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Review

Parameters affecting the photocatalytic degradation of dyes using TiO_2-based photocatalysts: A review

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ABSTRACT

This paper presents the review of the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO_2-based photocatalysts. It further examines various methods used in the preparations of the considered photocatalysts. The findings revealed that various parameters, such as the initial pH of the solution to be degraded, oxidizing agents, temperature at which the catalysts must be calcined, dopant(s) content and catalyst loading exert their individual influence on the photocatalytic degradation of any dye in wastewaters. It was also found out that sol–gel method is widely used in the production of TiO_2-based photocatalysts because of the advantage derived from its ability to synthesize nanosized crystallized powder of the photocatalysts of high purity at relatively low temperature.

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Contents

1. Introduction 520
   1.1. Photocatalysis 521
   1.2. Semiconductors 522
      1.2.1. Titanium dioxide photocatalyst 522
2. Operating parameters in photocatalytic processes 522
   2.1. Influence of pH on photocatalytic degradation of dyes in wastewaters 522
   2.2. Oxidizing agents effect on photocatalytic degradation of dyes in wastewater 523
   2.3. Catalyst loading effects on photocatalytic degradation of dyes in wastewaters 524
   2.4. Dopant content effect on photocatalytic activity of photocatalysts 524
   2.5. Influence of calcination temperature on the activity of photocatalysts 525
3. Methods of TiO_2-based photocatalysts preparation 526
4. Conclusion 526
   Acknowledgement 526
   References 527

1. Introduction

The effluents, gaseous or liquid produced by some of our industries are harmful to the health and general well-being of man. When undesirable substances are present in liquid effluents, it can be disastrous as their presence pose severe threat to the immediate recipients. Wastewaters from various industries, factories, laboratories, etc. are serious problems to the environment. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [1]. These deleterious effects of chemicals on the earth ecosystems are a cause for serious concern. Several of these chemicals such as azo dyes, herbicides, and pesticides are actually present in rivers and lakes, and are in part suspected of being endocrine-disrupting chemicals (EDCs) [2–5].

Konstantinou and Albanis [6] reported that textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger. About 1–20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents [7]. The release of those colored wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation,

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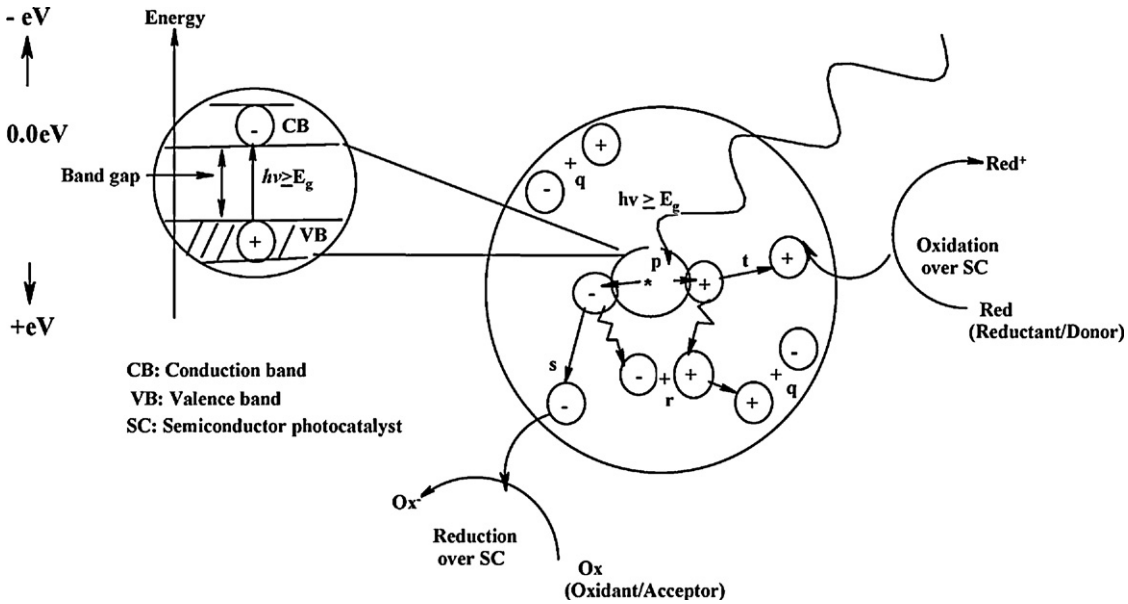

Fig. 1. Schematic diagram of photocatalytic process initiated by photon acting on the semiconductor [27].

hydrolysis, or other chemical reactions taking place in the wastewater phase. It must be noted that dyes can present toxic effects and reduce light penetration in contaminated waters [8].

Degradation of dyes in industrial wastewaters has therefore received increasing attention and some methods of remediation have been proffered. Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants [6,9]. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require a further treatment of solid-wastes and regeneration of the adsorbent which will add more cost to the process. Microbiological or enzymatic decomposition [10], biodegradation [11], ozonation [12], and advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions [6,13], H_2O_2/UV processes [14] have also been used for dyes removal from wastewaters.

Forgacs et al. [15] noted that traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants, and went further to verify that 11 out of 18 azo dyes selected for their investigations passed through the activated sludge process practically untreated. Most textile dyes are photocatalytically stable and refractory towards chemical oxidation [16], and these characteristics render them resistant towards decolorization by conventional biochemical and physico-chemical methods. All the aforementioned processes have a wide range of their deficiencies in the removal of dyes from wastewaters.

Recent studies [11,17–23] have been devoted to the use of photocatalysis in the removal of dyes from wastewaters, particularly, because of the ability of this method to completely mineralize the target pollutants [24].

The present work is slated to review the effects of operating parameters on the photocatalytic degradation of textile dyes using TiO_2-based photocatalysts. A brief review of the methods of preparation of the photocatalysts will also be presented.

1.1. Photocatalysis

Photocatalysis may be termed as a photoinduced reaction which is accelerated by the presence of a catalyst [25]. These types of reactions are activated by absorption of a photon with sufficient energy (equals or higher than the band-gap energy (E_{bg}) of the catalyst) [26]. The absorption leads to a charge separation due to promotion of an electron (e^-) from the valence band of the semiconductor catalyst to the conduction band, thus generating a hole (h^+) in the valence band (the schematic diagram of the process is presented in Fig. 1 [27]). The recombination of the electron and the hole must be prevented as much as possible if a photocatalyzed reaction must be favored. The ultimate goal of the process is to have a reaction between the activated electrons with an oxidant to produce a reduced product, and also a reaction between the generated holes with a reductant to produce an oxidized product. The photogenerated electrons could reduce the dye or react with electron acceptors such as O_2 adsorbed on the Ti(III)-surface or dissolved in water, reducing it to superoxide radical anion $O_2^{-\bullet}$ [6]. The photogenerated holes can oxidize the organic molecule to form R^+, or react with OH^- or H_2O oxidizing them into $OH^\bullet$ radicals. Together with other highly oxidant species (peroxide radicals) they are reported to be responsible for the heterogeneous TiO_2 photodecomposition of organic substrates as dyes. The resulting $^\bullet OH$ radical, being a very strong oxidizing agent (standard redox potential +2.8 V) can oxidize most azo dyes to the mineral end-products. According to this, the relevant reactions at the semiconductor surface causing the degradation of dyes can be expressed as follows [6]:

$$TiO_2 + h\nu(UV) \rightarrow TiO_2(e_{CB}^- + h_{VB}^+) \quad (1)$$

$$TiO_2(h_{VB}^+) + H_2O \rightarrow TiO_2 + H^+ + OH^\bullet \quad (2)$$

$$TiO_2(h_{VB}^+) + OH^- \rightarrow TiO_2 + OH^\bullet \quad (3)$$

$$TiO_2(e_{CB}^-) + O_2 \rightarrow TiO_2 + O_2^{-\bullet} \quad (4)$$

$$O_2^{-\bullet} + H^+ \rightarrow HO_2^\bullet \quad (5)$$

$$\text{Dye} + OH^\bullet \rightarrow \text{degradationproducts} \quad (6)$$

$$\text{Dye} + h_{VB}^+ \rightarrow \text{oxidationproducts} \quad (7)$$

$$\text{Dye} + e_{CB}^- \rightarrow \text{reductionproducts} \quad (8)$$

where $h\nu$ is photon energy required to excite the semiconductor electron from the valence band (VB) region to conduction band (CB) region.

1.2. Semiconductors

Semiconductors (such as TiO_2, ZnO, Fe_2O_3, CdS, and ZnS) can act as sensitizers for light-induced redox-processes due to the electronic structure of the metal atoms in chemical combination, which is characterized by a filled valence band, and an empty conduction band [28]. Upon irradiation, valence band electrons are promoted to the conduction band leaving a hole behind. These electron–hole pairs can either recombine or can interact separately with other molecules. The holes may react either with electron donors in the solution, or with hydroxide ions to produce powerful oxidizing species like hydroxyl (oxidation potential 2.8 V) or superoxide radicals [29].

In other word, semiconductor materials are materials whose valence band and conduction band are separated by an energy gap or band-gap. When a semiconductor molecule absorbs photons with energy equal or greater than its band-gap, electrons in the valence band can be excited and jump up into the conduction band, and thus charge carriers are generated. In order to have a photocatalyzed reaction, the e^-–h^+ recombination, subsequent to the initial charge separation, must be prevented as much as possible [30].

Among all these semiconductors, the most widely used semiconductor catalyst in photoinduced processes is titanium dioxide (TiO_2). Though TiO_2 has the disadvantage of not being activated by visible light, but by ultraviolet (UV) light, it is advantageous over the others in that it is chemically and biologically inert, photocatalytically stable, relatively easy to produce and to use, able to efficiently catalyze reactions, cheap and without risks to environment or humans [26].

1.2.1. Titanium dioxide photocatalyst

Titanium dioxide (TiO_2) or titania is a very well-known and well-researched material due to the stability of its chemical structure, biocompatibility, physical, optical and electrical properties. It exists in four mineral forms [31], viz: anatase, rutile, brookite and titanium dioxide (B) or TiO_2(B). Anatase type TiO_2 has a crystalline structure that corresponds to the tetragonal system (with dipyramidal habit) and is used mainly as a photocatalyst under UV irradiation. Rutile type TiO_2 also has a tetragonal crystal structure (with prismatic habit). This type of titania is mainly used as white pigment in paint. Brookite type TiO_2 has an orthorhombic crystalline structure. TiO_2(B) is a monoclinic mineral and is a relatively newcomer to the titania family. TiO_2, therefore is a versatile material that has applications in various products such as paint pigments, sunscreen lotions, electrochemical electrodes, capacitors, solar cells and even as a food coloring agent and in toothpastes [32].

The possible application for this material as a photocatalyst in a commercial scale water treatment facility is due to several factors:

(a) Photocatalytic reaction takes place at room temperature.
(b) Photocatalytic reactions do not suffer the drawbacks of photolysis reactions in terms of the production of intermediate products because organic pollutants are usually completely mineralized to non-toxic substances such as CO_2, HCl and water [33–36].
(c) The photocatalyst is inexpensive and can be supported on various substrates such as, glass, fibers, stainless steel, inorganic materials, sand, activated carbons (ACs), allowing continuous re-use.
(d) Photogenerated holes are extremely oxidizing and photogenerated electrons reduce sufficiently to produce superoxides from dioxygens [37].

The effectiveness of TiO_2 photocatalyst can be enhanced by doping metal and non-metal ions into it. The following investigations are the proofs of enhancement of the efficiency of TiO_2 by doping [23,38–47]. Krishna et al. [48] also reported a 2.6 times higher rate coefficient for PHF-TiO_2 over TiO_2 for the degradation of triazine monoazo compound Pricion red MX-5B.

2. Operating parameters in photocatalytic processes

In photocatalytic degradation of dyes in wastewaters, the followings are operating parameters which affect the process: pH of the solution to be degraded, and the pH of the precursor solution (catalyst's solution during preparation of catalyst); oxidizing agent, calcination temperature, dopant content, and catalyst loading. These parameters will be considered one after the other as they influenced the photocatalytic processes of the degradation of dyes in wastewaters.

2.1. Influence of pH on photocatalytic degradation of dyes in wastewaters

The interpretation of pH effects on the efficiency of dye photodegradation process is a very difficult task because of its multiple roles [6]. First, is related to the ionization state of the surface according to the following reactions,

$$TiOH + H^+ = TiOH_2{}^+ \quad (9)$$

$$TiOH + OH^- = TiO^- + H_2O \quad (10)$$

as well as to that of reactant dyes and products such as acids and amines. pH changes can thus influence the adsorption of dye molecules onto the TiO_2 surfaces, an important step for the photocatalytic oxidation to take place [49]. Bahnemann et al. [50] have already reviewed that acid-base properties of the metal oxide surfaces can have considerable implications upon their photocatalytic activity.

Second, hydroxyl radicals can be formed by the reaction between hydroxide ions and positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels [51]. It was stated that in alkaline solution, $^{\bullet}OH$ are easier to be generated by oxidizing more hydroxide ions available on TiO_2 surface, thus the efficiency of the process is logically enhanced [52]. Similar results are reported in the photocatalyzed degradation of acidic azo dyes and triazine containing azo dyes [9,53,54], although it should be noted that in alkaline solution there is a Coulombic repulsion between the negative charged surface of photocatalyst and the hydroxide anions. This fact could prevent the formation of $^{\bullet}OH$ and thus decrease the photoxidation.

Third, it must also be noted that TiO_2 particles tend to agglomerate under acidic condition and the surface area available for dye adsorption and photon absorption would be reduced [49]. The degradation rate of some azo dyes increases with decrease in pH as reported elsewhere [55].

The study of Baran et al. [56] also showed that the degradation of Bromocresol purple dye under acidic condition was better than in alkaline medium, and that the molecules are positively charged. Precisely, after the solution was acidified from pH 8.0 to pH 4.5, a six-fold increase in adsorption efficacy was observed. Such an increase in adsorption efficacy could not be explained only through changes of the TiO_2 surface (probably caused by a change of pH) [57].

The mechanism of the photocatalytic reaction in the presence of TiO_2 consists of a free radical reaction initiated by UV light [56]. The mechanism may depend on the ability of the degraded compound to be adsorbed on the surface of the catalyst. The extent of such adsorption depends on many factors, and one of it is the charge of the degraded compound. It was found that in photocatalytic degra-

Table 1
pH influence on the photocatalytic degradation of various pollutants and an insecticide.

Pollutant type	Light source	Photocatalyst	Tested pH range	Optimum pH	Ref.
Fast Green FCF	UV	TiO_2	3.0–11.0	4.4	[19]
Patent Blue VF	UV	TiO_2	3.0–11.0	11.0	[19]
Salicylic acid	UV	TiO_2	1.0–11.0	2.3[a]	[22]
Orange G	UV	$Sn/TiO_2/AC$	1.0–12.0	2.0	[23]
BRL	UV	$K\text{-}TiO_2$	4.5–11.8	7.2	[38]
Methyl orange	UV	$Pt\text{-}TiO_2$	2.5–11.0	2.5	[39]
Orange G	Visible	$N\text{-}TiO_2$	1.5–6.5	2.0	[43]
Acid Red B	UV	$Ce\text{-}TiO_2$	1.5–7.0	1.5	[44]
4-Chlorophenol	UV	$N\text{-}TiO_2$	2.0–5.0	3.0[a]	[45]
Orange II	Solar	$Zn\text{-}TiO_2$	3.0–10.0	3.0	[46]
Bromocresol purple	UV	TiO_2	4.5 and 8.0	4.5	[56]

[a] pH of precursor solution (catalysts solution during preparation of catalysts).

dation, the adsorption level on unmodified TiO_2 is higher for dyes with a positive charge (cationic) than for those with a negative charge (anionic) [58]. As the charge depends on the pH of a given solution, it follows that both pH and the nature of a particular dye influence the photocatalyst activity [9,29,59–62].

The degradation rate of azo dyes increases with decrease in pH [6]. At pH <6, a strong adsorption of the dye on the TiO_2 particles is observed as a result of the electrostatic attraction of the positively charged TiO_2 with the dye. At pH >6.8 as dye molecules are negatively charged in alkaline media, their adsorption is also expected to be affected by an increase in the density of TiO^- groups on the semiconductor surface. Thus, due to Coulombic repulsion the dyes are scarcely adsorbed [63,64].

The effects of pH on photocatalytic degradation of dyes have been studied by many Researchers [1,19,23,38,39,42–44,56,65]. In studying the effects of pH on the photocatalytic degradation of dyes, two things must be borne in mind; one, industrial effluents may not be neutral, and two; pH of the reaction mixture influences the surface-charge-properties of the photocatalysts [17].

Sleiman et al. [11] reported on the influence of pH on the photocatalytic degradation of Metanil Yellow, an anionic dye with a sulphonate group, over TiO_2 photocatalyst under UV illumination. Their results indicated that the process efficiency is not considerably affected over a wide range of pH (4–8). They added that the interpretation of pH effect can be principally explained by a modification of the electrical double layer of the solid–electrolyte interface, which consequently affects the sorption–desorption processes and the separation of the photogenerated electron–hole pairs at the surface of the semiconductor particles. Their study also explained that since Metanil Yellow is an anionic dye and has a sulphonate group, its adsorption is favored at low pH (the extent of adsorption is almost two-fold at pH 4.0 compared to that at neutral pH). The results of their findings showed that the nature of the substance to be degraded affects the operating pH of the system.

Zhiyong et al. [46] in their work – $ZnSO_4\text{-}TiO_2$ doped catalyst with higher activity in photocatalytic processes, reported on the effect of pH on the photocatalytic degradation of Orange II, an anionic dye with $-SO_3$ group. Their results showed that the photocatalytic activity was most favored at a lower pH (3.0), but went on at a slower and inefficient rate at pH 10.0. It is important to note that the photocatalytic degradation of some dyes is more effective at about neutral pH [38], and others in alkaline medium [19]. It has earlier been reported that in alkaline medium, there is a greater probability for the formation of hydroxyl radical ($^{\bullet}OH$), which can act as an oxidant, thus increasing the rate of photodegradation of the dye [66].

In summary, Table 1 presents pH influence on the photodegradation of various dyes. The table reveals that different dyes have different activity in photocatalytic reaction. Some are photocatalytically degraded at lower pH, while others do so at higher pH. All these may be attributed to the nature of the pollutant to be degraded. Therefore, it is important to study the nature of the pollutants to be degraded, and determine the probably right pH to photocatalytically degrade them.

Influence of pH of the solution of precursor on the photocatalytic activity of $Ni\text{-}TiO_2$ photocatalyst on the degradation of 4-chlorophenol under UV light had also been studied [45]. In this case, photocatalysts were prepared at different pH range (2.0–5.0), and calcined at the same temperature, 500 °C. The photocatalytic activity of N-doped TiO_2 nanoparticles was found to increase as the pH decreased from 5.0 to 3.0. Further decrease in pH to 2.0 affected the photocatalytic activity of the catalyst negatively. Hence, the optimum pH for that particular catalysts' preparation was 3.0. The reason advanced for the adverse effect of low pH on the photocatalyst performance is that the possible increase of H^+ concentration may restrain hydrolyzation of $Ti(OBu)_4$ and thereby reduces the crystal size of the prepared N-doped TiO_2 nanoparticles. Again, too low pH such as 2.0 would result in phase transformation from anatase to rutile [67].

2.2. Oxidizing agents effect on photocatalytic degradation of dyes in wastewater

Reports show that oxidizing agents have a great deal of influence on the photocatalytic degradation of dyes. It was demonstrated by Saquiba et al. [19] that hydrogen peroxide (H_2O_2), ammonium persulphate ($(NH_4)_2S_2O_8$) and potassium bromate ($KBrO_3$) have individual influence on the degradation of Fast Green FCF (1) and Patent Blue VF (2) using Hombikat UV 100 and Degussa P25 as respective photocatalysts. Their results revealed that potassium bromate and ammonium persulphate had a beneficial effect on the degradation rate for the decomposition of dye 1 in the presence of UV 100; whereas in the case of dye 2, all the electron acceptors were found to enhance the rate markedly in the presence of P25.

Huang et al. [39] also studied the effect of adding H_2O_2 on the decolorization of methyl orange. The decolorization rate was found to increase with increase in H_2O_2 concentration. The experiment was conducted at the concentration range of 0.4–2 mM/l H_2O_2. They reported an optimum addition of 1.2 mM/l H_2O_2 for photocatalytic decolorization of methyl orange solution by Pt modified TiO_2 loaded on natural zeolite. Actually, addition of H_2O_2 enhanced the reaction. Zhiyong et al. [47] also reported that addition of H_2O_2 (1 mM) to methyl orange solution mediated TiO_2 Degussa P25 (0.5 g/l) under sunlight irradiated photocatalyst brought about methyl orange degradation in 1 h.

Oxygen is required as electrons scavenger to keep the photocatalytic reaction, and the amount of oxygen going into the system is an important parameter. The air (oxygen) flow into the photocatalytic system should be well regulated, as poor flow of oxygen can bring

about an adverse effect on the photocatalytic reaction as reported elsewhere [17].

Konstantinou and Albanis [6] affirmed that H_2O_2 and $S_2O_8^{2-}$ were beneficial for the photoxidation of the dyes of different chemical groups including azo dyes. This is in conformity with the findings of Augugliaro et al. [68] and, Saquib and Muneer [69]. The reactive radical intermediates ($SO_4^{-\bullet}$ and $^\bullet OH$) formed from these oxidants by reactions with the photogenerated electrons can exert a dual function: as strong oxidant themselves and as electron scavengers, thus inhibiting the electron–hole recombination at the semiconductor surface [26] according to the following equations:

$$H_2O_2 + O_2^{-\bullet} \rightarrow {}^\bullet OH + OH^- + O_2 \quad (11)$$

$$H_2O_2 + h\nu \rightarrow 2{}^\bullet OH \quad (12)$$

$$H_2O_2 + e_{CB}^- \rightarrow {}^\bullet OH + OH^- \quad (13)$$

$$S_2O_8^{2-} + e_{CB}^- \rightarrow SO_4^{2-} + SO_4^{-\bullet} \quad (14)$$

$$SO_4^{-\bullet} + H_2O \rightarrow SO_4^{2-} + {}^\bullet OH + H^+ \quad (15)$$

It must be noted that the addition of peroxide increases the rate towards real reaction with adequate oxygen supply, because the solution phase may at times be oxygen starved as a result of either oxygen consumption or slow oxygen mass transfer. The presence of persulphate positively affects the mineralization rate, despite the decrease of pH as the oxidant properties of the system probably prevail on the effect of pH reduction.

Other works [23,43] have also revealed the effect of oxidants in photocatalytic reactions. It was pointed out as part of their findings that one practical problem in using TiO_2 as photocatalysts is the undesired electron–hole recombination, which in the absence of proper electron acceptor or donor, is extremely efficient and thus represents the major energy-wasting step, thereby limiting the achievable quantum yield. They therefore opined that, one strategy to inhibit electron–hole recombination is to add irreversible electron acceptors to the reaction system, and they used H_2O_2 to study its effect on photodegradation of Orange G (OG) on the N-doped TiO_2 under different light sources. The results indicated that there was an optimal dosage of H_2O_2, at which the degradation efficiency of OG on the N-doped TiO_2 attained the height. At higher dosage of H_2O_2 beyond the optimum, the degradation efficiency of OG decreased. This was because the very reactive $^\bullet OH$ radicals and valence band holes could be consumed by H_2O_2 itself as given in Eqs. (16)–(18) [70,71]. At the same time, radical–radical recombination as a competitive reaction must be taken into account, as described in Eq. (19) [6].

$$^\bullet OH + H_2O_2 \rightarrow HO_2^\bullet + H_2O \quad (16)$$

$$^\bullet OH + HO_2^\bullet \rightarrow O_2 + H_2O \quad (17)$$

$$TiO_2(h_{VB}^+) + H_2O_2 \rightarrow TiO_2 + O_2 + 2H^+ \quad (18)$$

$$HO^\bullet + HO^\bullet \rightarrow H_2O_2 \quad (19)$$

As both $^\bullet OH$ and h_{VB}^+ are strong oxidants for organic pollutants, the photocatalytic degradation of OG will be inhibited in the condition of excess of H_2O_2. Furthermore, H_2O_2 can be adsorbed onto TiO_2 particles to modify their surfaces and subsequently decrease its catalytic activity [72].

Again, the wavelength and intensity of the light sources affect the H_2O_2 performance as oxidizing agent in photocatalytic degradation of organic pollutants. This was also demonstrated by Sun et al. [23]. Their findings revealed that the optimal dosage of H_2O_2 for photodegradation of OG under sunlight was 5.0 mM/l, while under visible light was 15.0 mM/l.

In order to improve on the performance of photocatalytic reaction of Bi^{3+} doped TiO_2, Rengaraj and Li [73], used formic acid with a simple one-carbon molecular structure as a hole scavenger to investigate its effect on nitrate reduction. The oxidation of formic acid to carbon dioxide is straightforward and involves minimal intermediate product [74,75]. Also, formic acid is capable of forming reducing radicals, which could help in the reduction reaction [76]. Rengaraj and Li [73] confirmed from their study that without the use of the sacrificial hole scavenger (formic acid), there was no catalytic activity of either TiO_2 or Bi^{3+}-TiO_2 in the nitrate solution. They also agreed that there is an optimal dosage of the scavenger that must be used for the photodegradation of nitrate in the specific reaction considered.

Putting all together, there is the need to consider the effect of oxidizing agent in the photocatalytic degradation of textile dyes.

2.3. Catalyst loading effects on photocatalytic degradation of dyes in wastewaters

The effects of catalyst loading on photocatalytic degradation of dyes in wastewaters have been studied [6,19,38,39,43,77]. Konstantinou and Albanis [6], in their review of TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution reported that in any reactor system, the initial rates were found to be directly proportional to catalyst concentration, indicating the heterogeneous regime. They further observed that there is a limit of catalyst concentration that must be used for the photodegradation of a particular pollutant in wastewater, above which the rate of photocatalysis will even decrease. This is in agreement with recent reports [17,19,38,39,43,77]. Konstantinou and Albanis [6] also reported an enhanced degradation rates for optimum catalyst loading up to 0.4–0.5 g/l. This seems to vary from recent reports as shown in Table 2, though one of the reports agrees with their report.

The reason generally advanced for this is that the increase in the amount of catalyst increases the number of active sites on the photocatalyst surface, which in turn increase the number of hydroxyl and superoxide radicals. Again, when the concentration of the catalyst increases above the optimum value, the degradation rate decreases due to the interception of the light by the suspension [17]. Sun et al. [43] added that as the excess catalyst prevent the illumination, $^\bullet OH$ radical, a primary oxidant in the photocatalytic system decreased and the efficiency of the degradation reduced accordingly. Furthermore, the increase of catalyst concentration beyond the optimum may result in the agglomeration of catalyst particles, hence the part of the catalyst surface become unavailable for photon absorption, and degradation rate decrease [39].

2.4. Dopant content effect on photocatalytic activity of photocatalysts

Dopants contents on photocatalytic activity of photocatalysts have been investigated [44,78–83]. The results of Bouras et al. [78] revealed that the photocatalytic degradation of Basic Blue 41 dye under UV light was more favored in the presence of pure TiO_2, than in the presence of Fe-doped TiO_2. A continuous decrease in the percentage degradation of the dye from 80 to about 1 as the dopant content increased from 0 to 30 at% Fe was observed. The same trend was observed for Cr-TiO_2 and Co-TiO_2, though at varying % reduction. This is a pointer to the fact that transition metals TiO_2-doping can at times be detrimental to the photocatalytic degradation of some dyes.

On the other hand, metal–TiO_2-doping is always advantageous to the photocatalytic degradation of dyes in wastewaters as depicted in Table 3, but for Bouras et al. [78]. The optimum dopant, either mol% or wt% vary from catalyst to catalyst. Table 3 shows the effect of dopant content on photocatalytic activity of photocatalysts; and from the table, % optimum dopant vary from 0.06 to 1.0 for degradation of dyes in wastewater, and 1.25–2.25 for hydrogen

Table 2
Effects of catalysts loading on the photocatalytic degradation of dyes in wastewaters.

Pollutant	Light source	Photocatalyst	Range of catalyst wt. (g/l)	Optimum wt. cat. (g/l)	% Degradation	Ref.
Fast Green	UV	TiO_2	0.5–4.0	[a]	[b]	[19]
Acid Blue	UV	TiO_2	0.5–4.0	2.0	[b]	[19]
Orange G	UV	$Sn/TiO_2/AC$	5.0–15.0	12.5	99.1/h	[23]
Everdirect Blue (BRL)	UV	$K\text{-}TiO_2$	0–2.0	1.5	–	[38]
Methyl orange	UV	$Pt\text{-}TiO_2$	0.5–6.0	3	90.5[c]	[39]
Methyl orange	Visible	$SiO_2\text{-}TiO_2$	0–1.0	0.055	–	[77]

[a] Continuous increase.
[b] Not indicated.
[c] Time not indicated.

production. Any further increase in dopant content, exert negative effect on the activity of photocatalyst. Liao et al. [81] showed that there is a particular ratio of Zn to Ti that must produce an optimum degradation of methyl orange. Using two different surfactants (sodium dodecyl benzene sulphonate (DBS) and sodium dodecyl sulphonate (SDS)) Zn/Ti ratio of 0.25/1.0 gave the highest reaction rates at calcinations temperatures of 600, 700, and 800 °C. Zhiyong et al. [46] also reported on the effects of doping TiO_2 with $ZnSO_4$. They observed that there was a great deal of enhancement in the discoloration of Orange II by doping TiO_2 with different mol% Zn. Their report also showed that a doping level as high as 4 mol% Zn seemed to affect adversely the surface area of TiO_2 precluding reactant absorption. Their optimum doping level seems to be 2 mol% Zn. Boron- and cerium-codoped TiO_2 has also been reported [44]. The contents of different dopants at various ratios also exerted different effects on the photocatalytic activity of the prepared photocatalyst. In this case, the best doping content was 1.6 and 0.5 wt% B and Ce respectively.

Li et al. [80] offered explanation for the continuous increase in activity of photocatalyst with increase in dopant content until it reaches the optimum. One, using alkaline earth metals, the metal oxide (MO) deposited on the TiO_2 particles can form a space charge layer, which can separate the photoinduced electron–hole pairs. As the concentration of dopants increases, the surface barrier becomes higher and the electron–hole pairs within the region are efficiently separated by the large electric field. Two, due to the difference in electron negativity between Ti and M, the Ti–O–M formed via M^{2+} entering into the shallow surface of TiO_2 could promote the charges to transfer, resulting in an increase of photocatalytic activity. Three, alkaline earth metal ion doping can cause a lattice deformation and produce defects in the crystal. The defects can inhibit the recombination of electron–hole pairs and, eventually, enhance the activity.

When in excess, the existence of dopant on the particle surface of TiO_2 lessens the specific area of TiO_2, impedes the adsorption of reactant and thus, inhibits the photocatalytic activity [84]. Excess amount of dopant at the surface of TiO_2 could notably screen the TiO_2 from the UV light and inhibit the interfacial electron and hole to transfer, which would result in a low photo-activity [80]. On the other hand, Xin et al. [85] observed that the excessive oxygen vacancies and dopant (Cu) species can become the recombination centers of photoinduced electrons and holes, and that the excessive P-type Cu_2O can cover the surface of TiO_2, leading to decrease in the photocatalytic activity of the photocatalyst.

2.5. *Influence of calcination temperature on the activity of photocatalysts*

Depending on the method of the preparation and the end usage of the TiO_2 or doped TiO_2 photocatalysts, calcination temperatures have prominent influence on the activity of the prepared photocatalysts. Yu et al. [45] prepared nitrogen-doped TiO_2 nanoparticle catalyst and analyzed its catalytic activity under visible light. In their work, the influence of the calcination temperature on photocatalytic degradation of methylene blue (MB) under UV irradiation was examined. The N-doped TiO_2 samples were subjected to various calcination temperatures ranging from 300 to 700 °C. The results of their investigations revealed that the photocatalytic activity of the prepared photocatalysts increased with increase in temperature from 300 to 500 °C. At 500 °C, it reached the maximum, because of complete crystallization of anatase at this temperature. However, the catalytic activity of the N-doped TiO_2 decreased with further increase of calcination temperature from 500 to 700 °C. This was also found to be consistent with their TEM analysis, which showed that at 600 °C and above, a mixture of anatase and rutile phases of the sample were formed.

The effect of calcination temperature on the photocatalytic activity of $Zn\text{-}TiO_2$ has also been investigated on the photocatalytic degradation of Rhodamine B [84]. Their results also revealed that the photocatalytic activity of $Zn\text{-}TiO_2$ rapidly increased and was optimum at 500 °C as the calcination temperature increased

Table 3
The effect of dopant contents on photocatalytic activity of photocatalysts.

Degraded pollutant and hydrogen production	Light source	Photocatalyst	Range of doping (%)	Optimum doping (%)	Ref.
Acid Orange 7	UV	$Pt\text{-}TiO_2$	0–2.0	2.0	[40]
Orange II	Suntest lamp	$ZnSO_4\text{-}TiO_2$	0–6.0	2.0	[46]
Methyl orange	UV	($Pt\text{-}TiO_2$ pillared clay)	0–2.0	0.5	[79]
Hydrogen production					[80]
		$Be\text{-}TiO_2$	0–4.5	1.25	
		$Mg\text{-}TiO_2$	0–4.5	1.25	
		$Ba\text{-}TiO_2$	0–4.5	2.25	
		$Ca\text{-}TiO_2$	0–4.5	2.25	
		$Sr\text{-}TiO_2$	0–4.5	2.25	
Methyl orange	UV	$ZnO\text{-}TiO_2$	0–0.5	0.25	[81]
Bisphenol A	UV	$Ag\text{-}TiO_2$	0–2.0	1.0	[82]
Nitride	Visible	$Sm^{3+}\text{-}TiO_2$	0–2.0	0.5	[83]
Rhodamine B	UV	$Zn\text{-}TiO_2$	0–2.0	0.5	[84]
Rhodamine B	UV	$Cu\text{-}TiO_2$	0–3.0	0.06	[85]

Table 4
Effects of calcinations temperature on surface areas, pore volumes and pore sizes of photocatalysts [38].

Samples	T_C (K)	A_S (m^2/g)	Micropore surface area[a] (m^2/g)	External surface area[a] (m^2/g)	V_P (cm^3/g)	$V\mu_P$[a] (cm^3/g)	Pore size[b] (Å)
TiO_2-400	673	119.4	1.4	118.0	0.394	–	103.0
TiO_2-550	823	57.7	–	57.7	0.252	–	37.0
TiO_2-700	973	18.8	–	18.8	0.121	–	209.0
TiO_2-850	1123	1.48	1.0	0.5	0.016	–	645.9
K1-400	673	94.2	9.0	85.0	0.300	0.0035	118.1
K1-550	823	60.0	5.9	54.0	0.288	0.0023	177.8
K1-700	973	40.9	5.1	35.8	0.294	0.0021	278.2
K1-850	1123	7.8	1.5	6.3	0.027	0.0006	158.5
K4-400	673	68.3	7.9	60.4	0.249	0.0028	180.3
K4-550	823	25.4	4.3	21.0	0.143	0.0018	242.9
K4-700	973	22.8	2.0	20.8	0.113	0.0007	198.9
K4-850	1123	10.8	2.5	8.3	0.045	0.001	204.2

T_C: calcination temperature, A_S: surface area, V_P: pore volume, $V\mu_P$: micropore volume.
[a] *t*-Plot method.
[b] BJH adsorption/desorption average pore diameter.

from 300 to 500 °C. Further increase in the calcination temperature from 500 to 900 °C resulted in lower photocatalytic activity of the prepared catalyst. The reason given for this is that the increase in calcination temperature beyond 500 °C can promote the transformation of anatase to rutile, which has little photocatalytic activity. In the same vein Zhiyong et al. [46] considered the effect of calcination temperature on the $ZnSO_4$-TiO_2 coated Raschig ring (RR) photocatalytic degradation of Rhodamine B, and Orange II. In their study, the calcination temperature was fixed at 500 °C, and the varied parameter was the calcination time. Their findings revealed that the catalyst treated at 500 °C and 2 h led to the best enhancement during the discoloration of Rhodamine B. They went further to ascribe this trend to the diffusion of Zn-ions into TiO_2 lattice. On the other hand, the discoloration of Orange II was accelerated using the photocatalyst calcined at 500 °C for 5 h. The results also showed that there was a retrogressive effect on the discoloration of Orange II with $ZnSO_4$-TiO_2/RR calcined at 500 °C for 7 h. This, they also attributed to an increase in the rutile content in the TiO_2 sample, hence lowering the photocatalytic activity of the catalyst. At lower calcination time (3 h), the discoloration rate of Orange II was lower than that of 5 h. Therefore, the optimum time from their study for the calcination of $ZnSO_4$-TiO_2/RR is 5 h at 500 °C.

Sun et al. [23] also studied the effect of calcination temperature on photocatalytic activity of Sn(IV)/TiO_2/AC on the photocatalytic degradation of Orange G. Their results showed that photocatalytic activity of the prepared catalyst was significantly influenced by the calcination temperature and that; the optimal calcination temperature was 550 °C. Their XRD revealed that the sample calcined at 550 °C contained both anatase and rutile phases of TiO_2, which may explain the higher photocatalytic activity for the degradation of OG. This appears contradictory to the position of Yu et al. [45], Zhiyong et al. [46] and Liu et al. [84]. Nevertheless, the calcination temperature influence on the photocatalytic activity of the catalyst depends on the end usage of the catalyst. The instance of Chen et al. [38], where they prepared K^+-doped TiO_2 photocatalysts is a typical example of this. In their investigations, the effects of calcinations temperature on the surface areas, pore volume and pore sizes, together with its effects on the photocatalytic degradation of Everdirect Supra Blue BRL dyes were studied. The results of the effects on calcinations temperature on surface areas, pore volumes and pore sizes are presented in Table 4. Five sample types were considered in their study – 0, 4.6, 6.7, 9.0 and 14.3 % mole fractions of K^+ doped onto TiO_2 and were designated as TiO_2, K_1, K_2, K_3, and K_4 respectively. Their results on the effects of calcination temperature, on the degradation of RBL showed that sample K_1 degraded at a faster rate than the others, and its optimum calcinations temperature was 973 K (700 °C).

3. Methods of TiO_2-based photocatalysts preparation

Many methods have been reported for the production of TiO_2 nanopowders such as chemical solution decomposition (CSD) [86], chemical vapour decomposition [87–90], two-step wet chemical method [91], sol–gel [22,23,42,44,45,77,79–85,92–114], ultrasonic irradiation [115,116], ethanol thermal and hydrothermal [117–120]. The most widely used TiO_2 in photocatalysis is commercial Degussa P25 produced by flame hydrolysis of $TiCl_4$ at temperatures greater than 1200 °C in the presence of hydrogen and oxygen. Recent literature [22,23,42,44,45,77,79–85,92–114] revealed that sol–gel is the most commonly used method for the preparation of photocatalysts, whether only TiO_2 or doped TiO_2. The advantage of these methods (wet chemical methods, which include sol–gel) is that they facilitate the synthesis of nanometer sized crystallized TiO_2 powder of high purity at relatively low temperature [115]. Other Researchers used modified sol–gel method [121,122], ultrasonic assisted sol–gel method [72], aerogel method [123], method similar to sol–gel [38], sol–gel and photo-reductive decomposition [39], precipitation [43,124], two-step wet chemical method [91], and extremely low temperature precipitation [125].

4. Conclusion

Various operational parameters affect the effectiveness or activities of TiO_2-based photocatalysts. It is therefore necessary to study the nature of the sample to be degraded, as this will provide a clue on the type of photocatalyst to be used in its degradation. Some reactive dyes are degraded at higher pH, while others at lower pH; hence in photocatalytic degradation of dyes in wastewaters, the reaction should be undertaken at the proper pH. Oxidizing agents, calcination temperature and catalyst loadings are found to exert their individual influence on the photocatalytic degradation of any dye. Therefore, to study effectively, the photocatalytic degradation of any dye all the aforementioned parameters must be given due considerations. It is also discovered that many methods are used in the preparation of TiO_2-based photocatalysts. Nevertheless, sol–gel method is widely used because the method facilitates the synthesis of nanometer sized crystallized TiO_2-'based catalysts' powder of high purity at relatively low temperature.

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References

[1] P. Borker, A.V. Salker, Photocatalytic degradation of textile azo dye over $Ce_{1-x}Sn_xO_2$ series, Mater. Sci. Eng. B 133 (2006) 55–60.
[2] H.M. Coleman, B.R. Eggins, J.A. Byrne, F.L. Palmer, E. King, Photocataytic degradation of 17-β-oestradiol on immobilized TiO_2, Appl. Catal. B: Environ. 24 (2000) L1–L5.
[3] C.S. Hong, Y. Wang, B. Bush, Kinetics and products of the TiO_2, photocatalytic degradation of 2-chlorobiphenyl in water, Chemosphere 36 (1998) 1653–1667.
[4] Y. Ohko, I. Ando, C. Niwa, T. Tatsuma, T. Yamamura, T. Nakashima, Y. Kubota, A. Fujishima, Degradation of bisphenol A in water by TiO_2 photocatalyst, Environ. Sci. Technol. 35 (2001) 2365–2368.
[5] Y. Wang, C. Hong, TiO_2-mediated photomineralization of 2-chlorobiphenyl: the role of O_2, Water Res. 34 (2000) 2791–2797.
[6] I.K. Konstantinou, T.A. Albanis, TiO_2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—A review, Appl. Catal. B: Environ. 49 (2004) 1–14.
[7] H. Zollinger (Ed.), Color Chemistry: Synthesis, Properties and Applications of Organic Dyes and Pigments, 2nd revised ed., VCH, 1991.
[8] A.G.S. Prado, L.B. Bolzon, C.P. Pedroso, A.O. Moura, L.L. Costa, Nb_2O_5 as efficient and recyclable photocatalyst for indigo carmine degradation, Appl. Catal. B: Environ. 82 (2008) 219–224.
[9] W.Z. Tang, H. An, UV/TiO_2 photocatalytic oxidation of commercial dyes in aqueous solutions, Chemosphere 31 (1995) 4158–4170.
[10] O.J. Hao, H. Kim, P.C. Chiang, Decolorization of wastewater, Environ. Sci. Technol. 30 (2000) 449–502.
[11] M. Sleiman, D. Vildozo, C. Ferronato, J.-M. Chovelon, Photocatalytic degradation of azo dye Metanil Yellow: optimization and kinetic modeling using a chemometric approach, Appl. Catal. B: Environ. 77 (2007) 1–11.
[12] Y.M. Slokar, A.M.L. Marechal, Methods of decoloration of textile wastewaters, Dyes Pigm. 37 (4) (1998) 335–356.
[13] W.G. Kuo, Decolorizing dye wastewater with Fenton's reagent, Water Res. 26 (1992) 881–886.
[14] N.H. Ince, D.T. Gonenc, Treatability of a textile azo dye by UV/H_2O_2, Environ. Technol. 18 (1997) 179.
[15] E. Forgacs, T. Cserhati, G. Oros, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30 (2004) 953–971.
[16] I. Arslan, A.I. Balcioglu, Advanced oxidate of raw and biotreated textile industry wastewater with O_3, H_2O_2/UV-C and their sequential application, J. Chem. Technol. Biotechnol. 76 (2001) 53–60.
[17] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textile dyes in wastewater using ZnO as semiconductor catalyst, J. Hazard. Mater. B112 (2004) 269–278.
[18] M.P. Reddy, A. Venugopal, M. Subrahmanyam, Hydroxyapatite photocatalytic degradation of calmagite (an azo dye) in aqueous suspension, Appl. Catal. B: Environ. 69 (2007) 164–170.
[19] M. Saquiba, M.A. Tariqa, M. Faisala, M. Muneer, Photocatalytic degradation of two selected dye derivatives in aqueous suspensions of titanium dioxide, Desalination 219 (2008) 301–311.
[20] C.G. Silva, W. Wang, J.L. Faria, Photocatalytic and photochemical degradation of mono-, di- and tri-azo dyes in aqueous solution under UV irradiation, J. Photochem. Photobiol. A: Chem. 181 (2006) 314–324.
[21] M. Stylidi, D.I. Kondarides, X.E. Verykios, Visible light-induced photocatalytic degradation of Acid Orange 7 in aqueous TiO_2 suspensions, Appl. Catal. B: Environ. 47 (2004) 189–201.
[22] C. Su, B.Y. Hong, C.M. Tseng, Sol–gel preparation and photocatalysis of titanium dioxide, Catal. Today 96 (2004) 119–126.
[23] J. Sun, X. Wang, J. Sun, R. Sun, S. Sun, L. Qiao, Photocatalytic degradation and kinetics of Orange G using nano-sized Sn(IV)/TiO_2/AC photocatalyst, J. Mol. Catal. A: Chem. 260 (2006) 241–246.
[24] J. Madhavan, P. Maruthamuthu, S. Murugesan, S. Anandan, Kinetic studies on visible light-assisted degradation of acid red 88 in presence of metal-ion coupled oxone reagent, Appl. Catal. B: Environ. 83 (2008) 8–14.
[25] A. Mills, L. Hunte, An overview of semiconductor photocatalysis, J. Photochem. Photobiol. A: Chem. 108 (1997) 1–35.
[26] O. Carp, C.L. Huisman, A. Reller, Photoinduced reactivity of titanium oxide photoinduced reactivity of titanium oxide, Solid State Chem. 32 (2004) 33–177.
[27] U.I. Gaya, A.H. Abdullah, Heterogeneous photocatalytic degradation of organic contaminants over titanium dioxide: a review of fundamentals, progress and problems, J. Photochem. Photobiol. C: Photochem. Rev. 9 (2008) 1–12.
[28] M.R. Hoffmann, S.T. Martin, W. Choi, D.W. Bahenemann, Environmental application of semiconductor photocatalysis, Chem. Rev. 95 (1995) 69–96.
[29] W.Z. Tang, H. An, Photocatalytic degradation kinetics and mechanism of acid blue 40 by TiO_2/UV in aqueous solution, Chemosphere 31 (1995) 4171–4183.
[30] T.V. Gerven, G. Mul, J. Moulijn, A. Stankiewicz, A review of intensification of photocatalytic processes, Chem. Eng. Proc. 46 (2007) 781–789.
[31] L.P. Gianluca, A. Bono, D. Krishnaiah, J.G. Collin, Preparation of titanium dioxide photocatalyst loaded onto activated carbon support using chemical vapor decomposition: a review paper, J. Hazard. Mater. 157 (2–3) (2008) 209–219.
[32] G. Meacock, K.D.A. Taylor, M. Knowles, A. Himonides, The improved whitening of minced cod flesh using dispersed titanium dioxide, J. Sci. Food Agric. 73 (2) (1997) 221–225.
[33] M.A. Aramendia, A. Marinas, J.M. Marinas, J.M. Moreno, F.J. Urbano, Photocatalytic degradation of herbicide fluroxypyr in aqueous suspension of TiO_2, Catal. Today 101 (3–4) (2005) 187–193.
[34] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J.M. Hermann, Influence of chemical structure of dye, of pH and of inorganic salts on their photocatalytic degradation by TiO_2 comparison of the efficiency of powder and supported TiO_2, J. Photochem. Photobiol. A: Chem. 158 (2003) 27–36.
[35] S. Malato, J. Blanco, A. Compos, J. Caceres, C. Guillard, J.M. Herrmann, A.R. Fernandez-Alba, Effect of operating parameters on the testing of new industrial titania catalysts at solar pilot plant scale, Appl. Catal. B: Environ. 42 (4) (2003) 349–357.
[36] P. Pichat, Chemical degradation methods for wastes and pollutants: environmental and industrial applications, Marcel Dekker Inc., New York, Basel, 2003, pp. 77–119.
[37] A. Fujishima, T.N. Rao, D.A. Tryk, Titanium dioxide photocatalysis, J. Photochem. Photobiol. C: Photochem. Rev. 1 (2000) 1–21.
[38] L.-C. Chen, C.-M. Huang, F.-R. Tsai, Characterization and photocatalytic activity of K^+-doped TiO_2 photo catalysts, J. Mol. Catal. A: Chem. 265 (2007) 133–140.
[39] M. Huang, C. Xu, Z. Wu, Y. Huang, J. Lin, J. Wu, Photocatalytic discolorization of methyl orange solution by Pt modified TiO_2 loaded on natural zeolite, Dyes Pigm. 77 (2008) 327–334.
[40] G.N. Kryukova, G.A. Zenkovets, A.A. Shutilov, M. Wilde, K. Guther, D. Fassler, K. Richter, Structural peculiarities of TiO_2 and Pt/TiO_2 catalysts for the photocatalytic oxidation of aqueous solution of Acid Orange 7 Dye upon ultraviolet light, Appl. Catal. B: Environ. 71 (2007) 169–176.
[41] O. Ozcan, F. Yukruk, E.U. Akkaya, D. Uner, Dye sensitized artificial photosynthesis in the gas phase over thin and thick TiO_2 films under UV and visible light irradiation, Appl. Catal. B: Environ. 71 (2007) 291–297.
[42] S. Rengaraj, X.Z. Li, P.A. Tanner, Z.F. Pan, G.K.H. Pang, Photocatalytic degradation of methyl parathion—An endocrine disruptor by Bi^{3+}-doped TiO_2, J. Mol. Catal. A: Chem. 247 (2006) 36–43.
[43] J. Sun, L. Qiao, S. Sun, G. Wang, Photocatalytic degradation of Orange G on nitrogen-doped TiO_2 catalysts under visible light and sunlight irradiation, J. Hazard. Mater. 155 (2008) 312–319.
[44] C.-H. Wei, X.-H. Tang, J.-R. Liang, S. Tan, Preparation, characterization and photocatalytic activity of boron- and cerium-codoped TiO_2, J. Environ. Sci. 19 (2007) 90–96.
[45] H. Yu, X. Zheng, Z. Yin, F. Tao, B. Fang, K. Hou, Preparation of nitrogen-doped TiO_2 nanoparticle catalyst and its catalytic activity under visible light, Chin. J. Chem. Eng. 15 (6) (2007) 802–807.
[46] Y. Zhiyong, M. Bensimon, V. Sarria, I. Stolitchnov, W. Jardim, D. Laub, E. Mielczarski, J. Mielczarski, L. Kiwi-Minsker, J. Kiwi, $ZnSO_4$–TiO_2 doped catalyst with higher activity in photocatalytic processes, Appl. Catal. B: Environ. 76 (2007) 185–195.
[47] Y. Zhiyong, H. Keppner, D. Laub, E. Mielczarski, J. Mielczarski, L. Kiwi-Minsker, A. Renken, J. Kiwi, Photocatalytic discoloration of Methyl Orange on innovative parylene–TiO_2 flexible thin films under simulated sunlight, Appl. Catal. B: Environ. 79 (2008) 63–71.
[48] V. Krishna, D. Yanes, W. Imaram, A. Angerhofer, B. Koopman, B. Moudgil, Mechanism of enhanced photocatalysis with polyhydroxy fullerenes, Appl. Catal. B: Environ. 79 (2008) 376–381.
[49] M.A. Fox, M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 93 (1993) 341.
[50] D.W. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, N. Serpone, in: R.G. Zepp, G.R. Heltz, D.G. Crosby (Eds.), Aquatic Surface Photochemistry, Lewis Publishers, Boca Raton, 1994, p. 261.
[51] S. Tunesi, M. Anderson, Influence of chemisorption on the photodecomposition of salicylic acid and related compounds using suspended titania ceramic membranes, J. Phys. Chem. 95 (1991) 3399–3405.
[52] M.S.T. Concalves, A.M.F. Oliveira-Campos, M.M.S. Pinto, P.M.S. Plasencia, M.J.R.P. Queiroz, Photochemical treatment of solutions of azo dyes containing TiO_2, Chemosphere 39 (1991) 781.
[53] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, S. Malato, J. Blanco, M.I. Maldonado, J.M. Herrmann, Solar efficiency of a new deposited titania photocatalyst: chlorophenol, pesticide and dye removal applications, Appl. Catal. B: Environ 46 (2) (2003) 319–332.
[54] L.B. Reutergarth, M. Iangpashuk, Photocatalytic decolorization of reactive azo dye: a comparison between TiO_2 and CdS photocatalysts, Chemosphere 35 (1997) 585–596.
[55] S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy, V. Murugesan, Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2, Sol. Energy Mater. Sol. Cells 77 (2003) 65.
[56] W. Baran, A. Makowski, W. Wardas, The effect of UV radiation absorption of cationic and anionic dye solutions on their photocatalytic degradation in the presence of TiO_2, Dyes Pigm. 76 (2008) 226–230.
[57] K.-H. Wang, Y.-H. Hsieh, C.-H. Wu, C.-Y. Chang, The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO_2 aqueous suspension, Chemosphere 40 (2000) 389–394.
[58] W. Baran, A. Makowski, W. Wardas, The influence of $FeCl_3$ on the photocatalytic degradation of dissolved azo dyes in aqueous TiO_2 suspensions, Chemosphere 53 (2003) 87–95.
[59] I.A. Alaton, I.A. Balcioglu, Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes: a case study with hydrolyzed Reactive Black 5, J. Photochem. Photobiol. A: Chem. 141 (2001) 247–254.
[60] D. Grosse, N. Lewis, Handbook on Advanced Photochemical Oxidation Processes, Center for Environmental Research Information, National Risk Management Research Laboratory, Office of Research and Development, US, EPA, Cincinati, USA, 1998.

[61] I. Poulios, I. Aetopoulou, Photocatalytic degradation of the textile dye Reactive Orange 16 in the presence of TiO_2 suspensions, Environ. Technol. 20 (1999) 479–487.
[62] I. Poulios, A. Avrans, E. Rekliti, A. Zouboulis, Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides, J. Chem. Biotechnol. 75 (2000) 205–212.
[63] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaoui, G. Guillard, J.M. Hermann, Photocatalytic degradation of various types of dyes (alizarin S, crecein Orange G, methyl red, congo red, methylene blue) in water by UV-irradiated titania, Appl. Catal. B: Environ. 39 (2002) 75–90.
[64] M. Stylidi, D.I. Kondarides, X.E. Verykios, Pathways of solar light-induced photocatalytic degradation of azo dyes in aqueous TiO_2 suspension, Appl. Catal. B: Environ. 40 (2003) 271–286.
[65] Q. Xiao, J. Zhang, C. Xiao, X. Tan, Photocatalytic decolorization of methylene blue over $Zn_{1-x}Co_xO$ under visible light irradiation, Sci. Eng. B 142 (2007) 121–125.
[66] T. Zhang, T. Oyama, S. Horikoshi, H. Hidaka, J. Zhao, N. Serpone, Photocatalyzed N-demethylation and degradation of methylene blue in titania dispersions exposed to concentrated sunlight, Sol. Energy Mater. Sol. Cells 73 (2002) 287–303.
[67] X. Chen, G. Gu, Study on synthesis of nanometer TiO_2 crystal from organic compound in liquid phase at normal pressure and low temperature, Chin. J. Inorg. Chem. 18 (7) (2002) 749–752.
[68] V. Augugliaro, C. Baiocchi, A. Bianco-Prevot, E. Garcia-Lopez, V. Loddo, S. Malato, G. Marci, L. Palmisano, M. Pazzi, E. Pramauro, Azo-dyes photocatalytic degradation in aqueous suspension of TiO_2 under solar irradiation, Chemosphere 49 (2002) 1223–1230.
[69] M. Saquib, M. Muneer, TiO_2-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions, Dyes Pigm. 56 (2003) 37–49.
[70] H.M. Coleman, V. Vimonses, G. Leslie, R. Amal, Degradation of 1,4-dioxane in water using TiO_2 based photocatalytic and H_2O_2/UV processes, J. Hazard. Mater. 146 (2007) 496–501.
[71] N.M. Mahmoodi, M. Arami, N.Y. Limaee, N.S. Tabrizi, Kinetics of heterogeneous photocatalytic degradation of reactive dyes in an immobilized TiO_2 photocatalytic reactor, J. Colloid Interf. Sci. 295 (2006) 159–164.
[72] K. Tanaka, T. Hisanaga, K. Harada, Efficient photocatalytic degradation of chloral hydrate in aqueous semiconductor suspension, J. Photochem. Photobiol. A: Chem. 48 (1989) 155–159.
[73] S. Rengaraj, X.Z. Li, Enhanced photocatalytic reduction reaction over Bi^{3+}–TiO_2 nanoparticles in presence of formic acid as a hole scavenger, Chemosphere 66 (2007) 930–939.
[74] M.A. Aguado, M.A. Anderson, Degradation of formic acid over semiconducting membranes supported on glass: effects of structure and electronic doping, Sol. Energy Mater. Sol. Cells 28 (1993) 345–361.
[75] S. Sanuki, T. Kojima, K. Arai, S. Nagaoka, H. Majima, Photocatalytic reduction of selenate and selenite solutions using TiO_2 powders, Metall. Mater. Trans. B 30 (1999) 15–20.
[76] M. Kaise, H. Nagai, K. Tokuhashi, S. Kondo, S. Nimura, O. Kikuchi, Electron spin resonance studies of photocatalytic interface reactions of suspended M/TiO_2 (M = Pt, Pd, Ir, Rh, Os, or Ru) with alcohol and acetic acid in aqueous media, Langmuir 10 (1994) 1345–1347.
[77] S. Liu, J.-H. Yang, J.-H. Choy, Microporous SiO_2-TiO_2 nanosols pillared montmorillonite for photocatalytic decomposition of methyl orange, J. Photochem. Photobiol. A: Chem. 179 (2006) 75–80.
[78] P. Bouras, E. Stathatos, P. Lianos, Pure versus metal-ion-doped nanocrystalline titania for photocatalysis, Appl. Catal. B: Environ. 73 (2007) 51–59.
[79] X. Ding, T. An, G. Li, S. Zhang, J. Chen, J. Yuan, H. Zhao, H. Chen, G. Sheng, J. Fu, Preparation and characterization of hydrophobic TiO_2 pillared clay: the effect of acid hydrolysis catalyst and doped Pt amount on photocatalytic activity, J. Colloid Interface Sci. 320 (2) (2008) 501–507.
[80] Y. Li, S. Peng, F. Jiang, G. Lu, S. Li, Effect of doping TiO_2 with alkaline-earth metal ions on its photocatalytic activity, J. Serb. Chem. Soc. 72 (4) (2007) 393–402, JSCS-3569.
[81] D.L. Liao, C.A. Badour, B.Q. Liao, Preparation of nanosized TiO_2/ZnO composite catalyst and its photocatalytic activity for degradation of methyl orange, J. Photochem. Photobiol. A: Chem. 194 (2008) 11–19.
[82] S. Rengaraj, X.Z. Li, Photocatalytic degradation of bisphenol A as an endocrine disruptor in aqueous suspension using Ag-TiO_2 catalysts, Int. J. Environ. Pollut. 27 (1/2/3) (2006) 20–37.
[83] A.-W. Xu, Y. Gao, H.-Q. Liu, The preparation, characterization, and their photocatalytic activities of rare-earth-doped TiO_2 nano-particles, J. Catal. 207 (2002) 151–157.
[84] G. Liu, X. Zhang, Y. Xu, X. Niu, L. Zheng, X. Ding, The preparation of Zn^{2+}-doped TiO_2 nanoparticles by sol–gel and solid phase reaction methods respectively and their photocatalytic activities, Chemosphere 59 (2005) 1367–1371.
[85] B. Xin, P. Wang, D. Ding, J. Liu, Z. Ren, H. Fu, Effect of surface species on Cu-TiO_2 photocatalytic activity, Appl. Surf. Sci. 254 (2008) 2569–2574.
[86] T.K. Ghorai, D. Dhak, S.K. Biswas, S. Dalai, P. Pramanik, Photocatalytic oxidation of organic dyes by nano-sized metal molybdate incorporated titanium dioxide ($M_xMo_xTi_{1-x}O_6$) (M = Ni, Cu, Zn) photocatalysts, J. Mol. Catal. A: Chem. 273 (2007) 224–229.
[87] P. Babelon, A.S. Dequidt, H. Mostefa-Sba, S. Bourgeois, P. Sibillot, M. Sacilotti, SEM and XPS studies of titanium dioxide thin films grown by MOCVD, Thin Solid Films 322 (1998) 63–67.
[88] B.-H. Kim, J.-Y. Lee, Y.-H. Choa, M. Higuchi, N. Mizutani, Preparation of TiO_2 thin film by liquid spray mist CVD method, Mater. Sci. Eng. B107 (2004) 289–294.
[89] K. Okuyama, M. Shimada, T. Fujimoto, T. Maekawa, K. Nakaso, T. Seto, Effects of preparation conditions on the characteristics of titanium dioxide particles produced by a CVD method, J. Aerosol Sci. 29 (1) (1998) S907–S908.
[90] X. Zhang, M. Zhou, L. Lei, Preparation of anatase TiO_2 supported on alumina by different metal organic chemical vapor decomposition methods, Appl. Catal. A: Gen. 282 (2005) 285–293.
[91] D.-E. Gu, B.-C. Yang, Y.-D. Hu, V and N co-doped nanocrystal anatase TiO_2 photocatalysts with enhanced photocatalytic under visible light irradiation, Catal. Commun. 9 (2008) 1472–1476.
[92] S. Bu, Z. Jin, X. Liu, T. Yin, Z. Cheng, Preparation of nanocrystalline TiO_2 porous films from terpineol-ethanol-PEG system, J. Mater. Sci. 41 (7) (2006) 2067–2073.
[93] J.C. Colmenares, M.A. Aramendia, A. Marinas, J.M. Marinas, F.J. Urbano, Synthesis, characterization and photocatalytic activity of different metal-doped titania systems, Appl. Catal. A: Gen. 306 (2006) 120–127.
[94] R. Campostrini, M. Ischia, L. Palmisano, Pyrolysis study of sol–gel derived TiO_2 powders. Part I. TiO_2-anatase prepared by reacting titanium (IV) isopropoxide with formic acid, J. Therm. Anal. Calorim. 71 (3) (2003) 997–1009.
[95] R. Campostrini, M. Ischia, L. Palmisano, Pyrolysis study of sol–gel derived TiO_2 powders. Part II. TiO_2-anatase prepared by reacting titanium (IV) isopropoxide with oxalic acid, J. Therm. Anal. Calorim. 71 (3) (2003) 1011–1021.
[96] R. Campostrini, M. Ischia, L. Palmisano, Pyrolysis study of sol–gel derived TiO_2 powders. Part III. TiO_2-anatase prepared by reacting titanium (IV) isopropoxide with acetic acid, J. Therm. Anal. Calorim. 75 (3) (2004) 13–24.
[97] R. Campostrini, M. Ischia, L. Palmisano, Pyrolysis study of sol–gel derived TiO_2 powders. Part IV. TiO_2-anatase prepared by hydrolysing titanium (IV) isopropoxide without chelating agents, J. Therm. Anal. Calorim. 75 (1) (2004) 25–34.
[98] M. Crisan, A. Braileanu, M. Raileanu, M. Zaharescu, D. Crisan, N. Dragan, M. Anastasescu, A. Ianculescu, I. Nitoi, V.E. Marinescu, S.M. Hodorogea, Sol–gel S-doped TiO_2 materials for environmental protection, J. Non-Cryst. Solids 354 (2008) 705–711.
[99] X. Fan, X. Chen, S. Zhu, Z. Li, T. Yu, J. Ye, Z. Zou, The structural, physical and photocatalytic properties of the mesoporous Cr-doped TiO_2, J. Mol. Catal. A: Chem. 284 (2008) 155–160.
[100] V. Gombac, L.D. Rogatis, A. Gasparotto, G. Vicario, T. Montini, D. Barreca, G. Balducci, P. Fornasiero, E. Tondello, M. Graziani, TiO_2 nanopowders doped with boron and nitrogen for photocatalytic applications, Chem. Phys. 339 (2007) 111–123.
[101] X.Z. Li, F.B. Li, C.L. Yang, W.K. Ge, Photocatalytic activity of WO_x-TiO_2 under visible light irradiation, J. Photochem. Photobiol. A: Chem. 141 (2001) 209–217.
[102] Y. Li, T.J. White, S.H. Lim, Low-temperature synthesis and microstructural control of titania nano-particles, J. Solid State Chem. 177 (4–5) (2004) 1372–1381.
[103] A. Peng, E. Xie, C. Jia, R. Jiang, H. Lin, Photoluminescence properties of TiO_2: Eu_3^+ thin films deposited on different substrates, Mater. Lett. 59 (29–30) (2005) 3866–3869.
[104] M. Saif, M.S.A. Abdel-Mottaleb, Titanium dioxide nanomaterial doped with trivalent lanthanide ions of Tb, Eu and Sm: preparation, characterization and potential applications, Inorg. Chim. Acta 360 (2007) 2863–2874.
[105] J.-W. Shi, J.-T. Zheng, Y. Hu, Y.-C. Zhao, Influence of Fe^{3+} and Ho^{3+} co-doping on the photo catalytic activity of TiO_2, Meter. Chem. Phys. 106 (2007) 247–249.
[106] S. Sivakumar, P.P. Krishna, P. Makundan, K.G.K. Warrier, Sol–gel synthesis of nanosized anatase from titanyl sulfate, Mater. Lett. 57 (2) (2002) 330–335.
[107] S. Srinivasan, S.J. Wade, E.K. Stefanakos, Y. Goswami, Synergistic effects of sulfation and co-doping on the visible light photocatalysis of TiO_2, J. Alloys Compd. 424 (2006) 322–326.
[108] M. Stir, R. Nicula, E. Burkel, Pressure-temperature phase diagrams of pure and Ag-doped nanocrystalline TiO_2 photo catalyst, J. Eur. Ceram. Soc. 26 (2006) 1547–1553.
[109] S.S. Watson, D. Beydoun, J.A. Scott, R. Amal, The effect of preparation method on the photoactivity of crystalline titanium dioxide particles, Chem. Eng. J. 95 (1) (2003) 213–220.
[110] K. Wilke, H.D. Breuer, The influence of transition metal doping on the physical and photo catalytic properties of titania, J. Photochem. Photobiol. A: Chem. 121 (1999) (1999) 49–53.
[111] W. Xu, W. Hu, M. Li, C. Wen, Sol–gel derived hydroxyapatite/titania biocoatings on titanium substrate, Mater. Lett. 60 (13–14) (2006) 1575–1578.
[112] Y. Yang, X.-J. Li, J.-T. Chen, L.-Y. Wang, Effect of doping mode on the photocatalytic activities of Mo/TiO_2, J. Photochem. Photobiol. A: Chem. 163 (2004) 517–522.
[113] A. Zaleska, J.W. Sobczak, E. Grabowska, J. Hupka, Preparation and photocatalytic activity of boron-modified TiO_2 under UV and visible light, Appl. Catal. B: Environ. 78 (2008) 92–100.
[114] X. Zhang, Q. Liu, Preparation and characterization of titania photo catalyst co-doped with boron, nickel, and cerium, Mater. Lett. 62 (2008) 2589–2592.
[115] F. Peng, L. Cai, L. Huang, H. Yu, H. Wang, Preparation of nitrogen-doped titanium dioxide with visible-light photocatalytic activity using a facile hydrothermal method, J. Phys. Chem. Solids 69 (7) (2008) 1657–1664.
[116] F. Peng, L. Cai, L. Huang, H. Yu, H. Wang, Synthesis and characterization of substitutional and interstitial nitrogen-doped titanium dioxides with visible light photocatalytic activity, J. Solid State Chem. 181 (2008) 130–136.
[117] X. Feng, Q. Wang, G. Wang, F. Qiu, Preparation of nano-TiO_2 by ethanol-thermal method and its catalytic performance for synthesis of dibutyl carbonate by transesterification, Chin. J. Catal. 27 (3) (2006) 195–196.

[118] F. Wang, Z. Shi, F. Gong, J. Jiu, M. Adachi, Morphology control of anatase TiO_2 by surfactant-assisted hydrothermal method, Chin. J. Chem. Eng. 15 (5) (2007) 754–759.
[119] W. Zhiyu, C. Haifeng, T. Peisong, M. Weiping, Z. Fuan, Q. Guodong, F. Xianping, Colloids Surf. A: Physicochem. Eng. 289 (2006) 207–211.
[120] J. Zhu, Z. Deng, F. Chen, J. Zhang, H. Chen, M. Anpo, J. Huang, L. Zhang, Hydrothermal doping method for preparation of Cr^{3+}-TiO_2 photocatalysts with concentration gradient distribution of Cr^{3+}, Appl. Catal. B: Environ. 62 (2006) 329–335.
[121] M. Bettinelli, V. Dallacasa, D. Falcomer, P. Fornasiero, V. Gombac, T. Montini, L. Romano, A. Speghini, Photocatalytic activity of TiO_2 doped with boron and vanadium, J. Hazard. Mater. 146 (2007) 529–534.
[122] C. Liu, X. Tanga, C. Moa, Z. Qiang, Characterization and activity of visible-light-driven TiO_2 photocatalyst co-doped with nitrogen and cerium, J. Solid State Chem. 181 (4) (2008) 913–919.
[123] T. Horikawa, M. Katoh, T. Tomida, Preparation and characterization of nitrogen-doped mesoporous titania with high specific surface area, Microporous Mesoporous Mater. 110 (2008) 397–404.
[124] A.-C. Lee, R.-H. Lin, C.-Y. Yang, M.-H. Lin, W.-Y. Wang, Preparations and characterization of novel photocatalysts with mesoporous titanium dioxide (TiO_2) via a sol–gel method, Mater. Chem. Phys. 109 (2–3) (2007) 275–280.
[125] M.S. Jeon, W.S. Yoon, H. Joo, T.K. Lee, H. Lee, Preparation and characterization of a nano-sized Mo/Ti mixed photocatalyst, Appl. Surf. Sci. 165 (2000) 209–216.