for the dye and other organic pollutant degradation due to its constituent favourable position to adsorb the pollutant. The oxygen ions on the anatase are in the triangular position, which efficiently increase the absorption of organic molecules, whereas the titanium ions in the anatase phase are oriented in such a way to favour the reaction with the adsorbed species. Among others,  $\text{ZnO}$  (3.3 eV),  $\text{SnO}_2$  (3.57 eV) and  $\text{CeO}_2$  (3.19 eV) can be considered as alternative for  $\text{TiO}_2$  for the degradation of organic pollutants due to their high adsorbing capacity (Shinde et al. 2017).

However, due to large bandgap of these metal oxide catalyst(s), it can only absorb UV light which limits the efficient use of its applicability in degradation of organic pollutants and dyes since only about 10% of the solar spectrum consists of ultraviolet light ( $< 400$  nm). In the rest of the radiant energy emitted from the sun, about 50% lies in the infrared (IR) region ( $> 700$  nm) and about 40% in the visible region (400–700 nm) (Qiang and James 2003). On the earth crust, sunlight consists of only 3–5% of UV light, which makes it insufficient for the efficient degradation of dyes (Wang et al. 2019). To make use of enormous potential of sunlight, researchers are concentrating on to develop materials, which can absorb lower energy photon especially of visible light to make the degradation of dyes more efficient (Nakata and Fujishima 2012; Saravanan et al. 2017). Although there are certain metal sulphides like  $\text{CdS}$  (2.42 eV) and  $\text{PbS}$  (0.37 eV) which can absorb visible light photon due to their relatively lower bandgap; however, these metal sulphides are not stable, toxic in nature and composed of rare earth element which limits its application for the degradation of dyes (Boldish and White 1998; Shiga et al. 2016). It has been suggested that the bandgap of the above metal oxide(s) can be tuned in the visible light wavelength by adopting some techniques, which may improve the structure for high photocatalytic degradation of dyes. The next section will discuss about those improvement methods.

**Table 15.2** Influence of various parameters on the photocatalytic degradation of pollutants

Pollutant	Catalyst	Catalyst concentration (Optimized)	Pollutant concentration (Optimized)	pH range (Optimized pH)	Light source (intensity)	Removal	Reference
Crystal violet (CV)	TiO <sub>2</sub>	0.2 g	2.5 × 10 <sup>-5</sup> mol/L for CV in 50 mL	–	UV light 125 W Hg lamp	96.7%	Ren et al. (2014)
Azo dye 2-(2-naphthyl azo)-4,5-diphenyl imidazole	ZnO	0.03–0.60 g/100 mL (0.15 g/100 mL)	50–100 ppm (50 ppm)	4–11 (8.1)	UV light (8.44 mW/cm <sup>2</sup> )	84.06%	Saad et al. (2018)
Methylene blue (MB)	TiO <sub>2</sub>	0–35 mg/10 mL (20 mg/10 mL)	5–15 ppm (15 ppm)	5.5	UV LED (395 nm)	–	Zulmajdi et al. (2017)
Gentian violet	TiO <sub>2</sub> -P25	0.25–3 g/L (2 g/L)	2.5–20 mg/L (15 mg/L)	5.74	UV light (1.8 mW/cm <sup>2</sup> at 365 nm)	Complete decolorization in 30 min	Bendjabeur et al. (2017)
Methylene blue	SiO <sub>2</sub>	0.05–0.2 g/20 mL (0.2 g/20 mL)	50–200 ppm (100 ppm)	1–11 (low pH-1 High pH-11)	UV light	Complete degradation in 90 s	Aly and Abd-Elhamid (2018)
Methylene blue	TiO <sub>2</sub>	0.2–1.2 g/L (0.2 g/L)	1–15 ppm (10 ppm)	3–13.3 (13.3)	UV light 24 W	85% in 60 min	Salehi et al. (2012)
Methyl orange	ZnO	0.1–0.8 g/L (0.8 g/L)	10–50 mg/L (30 mg/L)	2–10 (2)	UV light	99.7%	Chen et al. (2017)

## 15.5 Modification of Catalyst

In spite of the extensive R&D on  $\text{TiO}_2$  as a photocatalyst for degradation of dyes and other organic pollutants, the low photo-quantum efficiency of  $\text{TiO}_2$  is still a major problem. This may be due to the rapid recombination of photo-generated electron and hole. In order to inhibit the electron–hole recombination process and to tune the bandgap of catalyst to absorb the visible energy for high photocatalytic activity, the surface of the semiconductor catalyst can be modified in the following ways: (1) Making a composite with metal/metal oxides or with carbon based materials like activated carbon, graphite, graphene and carbon nanotubes (CNTs); (2) Doping of certain metal and non-metal in the structure of semiconductor photocatalyst; and (3) Surface sensitization by dye/polymer.

### 15.5.1 Modification by Making Composite

One of the possible approaches for inhibiting the electron–hole recombination and modifying the bandgap of catalyst to work in visible region of solar radiation is to make coupled semiconductor photocatalyst(s). Recently, many semiconductor composites like  $\text{Ag}_2\text{O}/\text{TiO}_2$ ,  $\text{CuO}@\text{ZnO}$  core shell,  $\text{CdS}/\text{TiO}_2$ ,  $\text{PbS}/\text{TiO}_2$ ,  $\text{CdS}/\text{ZnO}$ , and so on have been reported (Liu et al. 2017; Mansournia and Ghaderi 2017; Aziz et al. 2019; Jana et al. 2016). It has been found that the photocatalytic activity can be enhanced by making composite system as compared to single component photocatalyst. This is because the composition of two-semiconductor photocatalyst having different bandgaps can inhibit the electron–hole recombination. Recently, Aziz et al. (2019) have reported the composites  $\text{PbS}/\text{TiO}_2$  and  $\text{CdS}/\text{TiO}_2$  for enhancing the photocatalytic degradation of azo-based dye (acid orange-56) in the visible light by using the above principle. It has been shown that the activity of composite (s)  $\text{PbS}/\text{TiO}_2$  and  $\text{CdS}/\text{TiO}_2$  is significantly enhanced towards acid orange-56 in the visible light, while anatase- $\text{TiO}_2$  alone did not show photocatalytic activity with the same conditions. This is because in the presence of visible light, there is rapid generation of electron–hole in the  $\text{PbS}$  and  $\text{CdS}$  due to their harmonized bandgap energy with visible light as compared to anatase- $\text{TiO}_2$ . Since the conduction band of  $\text{TiO}_2$  is situated at lower position to the conduction band of  $\text{PbS}$  and  $\text{CdS}$ , the photo-generated electron in  $\text{PbS}$  and  $\text{CdS}$  transfer to the conduction band of  $\text{TiO}_2$ . In this way, the electron–hole recombination process inhibits and thus the photochemical activity toward the acid orange-56 degradation increases (Aziz et al. 2019).

In another approach, the composite of semiconductor with carbon based materials like activated carbon, graphite, graphene and CNTs and graphitic  $\text{C}_3\text{N}_4$  have been explored. These heterostructure(s) enhance the photocatalytic activity because of high electrical conductivity, high surface area, high adsorption capacity and increase in charge separation and transfer at the heterojunction. Recently, Lin et al. (2018) have reported the hybrid structure of reduced graphene oxide/ $\text{TiO}_2$ /graphitic carbon

nitride ( $g\text{-C}_3\text{N}_4$ ) for the enhanced photocatalytic degradation of methylene blue (MB) under solar light irradiation. In this heterostructure, the porous structure of reduced graphene oxide (rGO) and  $g\text{-C}_3\text{N}_4$  increase the adsorption and photocatalytic reaction sites by making excellent dispersion of  $\text{TiO}_2$  nanoparticles on the heterostructure, while  $g\text{-C}_3\text{N}_4$  increases the visible light absorption due to its lower bandgap. Furthermore, rGO helps to improve the photo-generated charge separation due to its high electronic conductivity. This ternary heterostructure has shown significant enhancement in the photocatalytic activity, which is about 17.2, 8.6 and 2.7 times more than that of  $g\text{-C}_3\text{N}_4$ ,  $\text{rGO}/\text{TiO}_2$  and  $\text{TiO}_2/g\text{-C}_3\text{N}_4$ . Similar reports comprising effect of composite materials with metal oxide(s) and carbon materials on the photocatalytic degradation of dyes and other pollutants are presented in Table 15.3.

### 15.5.2 Modification by Doping of Metal/Non-metal

The doping of certain metal/metal ion(s) into the semiconductor lattice is another approach to inhibit the electron–hole recombination and to extend the absorption of light in visible region. Many transition metals such as V, Cr, Fe, Ni, Co, Zn, W, Mo; and noble metals such as Pt, Au, Ag and Pd have been used as a dopant in the lattice of semiconductor to increase the charge separation (Garcia et al. 2017; Liu et al. 2013; Inturi et al. 2014; Sowmya et al. 2018). Inturi et al. (2014) have reported the doping of many transition metals ( $M = \text{V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce}$  and  $\text{Zr}$ ) in the lattice of  $\text{TiO}_2$  for the visible light photocatalytic degradation of acetonitrile. In their study, Cr doped  $\text{TiO}_2$  showed the superior photocatalytic activity, which is 8–19 times higher than other metal-doped catalyst. It has been observed that during doping of Cr in  $\text{TiO}_2$  lattice,  $\text{Ti}^{3+}$  species originate in the structure. The  $\text{Ti}^{3+}$  energy level lies in between the valence and conduction band of  $\text{TiO}_2$ , which helps to absorb the photon in visible region. On the other side, Cr nanoparticles may serve as trapping centre for the photo-generated electron in the conduction band of  $\text{TiO}_2$ . In this way, the doping of Cr in the  $\text{TiO}_2$  inhibits the electron–hole recombination and increases the overall efficiency toward the acetonitrile degradation.

Doping/co-doping with non-metal(s) such as B, C, N and S in the semiconductor lattice can also increase the photocatalytic efficiency in visible light by red shifting the bandgap of semiconductor (Giannakas et al. 2016; Helmy et al. 2018). Jin et al. (2018) reported the efficient photocatalytic degradation of methyl orange (MO) on N doped anatase  $\text{TiO}_2$  catalyst and with increasing concentration of nitrogen, the activity toward degradation increases, whereas bare anatase  $\text{TiO}_2$  have no catalytic activity in visible light. Koltsakidou et al. (2018) reported the photocatalytic degradation of fluorouracil using  $\text{TiO}_2\text{-P25}$  and N/S doped  $\text{TiO}_2$  catalyst under visible light and found the best activity with codoped catalyst at the optimum molar concentration ratio of one.

**Table 15.3** Influence of making composite with metal oxide and carbon material(s) on photocatalytic degradation of various pollutants

Pollutant	Light source	Catalyst	Comment	Reference
Methylene blue	Visible light	TiO <sub>2</sub> /Ag <sub>2</sub> O	In visible light. Composite TiO <sub>2</sub> /Ag <sub>2</sub> O (1:4) shows best activity compared to bare TiO <sub>2</sub> and Ag <sub>2</sub> O with complete degradation in 50 min. The rate constant of TiO <sub>2</sub> /Ag <sub>2</sub> O (1:4), TiO <sub>2</sub> and Ag <sub>2</sub> O toward degradation is 0.085 min <sup>-1</sup> , 0.005 min <sup>-1</sup> and 0.065 min <sup>-1</sup> , respectively	Liu et al. (2017)
Methylene blue	Sunlight (100 mW/cm <sup>2</sup> )	TiO <sub>2</sub> /CdSe	The composite TiO <sub>2</sub> /CdSe film shows high photocatalytic degradation of 81.77% in 180 min, whereas TiO <sub>2</sub> film alone shows only 27.99% degradation of methylene blue	Lu et al. (2016)
Methylene orange	Visible light (500 W)	CdS/ZnO	The composite CdS/ZnO shows high activity of 94.6% towards methyl orange degradation compared to CdS and blank experiment, which have activity of 75.8% and 8.1% in 180 min. The rate constant of CdS/ZnO, CdS and blank for methyl orange degradation is 0.0142, 0.0079 and 0.0005 min <sup>-1</sup> , respectively	An et al. (2015)
Rhodamine B	Visible light (1000 W halogen lamp)	CdS/ZnO	This report provides that the photocatalytic activity depends upon the mass ratio of components of composite. CZ1:1 shows complete degradation of Rhodamine B in 190 min, whereas within same time, only 25% and 40% dye degraded in CZ1:2 and CZ1:3, respectively	Jana et al. (2016)
Phenol	Visible light (300 W Xe lamp)	Bi <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	Bi <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub> shows higher photocatalytic activity than Bi <sub>2</sub> O <sub>3</sub> toward phenol degradation despite having low content of Bi <sub>2</sub> O <sub>3</sub> (3%) in Bi <sub>2</sub> O <sub>3</sub> /g-C <sub>3</sub> N <sub>4</sub>	He et al. (2018)
Methylene blue and 4-Nitrophenol	Visible light	ZnO/ZnSe	The optimized ZnO/ZnSe composite shows better activity toward photocatalytic degradation of methylene blue (100%) and 4-Nitrophenol (92.5%) in 360 min, whereas pure ZnO has lower photocatalytic activity	Liu et al. (2015)
Methyl orange (MO)	Visible light	SnO/activated carbon (AC)	The SnO/AC(3%) composite shows better photocatalytic activity than bare SnO for MO degradation which is 97.6% in 80 min	Liang et al. (2019)

### 15.5.3 *Modification by Dye/Polymer Sensitizer*

The photocatalytic activity of semiconductor in the visible light can also be influenced by using certain dye/polymer molecules such as reactive red dye 198 (RR 198), eosin-Y, merbromine, 2,7-dichlorofluorescein, curcumin, cobalt(II)-phthalocyanine-tetrasulfonate, chrysoidine G, tolylene diisocyanate and polymer such as poly(fluorine-co-thiophene) (PFT) as the sensitizers (Rehman et al. 2009; Buddee et al. 2014; Behjou et al. 2013). When visible light is incident, dye/polymer molecule get excited and the excited electron moves to the conduction band of the semiconductor where these electrons are trapped by molecular oxygen to form superoxide radical ( $O_2^-$ ) which can further increase the rate of degradation of organic pollutants. The literature reports comprising effect of doping of various metals, non-metals and surface sensitizers (dyes/polymers) on the photocatalytic degradation of organic pollutants are presented in Table 15.4.

The above modification(s) in the structure of semiconductor catalyst especially  $TiO_2$  have efficiently enhanced its activity in visible light. However, to apply a particular photocatalyst at the industrial scale, long-term stability and large-scale production have to be considered. Black  $TiO_2$  having high visible light response and thus high photocatalytic activity can be another interesting alternative to be used in the industry. Black  $TiO_2$  can be synthesized via hydrogenation of P25  $TiO_2$  and can have a very low bandgap of about 1.0 eV which is lower than the P25 itself. However, the method used for the hydrogenation of P25 generally requires hydrogen atmosphere at high temperature and pressure, which impose a safety issue during its preparation. However, recently, Wang et al. (2019) introduced a hydrothermal method to overcome the shortcomings of hydrogenation method to reduce the P25  $TiO_2$  with reducing agent like zinc (Zn) and aluminium (Al). The processed black  $TiO_2$  from this method have very low band in the visible region.

## 15.6 Conclusion

Based on recent studies, this chapter dealt with the mechanistic understanding of various operating parameters such as catalyst physical parameters, pH, light intensity, catalyst concentration, pollutant concentration and presence of oxidizing agent, which effect the photocatalytic degradation of various dyes and other organic pollutants. The studies exhibit that these parameters can significantly influence the photocatalytic degradation process. Photocatalyst degradation process has emerged as an excellent method for the mineralization of wastewater pollutants. However, the finding of an appropriate low cost, scalable photocatalyst, which can absorb visible light or sunlight, is still a challenge. The future work should concentrate on this issue in a very specific mode to provide a low cost, non-toxic, scalable, durable and reproducible photocatalyst, which can increase the efficiency of photocatalytic degradation by working in sunlight as the light source.

**Table 15.4** Influence of doping of various metal(s), non-metal(s) and surface sensitizer (dyes and polymers) on photocatalytic degradation of various pollutants

Pollutant	Light source	Catalyst	Doping conc. (%) (optimum)	Comment	Reference
Congo red	Sunlight	Ag-TiO <sub>2</sub>	0.005–0.5% (0.1%)	Ag-TiO <sub>2</sub> with 0.1% Ag doping shows relatively better photodegradation activity of complete degradation in 80 min, whereas TiO <sub>2</sub> without doping shows 59% degradation in 80 min	Sowmya et al. (2018)
Methylene blue (MB) and RR-241	Visible light (500 W)	Nd and Er doped ZnO	Nd-2% Er-5%	Doped ZnO shows better activity compared to undoped ZnO. In 10 min, 100% degradation for MB and 78.6% for RR-241 take place in the presence of 2% Nd/ZnO and 5% Er/ZnO, respectively	Raza et al. (2016)
DB 71 dye	Visible light (500 W)	Mn doped ZnO	1.5% doping of Mn	Mn doped ZnO shows highest photocatalytic activity of about 98.9% at neutral pH. It follows pseudo first-order kinetics	Thennarasu Sivasamy (2019)
Methylene blue	Visible light (400 W)	Ni/co/Ce/Sb doped CdS	2% doping	Co-CdS shows best activity of 87% degradation, whereas Ni-, Ce-, Sb- and bare CdS show 73%, 76%, 70% and 68% degradation, respectively	Ertis and Boz (2017)
Bisphenol A	UV-Vis light (500 W)	Ag doped ZnO	3% doping of Ag	The Ag doped ZnO with 3% doping shows relatively much better photocatalytic activity as compared to bare ZnO. It follows first-order rate kinetics	Hoshiyama et al. (2016)
Methyl orange	Visible light	N-TiO <sub>2</sub>	3.8%, 13.6%	With increase in conc. of N, the photocatalytic activity increases which is due to the decrease in the bandgap with increasing N conc.	Jin et al. (2018)
5-fluorouracil	Blue light (16 W)	N-TiO <sub>2</sub>	—	The optimum N-TiO <sub>2</sub> shows 88.8% photocatalytic degradation, whereas Degussa P25 TiO <sub>2</sub> shows 61.5% degradation	Lin et al. (2015)



4-Nitrophenol	Simulated sunlight	C,N-TiO <sub>2</sub>	C-15.07% N-1.25%	The C,N-TiO <sub>2</sub> shows better photocatalytic activity of 87% and rate constant 0.00487 min <sup>-1</sup> , whereas anatase TiO <sub>2</sub> shows 65% activity and rate constant of 0.00253 min <sup>-1</sup>	Osin et al. (2018)
Rhodamine B	Visible light	C,N,S doped rutile TiO <sub>2</sub> nanorod and C,N,S doped anatase TiO <sub>2</sub> nanoparticle	—	Bandgap become narrow due to ternary doping which support photocatalytic activity in visible light. Optimized CNS rutile TiO <sub>2</sub> nanorod shows complete degradation in 60 min, which is better compared to anatase nanoparticles	Wang et al. (2017)
Phenol and Rhodamine B	Visible light	N, F codoped oxygen deficient TiO <sub>2</sub>	N-0.31% F-3.92%	Doping increase the activity of the material towards degradation, whereas P25 shows lesser photocatalytic activity towards degradation	Kang et al. (2018)
Methylene blue (MB) and orange II	Visible light	Curcumin sensitized TiO <sub>2</sub>	7.5% of Curcumin	The photocatalytic activity with Curcumin sensitized TiO <sub>2</sub> for MB is high in basic medium, whereas for orange II, it is high in acidic medium	Buddee and Wongnawa, (2015)
Rhodamine B	Visible light (90 W)	Tetra (4-carboxyphenyl) Porphyrin(TCPP)-TiO <sub>2</sub>	0.05–1% (0.1%)	TCPP provide 93% degradation of Rhodamine B under visible light in 10 h	Ahmed et al. (2017)

## References

- Ahmed S, Rasul MG, Martens WN, Brown R, Hashib MA (2011) Advances in heterogeneous photocatalytic degradation of phenols and dyes in wastewater: a review. *Water Air Soil Pollut* 215:3–29
- Ahmed MA, Abou-Gamra ZM, Medien HAA, Hamza MA (2017) Effect of porphyrin on photocatalytic activity of TiO<sub>2</sub> nanoparticles toward rhodamine B photodegradation. *J Photochem Photobiol B Biol* 176:25–35
- Akpan UG, Hameed BH (2009) Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>-based photocatalysts: a review. *J Hazard Mater* 170:520–529
- Akyol A, Yatmaz HC, Bayramoglu M (2004) Photocatalytic decolorization of Remazol Red RR in aqueous ZnO suspensions. *Appl Catal B* 54:19–24
- Aly HF, Abd-Elhamid AI (2018) Photocatalytic degradation of methylene blue dye using silica oxide nanoparticles as a catalyst. *Water Environ Res* 90(9):807–817. <https://doi.org/10.2175/106143017X15131012187953>
- An L, Wang G, Cheng Y, Zhao L, Gao F, Cheng Y (2015) Synthesis of CdS/ZnO Nanocomposite and its enhanced photocatalytic activity in degradation of methyl orange. *Russ J Phys Chem A* 89(10):1878–1883
- Aziz MI, Mughal F, Naeem HF, Zeb A, Tahir MA, Basit MA (2019) Evolution of photovoltaic and photocatalytic activity in anatase-TiO<sub>2</sub> under visible light via simplistic deposition of CdS and PbS quantum-dots. *Mater Chem Phys* 229:508–513
- Bahnemann W, Muneer M, Haque MM (2007) Titanium dioxide-mediated photocatalysed degradation of selected organic pollutants in aqueous suspensions. *Catal Today* 124:133–148
- Balciolu IA, Otker M (2003) Treatment of pharmaceutical wastewater containing antibiotics by O<sub>3</sub> and O<sub>3</sub>/H<sub>2</sub>O<sub>2</sub> processes. *Chemosphere* 50:85–95
- Behjou A, Aghaie H, Zare K, Aghaie M (2013) Synthesis and investigation of visible-light-activated rutile phase modified TiO<sub>2</sub>. *Asian J Chem* 25(2):880–882
- Bendjabeur S, Zouaghi R, Kaabeche ONH, Sehili T (2017) Parameter affecting adsorption and photocatalytic degradation behavior of gentian violet under UV irradiation with several kinds of TiO<sub>2</sub> as a photocatalyst. *Int J Chem React Eng* 15(4):20160206. <https://doi.org/10.1515/ijcre-2016-0206>
- Boldish SI, White WB (1998) Optical band gaps of selected ternary sulfides minerals. *Am Mineral* 83:865–871
- Bubacz K, Choina J, Dolat D, Morawski AW (2010) Methylene blue and phenol photocatalytic degradation on nanoparticles of anatase TiO<sub>2</sub>. *Pol J Environ Stud* 19:685–691
- Buddee S, Wongnawa S (2015) Removal of dyes by photocatalytically active curcumin-sensitized amorphous TiO<sub>2</sub> under visible light irradiation. *J Sol-Gel Sci Technol* 75:152–163
- Buddee S, Wongnawa S, Sriprang P, Sriwong C (2014) Curcumin-sensitized TiO<sub>2</sub> for enhanced photodegradation of dyes under visible light. *J Nanopart Res* 16:2336
- Cassano AE, Alfano OM (2000) Reaction engineering of suspended solid heterogeneous photocatalytic reactors. *Catal Today* 58:167–197
- Chen X, Wu Z, Liu D, Gao Z (2017) Preparation of ZnO photocatalyst for the efficient and rapid photocatalytic degradation of Azo dyes. *Nanoscale Res Lett* 12:143
- Chen L, Cai T, Cheng C, Xiong Z, Ding D (2018) Degradation of acetamiprid in UV/H<sub>2</sub>O<sub>2</sub> and UV/persulfate systems: a comparative study. *Chem Eng J* 351:1137–1146
- Chong MN, Jin B, Chow CWK, Saint C (2010) Recent developments in photocatalytic water treatment technology: a review. *Water Res* 44:2997–3027
- Ertis IF, Boz I (2017) Synthesis and characterization of metal-doped (Ni, Co, Ce, Sb) CdS catalysts and their use in methylene blue degradation under visible light irradiation. *Modern Research in Catalysis* 6:1–14
- Feilizadeh M, Attar F, Mahinpey N (2019) Hydrogen peroxide-assisted photocatalysis under solar light irradiation: interpretation of interaction effects between an active photocatalyst and H<sub>2</sub>O<sub>2</sub>. *Can J Chem Eng* 97(7):2009–2014

- Flores NM, Pal U, Galeazzia R, Sandovalb A (2014) Effects of morphology, surface area, and defect content on the photocatalytic dye degradation performance of ZnO nanostructures. *RSC Adv* 4:41099
- Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238(5358):37–38
- Fujishima A, Rao TN, Tryk DA (2000) Titanium dioxide photocatalysis. *J Photochem Photobiol C* 1(1):1–21
- García OA, Valencia JE, Romero R, Rico-Cerda JL, Albiter MA, Natividad R (2017) W and Mo doped TiO<sub>2</sub>: synthesis, characterization and photocatalytic activity. *Fuel* 198:31–41
- Gernjak W, Krutzler T, Glaser A, Malato S, Caceres J, Bauer R, Fernandez-Alba AR (2003) Photo-Fenton treatment of water containing natural phenolic pollutants. *Chemosphere* 50:71–78
- Ghaly MY, Hartel G, Mayer R, Haseneder R (2001) Photochemical oxidation of p-chlorophenol by UV/H<sub>2</sub>O<sub>2</sub> and photo-Fenton process. A comparative study. *Waste Manag* 21:41–47
- Giannakas AE, Antonopoulou M, Daikopoulos C, Deligiannakis Y, Konstantinou I (2016) Characterization and catalytic performance of B-doped, B–N co-doped and B–N–F tri-doped TiO<sub>2</sub> towards simultaneous Cr(VI) reduction and benzoic acid oxidation. *Appl Catal B Environ* 184:44–54
- Gleick PH (2015) Dirty water: estimated death from water-related diseases 2000–2020. Pacific Institute for Studies in Development, Environment, and Security, Oakland, pp 1–12. [www.pacinst.org](http://www.pacinst.org)
- Goncalves MST, Oliveira-Campos AMF, Pinto EMMS, Plasencia PMS, Queiroz MJRP (1999) Photochemical treatment of solutions of Azo dyes containing TiO<sub>2</sub>. *Chemosphere* 39:781–786
- Goswami L, Manikandan NA, Pakshirajan K, Pugazhenti G (2017) Simultaneous heavy metal removal and anthracene biodegradation by the oleaginous bacteria *Rhodococcus opacus*. *3 Biotech* 7:37
- Gupta VK, Ali I, Saleh TA, Nayak A, Agarwal S (2012) Chemical treatment technologies for wastewater recycling—an overview. *RSC Adv* 2:6380–6388
- He R, Zhou J, Fu H, Zhang S, Jiang C (2018) Room-temperature in situ fabrication of Bi<sub>2</sub>O<sub>3</sub>/g-C<sub>3</sub>N<sub>4</sub> direct Z-scheme photocatalyst with enhanced photocatalytic activity. *Appl Surf Sci* 430:273–282
- Helmy AT, Nemr AE, Mousa M, Arafa E, Eldafrawy S (2018) Photocatalytic degradation of organic dyes pollutants in the industrial textile wastewater by using synthesized TiO<sub>2</sub>, C-doped TiO<sub>2</sub>, S-doped TiO<sub>2</sub> and C, S co-doped TiO<sub>2</sub> nanoparticles. *J Water Environ Nanotechnol* 3(2):116–127
- Hoshiyama N, Dabwan AHA, Katsumata H, Suzuki T, Furukawa M, Kaneco S (2016) Enhanced photocatalytic degradation of bisphenol A in aqueous solution by Ag-doping ZnO. *Open J Inorg Non-Met Mater* 6:13–17. <https://doi.org/10.4236/ojinm.2016.63003>
- Inturi SNR, Boningari T, Suidanb M, Smirmiotis PG (2014) Visible-light-induced photodegradation of gas phase acetonitrile using aerosol-made transition metal (V, Cr, Fe, Co, Mn, Mo, Ni, Cu, Y, Ce, and Zr) doped TiO<sub>2</sub>. *Appl Catal B Environ* 144:333–342
- Jana TK, Maji SK, Pal A, Maiti RP, Dolai TK, Chatterjee K (2016) Photocatalytic and antibacterial activity of cadmium sulphide/zinc oxide nanocomposite with varied morphology. *J Colloids Interface Sci* 480:9–16
- Jin YJ, Linghu J, Chai J, Chua CS, Wong LM, Feng YP, Yang M, Wang S (2018) Defect evolution enhanced visible-light photocatalytic activity in nitrogen-doped anatase TiO<sub>2</sub> thin films. *J Phys Chem C* 122:16600–16606
- Kang X, Han Y, Song X, Tan Z (2018) A facile photo assisted route to synthesis N, F-codoped oxygen-deficient TiO<sub>2</sub> with enhanced photocatalytic performance under visible light irradiation. *Appl Surf Sci* 434:725–734
- Kazeminezhad I, Sadollahkhani A (2016) Influence of pH on the photocatalytic activity of ZnO nanoparticles. *J Mater Sci Mater Electron* 27(5):4206–4215

- Khataee V, Vatanpour V, Amani AR (2009) Decolorization of C.I. acid blue 9 solution by UV/nano-TiO<sub>2</sub>, Fenton, Fenton-like, electro-Fenton and electrocoagulation processes: a comparative study. *J Hazard Mater* 161:1225–1233. <https://doi.org/10.1016/j.jhazmat.2008.04.075>
- Koltsakidou A, Antonopoulou M, Evgenidou E, Konstantinou I, Lannakas AE, Papadaki M, Bikiaris D, Lambropoulou DA (2018) Photocatalytic removal of fluorouracil using TiO<sub>2</sub>-P25 and N/S doped TiO<sub>2</sub> catalysts: a kinetic and mechanistic study. *Sci Total Environ* 578:257–267
- Kushwaha A, Rani R, Kumar S, Thomas T, David AA, Ahmed M (2017) A new insight to adsorption and accumulation of high lead concentration by copolymer and whole cells of lead-resistant bacterium *Acinetobacter junii* L. Pb1 isolated from coal mine dump. *Environ Sci Pollut Res* 24:10652–10661
- Lee JC, Park H-J, Lee J-H, Kim H-S, Chung Y-J (2009) Photocatalytic degradation of TOC from aqueous phenol solution using combusted ZnO nanopowder. *J Electroceram* 22:110–113
- Liang B, Zhang W, Zhang Y, Zhang R, Liu Y (2019) Efficient visible-light photocatalyst synthesized by modifying SnO with activated carbon. *Mater Res Express* 6:015603
- Lin HH-H, Lin AY-C, Hung C-L (2015) Photocatalytic oxidation of cytostatic drugs by microwave-treated N-doped TiO<sub>2</sub> under visible light. *J Chem Technol Biotechnol* 90:1345–1354
- Lin P, Hu H, Lv H, Ding Z, Xu L, Qian D, Wang P, Pan J, Li C, Cui C (2018) Hybrid reduced graphene oxide/TiO<sub>2</sub>/graphitic carbon nitride composites with improved photocatalytic activity for organic pollutant degradation. *Appl Phys A* 124:510
- Lindner M, Bahnemann DW, Hirthe B, Griebler WD (1995) Novel TiO<sub>2</sub> powders as highly active photocatalysts. In: Stine WB, Tanaka T, Claridge DE (eds) *Solar water detoxification; solar engineering*. ASME, New York, pp 339–408
- Ling CM, Mohamed AR, Bhatia S (2004) Performance of photocatalytic reactors using immobilized TiO<sub>2</sub> film for the degradation of phenol and methylene blue dye present in water stream. *Chemosphere* 57:547–554
- Liu M, Qiu X, Miyauchi M, Hashimoto K (2013) Energy-level matching of Fe(III) ions grafted at surface and doped in bulk for efficient visible-light photocatalysts. *J Am Chem Soc* 135(27):10064–10072
- Liu H, Hu Y, He X, Jia H, Liu X, Xu B (2015) In-situ anion exchange fabrication of porous ZnO/ZnSe heterostructural microspheres with enhanced visible light photocatalytic activity. *J Alloys Compd* 650:633–640
- Liu B, Mu L, Han B, Zhang J, Shi H (2017) Fabrication of TiO<sub>2</sub>/Ag<sub>2</sub>O heterostructure with enhanced photocatalytic and antibacterial activities under visible light irradiation. *Appl Surf Sci* 396:1596–1603
- Lu A, Li Y, Lv M, Wang C, Yang L, Liu J (2007) Photocatalytic oxidation of methyl orange by natural V bearing rutile under visible light. *Sol Energy Mater Sol Cells* 91:849–1855
- Lu C, Zhang L, Zhang Y, Liu S (2016) Electrodeposition of TiO<sub>2</sub>/CdSe heterostructure films and photocatalytic degradation of methylene blue. *Mater Lett* 185:342–345
- Mahmoodi NM, Arami M, Limaee NY, Tabrizi NS (2006) Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized TiO<sub>2</sub> photocatalytic reactor. *J Colloid Interface Sci* 295:159–164
- Mansournia M, Ghaderi L (2017) CuO@ZnO core-shell nanocomposites: novel hydrothermal synthesis and enhancement in photocatalytic property. *J Alloys Compd* 691:171–177
- Martin ST, Herrmann H, Choi W, Hoffmann MR (1994) Time-resolved microwave conductivity. Part 1.-TiO<sub>2</sub> photoreactivity and size quantization. *J Chem Soc Faraday Trans* 90:3315–3322
- Muneer M, Singh HK, Bagnemann D (2002) Semiconductor-mediated photocatalysed degradation of two selected priority organic pollutants, benzidine and 1, 2-diphenylhydrazine, in aqueous suspension. *Chemosphere* 49:193–203
- Nakata K, Fujishima A (2012) TiO<sub>2</sub> photocatalysis: design and applications. *J Photochem Photobiol C* 13(3):169–189

- Oller I, Malato S, Sanchez-Perez JA (2011) Combination of advanced oxidation processes and biological treatments for wastewater decontamination—a review. *Sci Total Environ* 409 (20):4141–4166
- Ollis DF (1985) Contaminant degradation in water. *Environ Sci Technol* 19(6):480–484
- Ollis DF, Pelizzetti E, Serpone N (1992) Photocatalyzed destruction of water contaminants. *Environ Sci Technol* 25:1522–1529
- Osin OA, Yu T, Cai X, Jiang Y, Peng G, Cheng X, Li R, Qin Y, Lin S (2018) Photocatalytic degradation of 4-nitrophenol by C, N-TiO<sub>2</sub>: degradation efficiency vs. embryonic toxicity of the resulting compounds. *Front Chem* 6:192. <https://doi.org/10.3389/fchem.2018.00192>
- Pimental D (1991) Global warming, population growth, and natural resources for food production. *Soc Nat Resour* 4:347–363. <https://doi.org/10.1080/08941929109380766>
- Poulios I, Avranas A, Rekliti E, Zouboulis A (2000) Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides. *J Chem Technol Biotechnol* 75:205–212
- Qamar M, Muneer M (2009) A comparative photocatalytic activity of titanium dioxide and zinc oxide by investigating the degradation of vanillin. *Desalination* 249:535–540
- Qiang F, James R (2003) *Encyclopedia of atmospheric sciences*. Academic Press, Amsterdam, pp 1859–1863
- Rajeshwar K, Osugi ME, Chanmanee W, Chenthamarakshan CR, Zaroni M, Kajitvichyanukul P, Krishnan-Ayer R (2008) Heterogeneous photocatalytic treatment of organic dyes in air and aqueous media. *J Photochem Photobiol C* 9(4):171–192
- Raza W, Faisal SM, Owais M, Bahnemann D, Muneer M (2016) Facile fabrication of highly efficient modified ZnO photocatalyst with enhanced photocatalytic, antibacterial and anticancer activity. *RSC Adv* 6:78335
- Rehman S, Ullah R, Butt AM, Gohar ND (2009) Strategies of making TiO<sub>2</sub> and ZnO visible light active. *J Hazard Mater* 170(2–3):560–569
- Rehman F, Sayed M, Khan JV, Shah NS, Khan HM, Dionysiou DD (2018) Oxidative removal of brilliant green by UV/S<sub>2</sub>O<sub>8</sub><sup>2-</sup>, UV/HSO<sub>5</sub><sup>-</sup> and UV/H<sub>2</sub>O<sub>2</sub> processes in aqueous media: a comparative study. *J Hazard Mater* 357:506–514
- Ren L, Li Y, Hou J, Zhao X, Pan C (2014) Preparation and enhanced photocatalytic activity of TiO<sub>2</sub> nanocrystals with internal pores. *ACS Appl Mater Interfaces* 6:1608–1615
- Reza KM, Kurny AS, Gulshan F (2017) Parameters affecting the photocatalytic degradation of dyes using TiO<sub>2</sub>: a review. *Appl Water Sci* 7:1569–1578
- Saad ST, Al-Gubury HY, Alrazzak NA (2018) Photocatalytic degradation of monoazo dye in ethanol using zinc oxide in ultra-violet radiation. *Asian J Chem* 30(10):2334–2336
- Saggiaro EM, Oliveira AS, Moreira JC (2016) Heterogeneous photocatalysis remediation of wastewater polluted by indigoid dyes. In: *Textile wastewater treatment*. Intech Open, London, p 94. <https://doi.org/10.5772/63790>
- Salehi M, Hashemipour H, Mirzaee M (2012) Experimental study of influencing factors and kinetics in catalytic removal of methylene blue with TiO<sub>2</sub> nanopowder. *Am J Environ Eng* 2 (1):1–7
- Saqib M, Tariq MA, Faisal M, Muneer M (2008) Photocatalytic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide. *Desalination* 219:301–311
- Saravanan R, Gracia F, Stephen A (2017) Basic principles, mechanism, and challenges of photocatalysis. In: Khan MM et al (eds) *Nanocomposites for visible light-induced photocatalysis*. Springer, Cham, pp 19–40. [https://doi.org/10.1007/978-3-319-62446-4\\_2](https://doi.org/10.1007/978-3-319-62446-4_2)
- Serpone N, Horikoshi S, Emeline AV (2010) Microwaves in advanced oxidation processes for environmental applications: a brief review. *J Photochem Photobiol C* 11:114–131
- Serpone N, Emeline AV, Horikoshi S, Kuznetsov VN, Ryabchuk VK (2012) On the genesis of heterogeneous photocatalysis: a brief historical perspective in the period 1910 to the mid-1980s. *Photochem Photobiol Sci* 11:1121
- Sharma MVP, Kumari VD, Subrahmanyam M (2008) TiO<sub>2</sub> supported over SBA-15: An efficient photocatalyst for the pesticide degradation using solar light. *Chemosphere* 73:1562–1569

- Shifu C, Gengyu C (2005) Photocatalytic degradation of pesticides using floating photocatalyst  $\text{TiO}_2\text{SiO}_2$  beads by sunlight. *Sol Energy* 79:1–9
- Shiga Y, Umezawa N, Srinivasan N, Koyasu S, Sakai E, Miyauchi M (2016) A metal sulfide photocatalyst composed of ubiquitous elements for solar hydrogen production. *Chem Commun* 52:7470–7473
- Shinde DR, Tambade PS, Chaskar MG, Gadave KM (2017) Photocatalytic degradation of dyes in water by analytical reagent grades  $\text{ZnO}$ ,  $\text{TiO}_2$  and  $\text{SnO}_2$ : a comparative study. *Drink Water Eng Sci* 10:109–117
- Singh PK, Kushwaha A, Hans N, Gautam A, Rani R (2019) Evaluation of the cytotoxicity and interaction of lead with lead resistant bacterium *Acinetobacter junii* Pb<sub>1</sub>. *Braz J Microbiol* 50 (1):223–230
- Sowmya SR, Madhu GM, Hashir M (2018) Studies on nano-engineered  $\text{TiO}_2$  photo catalyst for effective degradation of dye. *IOP Conf Ser Mater Sci Eng* 310:012026. <https://doi.org/10.1088/1757-899X/310/1/012026>
- Su Y, Deng L, Zhang N, Wang X, Zhu X (2009) Photocatalytic degradation of C.I. acid blue 80 in aqueous suspensions of titanium dioxide under sunlight. *React Kinet Catal Lett* 98(2):227–240. <https://doi.org/10.1007/s11144-009-0059-4>
- Teoh WY, Scott JA, Amal R (2012) Progress in heterogeneous photocatalysis: from classical radical chemistry to engineering nanomaterials and solar reactors. *J Phys Chem Lett* 3:629–639
- Thennarasu G, Sivasamy A (2019) Mn doped  $\text{ZnO}$  nano material: a highly visible light active photocatalyst for environmental abatement. *Inorg Nano-Metal Chem* 48(4–5):239–246
- Viswanathan B (2018) Photocatalytic degradation of dyes: an overview. *Current Catalysis* 7 (1):1–25
- Wang S, Shiraishi F, Nakano K (2002) A synergistic effect of photocatalysis and ozonation on decomposition of formic acid in an aqueous solution. *Chem Eng J* 87:261–271
- Wang F, Ma Z, Ban P, Xu X (2017) C, N and S codoped rutile  $\text{TiO}_2$  nanorods for enhanced visible-light photocatalytic activity. *Mater Lett* 195:143–146
- Wang T, Zhang Y-L, Pan J-H, Li B-R, Wu L-G, Jiang B-Q (2019) Hydrothermal reduction of commercial P25 photocatalysts to expand their visible-light response and enhance their performance for photodegrading phenol in high-salinity wastewater. *Appl Surf Sci* 480:896–904
- Yoon J, Lee Y, Kim S (2001) Investigation of the reaction pathway of OH radicals produced by Fenton oxidation in the conditions of wastewater treatment. *Water Sci Technol* 44(5):15–21
- Zulmajdi SLN, Ajak SNFH, Hobley J, Duraman N, Harunsani MH, Yasin HM, Nur M, Usman A (2017) Kinetics of photocatalytic degradation of methylene blue in aqueous dispersions of  $\text{TiO}_2$  nanoparticles under UV-LED irradiation. *Am J Nanomater* 5(1):1–6