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Review

Roles of titanium dioxide and ion-doped titanium dioxide on photocatalytic degradation of organic pollutants (phenolic compounds and dyes) in aqueous solutions: A review

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ABSTRACT

Water pollution by organic pollutants is an ever increasing problem for the global concerns. This paper presents a critical review on the abatement of organic pollutants, dyes and phenolic compounds in particular, using photocatalytic reaction by titanium dioxide (TiO_2). Mechanism of photocatalytic reaction is briefly discussed. A detailed search of published reports on the advancement in photocatalytic degradation of organic pollutants in wastewater by doping titanium dioxide with foreign species such as metal and non-metal component has also been carried out and analyzed in this paper.

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1. Introduction

The world's most precious and important natural resource, water, is under threat from various contaminants, causing a water contamination crisis. While the world's population has been tripled in the 20th century, use of renewable water resources has grown six-fold, and global population is expected to increase by another 40–50% within the next 50 years. The increasing demand for water generated by this population growth will cause serious consequences on the environment [1]. According to the World Health Organization (WHO), in 2002 more than one out of six people lacked access to safe drinking water, namely 1.1 billion people, representing 17% of the global population. Moreover, in the same year, 2.6 billion people, i.e. 42% of the world's populations were without even the most basic sanitation facilities. A Lack of clean drinking water and sanitation kills about 4500 children each day and condemns their parents, siblings, and neighbors to sickness, pollution, and enduring poverty [2]. It should be noted that these figures represent only those people living in very poor conditions. In reality, the overall figures are expected to be much higher.

Humans are generating and disposing more wastewater today than any other time. The disposal of toxic contaminants, such as dyes and phenolic compounds which are harmful to the environment, hazardous to humans, and difficult to degrade by natural means, is pervasively associated with industrial development and these contaminants are frequently found in the industrial effluents [3]. Chemical precipitation, filtration, electro-deposition, ion-exchange adsorption, and membrane systems are some of the conventional methods for water treatment and have found certain practical applications. However, these methods may not be very effective, because they are either slow or non-destructive to some or most persistent organic pollutants. Besides, large scale implementations of these methods have some limitations, owing to the expensive equipments involved in these processes [4]. It is therefore essential to investigate the use of efficient catalytic materials to remove highly toxic compounds from potential sources of drinking water. Semiconductor heterogeneous photocatalysis is a popular technique that has the great potential to control the organic contaminants in water or air [5]. This process which is also known as "Advanced Oxidation Process (AOP)" is suitable for the oxidation of recalcitrant contaminants such as dyes and phenolic compounds [6]. Heterogeneous photocatalytic oxidation, developed in the 1970s, has attracted considerable attention particularly when used under solar light [7]. In the past decades, numerous studies have been carried out by researchers from all over the world on the application of heterogeneous photocatalytic oxidation process to decompose and mineralize certain recalcitrant contaminants. The photocatalytic activity of various forms of TiO_2, such as TiO_2 film [8], TiO_2 powders [9], TiO_2 nanotubes [10], supported TiO_2 [11–13] and doped TiO_2 [14,15] have been evaluated through degradation of dyes and/or phenolic compounds under light irradiation. Results of these studies showed that TiO_2 was effective for removing dyes and phenolic compounds from aqueous solutions. In the present review, some advances in photocatalytic removal of organic pollutants, particularly dyes and phenolic compounds from fluid streams have been presented.

2. Organic pollutants in wastewater

2.1. Dyes

The widespread disposal of industrial wastewater containing dyes on land and in bodies of water often has received the most attention in studies because of the color and toxicity of some of the raw materials used to synthesize dyes, such as certain aromatic amines used to produce azo dyes. Their disposal has led to serious contamination in many countries worldwide [16,17]. Dyes are usually the first contaminant to be recognized in wastewater because they are highly visible and undesirable in water, even in very small amounts (<1 ppm for some dyes) [18,19]. Nevertheless, dyes are still widely used in many contemporary fields of technology [20]. Over 100,000 commercially available dyes exist, and more than 7×10^5 tonnes of dyes are produced annually [21].

Dyes play a very important role in various branches of the textile industry; dyes used in this industry are often synthetic, usually derived from two sources: coal tar and petroleum-based intermediates [20–25]. Synthetic dyes have become common water pollutants and are usually found in trace quantities in industrial wastewater owing to their good solubility in water [26,27]. It has been estimated that approximately 15% of the total world production of dyes is lost during the dyeing process and then released to the environment through textile effluents [17]. Apart from the textile industry, leather tanning industry [28–30], paper industry [31], food technology [32,33], hair colorings [34–36], photoelectrochemical cells [37–39] and light-harvesting arrays [40–42] also contribute to the presence of dyes in wastewater.

Many of the dyes used in industry are toxic and carcinogenic, and this poses a serious hazard to aquatic living organisms. The toxicity and impact of dyes released to the environment have therefore been extensively studied [43,44]. Furthermore, because of the increasingly strict restrictions on the organic composition of industrial effluents, it is essential to eliminate dyes from wastewater before they can be discharged into the environment. However, many dyes are difficult to decolorize, owing to their synthetic origin and complex structure. These dyes usually have many structural varieties, for example, acidic, basic, azo, diazo, disperse, anthroquinone-based, and metal complex dyes. As a result, traditional wastewater treatment technologies are markedly ineffective in handling synthetic dye-contained wastewater, because of the chemical stability of these pollutants [45]. A wide range of technologies have been developed to remove synthetic dyes from wastewaters so as to reduce their impact on the environment. Chemical precipitation, adsorption on organic or inorganic matrices, and decolorization by photocatalysis and/or by chemical oxidation processes are some of the technologies currently being used for the removal of synthetic dyes [46].

2.2. Phenolic compounds

Besides dyes, presence of phenols and their derivatives in water supplies and industrial effluents is another problem attracting global concern. These hazardous water-soluble phenolic compounds are continuously released to the environment through domestic and industrial activities, representing a severe toxicological risk to the earth as well as all living creatures on it.

Phenolic compounds are aromatic compounds with one or more hydroxyl groups attached to the aromatic ring. These compounds are usually found in wastewater discharged from a variety of industries, such as petroleum refineries, chemical synthesis, plastics, coke plants, dyes, pulp and paper, textiles, detergents, pharmaceutics, as well as pesticides and herbicides synthesis [47,48]. Phenolic compounds can also arise from natural sources in the aquatic environment, such as algal secretion, lignin transformation, hydrolysable tannins and flavanoids, and humidification processes at low concentration [49].

Humans are potentially exposed to phenols in all places, as they are found in tea, fruits, and vegetables and are widely used in industrial processes, pharmaceuticals, and consumer products [50]. Exposure to phenols poses hazards to humans as the compounds are corrosive to the respiratory tract, eyes, and skin. Repeated or long-term exposure of skin to phenols will cause dermatitis, or even second- and third-degree burns because of the phenol's defatting and caustic properties [51,52]. Phenol derivatives such as bisphenol A (BPA), chlorophenol, and nitrophenol are also known to be hazardous to humans. BPA is an organic compound with two phenol functional groups widely used in the plastics industry for the production of polycarbonate plastics and epoxy resins. Dental composites/sealants, baby bottles, the lining of food cans, and drinking-water bottles are some of the consumer products developed from BPA. The presence of BPA in industrial effluents has received wider attention since it was listed as an endocrine-disrupting chemical (EDC), which can influence the generative function of humans and other living creatures by mimicking the body's own hormones and leads to negative health effects [53–56].

The next phenol derivative, chlorophenol, is an organochloride of phenol, usually consisting of one or more covalently bonded chlorine atoms. It is also a known endocrine disruptor that is toxic and non-biodegradable. This compound is an important xenobiotic micropollutant of aquatic environments and is usually present in wastewater as by-products of the pulp and paper, dyestuff, pharmaceutical, and agrochemical industries [57,58]. Biodegradation of chlorophenol is slow and incomplete, eventually generating by-products that are more toxic and hazardous than chlorophenol to the environment as well as to human health [59,60]. In addition, nitrophenols, another family of common phenolic compounds found in industrial effluents, are continually detected in urban and agricultural waste as they are among the most widely used and versatile industrial organic compounds. These compounds are usually used in the manufacture of pharmaceuticals, pesticides, explosives, dye, pigments, wood preservatives, and rubber chemicals. Nitrophenols have been proven to be carcinogenic and may pose significant health risks to humans and other organisms. Among the nitrophenols, 2-nitrophenol, 4-nitrophenol, and 2,4-dinitrophenol have been listed as "Priority Pollutants" by the US Environmental Protection Agency, which recommended that their concentrations in natural waters should be restricted to below 10 ng/L [61–64].

3. Decomposition of organic pollutants in wastewater by photocatalytic reactions

From the perspective of environmental science, regulatory laws, and human health, it is urgent that the release of toxic chemicals from industrial processes and commercial products must be restricted. In fact, many processes and technologies for destroying these toxins have been proposed over the years, and some are currently employed in a number of wastewater treatment plants. Among the various methods for decomposition of these toxic compounds, a more promising technology based on an advanced oxidation process has been extensively studied. This process involves the degradation of pollutants by irradiating suspensions of metal oxide semiconductor particles such as TiO_2 or zinc oxide (ZnO) with light. It is a promising method because it not only degrades the pollutants but also completely mineralizes them to carbon dioxide (CO_2), water (H_2O), and mineral acids [65–67]. The low-cost and mild operating conditions (mild temperature and pressure) of this photocatalytic degradation process are also factors in its popularity in wastewater treatment [68].

A semiconductor is a material with electrical resistivity between that of an insulator and a conductor and is usually characterized by an electronic band structure in which the lowest empty energy bands, called the conduction band (CB), and the highest occupied energy band, called the valence band (VB), are separated by a band-gap. The ability of a photocatalytic reaction to degrade organic and inorganic pollutants arises from the redox environment generated from the photoactivation of a semiconductor such as titanium dioxide (TiO_2). In general, three components must be present so that the heterogeneous photocatalytic reaction can occur: an emitted photon (in the appropriate wavelength), a strong oxidizing agent (usually oxygen), and a catalyst surface (a semiconductor material) [69].

3.1. Titanium dioxide (TiO_2)

Titanium dioxide (TiO_2) is a natural occurring oxide of titanium; it is also named as titania or titanium(IV) oxide. In nature, TiO_2 exists in five different forms, i.e. rutile, anatase, brookite, monoclinic and orthorhombic. However, monoclinic and orthorhombic phase of TiO_2 are two exceptions found only in shocked granet gneisses from Ries crater in Germany [70,71]. Rutile appears to be the most common form of TiO_2, while anatase and brookite forms of TiO_2 tend to convert into rutile form upon heating at high temperature. Calcinated TiO_2, especially in rutile form is very stable and insoluble in water; it is also insoluble or only moderately soluble in concentrated and hot acids [72].

TiO_2 is well known for its widespread applications in paints, sunscreens, environmental treatment and purification purposes [73–76]. These widespread applications of TiO_2 are credited to its high level of photoconductivity, ready availability, low toxicity, inertness, low cost as well as high photoefficiency and activity. TiO_2 has drawn great attentions of researchers in photovoltaic and photocatalysis fields since Fujishima and Honda first discovered the ability of TiO_2 in splitting of water under ultraviolet (UV) light [77]. Crystalline structure of TiO_2 has been reported as one of the factors affecting its photocatalytic activity. Anatase form of TiO_2 has the best photocatalytic activity, followed by rutile form [78].

TiO_2 can utilize natural UV radiation from sunlight for photocatalysis because it has suitable energetic separation between its conduction and valence band [79]. Band-gap energy of TiO_2 (3.2 eV for anatase; 3.03 for rutile) is relatively smaller compared to other semiconductors, such as ZnO (3.35 eV) and SnO_2 (3.6 eV) [80]. Therefore, TiO_2 is able to absorb photons energy in the near UV range ($\lambda < 387$ nm). Photocatalytic reaction is initiated with the sufficient input of radiation equal or higher than the band-gap energy of the target semiconductor which causes molecular excitation and charge separation. As a result, mobile electrons and holes will be generated and migrate to the surface of the semiconductor to take part in the photocatalytic reaction [81]. Mechanism of the photocatalytic reaction will be further discussed in later part of this article.

3.2. Mechanism of photocatalytic reaction

The heterogeneous photocatalytic reaction is initiated with the absorption of radiation equal to or higher than the band-gap energy (E_{bg}) of the target semiconductor. E_{bg} is defined as the difference between the filled VB and the empty CB; in this case TiO_2 has a band-gap of 3.2 eV in the form of anatase or 3.0 eV as rutile. When photons with energy equal to or higher than E_{bg} reach the surface of the photocatalyst, they will cause molecular excitation. As a result, mobile electrons will be generated in the higher-energy CB simultaneously with the generation of positive holes in the lower-energy VB of the photocatalyst. After the initiation of photogenerated electron–hole pairs, the photocatalytic reaction will proceed through a series of chemical events. The photogenerated holes and electrons can either recombine and dissipate the absorbed energy as heat or be available for use in the redox reaction. Photogenerated holes and electrons that do not recombine migrate to the surface of catalyst for redox reaction. The redox reaction will utilize both the electron and hole, with the positive holes (h^+) for oxidation processes and the electrons (e^-) for reduction processes on the surface of the photocatalysts. The positive holes break apart the water molecule to form hydron (positive hydrogen cation, H^+)

Table 1
General mechanism of the photocatalytic reaction on illuminated TiO_2.

Process	Reaction steps
Photo-excited TiO_2 generates electron–hole pairs ($h\nu \geq E_G$)	$TiO_2 \xrightarrow{h\nu} e^- + h^+$
Photogenerated holes, h^+ migrate to catalyst surface and react with water molecules adsorbed on the catalyst surface H_2O_{ad}	$TiO_2(h^+) + h_2O_{ad} \rightarrow TiO_2 + HO\cdot + h^+$
Photogenerated electrons, e^- migrate to catalyst surface and molecular oxygen acts as an acceptor species in the electron-transfer reaction	$TiO_2(e^-) + O_2 \rightarrow TiO_2 + O\cdot_2^-$
Reactions of superoxide anions, $O_2{}^-$	$O\cdot_2^- + H^+ \rightarrow HO\cdot_2$ $O\cdot_2^- + 3HO\cdot_2 \rightarrow HO\cdot + 3O_2 + H_2O + e^-$ $2HO\cdot_2 \rightarrow O_2 + H_2O_2$
Photoconversion of hydrogen peroxide to give more $HO^\bullet$ free-radical groups	$H_2O_2 + TiO_2(e^-) \rightarrow TiO_2 + HO^- + HO\cdot$
Oxidization of organic adsorbed pollutants (S_{ad}) by $HO^\bullet$ onto the surface of the TiO_2	$HO\cdot_2 + S_{ad} \rightarrow$ Intermediates
Overall reaction	Organic Pollutant $\xrightarrow{TiO_2/h\nu}$ Intermediates $\rightarrow CO_2 + H_2O$

and the hydroxyl radical (OH^-). This OH^- will then lead to the production of strong oxidizing $HO^\bullet$ radicals. Meanwhile, the negative electrons react with the oxygen molecule to form a superoxide anion ($O_2{}^{\bullet-}$). This superoxide anion also produces $HO^\bullet$ radicals via the formation of $HO_2{}^\bullet$ radicals and H_2O_2. The electron–hole recombination step is undesirable as it will result in process inefficiencies and waste the energy supplied by the photon. Therefore, it is often considered as one of the major factors limiting the efficiency of the photocatalytic processes. Besides, it is found that $HO^\bullet$ is the most plentiful radical species in TiO_2 aqueous suspension and the reaction of $HO^\bullet$ with organic pollutants is the most important step that leads to the mineralization of organic pollutants. The heterogeneous photocatalytic reaction can basically be represented by a number of mechanistic steps. The general mechanism of the photocatalytic reaction on light-illuminated TiO_2 is summarized in Table 1 [79,82,83].

4. Photocatalytic degradation of organic pollutants using undoped TiO_2

4.1. Dyes

Many studies have been carried out to examine the photocatalytic degradation of dyes in wastewater in the presence of TiO_2 as photocatalyst. Table 2 summarizes these studies. It is seen that TiO_2 is able to photodegrade various types of dyes in the presence of light. Light intensity, catalyst concentration, solution pH, dye concentration, and the presence of electron acceptor were found to be factors affecting the rate and efficiency of the photocatalysis.

4.2. Phenolic compounds

Apart from dyes, the feasibility and efficiency of the photodecomposition of phenol and its derivatives in water using TiO_2 as photocatalyst have also been investigated. The results of these studies are summarized in Table 3. As with dyes, the efficiency and rate of the photodegradation of phenol and its derivatives were found to be dependent on light intensity, catalyst concentration, solution pH, substrate (phenol and its derivatives) concentration, and the presence of electron acceptor.

5. Photocatalytic degradation of organic pollutants using single-doped TiO_2

TiO_2 is well known as a promising photocatalyst owing to its non-toxicity, low cost, and capability of degrading a wide range of both gaseous and liquid pollutants. However, this semiconductor displays its photoactivity only under ultraviolet (UV) light excitation. The relatively wide band-gap of TiO_2 (3.2 eV) means that it can be stimulated only by UV radiation with a wavelength of about 387 nm. As a result, only about 3–5% of incoming solar energy on the earth's surface can be utilized and is therefore not practical for wastewater treatment applications [113,115]. In addition, the photocatalytic activity of TiO_2 is limited by the low interfacial charge-transfer rates of photogenerated carriers as well as its high charge carrier recombination rate [116]. In this regard, several strategies have been developed to increase the efficiency of the photocatalytic process in TiO_2 [117,118]. One route for sensitizing TiO_2 to visible light so as to permit the use of the main part of the solar spectrum and also forming charge traps to keep electron–hole pairs separate is by doping pure TiO_2 with foreign ions [119]. For instance, TiO_2 doped with metals or metallic cations as a photocatalyst, such as transition metals, rare earth metals, and noble metals, have been widely investigated. Generally, metal-ion-doped TiO_2 could improve the redox potential of the photogenerated radicals, widen the light absorption range, and enhance quantum efficiency via inhibiting the recombination of photogenerated electrons and holes as the ions act as electron traps [120].

5.1. TiO_2 doped with rare earth metals

Rare earth metals or rare earth elements are a group of 17 chemical elements in the periodic table and include scandium (Sc), yttrium (Y), and the 15 lanthanoids. These metals having incompletely occupied 4f and empty 5d orbitals often serve as catalysts or promote catalysis. Therefore, the incorporation of rare earth metal ions into the TiO_2 matrix could provide a mean to increase the concentration of organic pollutants at the semiconductor surface, hence improving the photoactivity of TiO_2 [121].

Doping TiO_2 with rare earth metals that have incompletely occupied 4f orbitals, such as neodymium (Nd) has been investigated by Štengl et al. [122] and Xu et al. [123] to show its better photocatalytic activity. It was inferred that the increase in photocatalytic activity was due to the transition of 4f electrons in rare earth ions, which led to the enforcement of optical adsorption of the photocatalysts and supported the separation of photogenerated electron–hole pairs [122]. It was also concluded that the presence of a 4f level in Nd ions helped to decrease the TiO_2 energy band-gap by allowing charge transfer between the TiO_2 valence/conduction band and the Nd ion 4f level [123].

Research done by El-Bahy et al. [121] showed that the photocatalytic activity of TiO_2 depends on its band-gap, surface area, and pore volume. Thus, gadolinium (Gd)-doped TiO_2 prepared by El-Bahy et al., a doped TiO_2 with high surface area, large pore volume, small particle size, and small band-gap, presented the highest photocatalytic activity. In addition, TiO_2 doped with cerium (Ce) and holmium (Ho) were found to be able to retard grain growth of TiO_2 [124] as well as decrease its crystallite size while increasing its specific surface area [125]. Shi et al. [125] claimed that Ho-doped TiO_2 with a smaller crystallite size favored the shifting of photogenerated carriers to the surface of the photocatalysts and interaction with the reactants. Increased surface area, on the other hand, was

Table 2
Summary of studies on photocatalytic degradation of dyes in wastewater in the presence of TiO_2 as photocatalyst.

Compound degraded	Photocatalyst used	Parameter studied	Comments	References
Methyl Orange (MO)	Natural zeolites supported TiO_2	Initial concentration of MO, catalyst concentration, pH and species of natural zeolite	• Supported TiO_2 showed higher reaction rate than pure TiO_2 regardless of the initial MO initial concentration. • Photocatalytic degradation rate constant, k_1 increased sharply from $0.025\,min^{-1}$ to $0.060\,min^{-1}$ while increasing the catalyst dosage from 0.006 to 0.04 g/10 mL. • Both decolorization efficiency and reaction rate constant (k_1) decreased with increasing initial pH from acidic to basic. • Natural zeolites did not directly participate in photocatalytic degradation, however their species and the presence of impurities played minor role in enhancing the photodegradation of MO.	Li et al. [84]
C.I. Basic Violet 10	Y zeolite supported TiO_2	TiO_2 content, calcinations temperature, pH, initial dye concentration and catalyst loading	• The photocatalytic degradation of C.I. Basic Violet 10 by Y zeolite supported TiO_2 was a first-order kinetics reaction. • Optimum photocatalytic performance was achieved with high TiO_2 content (20%), high calcinations temperature (600 °C), alkaline pH (9–10) catalyst concentration of 5333 ppm and small initial dye concentration (10 ppm).	Wang et al. [85]
Acid Orange 7 (AO7)	Silica gel supported TiO_2	Calcinations temperature, catalyst loading	• The photocatalytic activity of silica gel supported TiO_2 (31% TiO_2/SiO_2) was reduced when the catalyst was calcined at higher temperature, which attributed to the decrease in BET surface area available for the adsorption of AO7. • 31% TiO_2/SiO_2 showed 2.3 and 12.3 times faster photodegradation rate than P-25 and TiO_2 (Shanghai), respectively. This could be explained by the strong adsorption of AO7 on 31% TiO_2/SiO_2 as well as the higher surface area of 31% TiO_2/SiO_2 compared to P-25 and TiO_2 (Shanghai).	Chen et al. [86]
Rhodamine B	TiO_2 loaded on mesoporous graphitic carbon (TiO_2/GC-950)	N/A	• TiO_2/GC-950 showed better photoactivity than pure TiO_2 with reaction constant, k_1 of $0.012\,min^{-1}$ ($0.006\,min^{-1}$ for pure TiO_2). This enhancement in photoactivity was due to the confinement in the mesopores of graphitic carbon (GC-950), high degree of anatase crystallization as well as the graphitic property of GC-950.	Xiao et al. [87]
Malachite Green (MG)	TiO_2 Degussa P-25	TiO_2 quantity and pH	• 99.9% of MG was degraded with the addition of 0.5 g/L TiO_2. • Photodegradation rate of MG increased along with increasing pH as pH higher than pH_{ZPC} (ZPC = zero point charge).	Chen et al. [88]
Malachite Green	TiO_2 prepared by hydrothermal crystallization in organic media	Physical properties of TiO_2	• TiO_2 prepared from this method exhibited a higher level of activity than commercial P-25 TiO_2. • Adsorptivity and desorptivity of MG on the catalyst as well as the crystallinity of TiO_2 are decisive factors in the bleaching of MG. • Decomposition of MG increases with higher degree of crystallinity and adsorptivity and desorptivity.	Kominami et al. [89]
Triphenylmethane dye (Gentian Violet)	TiO_2 Degussa P-25	pH, catalyst concentration, substrate concentration, types of TiO_2	• Degussa P-25 showed better performance than other TiO_2, i.e., UV100 and PC500. • pH value of 3.5 and 11 and higher substrate concentration (no more than 0.25 mM) are the criteria for better photocatalytic performance.	Muneer and Saquib [90]
Methyl Orange (MO)	Nanocrystalline TiO_2 prepared by stearic acid gel method	Loading of TiO_2	• Photocatalytic degradation of MO increases with increasing loading of TiO_2 because the probability of absorbing photons increases with increasing loading of TiO_2.	Ruan et al. [91]
Reactive Red 195 (RR 195)	TiO_2 nanoparticles	Initial pH, concentration of dye, and concentration of adsorbent	• Optimum pH of sorption = 3. Acidic pH promotes the electrostatic attractions between the positively charged surface of the adsorbent and anionic dye. • Percentage of color removal decreased with increasing initial dye concentration, while the amount of dye adsorbed per unit of adsorbent mass was enhanced. • Dye adsorption yield increased with increasing adsorbent dose.	Belessi et al. [92]
C.I. Reactive Red	TiO_2 Degussa P-25	pH, dye concentration, electron acceptor (hydrogen peroxide, persulfate, and copper ions), and hydroxyl radical trap (ethanol)	• Increasing quantity of persulfate ions added would increase the decolorization rate because persulfate (as electron acceptor) suppressed the recombination of photogenerated electron–hole pairs. • Addition of ethanol inhibited decolorization as the predominant decolorization pathway involves hydroxyl radicals.	Wu [93]

Table 2 (*Continued*)

Compound degraded	Photocatalyst used	Parameter studied	Comments	References
Rhodamine B solution	TiO_2 Degussa P-25 modified by post-treatment with phosphorous acid	The effects of surface modification on the thermal stability of TiO_2	• Modified TiO_2 has enhanced anatase thermal stability and larger surface area. This is because the PO_4^{3+} groups of phosphorus acids inhibit the surface mass diffusion and aggregation among TiO_2 particles during thermal treatment. • The enhanced anatase thermal stability and larger surface area are beneficial in inhibiting photo-induced charge recombination.	Qin et al. [94]
Acridine Orange (AO)	TiO_2 Degussa P-25	pH, TiO_2 dosage	• Photocatalytic reactions were enhanced in alkaline media because, under alkaline conditions, TiO_2 surface carries weak negative charge, which will attract positively charged AO and promote photocatalytic degradation. • Rate of photocatalytic degradation of dye increased with increasing concentration of TiO_2. However, at high catalyst concentrations, the increase in opacity and light scattering by the TiO_2 particle will reduce the degradation rate.	Lu et al. [95]
Acridine Orange (AO) and ethidium bromide	TiO_2 Degussa P-25	pH, substrate concentration, electron acceptors, and types of TiO_2	• Highest efficiency of degradation was achieved under alkaline conditions (pH 10). • Degussa P-25 showed superior photocatalytic activity compared to other catalyst powders, i.e., UV100 (Hombikat) and PC500 (Millennium Inorganic Chemicals Ltd). This is because P-25 is composed of small nanocrystallites of rutile that disperse within an anatase matrix. Rutile with a narrower bandgap "catches" photons to generate electron–hole pairs. The recombination is inhibited by the transfer of photogenerated electrons from the rutile conduction band to electron traps in the anatase phase, thus allowing the hole to move to the surface of the particle and react.	Faisal et al. [96]
Azure (A and B) and Sudan (III and IV)	Solution combustion synthesized TiO_2 (CS TiO_2)	Effect of solvent and mixed-solvent system, pH, and effects of metal ions	• Solvents with higher polarity showed higher photodegradation rates. • Metal ions reduced the photocatalysis rates.	Aarthi et al. [97]
Bromothymol Blue	TiO_2 Degussa P-25	pH, catalyst concentration, substrate concentration, types of TiO_2, effects of electron acceptors	• Degussa P-25 showed better photocatalysis than other TiO_2, i.e., Hombikat UV100, PC500, and TiO_2 obtained from Travancore Titanium Products. • Electron acceptors (hydrogen peroxide, potassium bromate, and ammonium persulfate) enhanced the degradation rate of the pollutant because of their ability to improve the formation of hydroxyl radicals and suppress electron–hole pair recombination.	Haque and Muneer [98]
Methyl Red	TiO_2 nanoparticles immobilized onto the inner wall of a cylindrical glass photoreactor	Comparison of supported TiO_2 and conventional TiO_2 Degussa P-25 catalyst	• TiO_2 Degussa P-25 showed higher efficiency than supported nano-TiO_2 particles because the immobilization process reduces the active surface area available for adsorption and photocatalysis. • However, it was proposed that this could be overcome by optimizing the deposition procedures.	Mascolo et al. [99]

found to enable the photocatalysts to preadsorb more reactant molecules and hence avoided the recombination of electron–hole pairs.

Furthermore, Ho doping leads to lattice distortion and expansion of TiO_2 and creates charge imbalance in it. Lattice distortion and expansion of TiO_2 reduces the recombination rate of electron–hole pairs and produces more hydroxyl radical; whereas charge imbalance in TiO_2 restrains the recombination of excited electrons and positive holes in the photocatalysts during their transference to the surface. Thus, the synergistic effects of the above factors could improve the efficiency of TiO_2 photocatalytic activity [125].

The redox pair of Ce (Ce^{3+}/Ce^{4+}) could act as an electron scavenger that traps the bulk electrons in TiO_2. Ce also extends the photoresponse of TiO_2 into the visible region by reducing the bandgap of the original material. All these factors lead to an increase in TiO_2 photocatalytic performance [124,126].

5.2. TiO_2 doped with transition metals

According to the current IUPAC definition, a transition metal is defined as an element whose atom has an incomplete d subshell or that can give rise to cations with an incomplete d subshell. Doping TiO_2 with transition metals tunes the optical bandgap, thus shifting the light absorption region from UV to visible light [127].

A characteristic of transition metals is that they exhibit two or more oxidation states usually differing by one. This trait enables the enhancement of the photocatalytic activity of TiO_2 when doped with transition metals [128]. For example, the ability of iron (Fe) to form $Fe^{4+}/Fe^{3+}/Fe^{2+}$ ions inhibits the recombination of photogenerated carriers as the ions act as traps for the photogenerated electron–hole pairs. Another reason that Fe^{3+} ions can act as charge traps in the TiO_2 lattice is that the radius of Fe^{3+} (0.79 Å) is similar to that of Ti^{4+} (0.75 Å), so Fe^{3+} can be easily incorporated into the crystal lattice of TiO_2 [129].

In a study by Asiltürk's research group [130], it was found that Fe^{3+} doping may prevent particle agglomeration, forming well-defined nanocrystalline particles with high surface area. These may result in high photocatalytic performance, owing to improved adsorption of photons and pollutant molecules. Introducing iron into the crystal structure of TiO_2 may also improve the wettability of the nanoparticles, thus avoiding high aggregation in the

Table 3
Summary of studies on photocatalytic degradation of phenolic compounds in wastewater in the presence of TiO_2 as photocatalyst.

Compound degraded	Photocatalyst used	Parameter studied	Comments	References
Phenol	Supported nano-TiO_2/ZSM-5/silica gel (SNTZS)	TiO_2 loading, adsorbent (zeolite) loading, support loading, and binder (colloidal silica gel) loading	• Optimum formulation of SNTZS = nano-TiO_2:ZSM-5:silica gel:colloidal silica gel = 1:0.6:0.6:1. • High photocatalytic activity of SNTZS was due to its large surface area (275.7 m^2/g), high crystalline quality of the synthesized catalyst, small particle size, and low electron–hole pair recombination rate.	Zainudin et al. [49]
Phenol	TiO_2 loaded on mesoporous graphitic carbon (TiO_2/GC-950)	N/A	• TiO_2/GC-950 showed better photoactivity than pure TiO_2 with reaction constant, k_1 of 0.012 min^{-1} (0.008 min^{-1} for pure TiO_2). • This enhancement in photoactivity was due to the confinement in the mesopores of graphitic carbon (GC-950), which improved the adsorption ability of phenol molecules by providing larger surface area. • Besides, high degree of anatase crystallization with less defect sites which could reduce recombination of electrons/holes as well as the graphitic property of GC-950 that facilitated the diffusion of reactants and products from the active site also led to the improvement in photocatalytic activity.	Xiao et al. [87]
Phenol	Pellet and powder forms of TiO_2 deposited on activated carbon (AC)	N/A	• Both TiO_2/AC pellet and TiO_2/AC powder showed good performance in photodegradation of phenol in aqueous solution.	Carpio et al. [100]
Phenol	TiO_2 coated on perlite	Effect of light intensity	• High porosity of perlite (>95%) allowed TiO_2 coated on it to float on water surface and thus no filtration and recirculation were needed to get back the catalyst after the reaction. • Photocatalytic efficiency increased about twice with the increase of UV intensity from 80 W lamp to 125 W lamp.	Hosseini et al. [101]
Phenol	Nanocrystalline TiO_2 prepared by acid-catalyzed sol-gel method	Catalyst loading, initial phenol concentration, pH, irradiation intensity, and presence of oxidant species	• Photocatalytic process was influenced by operating parameters. • Introduction of oxidant moderately increased the oxidation rate, but the increase did not depend on the nature of the oxidant. This suggests that the oxidant process is mainly due to the $HO^\bullet$ adsorbed radicals generated from positive holes at the surface.	Silva and Faria [102]
Phenol	TiO_2 Degussa P-25	Effect of adding hydrogen peroxide (H_2O_2)	• The combined use of TiO_2 photocatalyst, H_2O_2, and UV light greatly improved the efficiency of phenol degradation. This could be explained by the ability of H_2O_2 to produce hydroxyl radicals under UV irradiation, thereby increasing photodegradation.	Chiou et al. [103]
Phenol	Nano-sized TiO_2 prepared by hydrogen-air flame hydrolysis	Effect of particle shape on the activity of nanocrystalline TiO_2	• Particle shape played a crucial role in the photocatalytic activity, where samples with only polyhedral (faceted) nanocrystals significantly showed better photocatalytic degradation of phenol compared to those containing a mixture of spherical and polyhedral nanocrystals.	Balázs et al. [104]
Phenol	Nanocrystalline anatase TiO_2 prepared by sol-gel method	Size effects of TiO_2	• When the TiO_2 crystal size decreased from 9.9 to 4.5 nm, the semiconductor bandgap shifted toward a higher energy level.	Liu et al. [105]

Table 3 (*Continued*)

Compound degraded	Photocatalyst used	Parameter studied	Comments	References
Phenol	TiO_2	Influence of calcinations temperature (350ºC-750ºC)	• The optimal TiO_2 particle size (about 10 nm) for maximum photocatalytic efficiency is claimed to be a result of photogenerated electrons and holes, light absorption, defects, and surface area. • Lower calcinations temperature (350 °C) led to highest photocatalytic activity in visible light ($\lambda > 400$ nm). This is because lower calcinations temperature favors a larger surface area, more residual carbon in the form of carbonaceous C–C species (working as sensitizers), elimination of oxygen vacancies, and promotion of photocatalytic activity under visible light. • Increasing calcinations temperature to 450 °C diminishes the amount of carbonaceous species and suppresses the activity under visible light. However, TiO_2 calcined at this temperature had the best activity in UV light ($250 < \lambda < 400$ nm).	Górska et al. [106]
Bisphenol A (BPA)	Commercial TiO_2 powder	N/A	• After 20 h of UV light irradiation from a Hg-Xe lamp, BPA and its intermediate products were finally mineralized.	Ohko et al. [107]
Bisphenol A (BPA)	Commercial TiO_2 powder	Photocatalyst dosage, initial substrate concentration, temperature, pH, and light intensity	• Under sunlight irradiation for 11 h at optimal conditions (i.e., initial BPA concentration of 20 mg/L, TiO_2 dosage of 10 mg/L, temperature of 40 °C, initial pH of 6.0, and solar light intensity of 0.35 mW/cm^2), the organic substrate of BPA was completely mineralized in the TiO_2-catalyzed process.	Kaneco et al. [108]
Bisphenol A (BPA)	Commercial TiO_2	Thermal versus non-thermal effects of microwave radiation-assisted photocatalytic process driven by UV radiation	• Hybrid reactor with either external heating or microwave irradiation showed higher efficiency (90%).	Horikoshi et al. [109]
Bisphenol A (BPA)	TiO_2 Degussa P-25, Hombikat UV100, Millenium PC50, and prepared TiO_2 platinized catalyst	pH	• Photocatalytic activity in an annular jacket reactor at pH 3 and 10 could be improved 3–6-fold, but the degree of mineralization at pH 10 was relatively low. This is because TiO_2 particle surfaces become negatively charged at pH 10 and would inhibit the adsorption of substrate, which eventually lowers the degree of BPA mineralization.	Chiang et al. [110]
Bisphenol A (BPA)	Nano-TiO_2 purchased from Degussa AG Co.	Initial BPA concentration, photocatalyst dosage, initial pH, temperature	• Optimal conditions for photocatalytic degradation of BPA could be performed at initial BPA concentration = 20 mg/L, TiO_2 dosage = 0.5 g/L (100 mg/200 cm^3), initial pH 7.0, and temperature = 25°C. • Photodegradation kinetics for the destruction/removal of BPA in water can be well described by a pseudo-first-order reaction model, where the apparent first-order reaction constant (k_{obs}) is proportional to TiO_2 dosage.	Tsai et al. [56]
2,4-dinitrophenol (2,4-DNP)	Multi-walled carbon nanotubes (MWCNTs)/TiO_2 composite	pH, irradiation time, catalyst loading, 2,4-DNP concentration, reaction temperature and amount of MWCNTs in catalyst	• 0.05% (w/w) of MWCNTs:TiO_2 was found to be the optimal ratio for the 2,4-DNP degradation. • Optimum photocatalytic degradation of 2,4-DNP was achieved at initial 2,4-DNP concentration of 38.8 mg/L, pH 6.0 and 8 g/L of catalyst loading under 150 min solar irradiation with good recyclisation of catalyst. • The apparent rate constant K_{app} increased from 0.0179 to 0.0379 min^{-1} when increasing the reaction temperature from 293 K to 363 K. This might be ascribed to the improved diffusion rate of 2,4-DNP in solution and hence increased the opportunity of the 2,4-DNP molecules to adsorb on the catalyst surface.	Wang et al. [111]
2,4-dinitrophenol (2,4-DNP)	Nano-sized TiO_2	pH and light intensity	• UV light is more effective than sunlight, which enabled the maximum removal of 2,4-DNP to reach 70% at pH 8 within 7 h of irradiation. • Only 46.67% of 2,4-DNP removal could be achieved by sunlight irradiation under the same conditions.	Shukla et al. [112]
m-nitrophenol (m-NP)	TiO_2 Degussa P-25	Effects of catalyst pre-wetting on TiO_2 photocatalytic activity	• Pre-wetting of TiO_2, which meant pre-contacting m-NP with TiO_2 in the dark for 60 min without agitation, enhanced the photodegradation, especially in the initial stage of the degradation process (<0.5 h). This is because, during pre-wetting, the organic compounds are allowed to be dispersed uniformly and close to the surface of TiO_2 or even impregnated into its pores. As a result, more intermediates are available for adsorption on the TiO_2 surface, hence photodegrading m-NP at the beginning of the degradation process.	Chiou et al. [113]
2,4-dichlorophenol (DCP)	Granular activated carbon (GAC) supported TiO_2 (Ti-GAC)	Annealing temperature, catalyst loading, air flow rate, pH and DCP concentration	• DCP was removed by the synergistic effect of Ti-GAC and joint effect of adsorption and HO$^\bullet$ oxidation.	Gu et al. [114]

Table 3 (*Continued*)

Compound degraded	Photocatalyst used	Parameter studied	Comments	References
			• Ti-GAC annealed at 773K showed better performance because of its higher content of rutile phase which has lower band gap energy (3.0 eV). • Optimum removal of DCP was achieved at pH 7.0, catalyst loading of 9 g/L and air flow rate of 6 L/min. Removal of DCP decreased with the increase of initial DCP concentration, which due to multilayer of DCP molecules were adsorbed on the catalyst surface and prevented the contact between the molecules with photogenerated holes or hydroxyl radicals.	

aqueous suspension, which is obviously detrimental to the photocatalytic activity as many particles are hidden from light absorption [131].

Photocatalytic degradation of organic pollutants under visible light was made possible by doping TiO_2 with transition metals such as cobalt (Co) [127], copper (Cu) [132], vanadium (V) [133,134], tungsten (W) [135], and iron (Fe) [130]. The incorporation of transition metal ions into the matrix narrows the band-gap of TiO_2 and causes a redshift of the absorption edge to the visible-light region. This redshift is caused by the charge-transfer transition between the d electrons of the transition metals and the CB or VB of TiO_2. In addition, transition metal ions in the TiO_2 lattice that act as both electron and hole traps can restrain the recombination rate of photogenerated electrons and holes, improving the photocatalytic activity of TiO_2 [133].

5.3. TiO_2 doped with noble metals

Noble metals have high resistance to corrosion and oxidation in moist air, unlike most base metals. These metals tend to be precious because of their rarity in the earth's crust.

Silver (Ag)-doped TiO_2 has recently been developed to study its effects on enhancing catalyst performance. The presence of Ag results in improved photocatalytic activity, attributed to the larger specific surface area, and thus more reactive sites are available to take part in photoreactions than with undoped TiO_2. Ag doping also promotes the phase transformation from anatase to rutile, which also contributes to the increase in specific surface area. In addition, doping TiO_2 with Ag retards the rate of electron–hole pair recombination by enhancing the charge carrier separation and hence improves photocatalytic activity [116,136,137].

Binitha's research group also studied the effect of Ag-doped TiO_2 photocatalysts [138]. They found them to be promising photocatalysts where they show relatively high degradation rate. This result was explained in terms of increments in the wavelength of absorption for TiO_2 and dispersion stability exposing more TiO_2 surface to the target pollutants.

5.4. TiO_2 doped with poor metals

Metallic elements in the p-block of the periodic table are sometimes known as poor metals or post-transition metals, situated between the metalloids and the transition metals. Generally, these metals have lower melting and boiling points than the transition metals, and their electronegativity is higher; they are also softer. However, they are distinguished from the metalloids in the same row by their significantly higher boiling points. This group generally includes aluminum (Al), gallium (Ga), indium (In), tin (Sn), thalium (Tl), lead (Pb), and bismuth (Bi).

According to research conducted in the last several years, coupling TiO_2 with tin oxide (SnO_2) could be an effective way to increase photocatalytic activity, because the electronic levels of these two substances match [139–141]. The results reported by Li et al. [139] show that a suitable amount of Sn dopant could significantly increase the amount of hydroxyl radicals generated by the TiO_2 nanoparticles and enhance the separation rate of the photogenerated charge carriers for TiO_2. These hydroxyl radicals and the low recombination rate are responsible for the obvious increase of photocatalytic activity.

Meanwhile, the absorption edge for TiO_2 doped with another poor metal, e.g., Bi, showed a redshift as compared to that of undoped TiO_2. This shift means that Bi doping can enlarge the wavelength response range and also intrinsically narrows the band-gap transition of the catalyst, hence improving photocatalytic activity under visible light [142].

5.5. TiO_2 doped with non-metals

Over the last several years, it has been demonstrated by many researchers that TiO_2 doped with non-metal elements such as carbon (C) [143–147], nitrogen (N_2) [148–159], fluorine (F) [160], or sulfur (S) [161–165] shows positive response in the visible-light region and higher photocatalytic activity.

Among anion-doped TiO_2, carbon doping has been claimed theoretically to have a potential advantage. This is because the substitutional carbon atom in the TiO_2 matrix introduces new states (C 2p) close to the VB edge of TiO_2 (O 2p). Consequently, the VB edge shifts to a higher energy than the reference TiO_2, hence narrows the band-gap. This type of band-gap narrowing is important if the C-doped TiO_2 sample is to give a photoresponse in the visible-light region [143,146]. In the study conducted by Shen et al. [144], it was demonstrated that C-doped TiO_2 showed stronger absorption in the UV–visible range, attributed to carbon substitutions at oxygen sites in the sample, and therefore exhibited better photocatalytic activity. Another factor that may account for the high visible-light photocatalytic activity of C-doped TiO_2 is the higher surface area of the doped samples, which could provide more active sites and adsorb more reactive species for photodegrading targeted pollutants in water [147].

The incorporation of nitrogen into TiO_2 changes the hardness, refraction index, elastic modulus, electrical conductivity, and photocatalytic reactivity toward visible-light absorption [148–151]. Works by Peng et al. [148] and Ao et al. [150] showed that N-doped TiO_2 has a narrower energy band-gap and can be activated by visible light. Thus, more electrons and holes can be generated and take part in the photocatalytic redox reactions.

In addition to carbon and nitrogen doping, the effect of S-doped TiO_2 has been studied. It was found that in S-doped TiO_2 the residual S atoms did not turn into anatase TiO_2 occupied O-atom sites to form Ti-S bonds. The mixing of the S 3p states with the TiO_2 VB led to band-gap narrowing in the S-doped TiO_2, which caused the absorption edge of TiO_2 to shift to a lower-energy region. Therefore, S-doped TiO_2 is able to extend the photoactivity to the visible region and displays excellent visible-light photocatalytic activity in degrading organic pollutants [161,162,164]. Besides narrowing the energy band-gap of TiO_2, the ratio of the anatase to rutile phase could also be modified by introducing S into TiO_2. This would then control the development and crystallization of the S-doped TiO_2

Table 4
Optimum dopant concentration used by researchers to improve the efficiency of catalyst.

Pollutant	Light source	Photocatalyst	Range of doping	Optimum doping	References
Rare Earth Metals					
Direct Blue (DB 53)	Xenon lamp (>320 nm)	Gadolinium-doped TiO_2	–	0.03 mol%	El-Bahy et al. [121]
Methyl Orange	250 W high-pressure mercury lamp	Neodymium-doped TiO_2	0.05–2.00 mol%	0.3 mol%	Xu et al. [123]
Phenol	250 W UV light (365 nm)	Cerium-doped TiO_2	0.08–2.5 wt%	0.4 wt%	Fan et al. [124]
Methyl Orange	500 W high-pressure mercury UV lamp (365 nm)	Holmium-doped TiO_2	0.3–2.0 mol%	0.3 mol%	Shi et al. [125]
4-chlorophenol	Medium-pressure mercury UV–visible light (366, 405, & 436 nm)	Cerium-doped TiO_2	0.2–1.0 wt%	0.6 wt%	Silva et al. [126]
Transition Metals					
Methylene Blue	200 W high-pressure mercury UV lamp (365 nm)	Iron-doped TiO_2	0.05–0.20 mol%	0.10 mol%	Sun et al. [128]
Malachite Green dye	UV and visible light	Iron-doped TiO_2	0.19–4.89 wt%	0.19 wt%	Asiltürk et al. [130]
Phenol	UV and visible light	Iron-doped TiO_2	0–2.5 wt%	0.75 wt%	Ambrus et al. [131]
Methyl Orange	150 W mercury lamp	Copper-doped TiO_2	0–0.2 wt%	0.1 wt%	Chen et al. [132]
Methylene Blue and 2,4-dichlorophenol	1000 W tungsten halogen lamp (visible ë > 420 nm)	Vanadium-doped TiO_2	0.25–5.00 mol%	1 mol%	Tian et al. [133]
Methylene Blue	UV light (305 nm)	Vanadium-doped TiO_2	0–2 wt%	2 wt%	Doong et al. [134]
Methylene Blue	500 W Xenon lamp	Tungsten-doped TiO_2	3–10 wt%	3 wt%	Yang et al. [135]
Noble Metals					
Rhodamine 6G dye	Q-Sun solar test chamber (340 nm)	Silver-doped TiO_2	1–5 mol%	5 mol%	Seery et al. [116]
Methylene Blue	15 W germicidal lamp (254 nm)	Silver-doped TiO_2	0–3 mol%	3 mol%	Tomás et al. [137]
Methyl Orange	Direct sunlight	Silver-doped TiO_2	–	2 wt%	Binitha et al. [138]
Poor Metals					
Methylene Blue	300 W halogen lamp (visible light)	Bismuth-doped TiO_2	0–0.051 mol%	0.051 mol%	Ji et al. [142]
Non-Metals					
Rhodamine B	500 W tungsten halogen lamp (visible light ë > 420 nm)	Carbon-doped TiO_2	–	0.0135 mol%	Ren et al. [147]
Reactive Brilliant Red dye X-3B (C.I. Reactive Red 2)	250 W halogen lamp (visible light ë > 400 nm)	Nitrogen-doped TiO_2	1–2 mol%	2 mol%	Ao et al. [150]
Methyl Orange	400 W high-pressure mercury lamp	Sulfur-doped TiO_2	0.5–1.5 mol%	1.5 mol%	Tian et al. [163]
Methyl Orange	12 W LED lamp (460 nm)	Sulfur-doped TiO_2	0–4 wt%	0.8 wt%	Liu et al. [164]
Methyl Orange	400 W Osram lamp (UV and visible light)	Sulfur-doped TiO_2	0–4 mol%	0.05 mol%	Hamadanian et al. [165]
Metalloid					
C.I. Reactive Red 2 (X-3B) and 4-chlorophenol	250 W halogen lamp (ë > 400 nm)	Boron-doped TiO_2	–	0.015 mol%	Xu et al. [167]

photocatalysts so that the photocatalytic efficiency of TiO_2 could be improved [165].

5.6. TiO_2 doped with metalloid

Metalloids such as boron (B), silicon (Si), germanium (Ge), arsenic (As), antimony (Sb), tellurium (Te), and polonium (Po) are those elements in the periodic table with intermediate properties between metal and non-metal. Generally, metalloids often form amphoteric oxides and frequently behave as semiconductors (B, Si, Ge). Boron [162,163], for instance, has also been used as a dopant in TiO_2 and was found to have positive effects on the photocatalytic reactivity of the catalysts.

Geng and his co-workers [166] reported that B-doped TiO_2 is in an anatase state and appears to be a much more efficient and stable photocatalyst than pure TiO_2. They found that the boron atom tends to either be incorporated in the interstitial position or replace an oxygen but is very unlikely to replace Ti. For O-substituted doping, the boron atom is strongly bonded to two oxygen atoms as well as to two Ti atoms. The result is a new midgap that eventually redshifts the absorption edge and finally enhances the photocatalytic efficiency. Meanwhile, Xu et al. [167] suggested that boron atoms could retard the grain growth, promote change from brookite to anatase phase, and redshift the absorption edge to the visible region. Therefore, the synergistic effects of higher crystallinity, higher surface area, and stronger absorption in the visible region greatly enhance the photocatalytic activity of B-doped samples over pure TiO_2 and P25.

In general, single ion-doped TiO_2 could enhance its photocatalytic activity by reducing the undesirable recombination of photoinduced electrons and holes as well as extending the photoresponse of the catalyst to visible light region. However, doping with excess amount of dopant would be detrimental to the photocatalytic activity of the photocatalyst. Therefore, there is an optimum quantity of dopant that should be added so as to improve the efficiency of the catalyst as listed in Table 4.

6. Drawbacks of metal doping

Doping with metals or metallic cations has undeniably shown positive effects on photocatalysis as discussed in the previous section. However, metal doping also has several drawbacks. The doped TiO_2 has been known to suffer from thermal instability and more expensive ion-implantation facilities are required for doping metallic cations into TiO_2 [149,168,169]. Besides, the metal ions doped into TiO_2 have been identified as the main cause for the partial blockage of surface sites available for photocatalytic activity [170].

Furthermore, the metal centers in metal-doped materials usually tend to become electron traps that encourage the recombination of photogenerated electrons–holes pairs, and subsequently reduce the photocatalytic efficiency. P-type dopants such as aluminium (Al^{3+}), chromium (Cr^{3+}) and gallium (Ga^{3+}) are known to have the ability to create acceptor centers. These acceptor centers act as a trap for photogenerated electrons, and once these centers become negatively charged, positive holes will be attracted and recombine with the electrons. Similarly to N-type dopants such as (niobium) Nb^{5+}, tantalum (Ta^{5+}) and antimony (Sb^{5+}) which create donor centers and trap photogenerated holes, once positively charged, they will attract electrons and thus act as recombination centers. Electron–hole pairs separation in noble metal doped TiO_2 is ascribed to the difference in Fermi level of noble metals and that of TiO_2. Yet, once the metal centers become negatively charged, holes will be attracted and recombine with electrons. This is especially obvious for highly loaded samples where the metal content is more than 5 wt% (%M > 5) [171].

Some studies have shown that the desired band-gap narrowing can be achieved by doping with non-metal anionic dopant rather than metallic cations [168,169]. But, on the other hand, non-metal doping also has some drawbacks; researchers have found that the content of a doped non-metal component would decrease during the annealing process, thus reducing visible-light photoactivity [172]. Co-doping has been identified as one of the ways to compensate the drawbacks of single doped TiO_2 and will be further discussed in the following section.

7. Photocatalytic degradation of organic pollutants using TiO_2 with multiple dopants

Recently, co-doping with two types of ion has been investigated and attracted the interest of many investigators looking to compensate the drawbacks of single-doped TiO_2.

Zhao et al. [117] reported on doping TiO_2 with two different species, i.e., a non-metal element, boron (B), and a metal oxide, nickel oxide (Ni_2O_3), using a modified sol–gel method. Trichlorophenol (TCP), 2,4-dichlorophenol (2,4-DCP), and sodium benzoate were chosen as the target pollutants to evaluate the photocatalytic performance of the co-doped TiO_2. According to their results, Ni_2O_3 facilitates excited electron transfer and therefore efficiently suppresses the recombination of photo-induced electron–hole pairs. The incorporation of B atoms in TiO_2 can extend the spectral response to the visible region. The cooperative effects of B- and Ni_2O_3-co-doped TiO_2 efficiently degrade and mineralize all target pollutants to environmentally friendly elements under visible light.

TiO_2 co-doped with nitrogen (N) and lanthanum (La) was synthesized by Liu et al. using titanium tetrachloride ($TiCl_4$) sol–gel autoigniting synthesis [173]. The results indicated that both the nitrogen and the lanthanum atoms were incorporated into the lattice and interstices of the TiO_2. La^{3+} ions promote the transfer and separation of electron–hole pairs because they are effective at trapping electrons excited from the VB of TiO_2. On the other hand, N^{3-} ions incorporated into the lattice of TiO_2 help to narrow the band-gap and trap holes, resulting in a response to visible light. These two factors contribute to the enhanced photocatalytic activity of (La, N)-co-doped TiO_2. Besides nitrogen doping, the effect of co-doped lanthanum with sulfur (S) has been studied, by Liu and Gao [174]. In this study, a small amount of lanthanum (0.03 mol%) and sulfur were co-doped in rutile n-TiO_2. The S 3p states were delocalized, contributing to the formation of VB with O 2p and Ti 3p states. The mixing of the 3p states with VB then increased the width of the VB and finally decreased the energy band-gap. Meanwhile, replacing the Ti atom with La^{3+}, retarding the rate of electron–hole recombination and thus the synergistic effects of S and La_2O_3, resulted in a high degradation rate of methylene blue (98.4%) under visible light.

Chen et al. [172] prepared a series of cerium (Ce) and silicon (Si)-co-doped TiO_2 (Ce-Si-TiO_2), and their photocatalytic performance was evaluated by photodecomposing Rhodamine B (RB) under visible light. Doped Ce and Si were able to prevent TiO_2 nanocrystallites from aggregating because Ce prevents crystallite growth during heat treatment, while Si was able to move into the TiO_2 lattice to prevent particles from sintering. In addition, Ce additive enhanced visible-light adsorption, leading to a narrowing of the band-gap of TiO_2, and the addition of Si was also helpful in preventing the phase transformation from anatase to rutile. Through these effects, Ce-Si-TiO_2 has a higher visible-light photocatalytic activity in comparison to pure TiO_2. Recently, TiO_2 co-doped with Ce and N has also been prepared and studied by Yu et al. [175]. They found that the recombination of photogenerated electrons and holes can be inhibited by the synergistic effects of doping with both Ce and N. Ce- and N-co-doped TiO_2 showed improved photocatalytic efficiency in photodegrading methylene blue, which ascribed to the co-effects of Ce and N dopants where recombination of photogenerated electrons and holes had been inhibited and the absorption within the visible light region was enhanced.

Huang and co-workers [115] developed samarium (Sm)- and nitrogen (N)-co-doped TiO_2 (Sm-N-TiO_2) catalysts via a modified hydrothermal method. The nanocrystalline catalysts showed very good visible-light response and high photocatalytic activity for 4-chlorophenol decomposition under visible light (400–500 nm). It was concluded that the high photocatalytic performance of Sm-N-TiO_2 was probably due to the doped N atoms which greatly improved visible-light absorption, so that photoelectrons and holes were probably produced by visible light. Moreover, the Sm^{3+} ions acted as electron traps to improve the charge separation by suppressing the recombination of photoproduced electrons–holes, thus enhancing the photocatalytic activity of Sm-N-TiO_2.

Co-doping TiO_2 with two metals is also able to improve its photocatalytic performance. In the study carried out by Shi et al. [176], it was found that the photocatalytic activity of iron (Fe^{3+})- and holmium (Ho^{3+})-co-doped TiO_2 was significantly improved, which can be ascribed to the cooperative actions of the two dopants. Fe^{3+} broadens the absorption profile, improves photo-utilization of TiO_2, and generates more electron–hole pairs. Meanwhile, Ho^{3+} ions suppress any increase in grain size, lead to crystal expansion and matrix distortion, and reduce the photo-excited charge-carrier recombination rate. Yuan et al. [177] on the other hand studied the effect of co-doped TiO_2 with zinc (Zn) and iron (Fe). They concluded that co-doping zinc oxide (ZnO) and iron (III) oxide (Fe_2O_3) into TiO_2 could enhance the performance of the catalyst in phenol photodegradation. Nearly two-fold increase in the activity was achieved by using this Zn- and Fe-co-doped TiO_2. This increase in activity might be owing to the cooperative function between the dopants and TiO_2 energy bands.

Apart from co-doping with two metallic cations, the co-doping of two non-metal elements has also been studied. Yang et al. [178] doped TiO_2 films with both nitrogen (N) and carbon (C) by heating the TiO_2 gel in an ionized N_2 gas. The as-prepared N- and C-co-doped TiO_2 showed improvement over pure TiO_2 in optical absorption and photocatalytic activity, i.e., the photodegradation of methyl orange under visible light. The results of this study showed that both nitrogen and carbon were doped into the near-surface region of the TiO_2 film and take over oxygen to form N–Ti bonds and C–Ti bonds, respectively, which leads to improved band-gap narrowing and enhanced photocatalytic activity. Besides N- and C-co-doped TiO_2, N- and iodine (I-) co-doped TiO_2 has also been synthesized by Zhou et al. [179] by hydrolysis method and its performance in photo-discoloration of methyl orange (MO) has been studied. In that study, they found that N- and I-co-doped TiO_2 showed high efficiency of photo-discoloration in both UV and visible range. The high rate of MO discoloration was due to the co-effects of both dopants. N atoms narrow the energy band gap by substituting at some O sites in TiO_2, whilst I^{7+} and I^- of I inhibit the recombination of electron–hole.

8. Conclusions

This paper has reviewed studies addressing the non-strictly controlled discharge of industrial effluents, which has given rise to the current water contamination crisis. Sources of organic pollutants, dyes, and phenolic compounds in particular, and their effects on the environment, have been briefly discussed. The photocatalytic degradation of these organic pollutants using titanium dioxide is the most widely studied method of overcoming the problem of water contamination by organic pollutants. The effects of dopants on the photocatalysis efficiency of titanium dioxide have been reviewed. It can be concluded that the addition of dopants to pure titanium dioxide can significantly enhance catalyst performance. The limitations of pure titanium dioxide, such as wide band-gap (3.2 eV for crystalline anatase phase), which requires the use of UV light, and its high photogenerated electron–hole pair recombination rate, can be overcome by introducing foreign species into the titanium dioxide matrix.

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