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REVIEW ARTICLE

Parameters affecting the photocatalytic degradation of dyes using TiO_2: a review

Khan Mamun Reza[1] · **ASW Kurny**[2] · **Fahmida Gulshan**[2]

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Abstract Traditional chemical, physical and biological processes for treating wastewater containing textile dye have such disadvantages as high cost, high energy requirement and generation of secondary pollution during treatment process. The advanced oxidation processes technology has been attracting growing attention for the decomposition of organic dyes. Such processes are based on the light-enhanced generation of highly reactive hydroxyl radicals, which oxidize the organic matter in solution and convert it completely into water, CO_2 and inorganic compounds. In this presentation, the photocatalytic degradation of dyes in aqueous solution using TiO_2 as photocatalyst under solar and UV irradiation has been reviewed. It is observed that the degradation of dyes depends on several parameters such as pH, catalyst concentration, substrate concentration and the presence of oxidants. Reaction temperature and the intensity of light also affect the degradation of dyes. Particle size, BET-surface area and different mineral forms of TiO_2 also have influence on the degradation rate.

Keywords Photocatalytic degradation · Dye · Titanium dioxide · Parameters

Introduction

Synthetic dyes are widely used in textile industry (Vandevivere et al. 1998; Sakthivel et al. 2003), leather industry (Sakthivel et al. 2003; Tunay et al. 1999), paper production (Vandevivere et al. 1998; Ivanov et al. 1996), food technology (Slampova et al. 2001), medical (Haferlach et al. 2008), agricultural research (Cook and Linden 1997; Kross et al. 1996), light-harvesting arrays (Wagner and Lindsey 1996), photoelectrochemical cells (Wrobel et al. 2001), etc.

At present, 100,000 different types of dyes with annual production rate of 7×10^5 are produced of which about 36,000 tons dye/year are consumed by the textile industries. Up to 20 % of the total world production of dyes is lost during the dyeing process and is released in the textile effluents (Esplugas et al. 2002; Houas et al. 2001; Crini 1996; Weber and Stickney 1993). Synthetic dyes are produced and consumed in large scale and can cause considerable environmental pollution and serious health-risk due to their stability, and toxicity (Shukla and Gupta 1992). A wide range of methods has been developed for the removal of synthetic dyes from waters and wastewaters to decrease their impact on the environment. Conventional water treatment technologies such as solvent extraction, activated carbon adsorption, and chemical treatment process [such as oxidation by ozone (O_3)] often produce hazardous by-products and generate large amount of solid wastes, which require costly disposal or regeneration method (Slokar and Marechal 1998; Galindo et al. 2001; Pandurangan et al. 2001).

Over the past few years, advanced oxidation processes (AOP) has been proposed as an alternative route for water purification (Legrini et al. 1993). AOP is divided into two categories (heterogeneous and homogenous catalysis). Heterogeneous catalysis has been successfully employed

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✉ Fahmida Gulshan
fahmidagulshan@mme.buet.ac.bd

[1] Department of Electronics and Communication Engineering, Jatiya Kabi Kazi Nazrul Islam University, Trishal, Mymensingh, Bangladesh

[2] Department of Materials and Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh

for the degradation of various families of hazardous materials. Titanium dioxide (TiO_2), due to its non-toxic, inexpensive, and high reactive nature, has been extensively investigated as a heterogeneous photocatalyst for the remediation of contaminated environment (Hassan et al. 2014; Harbi et al. 2015; Kim et al. 2005). The advantage of TiO_2 as photocatalyst is that organic pollutants are usually completely mineralized to non-toxic substances such as CO_2, HCl and water and thus the reactions do not suffer the drawbacks of photolysis reactions in terms of the production of intermediate products. Moreover, the reaction can take place at room temperature (Aramendia et al. 2005; Malato et al. 2003; Chatterjee and Dasgupta 2005).

Upon irradiation by photons, electrons on the surface of TiO_2 are excited to the conduction band, and positive holes are formed in the valance band. The electrons and holes can either recombine and produce thermal energy or interact with other molecules (Venkatadri and Peters 1993). The holes can react with electron donors in the solution to produce powerful oxidizing free radicals such as hydroxyl radicals, which oxidize the organics on the surface. The holes can also oxidize the substrate by direct electron transfer. In brief, photogeneration of radical species in TiO_2/UV system can be described as follows (Kormann et al. 1988):

$$\mathrm{TiO_2} + hv \rightarrow e^-_{\mathrm{CB}} + h^+_{\mathrm{VB}} \tag{1}$$

$$h^+_{\mathrm{VB}} + \mathrm{OH}^-(\mathrm{surface}) \rightarrow \mathrm{OH}^{\cdot} \tag{2}$$

$$h^+_{\mathrm{VB}} + \mathrm{H_2O} \rightarrow \mathrm{OH}^{\cdot} + \mathrm{H}^+ \tag{3}$$

$$e^-_{\mathrm{CB}} + \mathrm{O_2} \rightarrow \mathrm{O_2^-} \tag{4}$$

$$e^-_{\mathrm{CB}} + h^+_{\mathrm{VB}} \rightarrow \mathrm{Heat} \tag{5}$$

Parameters effecting the photocatalytic degradation

Photocatalytic degradation of dyes are influenced by several parameters, such as pH, initial concentration of dyes, photocatalyst particle size and its concentration, reaction temperature, light intensity and the presence of electron acceptors.

Effect of oxidizing agent

Inorganic oxidants such as O_3 have been proposed to increase the efficiency of TiO_2/UV treatments (Wang et al. 2002; Li et al. 2003), H_2O_2 (Saggioro et al. 2011; Saquib et al. 2008), $BrO_3{}^-$ (Saquib et al. 2008; Muneer and Bahnemann 2002), $S_2O_8{}^{2-}$ (Saquib et al. 2008; Muneer and Bahnemann 2002) and $ClO_4{}^-$ (Pelizzetti et al. 1991). These oxidants increase the number of trapped electrons, which prevents recombination and generates oxidizing radicals, which may, in turn, enhance the photocatalytic degradation of dye.

It has been shown that potassium bromate and ammonium persulfate had a beneficial effect on the degradation rate for the decomposition of Fast Green FCF in the presence of UV 100, whereas in the case of Patent Blue VF, all the electron acceptors were found to enhance the rate noticeably in the presence of P25 (Saquib et al. 2008).

Mahmoodi et al. (2006) worked with Reactive Blue 8 (RB 8) and Reactive Blue 220 (RB 220) and found that when H_2O_2 concentration changed from 0 to optimal concentration (300 mg/l for RB 8 and 450 mg/l for RB 220). No nonappreciable changes at the decolonization rate were observed when the concentration further increased.

H_2O_2 increases the formation rate of hydroxyl radical in two ways: (1) the reduction of H_2O_2 at the conduction band and (2) self-decomposition by illumination (So et al. 2002; Lee et al. 2003). Hydrogen peroxide, in low concentrations, enhances the degradation of compounds due to a more efficient generation of hydroxyl radical and inhibition of electron–hole pair recombination (Saggioro et al. 2011; Prado et al. 2008; Aguedach et al. 2005). Moreover, the solution phase may, at times, be oxygen starved, due to either oxygen consumption or slow oxygen mass transfer. Peroxide addition thereby increases the rate toward what it would have been an adequate oxygen supply (Daneshvar et al. 2004). However, when the concentration of H_2O_2 increases, the electron acceptor reacts with hydroxyl radicals, and acts as scavenger of the photoproduced holes (Daneshvar et al. 2003; Malato et al. 1998). In addition, H_2O_2 can modify the TiO_2 surface. This fact probably decreases its photocatalytic efficiency (Zhu et al. 2000). In addition, in the presence of high concentration of peroxide, $OH^{\cdot}$ radicals preferentially react with the excess of H_2O_2. This undesirable reaction competes with the destruction of the dye chromophore (Galindo and Kalt 1999; Coleman et al. 2007). Radical–radical reaction must also be taken into account (Konstantinou and Albanis 2004).

The UV/H_2O_2 process involves the photolysis of H_2O_2 by the rupture of the O–O bond and the formation of two $OH^{\cdot}$ radicals (Beltran et al. 1997). Practical difficulties with the UV photolysis of H_2O_2 are: (1) low wavelength (below 200–400 nm) required to make the process efficient, and (2) turbid waters containing strong UV absorbers such as aromatics organic compounds require higher light concentration, which increases the cost of the process. Dixit et al. (2010) studied photochemical oxidation of phenol and chlorophenol by UV/H_2O_2/TiO_2 process and compared with UV/H_2O_2 and UV/TiO_2 processes. He showed that when compared with the UV/H_2O_2 and UV/TiO_2 processes, the UV/H_2O_2/TiO_2 process reduced the energy consumption by 40–50 %. It was found that application of both oxidation and photocatalysis enhanced the degradation mechanism and hence gives much higher removal.

An investigation on the decomposition of methylene blue by iron oxides at various concentrations of oxalate solutions showed that much higher concentration of hydroxyl radicals was generated by iron oxides compared with those from a commercial TiO_2 (ST-01), as determined by the coumarin method. It was also found that the photodecomposition rate increased with increasing the generation of $OH^{\cdot}$ radicals (Gulshan et al. 2010).

Effect of pH

The interpretation of pH effects on the efficiency of the photodegradation process is a very difficult task. This is because three possible reaction mechanisms can contribute to dye degradation, (1) hydroxyl radical attack, (2) direct oxidation by the positive hole, and (3) direct reduction by the electron in the conducting band. The contribution of each one depends on the substrate nature and pH (Tang et al. 1997). The solution pH modifies the electrical double layer of the solid electrolyte interface, and consequently affects the sorption–desorption processes and the separation of the photogenerated electron–hole pairs in the surface of the semiconductor particles. TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface (Poulios et al. 2000) and thus a pH variation can influence the adsorption of dye molecules onto the TiO_2 surfaces (Wang et al. 2008).

Bubacz et al. (2010) observed an increase in the rate of the photocatalytic degradation of methylene blue with an increase in pH. According to Ling et al. (2004), basic pH electrostatic interactions between negative TiO^- and methylene blue cation leads to strong adsorption with a corresponding high rate of degradation. Ling et al. (2004) noted that basic pH electrostatic interactions between negative TiO^- and methylene blue cation leads to strong adsorption with a corresponding high rate of degradation. The surface charge properties of TiO_2 were also found to change with a change of pH value due to the amphoteric behavior of semi conducting TiO_2 (Guillard et al. 2003; Zielińska et al. 2003; Senthilkumaar et al. 2006).

Neppolian et al. (2002a) did not find significant influence of acidic pH on the percentage degradation of Reactive Blue 4, whereas the inhibitory effect was found to be more pronounced in the alkaline range (pH 11–13).

In acidic solutions ($pH < 5$), the photodegradation of the dye is retarded by the high concentration of proton, resulting in lower degradation efficiency. In alkaline medium ($pH > 10$), on the other hand, the presence of hydroxyl ions neutralizes the acidic end-products that are produced by the photodegradation reaction. A sudden drop of degradation had been observed when the initial pH of the reaction mixture was kept at 11. The reactive blue dye substituents of an electron-donating group such as—NH_2 in the α-positions of the carbonyl group form intramolecular hydrogen bonds at high pH values (Rys and Zollinger 1972). Therefore, the dye structure becomes chemically stable at high pH ranges. The chromophores of the dye remain intact after light irradiation and hence reduce the degradation rate of the dye (Tsui and Chu 2001). Hence, the changes in the behavior of the dye molecule may be responsible for the change in the percentage degradation of dye at higher pH.

Baran et al. (2008) investigated degradation of Bromocresol Purple at pH 4.5 and 8.0 and noted that under acidic conditions, and the molecule has a positive charge.

When the solution was acidified from pH 8.0 to pH 4.5, a 6-fold increase in adsorption efficacy was observed. The observed increase was caused by a change in the charge of the Bromocresol Purple. The simultaneous significant increase in dye degradation rate may indicate that pH change also influences dye photodegradation. Unfortunately such an easy way to accelerate photocatalysis is impossible to achieve in the case of anionic dyes. The unavoidable increase in acidity will coagulate the photocatalyst and decrease its activity. Kansal et al. (2009) also found that the degradation of Reactive Black 5 and Reactive Orange 4 dyes was favored in acidic medium with TiO_2. Tanaka et al. (2000) found that positively charged TiO_2 surface adsorbed more Acid Orange 7 at lower pH value, and more decomposition was achieved. The acid black 1 has a sulfuric group in its structure, which is negatively charged. So the acidic solution favors adsorption of dye onto photocatalyst surface as TiO_2 surface is positively charged in acidic solution (Grzechulska and Morawski 2002).

Lachheb et al. (2002) in their work with Crocein Orange G (OG), Methyl Red (MR), Congo Red (CR), Alizarin S (AS) and Methylene Blue (MB) found that the pH had a little influence upon the kinetics of disappearance. Since MB is a cationic dye, it is conceivable that at high pH, its adsorption is favored on a negatively charged surface. By contrast, OG has its adsorption inhibited by high pH because of its negatively charged sulfonate $-\phi\text{-}SO_3^-$ function. The other dyes, having several functional groups, were found to have a resulting behavior similar to that of MB.

Kiriakidou et al. (1999) found strong dependence of pH of the solution on the degradation rate of Acid Orange 7 (AO7). They noted that AO7 has a negatively charged sulfonic group and at low pH, attractive forces between the TiO_2 surface and the dye favors adsorption. On the other hand, at high pH, the TiO_2 surface is negatively charged and repulsive forces leads to decreased adsorption. Finally, at pH values close to the pH_{zpc}, adsorption takes intermediate values. The degradation rate was rather insensitive in the pH range of 2–9; however, it increased significantly upon increasing pH of the solution above 10. It is expected that most of the adsorbed dye molecules are not in direct contact with the photocatalyst surface resulting in decreased degradation rates with decreased pH.

Hu et al. (2003a) studied the changes of adsorption and decolorization of Procion Red MX-5B (MX-5B) and Cationic Blue X-GRL (CBX) with pH. They found that adsorption of MX-5B decreased with increasing pH. However, the photodegradation rate of MX-5B increased under UV irradiation with the decrease in adsorption of MX-5B. It was confirmed that, in the decolorization of MX-5B, the more active bonds including the C–N bonds linked to the benzene ring or the naphthalene ring were hydroxylated first (Hu et al. 2003b). The photodegradation of MX-5B therefore occurred in the bulk aqueous phase. On the contrary, the adsorption of CBX increased with pH, and the decolorization of CBX was also accelerated with the adsorption of CBX. Because of the high dependency on adsorption, the decolorization of CBX occurred mainly on the surface of TiO_2.

Hung and Yuan (2000) found that Orange G decomposed more quickly in the more acidic or base conditions and degraded more slowly in neutral conditions. They attributed higher degradation in base condition to fact that more OH^- present in the solution may result in formation of more $OH^·$ radicals.

Effect of dye concentration

Saquib and Muneer (2003) studied the effect of substrate concentration on the degradation of gentian violet at varying concentrations such as 0.18, 0.25, 0.35 and 0.5 mM. The degradation rate increased with increasing the substrate concentration up to 0.25 mM and then declined. Kiriakidou et al. (1999) working with Acid Orange 7 (AO7) got similar result. The experiments were conducted at pH 6 and the initial AO7 concentration was varied between 25 and 600 mg/l the time required for the decolorization of AO7 solutions was found to depend significantly on the initial dye concentration. Complete decolorization of the solutions took place in less than an hour for relatively low C_0 values (25–100 mg/l), while this was not the case for higher initial dye concentrations (200–600 mg/l). Other works also revealed similar result (Sakthivel et al. 2003; Saquib and Muneer 2003; Augugliaro et al. 2002; Sohrabi et al. 2009; Sivalingam et al. 2003).

The effect of initial concentration of dyes on the percentage degradation was studied by Neppolian et al. (2002) They varied the initial concentration of Reactive Yellow 17 from 8×10^{-4} to 1.2×10^{-3} M, of Reactive Red 2 from 4.16×10^{-4} to 1.25×10^{-3} M and of Reactive Blue 4 from 1×10^{-4} to 5×10^{-4} M with optimum catalyst loading. They found that the percentage degradation decreases with increasing initial concentration of the dye. This is in agreement with the works of others (Saggioro et al. 2011; Daneshvar et al. 2003; Giwa et al. 2012; Zhang et al. 2002).

The probability of formation of $OH^·$ radicals on the catalyst surface and $OH^·$ radicals reacting with dye molecules determine the degradation rate. As the initial dye concentrations increase, more dye molecules are available for excitation and energy transfer (Avasarala et al. 2010). This dependence is perhaps related to the formation of several monolayers of adsorbed dye on the TiO_2 surface, which is favored at high dye concentrations. Till the critical level is reached, the surface is not completely covered leading to constant reaction rates (Kiriakidou et al. 1999). On the other hand, the decrease in degradation efficiency with the increase in dye concentration occurs due to several reasons. As the initial concentrations of the dye increase more and more, dye molecules are adsorbed on the surface of the catalyst and significant amount of UV is absorbed by the dye molecules rather than the TiO_2 particles. Hence, the penetration of light to the surface of the catalyst decreases (Daneshvar et al. 2003; Kiriakidou et al. 1999; Saquib and Muneer 2003; Augugliaro et al. 2002). The generation of hydroxyl radicals decreases since the active sites was occupied by dyes (Daneshvar et al. 2003; Grzechulska and Morawski 2002). The adsorbed dye on the photocatalyst also inhibits the reaction of adsorbed molecules with the photo-induced positive holes or hydroxyl radicals, since there is no direct contact of the semiconductor with them (Daneshvar et al. 2003; Grzechulska and Morawski 2002; Kiriakidou et al. 1999; Poulios and Aetopoulou 1999). High dye concentration also shields the UV light (Saggioro et al. 2011; Segne et al. 2011; Liu et al. 2006). This reduces the path length of the photons entering the solution (Saggioro et al. 2011; Davis et al. 1994). Again, as the initial concentration of the dye increases, the requirement of catalyst surface needed for the degradation also increases. Since illumination time and amount of catalyst are constant, the $OH^·$ radical (primary oxidant) formed on the surface of TiO_2 is also constant. So the relative number of free radicals attacking the dye molecules decreases with increasing amount of the dye (Mengyue et al. 1995).

Effect of photocatalyst concentration

TiO_2 dosage can affect the degradation rate. Wei and Wan (1991) have reported that the catalyst amount has both positive and negative impact on the photodecomposition rate. The initial reaction rates were found to be directly proportional to catalyst concentration indicating the heterogeneous regime. Different concentrations of Degussa P25 in the range 0.5–5 g/l were employed to study the effect of photocatalyst concentration on the degradation kinetics of gentian violet. The degradation rate for the decomposition of the dye was found to increase with an increase in catalyst concentration, (Saquib and Muneer 2003). Qamar et al. (2005) found that the degradation rate for the decomposition of chromotrope 2B and amido black 10B increase with the increase in catalyst concentration. The investigation was done in different concentrations of Degussa P25 varying from 0.5 to 5 g/l. Hung and Yuan (2000) also found that the degradation rate of Orange G is proportional to the TiO_2 concentrations. Here TiO_2 concentrations ranged from 300 to 2000 mg/l. This is also in agreement with the work of Saggioro et al. (2011).

Zhang et al. (2002) examined the dependence of the photooxidation kinetics of methylene blue on TiO_2 loading and found that the rates increase with TiO_2 loading up to a limit and then decrease to a constant value. Others (Daneshvar et al. 2003; Sohrabi and Ghavami 2008) also found the same characteristics.

The effect of TiO_2 loading on percentage degradation of the dyes Reactive Yellow 17(RY17), Reactive Red 2(RR2), Reactive Blue 4 (RB4) has been examined by varying its amount from 100 to 600 mg/100 ml of the dye solution (Neppolian et al. 2002b). The percentage degradation was found to increase rapidly with an increase in the amount of TiO_2 from 100 to 300 mg/100 ml for all the three dyes. In the case of RR2 and RB4, the percentage degradation increased only slightly in the range 300–500 mg of TiO_2, while in the case of RY17, percentage degradation was found to be constant with increase in TiO_2 loading suggesting that upper level for catalyst effectiveness exists.

Further increase in the amount of TiO_2 from 500 to 600 mg in RY17 decreased the percentage degradation. Neppolian et al. (2002a) found that the degradation percentage or Reactive Blue 4 increases linearly with catalyst loading up to 2.5 g/l. Catalyst loading was varied from 1 to 4 g/l of the dye solution (4×10^{-4} M).

An increased loading of catalyst increases the quantity of photons adsorbed and consequently the degradation rates (Herrmann 1995; Muruganandham and Swaminathan 2006). On the other hand, an increase in the catalyst loading increases the solution opacity and leads to a decrease in the penetration of the photon flux in the reactor and thereby decreases the photocatalytic degradation rate (Kamble et al. 2003; Gogate and Pandit 2004). Moreover, a loss in surface area by agglomeration (particle–particle interactions) at high solid concentration is also observed (Kaneco et al. 2004). Excessive light scattering by the suspended particles also has a progressively diminishing influence on the reaction rate. The available number of dye molecules can also be insufficient for adsorption to a greater number of TiO_2 particles (Zhang et al. 2002; Sohrabi and Ghavami 2008). This can be rationalized in terms of availability of active sites on TiO_2 surface and the light penetration of photoactivating light into the suspension (Neppolian et al. 2002b). An optimum amount of TiO_2 has to be added to avoid unnecessary excess catalyst and also to ensure total absorption of light photons for efficient photomineralization. Herrmann (1999) found that the optimum loading of photocatalyst was dependent on the initial solute concentration

Effect of different photocatalysts

Photocatalytic activity of different photocatalysts varies with the differences in the lattice mismatch, and BET-surface and impurities on the catalyst's surface affect the adsorption behavior of a pollutant and the lifetime and recombination rate of electron–hole pairs. A large surface area can be the determining factor in certain photodegradation reactions, as a large amount of adsorbed organic molecules promote the reaction rate (Watson et al. 2003; Chen et al. 2004; Xiaohong et al. 2003). On the other hand, the predominant way of electron–hole recombination may be different depending on the particle size (Zhang et al. 1998).

Titanium dioxide (TiO_2) or titania is a well-known photocatalyst material. Anatase, rutile, brookite and titanium dioxide (B) or TiO_2 (B) are the four mineral forms of TiO_2. It has been found that anatase TiO_2 takes part in photocatalytic reaction more efficiently than the other forms of titanium dioxide (Tanaka et al. 1991). This superiority originates from its band gap, which is 3.2 eV, compared to 3.0 eV of rutile. It means the conductive zone of anatase type is 0.2 eV higher and therefore is more favorable for driving conjugate reactions involving electrons. Moreover, during photooxidation reaction, very stable surface peroxide groups can be formed in the anatase type of this oxide (Baraton and Merhari 2004; Luo and Ollis 1996). Furthermore, there are also studies which claim that a mixture of anatase (70–75 %) and rutile (30–25 %) is more active than pure anatase (Muggli and Ding 2001; Ohno et al. 2001).

Degussa P-25 titanium dioxide is mainly used as the photocatalyst. It is mostly in the anatase form and has a BET-surface area of 50 m^2/g corresponding to a mean particle size of 20–30 nm (Rachel et al. 2002; Bickley et al. 1991). UV100 consists of 100 % anatase with a specific BET-surface area >250 m^2/g and primary particle size of 5 nm (Lindner et al. 1997). The photocatalyst PC500 has a BET-surface area of >250 m^2/g with 100 % anatase and primary particle size of 5–10 nm (Rachel et al. 2002). TiO_2-Tytanpol A11 is totally in the anatase form and has a crystalline size of 37.3 nm, specific surface area of 11.4 m^2/g, a mean pore diameter of about 7.7 nm and a band gap of 3.31 eV (Zielińska et al. 2003).

Saquib and Muneer (2003) investigated the influence of three different photocatalysts (P25, UV100 and PC500) on the degradation kinetics of gentian violet. They observed that the mineralization and degradation of dye proceeds much more rapidly in the presence of P25 as compared with other photocatalysts. Higher concentration of electrons and holes is available for suitable reactants to initiate the photocatalytic reaction due to slow recombination of (e^-/h^+) pair of P25.

Qamar et al. (2005) also tested the photocatalytic activity of three different commercially available TiO_2 powders (namely P25, UV100 and PC500) on the degradation kinetics of chromotrope 2B and amido black 10B. They observed that the degradation of both dyes proceeds much more rapidly in the presence of Degussa P25 as compared with other TiO_2 samples.

Sivalingam et al. (2003) experimented with Degussa P-25 TiO_2 and combustion synthesized TiO_2 for the degradation of methylene blue under UV exposure. Complete degradation of methylene blue of initial concentration of 200 ppm with the catalyst loading of 1 kg/m^3 of combustion synthesized TiO_2 occurred in 65 min, while Degussa P-25 showed reduction in concentration up to 100 ppm under identical conditions. The degradation of dyes under solar radiation with an initial concentration of 100 ppm and catalyst loading of 1 kg/m^3 was also investigated. Complete degradation occurred in 3 h and 40 min, whereas time required for the complete degradation of MB under similar operating condition was 5 h even for the initial concentration of 20 ppm (Nosaka and Fox 1988) for commercial Degussa P-25 catalyst. This indicates that the photocatalytic activity of the combustion synthesized TiO_2 is much higher than commercial Degussa P-25 catalyst for both UV and solar exposure. The higher photocatalytic activity of the combustion synthesized TiO_2 over commercial catalysts may be attributed to higher surface area, high crystallinity and pure anatase crystal structure.

Giwa et al. (2012) studied the degradation of Reactive Yellow 81 and Reactive Violet 1 by two commercially available catalysts TiO_2-P25 (Degussa) and TiO_2 anatase and found Degussa P25 to be more effective for degradation. The high photoreactivity of TiO_2-P25 has been attributed to two factors: the slow recombination of the electron–hole pair, and its large surface area (Muruganandham et al. 2006).

Zielińska et al. (2003) worked with TiO_2-Tytanpol A11 and TiO_2-Degussa P25 for the decomposition of Reactive Red 198 (RB198), Acid Black 1 and Acid Blue 7 (AB7). They found photocatalyst P25 to be more active than A11.

After 100 min of irradiation, new absorption bands that are characteristic of the intermediate by-products appeared in the region of 1700 and 2800–3100 cm^{-1} for RR198 and AB7. This suggests that created by-products are adsorbed on the photocatalyst. Higher specific surface area and lower band gap energy of P25 prevents by-product formation on active sites and accelerates activity for photocatalysis.

Effect of intensity and wavelength of light

TiO_2 has a wide band gap (3.2 eV—anatase, 3.00 eV—rutile and 3.13 eV—brookite), which limits its absorption in the UV region of solar spectrum (Kuang et al. 2009; Khan et al. 2002; Atta et al. 2011).

The wavelength and intensity of the UV light irradiation source affects the degradation of dye in aqueous solution using TiO_2 catalyst powder in photocatalytic reactor (Konstantinou and Albanis 2004). The artificial UV irradiation is more reproducible than sunlight and can bring higher efficiency in the degradation of textile dyes. However, solar energy, because of its abundance and non-hazardous nature, is expected to emerge as an alternative cost effective light source (Neppolian et al. 2002b; Muruganandham and Swaminathan 2004). Usually, solar photocatalytic degradation reactions are carried out by using solar illumination directly (Gonçalves et al. 2005) or using parabolic collectors (Malato et al. 2002).

Ollis et al. (1992) stated that:

(1) At low light intensities (0–20 mW/cm^2), the rate would increase linearly with increasing light intensity (first order).
(2) At intermediate light intensities beyond a certain value (approximately 25 mW/cm^2), the rate would depend on the square root of the light intensity (half order).
(3) At high light intensities the rate is independent of light intensity. There are more photons per unit time and unit area; thus, the chances of photon activation on catalyst surface increase and therefore the photocatalytic power is stronger. However, as the light intensity increases, the number of activation sites remains the same thus the reaction rate only reaches a certain level even when the light intensity continues to increase.

The photocatalytic degradation of Reactive Yellow 17, Reactive Red 2, Reactive Blue 4 dyes using TiO_2 as photocatalyst and solar/UV irradiation as light source has been carried out by Neppolian et al. (2002b). They found UV irradiation to be more effective than solar irradiation. The difference in the rate of degradation is attributed to difference in the input energy. The energy of UV irradiation is large compared to band gap energy of the catalysts. Hence, the problem of electron–hole recombination is largely avoided with UV source. But in sunlight only 5 % of the total radiation possesses the optimum energy for the band gap excitation of electrons (Fatin et al. 2012). Hence, the percentage degradation is found to be less in solar radiation of textile dyes. It was also found that the percentage degradation of all the three dyes increased with increasing solar light intensity. Under the higher intensity of light irradiation, the enhancement was considerably higher because the electron–hole formation is predominant, and hence, electron–hole recombination is negligible. However, at lower light intensity, electron–hole pair separation competes with recombination which in turn decreases the formation of free radicals, thereby causing less effect on the percentage degradation of the dyes (Bahnemann 1999).

Hung and Yuan (2000) studied the effect of light intensity for the degradation of Orange G. The light intensity ranged from 215 to 586 μW/cm^2. The reaction rates for photolysis of Orange G increased with increasing light intensity.

Chanathaworn et al. (2012) varied the irradiation intensity of black light lamp in the range of 0–114 W/m^2 and examined the effects of irradiation intensity on the decolorization of the Rhodamine B. The results indicated that an increase in the irradiation intensity of black light lamps enhanced the dye decolorization.

Liu et al. (2006) conducted the experiment in three different light intensities (1.24 mW/cm^2, 2.04 mW/m^2, 3.15 mW/m^2) and found that the decolorization of Acid Yellow 17 increases with increasing light intensity. Enhancement of the decolorization rate with increasing light intensity was also observed (Sakthivel et al. 2003; So et al. 2002).

Rao et al. (2004) found that the rate of photocatalytic decomposition of acid orange 7 (AO7) is approximately 1.5 times higher in full sunlight than in artificial UV light. Though in the case of AO7, the direct photolysis plays a minor role in sunlight, but it is not completely negligible due to the strong absorption of the dye in the visible range.

The wavelength of the irradiation can affect the efficiency of photolysis. It is believed that shorter wavelength of irradiation can promote the electron hole generation and consequently enhance the efficiency of the catalyst (Nguyen et al. 2014). This has been observed in the CO_2 photoreduction over Ag/TiO_2 or TiO_2, the photodegradation of 4-chlorophenol over TiO2 and the photodecomposition of organic contaminants over $CaBi_2O_4$. Many organic compounds absorb in the UV (e.g., higher energy region). Irradiating with too low a wavelength may result in unintended side reactions. Lower wavelength means more energy not more photons.

Effect of reaction temperature

Mozia et al. (2009) observed that in case of Acid Red 18, an increase in the reaction temperature resulted in an increase in the photodegradation rate constant. The effect was observed especially in case of the TiO_2 loadings equal to 0.3 and 0.5 g/dm^3. The increase in solution temperature from 313 to 323 K resulted in an 11 and 13 % increase in the rate constant for TiO_2 loadings of 0.3 and 0.5 g/dm^3, respectively. Rising the temperature up to 333 K resulted in the increase in the rate constant k for additional 10 % for both catalyst loadings. The decrease in temperature favors adsorption of the reactant which is a spontaneous exothermic phenomenon. In addition, the lowering in temperature also favors the adsorption of the final reaction product, whose desorption tends to inhibit the reaction. On the contrary, when temperature tends to the boiling point of water, the exothermic adsorption of reactant becomes disfavored and tends to limit the reaction (Mehrotra et al. 2005).

The effect of temperature on the reaction was also studied by Soares et al. (2007). The optimum range of operational temperatures was found to be in the range 40–50 °C. At low temperature, desorption of the products formed limits the reaction because it is slower than the degradation on the surface and the adsorption of the reactants. On the other hand, at a higher temperature, the limiting stage becomes the adsorption of the dye on TiO_2. Zhou and Ray (2003) postulated that the reduction of the adsorptive capacity associated with the organics and dissolved oxygen at higher temperatures decreases the rate constant. Therefore, the optimum temperature is generally comprised between 293 and 353 K (Mehrotra et al. 2005).

Summary

Effective destruction of dyes is possible by photocatalysis in the presence of TiO_2 suspensions. Various operational parameters affect the activities of TiO_2 photocatalysts. Since the influence of the parameters has been in some cases controversial, 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. The better understanding of the photocatalytic process and the operative conditions could give great opportunities for its application for the destruction of dyes.

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