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Principles and mechanisms of photocatalytic dye degradation on TiO₂ based photocatalysts: a comparative overview

Anila Ajmal,^a Imran Majeed,^b Riffat Naseem Malik,^a Hicham Idriss^c
and Muhammad Amtiaz Nadeem^{*ac}

The total annual production of synthetic dye is more than 7×10^5 tons. Annually, through only textile waste effluents, around one thousand tons of non-biodegradable textile dyes are discharged into natural streams and water bodies. Therefore, with growing environmental concerns and environmental awareness there is a need for the removal of dyes from local and industrial water effluents with a cost effective technology. In general, these dyes have been found to be resistant to biological as well as physical treatment technologies. In this regard, heterogeneous advanced oxidation processes (AOPs), involving photo-catalyzed degradation of dyes using semiconductor nanoparticles is considered as an efficient cure for dye pollution. In the last two decades TiO₂ has received considerable interest because of its high potential as a photocatalyst to degrade a wide range of organic material including dyes. This review starts with (i) a brief overview on dye pollution, dye classification and dye decolourization/degradation strategies; (ii) focuses on the mechanisms involved in comparatively well understood TiO₂ photocatalysts and (iii) discusses recent advancements to enhance TiO₂ photocatalytic efficiency by (a) doping with metals, non-metals, transition metals, noble metals and lanthanide ions, (b) structural modifications of TiO₂ and (c) immobilization of TiO₂ by using various supports to make it a flexible and cost-effective commercial dye treatment technology.

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Dye pollution-an overview

Dyes play a vital role in various branches of the dyeing and textile industries. Over 100 000 commercially available synthetic dyes are the most frequently used dyes in such industries. These dyes are usually derived from two main sources *i.e.* coal tar and petroleum intermediates with a total annual production of more than 7×10^5 tons.^{5–7} Annually, through textile waste effluents, around 15% (one thousand

tons) of these non-biodegradable textile dyes are discharged into natural streams and water bodies.^{1–4,8,9} Typically, on an average for every kilogram of cloth, being processed in dyeing and finishing plants, about 120–280 L of water is being consumed.¹⁰

Konstantinou and Albanis¹¹ reported that industrial dye stuffs and textile dyes constitute one of the largest groups of toxic organic compounds. According to an estimate made by World Bank, nearly 17–20% water pollution has the major contributors related to textile finishing and dyeing industries. According to a study by Kant, out of major identified wastewater toxic chemicals, 72 chemicals were solely released by the textile dyeing and nearly 30 of such chemicals were not treatable.¹² In

^aDepartment of Environmental Sciences, Quaid-i-Azam University, Islamabad 4200, Pakistan. E-mail: NadeemMI@SABIC.com

^bDepartment of Chemistry, Quaid-i-Azam University, Islamabad 4200, Pakistan

^cCRI-KAUST, Saudi Basic Industries Corporation, Thuwal, Saudi Arabia

Anila Ajmal has recently completed her M.Phil in Environmental Remediation from Quaid-i-Azam University, Islamabad, Pakistan. She has recently completed her M.Phil thesis project that focuses photocatalytic treatment of dye contaminated wastewater. She obtained her BS honors (2010) in Environmental Sciences from Lahore College for Women University, Lahore, Pakistan. Her main research interests include applications of photocatalytic techniques for the remediation of environmental contaminants.

Imran Majeed is currently doing his Ph.D at Department of Chemistry, Quaid-i-Azam University Islamabad, Pakistan. His Ph.D project is about hydrogen production from renewables using visible light active TiO₂ based photocatalysts. He completed Masters (2005) in Applied Chemistry from University of Engineering and Technology, Lahore, Pakistan and M.Phil (2008) in Analytical/Inorganic Chemistry from the same University. Before starting his Ph.D, he was been working as Senior Scientist in Pakistan Atomic Energy Commission, Islamabad, Pakistan.

1974, Ecological and Toxicological Association of the Dyestuffs Manufacturing Industry (ETAD) was formed with an aim to protect consumers by preventing and reducing environmental damages by fully cooperating with government over the concerns related to the toxicological impact of their own products.¹³ In an ETAD survey, of all 4000 tested dyes, 90% dyes were found to be having their LD₅₀ values greater than 2×10^3 mg kg⁻¹. Among all tested dyes diazo, direct and basic dyes showed the highest rates of toxicity.¹⁴

Bright coloured dyes such as reactive and acid dyes are water soluble and the most problematic dyes to remove.¹⁵ Conventional and municipal aerobic treatment systems have been proved to be ineffective on both type of dyes.^{16,17} Compared to other types of dyes, reactive dyes are least taken up by the fabric during dyeing process, implying that the remaining quantity of dye is directly lost into the wastewater.¹⁸ Leena and Raj¹⁹ reported that reactive dye effluent possess the ability to remain stable and unaffected in environment for several years *i.e.* hydrolyzed reactive blue 19 has a half-life of about 46 years. Dispersed dyes do not ionize in an aqueous medium enhancing

their ability to bioaccumulate in aquatic living organisms.²⁰ Currently concerns related to the dye effluents are arising as many dyes are synthesized by known carcinogens such as aromatic compounds and benzidine.²⁰

Chung *et al.*²¹ have illustrated the dye reduction in the intestinal environment, that resulted into the formation of toxic amines. Moreover, azo dyes are readily reduced into the aromatic amines that are potentially hazardous as a result of anaerobic treatment conditions.^{22–25}

In addition to dye pollution, in textile industries processing prior to dyeing procedure such as mercerization, scouring, sizing and bleaching results into the production of bleaching as well as scouring agents. However, amongst all of above mentioned concerns, colour removal from wastewater is the most complex and difficult task.¹⁸ Dyes are usually the first contaminant to be recognized in industrial wastewater due to their high visibility even in minute concentrations (<1 ppm).²⁶ These coloured wastewaters are a considerable source of eutrophication as well as non-aesthetic pollution that can produce dangerous by-products by further oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. Apart from the toxic effects of dyes in wastewater streams, presence of dyes can cause reduced light penetration resulting in reduced photo-synthetic activity thus making oxygen unavailable for biodegradation of microorganism in the water.²⁷

Apart from the textile industry, leather tanning industry,²⁸ paper industry,²⁹ food industry,³⁰ hair colourings,³¹ photo-electrochemical cells³² and light-harvesting arrays^{33,34} also contribute towards the presence of dyes in wastewater. Majority of dyes used in various industries are toxic and carcinogenic thus posing a serious hazard to humans as well as to marine ecosystem.³⁵ Therefore, the impact of dyes released into the environment have been studied extensively in last few years.^{36,37}

Riffat Naseem Malik is currently an Associate Professor as well as Chairperson of Department of Environmental Sciences, Quaid-i-Azam University Islamabad, Pakistan. Before this, she worked as Post-Doctoral Research Fellow (2001–2003) at Lancaster Environmental Centre, Lancaster University, UK. She has completed her Ph.D in Environmental Biology from The Reading University, Reading, UK. She had received Research Fellowship from Department of Geography, University of Turku, Finland after completing her M.Phil and M.Sc from Quaid-i-Azam University, Islamabad, Pakistan. She is the author and co-author of more than 90 scientific publications.

Hicham Idriss is currently working at CRI-KAUST, Saudi Basic Industries Corporation, Thuwal, Saudi Arabia as Chief Scientist. Formerly, he worked as Aberdeen Energy Futures Chair and Professor of Chemistry at the University of Aberdeen and Robert Gordon University, UK from 2008 to 2010. He is also Adjunct Professor at the Department of Chemical Engineering, Louisiana State University in the USA. Prior to 2008 he was Associate Professor at the Department of Chemistry, the University of Auckland in New Zealand where he worked for 13 years. He served as a member of the New Zealand National Energy Panel who delivered the 2020 Energy report to the New Zealand Government in 2008. He has obtained his B.Sc (1984), M.Sc (1985), Ph.D (1987) and habilitation (1997) from the University of Strasbourg in France and has postdoctoral and research associate positions at the University of Delaware and University of Illinois, Urbana (USA). He is the author and co-author of over 140 scientific papers and has served/is serving at the editorial board of scientific journals including Applied Catalysis A, Catalysis Today and Catalysis Survey from Asia. His main interest in surface science and catalysis is on metal oxides and their interface with transition metals at the fundamental and applied levels.

Muhammad Amtiaz Nadeem is currently an Assistant professor at Quaid-i-Azam University Islamabad. He completed Masters (2003) in Chemistry from University of the Punjab, Lahore, Pakistan and M.Phil in Analytical/Inorganic Chemistry (2006) from Quaid-i-Azam University Islamabad, Pakistan. He joined Prof. Hicham Idriss group based at University of Auckland as a Ph.D student in 2008 and in 2009 moved with him at the Energy Future Center in Aberdeen, UK, to complete his Ph.D in 2012. His Ph.D thesis has been placed in Dean, Faculty of Natural Sciences, University of Auckland theses excellence list. His thesis was also nominated for University of Auckland best thesis award for 2012. His main interest in surface science and catalysis is on metal oxides and their interface with transition metals at the fundamental and applied levels.

This paper presents an overview of the recent research improvements targeting the degradation of various dyes by using TiO_2 as a potential photocatalyst.

Dye classification

Dyes usually have many structural varieties and their complete classification with respect to one parameter is very difficult and of no use from practical understanding point of view. However, dyes are generally divided into different groups and classes depending on their source, general dye structure and the fiber type with which they are most compatible as shown in the Fig. 1.

Among major dye categories, azo dyes are the largest group of colourants and over 50% of all the dyes used in industries are azoic dyes. *Azo dyes are characterized by double bond of nitrogen ($-\text{N}=\text{N}-$), where at least one of the nitrogen atom is attached to an aromatic group (rings of naphthalene or benzene).* Moreover, they have amphoteric properties due to the presence of additional carboxyl, hydroxyl, amino or sulfoxyl functional groups. Azo dyes can behave anionic (deprotonation at the acidic group), cationic (protonated at the amino group) or non-ionic depending upon the pH of the medium.³⁸ Most notable azo dyes are: acid dyes, basic dyes (cationic dyes), direct dyes (substantive dyes), disperse dyes (non-ionic dyes), reactive dyes, vat dyes and sulfur dyes.³⁹ Dyes based on general structure can also be classified as anionic, non-ionic and cationic dyes. The anionic dyes mainly include direct acidic and reactive dyes.²⁶ Major nonionic dyes include; disperse dyes which does not ionizes in the aqueous environment and the major cationic dyes include basic and disperse dyes.³⁸

Acidic dyes are named so as they are normally applied to the nitrogenous fibers or fabrics in inorganic or organic acid solutions. Basic dyes give cations in the solution which are generally applied to acrylic and modacrylic fibers. Direct dyes are applied in aqueous bath containing ionic salts and electrolytes that bond to fibers/fabrics by electrostatics forces.^{40,41} Disperse dyes have low solubility in water, but they can interact with the

polyester chains by forming dispersed particles.⁴² The wash fastness with disperse dyes varies with the type of fibers being used for dyeing purpose *i.e.* poor on acetate, excellent on polyester.³⁸ Reactive dyes are primarily utilized on cellulosic fibers, but occasionally on protein fibers and nylon as well forming covalent bond with the appropriate textile functionality.⁴³ Sulfur dyes are used on cellulosic fibers to produce dull shades such as navy, black and brown. They have excellent fastness in most areas, but fades off when exposed to chlorine. Vat dyes that works with a special chemistry having excellent fastness in all areas and especially on exposure to chlorine and bleach.^{44–46} Further characteristics of these dyes are summarized in Table 1.

Dye treatment strategies

Apart from their physically unpleasant nature and toxicity, ever increasing massive production rate of dyes due to increasing industrialization have led to the necessity of effective treatment.^{47,48} Therefore, in order to treat such obvious and challenging effluents, a wide range of technologies have been tested to reduce their potential magnified impacts on environment. *Traditional physical techniques* such as activated carbon, adsorption, reverse osmosis, ultrafiltration can be used for dye removal. However, these processes simply transfer the pollutants from one to another medium causing secondary pollution. This generally requires further treatment of solid-wastes and regeneration of the adsorbent, which adds more cost to the process. *Chemical process* such as chlorination, ozonation,⁴⁹ adsorption on organic or inorganic matrices, precipitation, chemical oxidation processes,⁵⁰ advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions,⁵¹ $\text{H}_2\text{O}_2/\text{UV}$ processes⁵² and photodegradation through photocatalysis are also commonly being used for the synthetic dye removal.⁵³ However, toxic unstable metabolites as a result of most of these processes⁵⁴ imparts adverse effects on animal and human health.⁵⁵

Biological processes involving microbiological or enzymatic decomposition⁵⁶ and biodegradation have also been used for dye removal from wastewaters. Moutaouakkil *et al.*⁵⁷ isolated Azoreductase enzyme from *Enterobacter agglomerans* having ability to grow fast on methyl red dye under aerobic condition by catalyzing reductive cleavage of azo bonds. Anaerobic conditions also facilitates⁵⁸ the azo bond rupture leading to the colour disappearance but result in incomplete mineralization of toxic and carcinogenic by-products.⁵⁹ However, it has been found that these conventional biological treatment processes are ineffective for synthetic dyes having recalcitrant nature.^{60,61} In recent years, a broad range of synthetic dyes have been extensively studied to develop a more promising technology based on *advanced oxidation process (AOPs)* that has the ability to oxidize contaminants quickly and non-selectively.^{50,62,63} AOPs rely on *in situ* production of highly reactive hydroxyl radicals (OH^\bullet) which can virtually oxidize any compound present in the water matrix, often at a diffusion controlled reaction speed. These radicals are produced with the help of one or more primary oxidants (*e.g.* ozone, hydrogen peroxide, oxygen) and/or energy sources (*e.g.* ultraviolet light) or catalysts (*e.g.* titanium dioxide).^{64,65} This



Fig. 1 Flow chart indicating dye classification on the basis of dye chemical constitution and its application.

Table 1 Types and characteristic classification of azo dyes

| Dye class | Characteristics | Fiber | Dye fixation (%) | Pollutant |
|------------|---|--|------------------|--|
| Acidic | Water-soluble anionic compounds | Wool, nylon, cotton blends, acrylic and protein fibers | 80–93 | Colour; organic acids; unfixed dyes |
| Basic | Water-soluble, applied in weakly acidic dye baths, very bright dyes | Acrylic, cationic, polyester, nylon, cellulosic, and protein fibers | 97 and 98 | NA |
| Direct | Water-soluble, anionic compounds, applied without mordant | Cotton, rayon and other cellulosic fibers | 70–95 | Colour; salts; unfixed dye; cationic fixing agents; surfactant; defoamer; levelling and retarding agents; finish; diluents |
| Dispersive | Insoluble in water | Polyester, acetate, modacrylic, nylon, polyester, triacetate and olefin fibers | 80–92 | Colour; organic acids; carriers; levelling agents; phosphates; defoamers; lubricants; dispersants; delustrants; diluents |
| Reactive | Water-soluble, anionic compounds, largest dye class | Cotton, cellulosic and wool fibers | 60–90 | Colour; salt; alkali; unfixed dye; surfactants; defoamer; diluents; finish |
| Sulphur | Organic compounds containing sulfur or sodium sulfide | Cotton and other cellulosic fibers | 60–70 | Colour; alkali; oxidizing agent; reducing agent; unfixed dye |
| Vat | Oldest dyes, chemically complex, water-insoluble | Cotton, wool and other cellulosic fibers | 60–70 | Colour; alkali; oxidizing agents; reducing agents |

review focuses on mechanistic and practical aspects of dye degradation by TiO_2 based photocatalysts.

Photocatalytic dye treatment

Heterogeneous photocatalysis has proved to be as an efficient tool for degrading both atmospheric and aquatic organic contaminants.⁶⁶ It uses the sunlight in the presence of a semiconductor photocatalyst to accelerate the remediation of environmental contaminants and destruction of highly toxic molecules.^{67,68} The type of the radiation used depends on the type of catalyst *i.e.* pure TiO_2 works under UV light (370–415 nm). Visible light can also be used for the excitation purpose but due to unavailability of proper catalyst and other contributing factor, it has been considered as less effective source for irradiation. Generally speaking, final products of TiO_2 photocatalysis have not been reported properly, which often makes evaluation of the photocatalysis difficult. The reactions of dye molecules on TiO_2 photocatalysts are often confusing, and could be classified into the following categories according to the photocatalysis products. (1) Photodecolourization^{69–73} involves simple photooxidation or photoreduction where dyes can return to the original form by either corresponding back reduction or back oxidation, respectively. (2) Photodegradation^{74–79} involves dye decomposition to some stable products. It is the most widely used name for photocatalytic dye treatment. (3) Photomineralization^{80–84} is regarded as complete decomposition to CO_2 , H_2O , N_2 , NO_3^- , NO_2^- *etc.* The goal of ideal photocatalysis should be mineralization. (4) Photodecomposition^{76,77} could imply both photodegradation and mineralization differently, depending also on the researchers. However, it rarely involves decolourization. Hereafter in this

review care will be taken to use these terminologies as precisely as possible.

In order to assess the degree of dye photodegradation achieved during the treatment, generally formation of CO_2 and inorganic ions is determined.^{81,82,85–88} However, it is impossible to measure the exact concentration of these ions in case of real wastewaters. In such cases the determination of total organic carbon (TOC) or the measurement of the chemical oxygen demand (COD) or the biological oxygen demand (BOD) is used to monitor extent of dye mineralization.^{82,83,86,89–92} In general, at lower dye concentration and for compounds which do not form stable intermediates, complete mineralization proceed with similar half-lives for parent dye and the intermediates but at higher concentration intermediates mineralization is slower than the degradation of the parent dye. To date most azo dyes have been found to undergo complete mineralization except triazine containing dyes.^{81–84,90} The later does not undergo complete mineralization due to high stability of triazine nucleus and the stable cyanuric acid intermediates.⁹³ However, fortunately these intermediates are not toxic.^{80,91,92} Usually COD or TOC values decrease with irradiation time whereas the amount of NH_4^+ , Cl^- , SO_4^{2-} and NO_3^- ions increase.^{81,91,94}

For chlorinated dye molecules, Cl^- ions are the first of the ions which appear during photocatalytic degradation.^{90,92,95} This could be interesting in photocatalytic biological treatment which is generally not efficient for chlorinated compounds. Nitrogen is mineralized into NH_4^+ , NO_3^- and N_2 depending upon initial oxidation state of nitrogen, the substrate structure and irradiation time.^{96,97} The total amount of nitrogen-containing ions present in the solution at the end of the experiments is usually lower than that expected from stoichiometry indicating that N-containing species remain adsorbed

in the photocatalyst surface or most probably, that significant quantities of N_2 and/or NH_3 have been produced and transferred to the gas-phase.^{81,83,90}

The dyes containing sulfur atoms are mainly mineralized into sulfate ions stoichiometrically.^{92,95} Non-stoichiometric formation of sulphate ions is usually explained by a strong SO_4^{2-} adsorption on the photocatalyst surface which could partially inhibit the reaction rate.^{81,98,99} Generally, it is found that nitrate anions have little effect on the kinetics of reaction whereas sulfate, chloride and phosphate ions, especially at concentrations of greater than 10^{-3} mol dm⁻³, can reduce the rate by 20–70% due to the competitive adsorption at the photoactivated reaction sites.⁹⁸

TiO₂ as dye treatment photocatalyst

Among various types of photocatalysts, titanium dioxide (TiO₂) assisted photocatalytic oxidation has received much attention the last few years due to its non-toxicity, strong oxidizing power and long-term photostability.¹⁰⁰ Titanium dioxide (TiO₂) is a white powder semiconductor having a wide band gap of 3.0–3.2 eV.^{101–103} It can be excited by UV light with a wavelength below ca. 415 nm (in its rutile form). However, the use of TiO₂ is limited as only about 3–4% of the solar spectrum falls within UV range.^{102,104–106} In general, there are three types of titanium dioxide *i.e.* anatase, rutile and brookite. In general TiO₂ nanoparticles are widely available commercially or can be easily prepared using sol gel method. Typically, anatase phase is often found having particle size equal to 10 nm or less with a band gap of 3.2 eV corresponding to a UV wavelength of 385 nm.¹⁰⁷ Comparatively, though some exceptions exists, rutile phase generally exists having particle size in the order of 50 nm or so.¹⁰⁸ Moreover, rutile has a smaller band gap of 3.0 eV with excitation wavelengths extending to visible 410 nm range. Thermodynamics dictates that heating the anatase phase results in gradual phase transformation of anatase to rutile and therefore depending on the method of preparation mix phase anatase-rutile can be easily prepared or purchased. For example, some commercially available TiO₂ that is a mixture of two phases, 80% anatase and 20% rutile, and has usually a BET area of 50 m² g⁻¹ has widely been studied.¹⁰⁹

Most of the studies have been carried out with anatase phase due to its high photocatalytic efficiency and adsorption affinity for the organic compounds as compared to the rutile phase.^{110,111} Shiga *et al.*¹¹² using nanocrystalline film electrodes of TiO₂ for photoelectrochemical activities showed that the anatase has a higher photoactivity than rutile phase at a longer wavelength. This is due to the fact that anatase phase due to its greater hole trapping ability (about 10-fold) exhibits lower recombination rates compared to rutile type.^{113,114} Therefore, anatase is generally regarded as photochemically more active phase of TiO₂ due to these combined effect.¹⁰⁷ Moreover, recently developed various forms of TiO₂, such as TiO₂ powders, TiO₂ film,¹¹⁵ supported TiO₂,^{116,117} TiO₂ nanotubes¹¹⁸ and doped TiO₂^{119,120} have been evaluated through degradation of dyes and phenolic compounds. Such studies demonstrated the higher

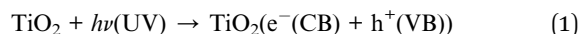
efficiency of various forms of TiO₂ used for removal of dyes and phenolic compounds from aqueous solutions.¹²¹

Basic principles and mechanism for photocatalyzed dye degradation

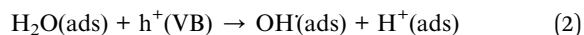
Indirect dye degradation mechanism

The indirect heterogeneous photocatalytic oxidation mechanism using semiconducting materials can be summarized as follows.^{122,123}

a. Photoexcitation. Photocatalytic reaction is initiated when a photoelectron is promoted from the filled valence band of a semiconductor photocatalyst *i.e.* TiO₂ to the empty conduction band as a result of irradiation. The absorbed photon has energy ($h\nu$) either equal or greater than the band gap of the semiconductor photocatalyst. The excitation process leaves behind a hole in the valence band (h_{VB}^+). Thus as a net result, electron and hole pair (e^-/h^+) is generated as indicated by the eqn (1) below.

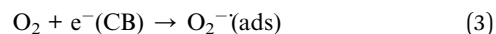


b. Ionization of water. The photogenerated holes at the valence band then react with water to produce OH[•] radical.



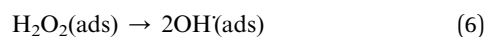
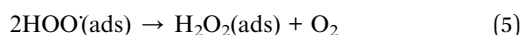
The HO[•] radical formed on the irradiated semiconductor surface are extremely powerful oxidizing agent. It attacks adsorbed organic molecules or those that are very close to the catalyst surface non-selectively, causing them to mineralize to an extent depending upon their structure and stability level. It does not only easily attack organic pollutants but can also attack microorganisms for their enhanced decontamination.¹²⁴

c. Oxygen ionosorption. While the photogenerated hole (h_{VB}^+) reacts with surface bound water or OH[•] to produce the hydroxyl radical, electron in the conduction (e_{CB}^-) is taken up by the oxygen in order to generate anionic superoxide radical (O_2^-).



This superoxide ion may not only take part in the further oxidation process but also prevents the electron-hole recombination, thus maintaining electron neutrality within the TiO₂ molecule.

d. Protonation of superoxide. The superoxide (O_2^-) produced gets protonated forming hydroperoxyl radical (HO_2^{\bullet}) and then subsequently H_2O_2 which further dissociates into highly reactive hydroxyl radicals (OH[•]).





Both oxidation and reduction processes commonly take place on the surface of the photoexcited semiconductor photocatalyst. The complete process has been represented by the Fig. 2.

Direct mechanism for dye degradation

Owing to their ability to easily absorb some of visible light, another mechanism of photocatalytic dye degradation can also occur under visible light. This mechanism involves the dye excitation under visible light photon ($\lambda > 400$ nm) from the ground state (Dye) to the triplet excited state (Dye*). This excited state dye species is further converted into a semi-oxidized radical cation (Dye⁺) by an electron injection into the conduction band of TiO₂.¹²⁵ Due to reaction between these trapped electrons and dissolved oxygen in the system superoxide radical anions (O₂^{•−}) are formed which in turn result into hydroxyl radicals (OH[•]) formation. These OH radicals are mainly responsible for the oxidation of the organic compounds represented by the equations and Fig. 3 below.^{126–128}



According to many studies, indirect mechanism is generally prevalent over direct mechanism and its contribution to the dye degradation is much more pronounced than the visible light initiated mechanism. The latter is believed to be a far slower reaction compared to indirect mechanism.^{126,129}

Factors affecting photocatalytic dye degradation

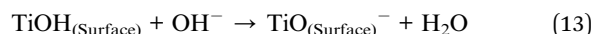
Effect of pH

The pH is one of the significant parameters for the photocatalytic dye degradation as it can influence dye reaction rates in multiple ways as explained here on. It can influence dye adsorption onto the semiconductor surface¹²¹ as catalyst surface charge depends on the pH of a given solution. Zhu *et al.*¹³⁰



Fig. 3 Pictorial representation of direct dye degradation process.

demonstrated that pH effect is related to the surface-charge properties of the photocatalysts, and could be explained on the basis of point of zero charge (PZC). The point of zero charge for TiO₂ particles is $\text{pH}_{\text{pzc}} = 6.8$.³ At a pH values lower than pH_{pzc} (pH < 6.8) or at acidic solution, the surface of the catalyst gets positively charged and *vice versa*^{131,132} according to the eqn (12) and (13) given below.



When the pH is lower than the PZC value the adsorbent surface is positively charged and the surface becomes anions attracting/cation repelling. Conversely, above PZC the surface is negatively charged and the surface becomes cation attracting/anion repelling.

Zhu *et al.*¹³⁰ explained that highest degree of decolourization of methyl orange observed at pH 2 is attributed to the electrostatic attraction between the positively charged catalyst surface and methyl orange anions, which led to the increase in degree of adsorption and 97% photodecolourization. However, the dye treatment results based on dye adsorption strength cannot be explained as there are many other parameters operating at the same time. For example, Muruganandham *et al.*¹³³ found that increasing pH from 1 to 9 increased decolourization rates for reactive orange 4 (an anionic dye) from 25.27% to 90.49% after 40 min and degradation from 15.16% to 87.24% within 80 minutes, respectively. However, the faster rate of color removal and photodegradation was observed at alkaline pH. In contrast, the degradation studies of some azo dyes showed conflicting results.¹³⁴ For example, acid yellow 17 (an anionic dye) has shown to be more degraded at pH 3, whereas, orange II (anionic dye) and amido black 10B (anionic dye) showed maximum degradation at pH 9.¹³⁵

The pH can also affect whole photocatalytic dye degradation mechanism and thus the degradation rate. For example positive holes generated at lower pH act as major oxidation species, however at higher or neutral pH range, hydroxyl radicals (OH[•]) are largely responsible for oxidation process.¹³⁶ On one hand, these radicals can be generated in an alkaline solution,¹³⁷ however, on the other hand sites the semiconductor surface may not adsorb dye anions due to electrostatic repulsion thereby decreasing their degradation and *vice versa*.¹³⁸ It is believed that hydroxyl radicals play an essential role in the fission of the -N=N- conjugated system in azo dyes in a TiO₂

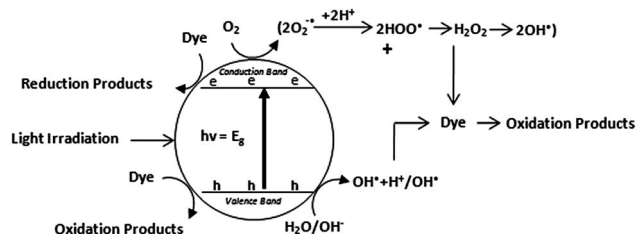


Fig. 2 Pictorial representation of indirect dye degradation process.²⁴

assisted photodegradation. The azo linkage ($-N=N-$) is mainly vulnerable to electrophilic attack by hydroxyl radical. Riga *et al.*¹⁰⁹ reported that dye decolourization and degradation rate increases with increasing pH. Whereas, at lower pH the concentration of H^+ exceeds and these H^+ ions interact with azo linkage reducing the azo group electron densities, resulting into decrease in hydroxyl reactivity of hydroxyl radicals by electrophilic mechanism.

It has been reported that a dye with positive charge shows higher adsorption rate on an unmodified TiO_2 than for dyes with a negative charge (anionic).¹³⁹ It has been studied that titanium dioxide has a higher oxidizing activity at lower pH; however, excess of H^+ at very low pH can decrease the rate of reaction too. This can be explained by the characteristic of TiO_2 particles that tend to agglomerate at lower or acidic condition, which may reduce surface area of catalyst for maximum dye adsorption as well as photon absorption.^{121,140,141} Bizani *et al.*¹⁴² reported that the pH effect on dye degradation rate can be explained mainly by the 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 on the surface of the semiconductor particles.¹⁴²

Effect of pollutant adsorption strength

In heterogeneous photocatalysis, competitive adsorption between water molecules and the target molecules that are to be degraded plays an important role in photocatalysis.^{143,144} This is due to the fact that photogenerated oxidizing species may not migrate far away from their formation centres resulting into negligible or a very slow rate of degradation at few nanometer layers around the catalyst particles surface.¹⁴⁵ However, in various studies many authors have not reported a direct relationship between adsorption and photodegradation. In some cases, adsorption of compounds or intermediates may act as poison on the catalyst surface. Vautier *et al.*¹⁴⁶ reported that an electrostatic interactions between the dye molecule and the hydroxyl groups of the photocatalyst is always required for proper dye adsorption.

Bizani *et al.*¹⁴² reported that strong adsorption may lead to a multilayer of dye molecules around the catalyst particles surface. This may result into limited interaction between excited dye molecule and the catalyst in case of direct degradation mechanism or between incoming light and the catalyst in case of indirect mechanism. In both of above cases the photooxidation process is expected to decrease. This could be the reason due to which the initial decolourization rate of the dye is reported lower in acidic solutions. On the other hand, in alkaline solutions, decrease in the initial rate of degradation reflects the difficulty of the anionic dye molecules to approach the catalyst surface.^{147–149}

Effect of light intensity

Band-gap sensitization mechanism does not have any influence on photocatalytic degradation rate or mechanism.¹⁰¹ However, various studies have revealed that with an increasing light

intensity, the rate of photocatalytic degradation increases.^{150–152} Collazzo *et al.*¹⁵³ compared the direct black 38 dye degradation ability of nitrogen doped TiO_2 under visible light source and sunlight. It was confirmed that nitrogen doped TiO_2 due to its higher absorption in visible region showed higher dye degradation (60% in 6 hours) under visible light. Under sunlight irradiation, N-doped TiO_2 exhibited degradation efficiency slightly higher than non-doped TiO_2 as shown in Fig. 4.

Effect of photocatalyst load

In order to avoid the excess use of the catalyst, it is necessary to calculate optimum dose or loading of the catalyst for efficient removal of dye. Of course the amount of catalysts required will depend on the configuration of the reactor, light intensity, type of the targeted dye and the type as well as particle morphology of the catalyst. Owing to these many contributing factors there are inconsistencies in the optimum catalyst dose used by different researchers. Several authors have investigated the function of catalyst loading on the reaction rate of photocatalytic oxidation process.^{133,154–156} Riga *et al.* reported that the amount of dye adsorbed on catalyst surface generally increases by increasing the TiO_2 loading or the catalyst used. It was found that generally TiO_2 loading increases rate of photo-decolourization, especially up to 1000 mg L^{-1} with an overall 60% TOC removal rate.¹⁰⁹

Kaur *et al.*¹⁰² reported that in all of the optimized conditions of efficiency, the catalyst dose for maximum photocatalytic degradation of reactive red 198 is 0.3 g L^{-1} . However, in another study, the optimized condition for TiO_2 consumption was stated to be 0.5 g L^{-1} .¹⁵⁷ Mahvi *et al.*¹³⁸ studied that an increase in the amount of catalyst to the level constant with the optimized level of light absorption (normally 0.4 g L^{-1}), increases the amount of the decolourization.^{157–159} Also, Muruganandham *et al.*¹³³ reported that an increase of catalyst weight from 1.0 to 4.0 g L^{-1} increases the dye decolourization sharply from 69.27% to 95.23% at 60 minutes and dye degradation from 74.54% to 97.29% at 150 min. A similar observation has been made by other authors, as well.^{137,148,160}

It is evident that initially photodegradation rate increases with an increase in the amount of photocatalyst and then decreases with increase in catalyst concentration (Fig. 5). This trend can be explained by three possibilities:

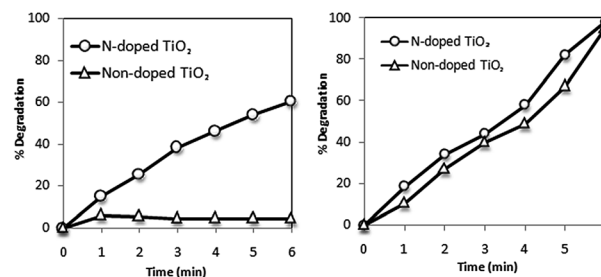


Fig. 4 Photocatalytic degradation of direct black 38 as a function of time under visible light (left) and sunlight (right). Experimental conditions: $C_o = 0.055\text{ g L}^{-1}$, $C_{\text{catalyst}} = 1.0\text{ g L}^{-1}$, $\text{pH} = 2.5$, $T = 25^\circ\text{C}$.¹⁵³



Fig. 5 Effect of increasing TiO₂ catalyst loadings (in grams) on rate of dye degradation.¹⁴¹

1 When all dye molecules are adsorbed on photocatalyst surface, the addition of higher quantities of photocatalyst would have no further enhancing effect on the degradation efficiency.

2 Another possible reason could be due to the fact that an excess of photocatalyst particles may increase opacity of the suspension which may retard the degradation rate.¹⁶¹ Zhu *et al.*¹³⁰ reported in their study that as the amount of photocatalyst was increased from 0.05 to 0.5 g L⁻¹ the number of absorbed photons increased indicating 97% photocatalytic decolorization of methyl orange solution. However, it was found that at photocatalyst dosages above 0.5 g L⁻¹, the rate constants decreased due to the blocking of light penetration by the excessive amount of photocatalysts.¹⁶²

3 Moreover, particle-particle interaction becomes significant as the amount of particles in solution increases. This may result in an enhanced rate of deactivation of activated molecules by collision with ground state titanium dioxide particles and hence decreases in dye concentration.^{141,163}

Effect of the initial dye concentration

It has been reported earlier that by increasing the dye concentration, the decolourization rate constant (*k*) decreases.¹³⁸ The initial dye concentration can affect the rate of photodegradation based upon two main aspects.

(1) In high dye concentrations, more active sites may be covered with dye ions. This further may lead to the decrease in the production of OH radicals on the surface of catalyst. Illinios *et al.*¹⁶⁴ studied the influence of various initial dye concentrations for reactive yellow 125 dye on the photocatalytic discolouration and degradation in the concentration range of 0.025–0.1 g L⁻¹. They concluded that increasing the dye concentration will render the process less efficient by decreasing degradation efficiency.

(2) Zhu *et al.*¹³⁰ reported that the path length of the photons entering the solution decreases as the initial concentration of methyl orange increased. The reversal occurred for the lower concentration, thereby increasing the number of photons absorbed by the catalyst.¹³² The same {Zhu, 2005 #167} effect was reported by Wang *et al.*¹⁶⁵ during their study of the photocatalytic degradation of commercial dyes using zinc oxide power as photocatalyst.

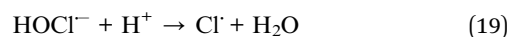
Effect of inorganic salts

The presence of mineral ions in dye contents of wastewater is common. Some cations such as copper, phosphate and iron have been reported to have the ability to decrease the photodegradation efficiency present in certain concentration. One of the major reasons is that these substances may compete with dyes for the active sites on the TiO₂ surface and thus deactivate the photocatalyst resulting in decreased degradation of targeted dyes. Whereas calcium, magnesium and zinc have been studied to have little effect on the photodegradation of organic compounds which is associated to the fact that these cations are present in their highest oxidation states causing no inhibitory effect.¹⁶⁶

The dye industry wastewater contains a considerable amount of inorganic anions such as carbonates, chlorides, nitrate, and sulphates. The presence of these salts causes colloidal instability, increases mass transfer and decrease in the surface contact between the target dye molecule and the photocatalyst.¹⁶⁶ Degradation of dyes decreases in the presence of these ions. These CO₃²⁻ and HCO₃⁻ ions may scavenge the HO radicals.²⁴

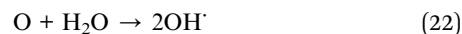


The decrease in degradation efficiency in the presence of chloride ion is due to the hole scavenging properties of chloride ion.



The chloride radical anions formed can also block the active sites of the catalyst surface. The inhibitory effect of chloride and phosphate ions on the photocatalytic degradation has also already been reported.¹⁶⁷ The inhibiting effect of CO₃²⁻ ion is greater than the inhibiting effect of Cl⁻ ion.

Wang *et al.*¹⁶⁸ reported the effect of NO₃⁻ and SO₄²⁻ on the photodegradation of reactive red 2 dye under UV irradiation, stating an increased in dye removal. Zhu *et al.*¹⁶⁹ also reported the same results that the presence of NO₃⁻ accelerated the photocatalytic degradation of an azo dye under visible light irradiation in their experiment. This can be attributed to the direct or indirect hydroxyl radical formation as follow:



SO_4^{2-} in photocatalytic dye degradation has two important roles. SO_4^{2-} , by driving the dye molecule to bulk interface, increases aqueous ionic strength that results into enhanced photocatalytic efficiency. Also, the adsorbed SO_4^{2-} reacts with generated valence band holes forming $\text{SO}_4^{\cdot-}$. This reaction between SO_4^{2-} and photogenerated h_{VB}^+ on the photocatalyst surface can prevent the electrons and holes recombination, enhancing photodegradation rate as:



$\text{SO}_4^{\cdot-}$ is a very strong oxidant with redox potential of +2.6 V, which can enhance dye degradation. Further, the degradation rates also depend on type of salt used. This effect has been studied by various authors.^{109,133,138,170–172}

Effect of addition of oxidizing species

Addition of powerful oxidizing species, such as hydrogen peroxide (H_2O_2) and potassium peroxydisulfate ($\text{K}_2\text{S}_2\text{O}_8$) to TiO_2 suspensions is a well-known procedure which increases rate of photooxidation.^{47,95,148,160,173} Hydrogen peroxide is believed to have a dual role during the process of photocatalytic degradation. It accepts an electron from the conduction band, thus, promotes the charge separation and it also forms OH radicals.



At H_2O_2 concentration greater than critical concentration, it may act as hole or OH^{\cdot} scavenger or react with TiO_2 to form peroxy compounds, which are detrimental to the photocatalytic action.^{148,174–177} Bizani *et al.*¹⁴² reported that the addition of oxidants such as H_2O_2 appears to be more effective in photocatalytic degradation of dyes than $\text{K}_2\text{S}_2\text{O}_8$ comparatively, although their effectiveness in decolourizing the solutions can be reversed. Dye intermediates showed higher toxicity values involving $\text{K}_2\text{S}_2\text{O}_8$ than photocatalytic process involving H_2O_2 , indicating partial DOC (dissolved organic carbon) and toxicity removal efficiency.

Strategies for enhancing photocatalytic properties of TiO_2

Photocatalysis by adopting advanced oxidation procedures

Recently cavitation methods have attracted attention as AOPs for the removal of carcinogenic chemicals present in water.^{178,179} Cavitation involves the growth, nucleation and implosive collapse of micro-bubbles and cavities that occur in fractions of microseconds, releasing large amount of energy over a small location that behave as micro-reactors.¹⁶⁸ In acoustic cavitation, pressure variations in liquid are effected through sound waves (16 kHz to 100 MHz) using ultrasonic transducers as represented in Fig. 6. This produces oscillating bubbles of various size moving at different velocities.¹⁸⁰ The motion of the bubbles

and their radial pulsation can be controlled by acoustic field in the resonating system.¹⁸¹ It has been observed that enhancement due to such synergistic mechanism is due to the deagglomerating effect of photocatalyst through ultrasound, resulting into increased surface area and catalytic performance.^{182–185} However, industrial application of ultrasonically induced cavitation is a problem due to ineffective distribution of the cavitation activity on a large scale.^{186,187} Wang *et al.*¹⁶⁸ studied the efficiency of combined treatment in which they used photocatalysis and water jet cavitation on reactive red 2 dye degradation. The results showed a significant enhancement of photocatalytic activity up to ca. 136%.

In hydrodynamic cavitation, cavitation is produced by pressure variations obtained by creating velocity variation and decrease in static pressure that occurs when the fluid passes through a constriction.¹⁸⁸ Saharan *et al.*¹⁸⁹ reported that hydrodynamic cavitation is more energy efficient compared to acoustic cavitation and has a higher degradation as for equivalent power/energy dissipation. In addition, other AOTs including organic contaminants degradation using $\text{SO}_4^{\cdot-}$ have recently been introduced.^{190–193} These include radiolytic or photolytic or thermal activation of persulfate or peroxide bond to break it down to produce $\text{SO}_4^{\cdot-}$. $\text{SO}_4^{\cdot-}$ showed a higher reduction potential of 2.5–3.1 V as compared with OH^{\cdot} having a standard reduction potential of 1.8–2.7 V. Moreover, it is more selective for the oxidation of organic contaminants over a wide range of pH.^{194,195} In addition, $\text{SO}_4^{\cdot-}$ have a longer half-life, depending on its preference for reactions related to electron transfer, whereas OH^{\cdot} with an equal preference participates in every reaction.^{172,194,196}

Development of efficient TiO_2 photocatalysts by doping

There are various research studies on photocatalytic degradation of dyes using TiO_2 in several modified forms for performance enhancement under visible light. These include adsorption and surface complexation on TiO_2 , non-metal doping, lanthanide ion doping, transition metal doping, noble metal doping and multi-atom doping. The main purpose of doping is to decrease the band gap of pure TiO_2 (3.2 eV for



Fig. 6 Application of cavitation technology to photocatalysis by using ultrasonic transducers for efficient treatment of organic contaminants.

anatase phase) to bring the absorption band from UV to visible region. The Fig. 7 below represents the simplified and relative band position and band gap of pure, metal and non-metal doped TiO_2 . The details about the doping methodologies and photocatalysis mechanisms can be found elsewhere.^{197–199}

Non-metal doping

There are various reports available on non-metal doping of TiO_2 , especially with boron,²⁰⁰ carbon,²⁰¹ sulfur, nitrogen and fluorine.²⁰² The main objective of non-metal doping is to bring the absorption band of TiO_2 to visible region. Apart from its advantages, however, long-term instability of the photocatalyst is a major drawback.²⁰² The detail about the dye degradation including nitrogen and carbon doped TiO_2 is given below under separate headings.

Nitrogen doping. The nitrogen-doped TiO_2 photocatalysts have been tested for the decomposition of aqueous solutions of organic compounds and dyes under UV and visible light illumination.^{201,203–207} Some examples of the N-doped TiO_2 catalysts used for different dye degradation studies along with their preparation technique are given in Table 2.

Asahi *et al.* and others reported that nitrogen due to its comparable size and electronegativity to that of oxygen is the most suitable element for reducing the band gap width of TiO_2 .^{216,217} Irie *et al.*²¹⁸ proposed that an isolated narrow band formed above the valence band in $\text{TiO}_{2-x}\text{N}_x$ powder is responsible for the visible light response. In addition, increasing nitrogen concentration lowered the quantum yield under UV illumination, indicating that the doping sites could also work as recombination centers. Parida and Naik²¹⁹ reported the degradation of methylene blue and methyl orange using N-doped TiO_2 showing 67% and 59% of degradation after 4 hours irradiation under visible light source. Selvaraj *et al.*²²⁰ measured the photocatalytic degradation of the reactive triazine dyes including reactive yellow 84, reactive red 120 and reactive blue 160 on N-doped TiO_2 anatase and P25 in the presence of natural sunlight. It was reported that reactive yellow 84 indicated a faster degradation on N-doped TiO_2 in sunlight than the commercial Aeroxide P25. However, the P25 indicated higher photocatalytic activity for the other two dyes. The COD level within 3 h sunlight exposure, reduced to 65.1, 73.1, and 69.6% for reactive yellow-84, reactive red 120 and reactive blue 160 respectively. In two separate studies, Ihara *et al.*²²¹ and

Serpone²²² argued that synthesized nitrogen doped TiO_2 with the sites that were oxygen deficient formed in the grain boundaries were responsible for the visible light response, whereas presence of nitrogen had only enhanced the stabilization of these oxygen vacancies. Songkhum and Tantirungrotechai²²³ prepared nitrogen and iron(III) co-doped TiO_2 (N-Fe- TiO_2) and reported active for the photodegradation of methyl orange. However, corresponding to the absorption spectra the synthesized TiO_2 photocatalysts except, under UV irradiation, were not found to be photocatalytically active under visible light irradiation. In summary, it can be concluded that, apart from vague understanding of dye degradation mechanism under visible light and various disadvantages, use of nitrogen doped TiO_2 may outweigh non-doped TiO_2 in near future due to its dye degradation activity under practically available sunlight.²²⁴

Carbon doping. In recent years, dopants such as carbon and nitrogen have received more attention owing to their low cost with demonstration of narrow band gap which results in significant visible light absorption capability.²²⁵ Different routes have been developed to synthesize carbon doped TiO_2 which can broadly be divided into two categories *i.e.* inner and outside synthetic route. Inner approach includes incorporation of carbon into TiO_2 structure during its synthesis while outside approach includes the incorporation after TiO_2 has already been synthesised. Khan *et al.*²²⁶ manufactured carbon doped TiO_2 by controlled combustion of Ti metal in a natural gas flame. Irie *et al.*²¹⁸ prepared carbon doped anatase TiO_2 nanoparticles by oxidative annealing of TiC under O_2 flow at 873 K. Sakthivel and Kwasch²²⁷ synthesized carbon-doped TiO_2 nanoparticles by hydrolysis of TiCl_4 with tetrabutylammonium hydroxide followed by calcination of the precipitate obtained as a result of wet process.

Ren *et al.*²²⁸ prepared doped TiO_2 using outside preparation approach. They added required amounts of amorphous TiO_2 , glucose, deionized water in a Teflon lined stainless steel autoclave by marinating the temperature at 160 °C for 12 hours.

Velmurugan *et al.*²²⁹ recently synthesized carbon nanoparticle loaded TiO_2 (CNP- TiO_2) through sonochemical method. CNP- TiO_2 was found to be stable and reusable. Comparatively, photocatalytic activity of CNP- TiO_2 under solar light for degradation of reactive red 120 was found higher than TiO_2 P-25 and as prepared TiO_2 . Increase in activity was related to suppression in recombination of photogenerated electron-hole pair by loaded CNP indicated by a decrease of measured photoluminescence intensity.

Lanthanide ions doping

Lanthanide ions are known for their complex formation with various Lewis bases *e.g.* aldehydes, acids, amines, alcohols, thiols. These Lewis bases interact with the f-orbitals of the lanthanides through their functional groups. Thus, incorporation of lanthanide ions into a TiO_2 matrix could provide a mean to concentrate the organic pollutant at the semiconductor surface and consequently enhance the photoactivity of TiO_2 .^{230–232} It has been reported in literature that the optimum



Fig. 7 Simplified relative energy band positions and band widths for pure ($h\nu$) metal doped ($h\nu_m$) and non-metal doped ($h\nu_{nm}$) TiO_2 anatase.¹⁹⁷

Table 2 Studies on N-doped TiO₂ assisted photodegradation of different dyes

| Catalyst | Dyes used for analysis | Techniques for preparation of N-doped TiO ₂ catalysts | Ref. |
|---|-------------------------------|--|------|
| N-Doped TiO ₂ | Rhodamine B | Microemulsion-hydrothermal method | 208 |
| N-Doped anatase and rutile | Methyl blue | Calcination of acidified TiCl ₃ in presence of urea and oxalic acid | 209 |
| N-Doped TiO ₂ nanotubes | Methyl orange | Solvothermal process | 210 |
| Microarrays of N-doped flower-like TiO ₂ | Methyl orange | Electrochemical anodization of Ti in NH ₄ F aqueous solution | 211 |
| N-TiO ₂ | Methyl orange and phenol | Microwave method | 212 |
| N-TiO ₂ nano colloid | Methyl blue | Nitridation of a porous TiO ₂ | 213 |
| N-TiO ₂ | Ethyl blue and 4-chlorophenol | Sol gel using NH ₄ Cl as nitrogen source | 207 |
| N-TiO ₂ | Methyl blue | Simple method | 214 |
| N-TiO ₂ | Rhodamine B | Plasma based ion implantation | 215 |

level of rare earth metal doping is 1–2% to hinder the crystal growth of TiO₂ during calcinations.²⁰² Although doping of lanthanide ions into TiO₂ attracted some attentions still such works are little so far. Additionally, lanthanides ions can in fact trap conductive band electrons when restricted to the TiO₂ surface.²³³ Recently, La³⁺, Nd³⁺, Sm³⁺, Eu³⁺, Gd³⁺, and Yb³⁺ modified TiO₂ nanoparticles with their ability to increase the anatase phase stability and preventing the segregation of TiO₂ have excessively been investigated for maximizing the efficiency of photocatalytic reactions.^{234–236} Xie *et al.*^{237,238} prepared three types of lanthanide ion-modified titanium dioxide *i.e.* Eu³⁺-TiO₂, Nd³⁺-TiO₂ and Ce⁴⁺-TiO₂ and tested for the photodegradation of azo dye X-3B under visible light irradiation. The results showed that Lnⁿ⁺-TiO₂ system had a higher photocurrent generation. They ranked reaction rates as Nd³⁺-TiO₂ sol > Eu³⁺-TiO₂ sol > Ce⁴⁺-TiO₂ sol > TiO₂ sol > P-25 TiO₂ powder. Zhang *et al.*²³⁹ prepared TiO₂ particles co-doped with boron and lanthanum (B-La-TiO₂) at a molar ratio of 1 : 4 and investigated their photocatalytic performance to photodegrade methyl orange dye. The result showed organic dye degradation to 98% within 90 min compared to 24% with undoped TiO₂. It was speculated that the reason behind enhanced photocatalytic activity of B-La-TiO₂ photocatalysts is its excellent photocatalytic effect under the visible light region.

Very recently, Lan *et al.*²⁴⁰ successfully prepared lanthanum and boron co-doped TiO₂ (La-B-TiO₂) by modified sol-gel method to enhance the visible-light photocatalytic performance by improving the quantum efficiency of the photocatalytic reaction. 1% La-B-TiO₂ catalysts showed highest photocatalytic degradation of acid orange 7 up to 93% under visible-light irradiation for 5 h. Nasir *et al.*²⁴¹ synthesized 0.1 Ce/C co-doped TiO₂ *via* hydrothermal method for the efficient degradation of an aqueous solution of acid orange 7 dye under visible light irradiation. Co-doped catalysts showed higher photocatalytic activity compared to C-doped catalyst. However, increasing Ce concentration above 0.1 Ce/C-TiO₂ resulted in an increase of electrons and holes recombination. In another study Nasir *et al.*²⁴² again used Ce to prepared Ce-S co-doped TiO₂ because of its Ce³⁺/Ce⁴⁺ redox couple, which contains the ability to shift between Ce₂O₃ and CeO₂ under reducing and oxidizing conditions.²⁴³ Results indicated that decrease in the particle size, increase in the surface area, abundance of surface hydroxyl

groups, and reduction of recombination of e⁻ and h⁺ assisted the enhanced photocatalytic degradation of acid orange dye.

Transition metal doping

Incorporating transition metals in the TiO₂ crystal lattice may result in the formation of new energy levels between valence and conduction band, inducing a shift of light absorption towards the visible light region. However, it has been reported as well that transition metals may cause thermal instability for the anatase phase of TiO₂.²⁴⁴

Cadmium doping. Cadmium is one of the heavy metals which could be present in real dyes containing wastewater. It can modify the photocatalytic activity of the catalyst by being absorbed on the photocatalyst surface.²⁴⁵ Andronic *et al.*²⁴⁵ investigated the photocatalytic efficiency of cadmium doped TiO₂ thin films obtained using the doctor blade deposition method to degrade methyl orange and methylene blue dyes. Results showed a linear correlation between the band gap energy of the cadmium doped TiO₂ films and dyes photodegradation efficiency. Some authors have reported negative or overall no effect of cadmium ion on the photocatalytic activity.²⁴⁶ However, these effects highly depend on the cadmium concentration and doping method used. More studies are needed to understand the system completely as Cd may be oxidized to CdO which is a *p*-type semiconductor thus modifying the electronic properties of the system.

Copper doping. It has been reported that Cu(II) has the ability to extend the light absorption to visible region by modifying the TiO₂ valence band spectrum resulting into improved photocatalytic activity.^{247–249} Copper sulphides have also largely been investigated in recent years due to their remarkable optical and electrical properties as a result of variations in composition, morphology, stoichiometry and their potential applications as absorbers for solid state solar cells.^{250,251} Andronic *et al.*²⁵² studied the photocatalytic process by using Cu_xS and coupled Cu_xS/TiO₂ thin films for methyl orange and methylene blue photodegradation. The photocatalytic activity of Cu_xS/TiO₂ nanocomposites depended on Cu_xS : TiO₂ ratio. The best results were achieved under UV irradiation, when H₂O₂ is added in photocatalytic process at Cu_xS : TiO₂ = 3 : 7, with high degradation efficiency of almost 99% using methyl orange in 300 min and methylene blue in 180

min. This semiconductors association and the films homogeneity have the ability to limit the electron-hole recombination facilitating good efficiency in dyes photodegradation even under visible light irradiation. Huang *et al.*²⁵³ prepared Cu₂O nanoparticles and microparticles. They tested these particles for the photodegradation of methyl orange. It was observed that nanoparticles were stable in ambient atmosphere, whereas microparticles were found stable as a Cu₂O/CuO core structure. The Cu₂O microparticles with very slow photocorrosion rate exhibited a higher photocatalytic activity for methyl orange dye than that of the deactivated nanoparticles during the photocatalytic reaction.

Sn⁴⁺ doping. Sn⁴⁺ doped nanosized TiO₂ particles have several advantages compared to other TiO₂ powders. They have pure anatase crystalline form having high-dispersion ability both in polar or non-polar solvents. They also have fine particle size with more uniform distribution with stronger interfacial adsorption facilitating its easy coating on different supporting material.²⁵⁴ The Sn⁴⁺-doped TiO₂ nanoparticles having molar doping ratio for Sn⁴⁺ and tetrabutylorthotitanate of *ca.* 5 were synthesized by hydrothermal process at 225 °C. The double layers of these nanoparticles coated on glass surfaces were found to be having much higher photocatalytic performance under UV and Vis lights than pure TiO₂.

Noble metal modified TiO₂

Deposition of noble metals on TiO₂ surface has been reported to improve the photocatalytic efficiency by acting as an electron trap due to the Schottky barrier formation thereby reducing electron-hole recombination process and helping interfacial charge transfer.^{79,255–261} TiO₂ modified with noble metal exhibits excellent stability as well as high reproducibility. Doping of TiO₂ with noble metals for photo-oxidation has been studied for at least two decades. However, the detail about the most recent dye degradation work including Silver and Platinum doped TiO₂ is given below under separate headings.

Silver modified TiO₂. Silver modified TiO₂ has shown promising results towards increased degradation efficiency and stability. Gupta *et al.*²⁶² were able to regenerate Ag⁺ doped TiO₂ catalyst just by washing the catalyst thoroughly with distilled water. Photocatalytic activity of Ag⁺ doped TiO₂ indicated >99% decolorization of basic violet 3 and methyl red within 90 min with a 86% mineralization efficiency. Seery *et al.*²⁵⁵ reported an enhanced decolorization of rhodamine 6 G with Ag modified TiO₂ under visible light photocatalysis. Increase in decolorization is attributed to the increase in visible absorption capacity of silver nanoparticles. Whereas, Gunawan *et al.*²⁶³ demonstrated the reversible photo-switching of nano silver on TiO₂. Reduced silver on a TiO₂ support when exposed to visible light ($\lambda > 450$ nm) resulted in electron excitation and its reverse flow to the TiO₂ support from silver by oxidizing silver ($\text{Ag}^0 \rightarrow \text{Ag}^+$) in the process. For improved optical properties it would be more attractive to further tailor the band gap width of TiO₂/Ag₂O with some potential transition metals.²⁶⁴

Platinized TiO₂ nanoparticles. Platinum deposited TiO₂ has been repeatedly used in a variety of photoreactions that speeds

up the water splitting reaction^{265,266} and oxidation of organic compounds^{145,267,268} and CO.²⁶⁹ Platinum nanoparticles can be beneficial for the subsequent oxidative reaction steps in the presence of molecular oxygen, which allows direct oxidation of the organic compounds by holes and HO[•] radicals as well. The main effect of Pt-loaded TiO₂ is due to its higher production rate of oxidizing species, *e.g.* holes or HO[•] radicals than conventional heating operation.

Multi-atom doped TiO₂

Many studies have revealed that TiO₂ mono-doping may lead to recombination centers thereby inhibiting light-induced migration of charge carriers to the surface.²⁷⁰ However, it has been recognized that co-doping of TiO₂ with both nonmetal and metal can reduce the number of recombination centers by neutralizing positive and negative charges inside the TiO₂, which can effectively improve the efficiency of migration of the charge carriers and thus enhance photocatalytic activity.²⁷¹ Xing *et al.*²⁷² prepared carbon and lanthanum co-doped TiO₂ by a hydrothermal method and reported their high photocatalytic activity under both UV and visible-light irradiation. Recently, Yang *et al.*²⁷³ synthesized Mo and C co-doped TiO₂ photocatalysts and reported that 1% Mo-C4/TiO₂ showed an excellent visible light photocatalytic degradation of rhodamine B dye. The prepared co-doped catalysts showed greater photocatalytic activity than pure anatase TiO₂ and the mono-doped catalysts, because a synergistic effect between molybdenum and carbon increases absorption of visible light and affects separation of photoinduced electrons and holes. Also, Yan *et al.*²⁷⁴ investigated photocatalytic degradation of methyl orange by TiO₂-SiO₂-NiFe₂O₄ suspensions and reported that OH[•] radicals and h⁺ plays important roles in the degradation by TiO₂-SiO₂-NiFe₂O₄. Akpan and Hameed²⁷⁵ compared electronically stable composite photocatalyst of the type $\text{Ti}^{(1-x-y)}\text{Ca}^{(3x-y)}\text{Ce}^{(2x-y)}\text{W}^{(y/6)}\text{O}_2^{(1-2(y-x))}$ (at $y < 2x$ and $x + y < 1$) prepared by sol-gel method with commercially available Degussa P-25 and TiO₂ photocatalysts for acid red 1 (AR1) photocatalytic degradation. The performance of the composite catalyst excelled that of TiO₂, but was as good as Degussa P-25 in terms of the solar photodegradation. However, composite photocatalyst was found better than Degussa P-25 in terms of reusability since it could settle out of solution in less than one hour after solar experiment. The composite photocatalyst was found to have narrowed band gap as compared to TiO₂ by 0.26 eV with its activities more into visible region.

Dye sensitization in photocatalysis

On a broader scale, waste water remediation with dye sensitization method is beneficial in two ways. *Firstly*, the adsorption of the dye on the surface of TiO₂ catalyst extends the absorption spectrum of TiO₂ from UV to visible regime.¹⁰² *Secondly*, the system containing the dye and the phenolic compound represents a classic model of a real effluent stream, which is usually a mixture of different organic compounds, surfactants and metal ions. Dye sensitized degradation is primarily aided by enhanced adherence of the dye molecule onto TiO₂ surface in the presence

of O₂ that can easily scavenge the injected electrons from the conduction band of TiO₂.⁷⁶ General mechanism of dye sensitized photocatalysis has been explained in detail in basic principles and mechanism section of this review. Zhang *et al.*²⁷⁶ recently studied the aerobic selective oxidation of alcohols in the presence of an anthraquinonic dye (alizarin red S) sensitized TiO₂, and a nitroxyl radical (2,2,6,6-tetramethyl-piperidinyloxy). They found that the whole mechanism involved was the formation of a dye radical cation, which oxidized the nitroxyl radical. This oxidized radical species was found to be mainly responsible for the selective oxidation of alcohols into aldehydes. Other conjugated polymers such as poly(aniline)²⁷⁷ and poly(thiophene)²⁷⁸ has also been used as TiO₂ sensitizers for the degradation of dyes.

Recently, there have been new discoveries related to the adsorption of complexants on TiO₂ surface leading to a sharp enhancement in its activity under visible light by using absorbent such as salicylic acid.²⁷⁹ In a study, Moser *et al.*²⁸⁰ proved that surface complexation of colloidal semiconductors strongly enhance interfacial electron transfer rates. Ikeda *et al.*²⁸¹ demonstrated that phenolic compounds with TiO₂ can work as catalyst under visible light below *ca.* 550–600 nm for water reduction in the presence of a sacrificial donor. Also, Zhang *et al.*²⁸² chemically modified TiO₂ nanoparticles with catechol (4.0 wt% catechol/TiO₂) without changing the crystalline structure of TiO₂. Surface complexation of catechol lead to an enhanced acid orange 7 dye photocatalytic degradation by shifting onset wavelength of the optical absorption to the visible range.

Structurally modified TiO₂

For enhancement of photocatalysis, nanostructured materials with different shapes of TiO₂ including nanoparticles, nanotubes, nanofibers, nanocages, nanorods, nanorings, nanosheets, nanocombs, nanobowls, nanosprings and nanobelts have been employed.²⁸³ The discussion below illustrates the use of most common TiO₂ structural modification to enhance its photocatalytic activity. TiO₂ can be synthesized in the form of a nanometer scale tube like structure called TiO₂ nanotubes.²⁸⁴ The photoactivity of the TiO₂ nanotube films has been found as strongly influenced by the tube diameter and thickness.^{285,286} Increasing tube thickness increases the photodegradation efficiency till a maximum and then decreases till a steady value. In much longer tubes active species have a longer diffusion path that may cause the decrease in photocatalytic degradation rate. The nanotube arrays have been found to be more active than anatase or P-25 TiO₂ nanoparticulate films with similar thickness and geometric area. The enhanced dye degradation activity is attributed to a more effective separation of electron-hole pairs taking place in a well ordered way in TiO₂ nanotube array film and due to higher internal surface area of the nanotube structure.^{285–290}

Graphene modified TiO₂

Carbon can also be used in the form of graphene to synthesize graphene/TiO₂ photocatalysts.²⁹¹ Graphene is an atomic sheet of sp²-bonded carbon atoms with unique properties having high

conductivity, large specific surface area and high transparency due to its one-atom thickness.²⁹² Zhang *et al.*²⁹³ prepared a P-25-graphene composite by hydrothermal treatment of a suspension of P-25 and graphene oxide. Graphene oxide was reduced to graphene and then P-25 nanoparticles were deposited simultaneously on this graphene sheet. The P-25-graphene composite was found more active than P-25 for the photodegradation of methylene blue due to reduced charge recombination and enhanced absorptivity. The P-25-graphene composite exhibited higher efficiency than P-25 having same carbon content, due to its giant two-dimensional planar structure, which facilitated a better platform for the adsorption of the dye and charge transportation.²⁸³ Moreover, TiO₂/graphene composites have been well studied as a solar light photocatalysts and electrode materials for lithium-ion batteries. Recent reports have shown that ultralight 3D-graphene aerogels (GAs) can better adsorb organic pollutants and can provide multidimensional electron transport pathways. Qiu *et al.*²⁹⁴ prepared 3D-structured TiO₂/GA composites by one-step hydrothermal method using glucose. Glucose acts as facet-controlling agent to achieve *in situ* growth of TiO₂ nanocrystals on GAs surfaces. TiO₂ nanocrystals exposed with {001} facets and mesoporous structure were highly dispersed on the GAs surface. Affording high surface area, massive appearance, and hydrophobic properties determine its high recyclability and to efficiently photodegrade methyl orange dye.

Fullerenes modified TiO₂

A fullerene is any molecule composed entirely of carbon, in the form of a hollow sphere, ellipsoid, tube, and many other shapes. Spherical fullerenes are also called buckyballs. Cylindrical fullerenes are called carbon nanotubes or buckytubes. Fullerenes are similar in structure to graphite, which is composed of stacked graphene sheets of linked hexagonal rings; but they may also contain pentagonal or sometimes heptagonal rings. Fullerenes are extremely hydrophobic, therefore, their use in aqueous media is quite limited. However functionalizing the molecules with hydroxyl groups can improve water solubilizing properties of fullerenes.²⁸³ Krishna *et al.*²⁹⁵ employed polyhydroxy fullerenes (PHF) to enhance the photocatalytic efficiency of TiO₂ for the degradation of the procion red dye. The PHF molecules adsorbed on the surface of TiO₂ by electrostatic forces enabled the scavenging of the photogenerated electrons decreasing the electron/hole recombination. The surface coverage of the TiO₂ nanoparticles by the PHF molecules (C₆₀(OH)_{*n*}, *n* = 18–24) determined the extent of enhancement in dye degradation, with an optimum PHF/TiO₂ weight ratio equal to 0.001.^{296,297}

Improvement by enhancing TiO₂ reactive facets

For anatase TiO₂, theoretical and experimental studies have so far revealed that {001} facet compared to thermodynamically stable {101} facet is much more reactive being the dominant source of active sites for various applications.²⁹⁸ Whereas, most of the synthetic anatase crystals due to its crystal growing process are dominated by the less-reactive {101} facets

diminishing the reactive {001} facets to minimize the surface energy. Chen *et al.*²⁹⁹ presented a simple hydrothermal approach for synthesizing uniform, hierarchical spheres self-organized from ultrathin anatase TiO₂ nanosheets with nearly 100% exposed {001} facets. Also, Liu *et al.*³⁰⁰ reported fabricating hollow TiO₂ microspheres composed of anatase polyhedra with 20% exposed {001} facets by fluoride-mediated self-transformation method, exhibiting tunable photocatalytic selectivity in decomposing azo dyes in water. Very recently, Yu *et al.*³⁰¹ synthesized of layered TiO₂, composed of nanosheets with exposed {001} facets, by a simple hydrothermal method. It was observed that layered TiO₂ with {001} facet nanosheets exhibited excellent photocatalytic activity for the degradation of rhodamine B dye.

Practical aspects of TiO₂ photo-processes

Limitations of TiO₂ photo-processes

Performance of a catalyst depends upon its configurations *i.e.* suspended or fixed-bed catalyst impart different performances. Although, coating a catalyst eliminates the need for its post-filtration and centrifugation but it generally reduces the system efficiency significantly largely due to loss in exposed surface area.^{302,303} On the other hand disadvantages using powder form of catalyst include stirring during the reaction and separation of catalyst from the treated water after each run. To address the later, filtration, sedimentation and centrifugation processes have been used to recover highly dispersed and suspended catalyst from the treated water. However, with this method a fraction of TiO₂ particles usually remains in the treated water and a further microfiltration step is usually required for final purification. Besides its time consuming problem, the filtration process become increasingly inefficient as the particle size diminishes. Smaller particles suspended in the water may penetrate through filtration materials causing membranes filter clogging.³⁰⁴

The other common way to perform the separation is by sedimentation of TiO₂ particles after pH adjustment by coagulation–flocculation process. Separation by sedimentation has been enhanced by attaching TiO₂ particles onto other support particles like quartz, silica gel, alumina, zeolites, activated carbon or glass spheres but the loss of photocatalytic activity has usually been observed.³⁰⁵ In addition to this the fast aggregation of TiO₂ in suspension leads to a decrease in effective surface area which reduces its catalytic efficiency. A filtration step after photocatalytic reaction is still required because of TiO₂ suspension.¹⁶⁴ Moreover, TiO₂ absorption wavelength corresponding to the band-gap energy of 3.02 eV is at near ultraviolet radiation.³⁰⁶ Thus either the need of an UV excitation source or ability of TiO₂ to absorb only 5% energy of the solar spectrum has restricted its technological applications.

Trends in improving TiO₂ photo-processes

Despite of drawbacks discussed in the above section, more coated photocatalysts and immobilization techniques are still

been investigated.^{164,307–311} In many cases TiO₂ coated on a support is found to be more efficient for organic compound removal in contrast to uncoated TiO₂, reducing overall operating costs.³¹² Many researchers have examined some methods for fixing TiO₂ on supporting materials including glass beads,³¹³ fiber glass,^{161,314} activated carbon,³¹⁵ silica³¹⁶ and zeolite³¹⁷ as given in Table 3.

Zeolite as TiO₂ support

Zeolites are the aluminosilicate members of the family of microporous solids known as molecular sieves. The term molecular sieve refers to the ability to selectively sort molecules based primarily on a size exclusion process. This is due to a very regular pore structure of molecular dimensions. Among variety of supports available, zeolites are considered to provide an effective electric field of their framework for separation of photogenerated electrons and holes.^{318,324} However care should be taken while using zeolite as TiO₂ support so that it may not affect the TiO₂ photoactivity and the adsorptive properties of zeolite. Mathews³²⁵ reported that photoefficiency of TiO₂ is suppressed when Ti interacts with zeolite. The OH[−] available on the surface of TiO₂ can be easily transferred onto zeolite surface as shown in Fig. 8. Additionally, the presence of zeolite on TiO₂ maintains dye molecules near the photocatalyst (local concentration effect) which may result in an increase of degradation rate.

TiO₂ loaded hydrophobic mesocellular foams

Hydrophobic materials based on zeolites and mesoporous silicas such as hexagonal mesoporous silica (HMS), SBA-15 and mesocellular foams could offer excellent ability of adsorption of organic compounds owing to their weak adsorption of water molecules and the large surface areas.³²⁶ Though simple surface fluorination on TiO₂ can induce an enhanced UV light photocatalytic oxidation activity, however it is difficult to improve the visible light photocatalytic activity of TiO₂, owing to the lack of photo-excited holes in the visible light irradiation.³²⁷

In 2012, Xing *et al.*³²⁸ prepared a novel hydrophobic TiO₂ photocatalyst, which can enhance visible light response by using cheaper and low-toxic inorganic NH₄F. They prepare the super-hydrophobic mesocellular foams loaded with nanosized TiO₂ photocatalyst. Mesoporous catalyst greatly facilitated the surface fluorination, which together with Ti³⁺ (a self-doped TiO₂ catalyst) generation promoted its visible light photocatalytic activity³²⁹ and the surface fluorination enhanced UV light photocatalytic activity. It was reported that the catalyst exhibit permanent and excellent super-hydrophobic property, high adsorption capacity, and enhanced photocatalytic activity for rhodamine B (RhB) degradation. Recently, Qi *et al.*³³⁰ prepared carbon-doped TiO₂/mesocellular-F photocatalysts hydrophobically modified by the hydrothermal method. Catalyst indicated an efficient visible light photodegradation of methyl orange solution because of the synergistic effect of small crystal size, carbon dopants, and hydrophobic modification due to the fluorination of NH₄F.

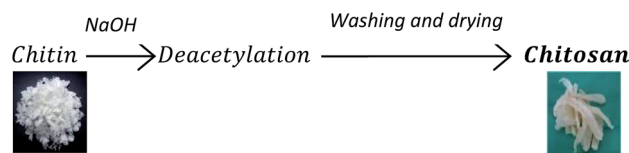
Table 3 Types of the supports used for enhancing TiO₂ photocatalytic degradation of different dyes

| Support type | Dye used for degradation | Technique used for preparation | Performance | Ref. |
|--|---|---|--|------|
| Clinoptilolite (CP) (Iranian Natural Zeolite) | Acid red 114 | — | TiO ₂ /clinoptilolite (SSD) proved to be an active photocatalyst with a first order reaction, $k = 0.0108 \text{ min}^{-1}$. With increasing dye conc. photodegradation conversion of AR 114 decreased | 318 |
| Chitosan [β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose] | Methyl orange | Solution casting technology | The TiO ₂ /ZnO/chitosan NTFs showed high photocatalytic activity under solar irradiation | 319 |
| Polymethylmethacrylate (PMMA) rings | Methylene blue | Ultrasonically spray-coated with TiO ₂ sol | Results showed 80% degradation of methylene blue after 10 min at pH 9 | 320 |
| Polyamide 6 (PA6) fiber | Methylene blue | Low temperature hydrothermal method | Compared with the untreated fabric, the protection against UV radiation improved. The titanium dioxide coated fabric could degrade methylene blue efficiently dye under UV irradiation | 321 |
| Glass plates | Acid red 27 (AR27) | Immobilized | Outlet stream from photoreactor was mineralized with products such as NH_4^+ , NO_3^- , O_2^- and SO_4^{2-} ions | 322 |
| Non-woven paper with SiO ₂ | Reactive black 5 (RB5) | — | Degradation of RB5 azo dye was strongly influenced by the ionic strength of the solution. Above pH PZC of SiO ₂ , the cations of the solution increased the amount of dye adsorbed onto the photocatalyst support | 170 |
| Sand | Methylene blue, rhodamine B and methyl orange | — | TiO ₂ /UV process supported on sand is effective in totally mineralizing these compounds | 323 |

**Fig. 8** Synergistic effect of TiO₂ and clinoptilolite catalyst on dye degradation by producing OH free radicals.³¹⁸

Chitosan as TiO₂ support

Chitosan [β -(1 \rightarrow 4)-2-amino-2-deoxy-D-glucose] is a natural cationic biopolymer that is produced by *N*-deacetylation of chitin. Chitin is considered as the second most abundant natural polysaccharide after cellulose.³³¹ The extraction of chitin from shells and its subsequent deacetylation to chitosan is a relatively low cost process.³³²



Chitosan molecules contain a large number of reactive hydroxyl (–OH) and amino (–NH₂) groups. Also, chitosan has

high affinity for metal ions and this property has been used to prepare metal–chitosan nanocomposites.³³³ This enables Chitosan to exhibit unique adsorption and chelating properties for all kinds of heavy metal ions,^{334–336} making chitosan an appropriate and excellent bio-matrix for synthesizing nanosized particles for various inorganic photocatalysts such as titanium oxide,^{337,338} cadmium sulfide,^{319,339} zinc sulfide,³⁴⁰ zinc oxide³⁴¹ and cuprous oxide.³⁴² In addition, immobilizing nanosized photocatalysts onto chitosan bio-matrix can effectively prevent agglomeration of nanoparticles during growth and can overcome the difficulties related to separation and recovery of nanosized powder materials.³³⁶

Activated carbon as TiO₂ support

Activated carbon also known as activated charcoal (AC) is a highly porous form of carbon with porosity spanning the macro ($\lambda > 50$ nm), meso (0.5–1 μ m) and micro (<1 μ m) pore ranges¹¹⁶ and very high-surface typically up to 900–1200 m² g^{−1}.³⁴³ It is generally produced from cheap carbonaceous source materials such as nutshells, coconut husk, peat, wood, coir, lignite, coal, and petroleum pitch. Use of activated carbon is the most common method applied for dye removal by adsorption.³⁴⁴ In particular, activated carbon (AC) has been extensively researched as a support for heterogeneous catalysis,³⁴⁵ and there exists over 650 studies and well over 1000 patents³⁴⁶ concerning AC–TiO₂ mixtures or composites.^{347–351} Due to its higher effectiveness, it has been applied on adsorbing cationic, mordant, and acid dyes and to dispersed, vat, direct, pigment and reactive dyes on a slightly lesser extent.^{26,352}

Effective performance using activated carbon mainly depends upon the type of carbon being used and the characteristics of the aqueous solution containing various chemicals and non-targeted contaminants. Regeneration or reuse can result in a steep reduction in performance, and efficiency of dye removal. Activated carbon, like many other dye-removal treatments is considered suitable for one particular type of pollutant or waste system and ineffective on another. Although, activated carbon is expensive it comes with the advantage of regeneration. However, this reactivation usually results into 10–15% loss of the sorbent. Arana *et al.*³⁵³ prepared AC and TiO₂ catalysts having varying proportion. The results showed that the AC in addition to increasing surface area can also modify the acid–base properties and the UV spectrum of TiO₂. It was reported that activity of AC was increased under solar irradiation.

In AC–TiO₂ system, the adsorption capacity of AC enhances the chances of high concentration of reactants to come in contact with TiO₂ and possibly turning them into their intermediates as explained in the Fig. 9. Zhang *et al.*²³⁶ proposed a similar illustration for the photocatalyzed mineralization of methyl orange to understand the effect of presence of AC onto TiO₂ for effective dye degradation. On the other hand, a disadvantage of using AC is the excessive formation of nanosized pores resulting into rare infiltration, leaving TiO₂ on the outer macropores.^{116,354,355} Moreover, the band gap tuning problem of TiO₂ is not resolved by the use of AC as a support.



Fig. 9 Synergistic mechanism between AC–TiO₂ composites. The arrow labelling un-reacted emphasizes that in the absence of Absorbent the reactants may remain un-reacted into the solution resulting in low photoactivity of methyl orange.²³⁶

Silica as TiO₂ support

Use of supported TiO₂ catalysts depends on the nature of supports, one of the most important factors influencing photocatalytic performance.^{169,356,357} Recently, amorphous SiO₂ due to its special physicochemical properties such as high adsorption capacity has been studied showing advantages towards highly active support for catalysts. The presence of considerably large number of acid sites and hydroxyl groups on the surface of amorphous SiO₂ material make it more absorptive.^{358,359} Studies have shown that silica gel can be an effective support for binding TiO₂ that is effective for removal of basic dyes. However, in such processes, there can be side reaction taking place along with photocatalysis and therefore such limiting factors can prevent its commercial application.²⁶ Additionally, immobilization TiO₂ on a suitable and inert matrix has shown an advanced organic and inorganic pollutant photodecomposition than that of pure TiO₂.^{169,360}

Sun *et al.*³⁶¹ investigated the catalytic properties of three porous amorphous silica including diatomite, opal and porous supported photocatalysts (TiO₂/SiO₂) by UV-assisted degradation of rhodamine B. Through morphology and physical properties of the resulting TiO₂/amorphous SiO₂ catalysts, it was suggested that the nature of silica supports could affect the particle size and the crystal form of TiO₂. TiO₂/diatomite photocatalyst, compared with pure TiO₂ (P-25) and the other two TiO₂/amorphous SiO₂ catalysts, exhibited better catalytic performance at different calcination temperatures with a discoloration rate of up to over 85%. Photocatalytic properties such as mixed-phase TiO₂ with small particle size might be responsible for efficient performance. Furthermore, its stable and inert porous structure improves its activity.

Carbon nanotubes as TiO₂ support

The carbon nanotubes (CNTs) are interesting materials having unique electronic properties associated with their special 1D structure which facilitates the charge transfer.³⁶² The CNTs are described as tubular assemblies made exclusively of rolled-up films of interlocked carbon atoms. These are classified as single-walled carbon nanotubes (SWCNTs) which consist of a

single layer of graphene sheet rolled into a cylindrical tube or multi-walled carbon nanotubes (MWCNTs), which contain multiple concentric tubes. CNTs have a large specific surface area due to their hollow geometry. CNTs-TiO₂ hybrids have been tested for the photodegradation of acetone,³⁶³ methylene blue^{364,365} and phenol.^{366,367} All such studies emphasized that the addition of CNTs had enhanced the photocatalytic effectiveness of TiO₂.

Yu *et al.*³⁶⁸ compared the effect of MWCNTs on the adsorption and the photocatalytic properties of TiO₂ P-25. The results showed that the mixture of CNTs and TiO₂ significantly improved the photocatalytic activity of TiO₂ for the treatment of three azo dyes and was found more efficient than the mixture of TiO₂ with activated carbon. Luo *et al.*³⁶⁹ prepared short MWCNTs that can be suspended, sorted and manipulated more easily so that the light can well penetrate into the inner tubes. The short MWCNTs were used as initial materials to fabricate TiO₂/short MWCNTs nano-composites that were tested for the photodegradation of reactive brilliant red X-3B. The photo-activity of the TiO₂/short MWCNTs samples with optimum weight ratio (1 : 100) was studied and rates much higher than that of various active photocatalysts (TiO₂/short MWCNTs > TiO₂/MWCNTs > TiO₂ > P-25) were reported.

TiO₂ embedded in polymer matrix

Difficulties such as low quantum yield and low adsorption capacity of TiO₂ photocatalyst limits its practical application.¹²² Among multiple techniques to overcome these issues, incorporation of semiconductors into the polymer matrix have been achieved. Example such as polypyrrole (PPy)-TiO₂ composite films, polyethylene-TiO₂, and polyvinylchloride (PVC)-TiO₂ as resulting composites were found to enhance degradation reactions more effectively than a suspension of TiO₂ nanoparticles.³⁷⁰ Cheng *et al.*³⁷¹ report efficient adsorption and photodegradation of textile dyes orange II and methyl orange under UV irradiation using polyaniline (PANI) and PANI-TiO₂ composite nanotubes as photocatalyst, respectively. Decolorization up to 98.6% of orange II and 98.1% of methyl orange in the presence of PANI-TiO₂ composite nanotubes were reported. Addition of TiO₂ nanoparticles to the one-dimensional polymer matrix gradually increased the removal rate of organic dyes due to higher specific surface area and the positive form of titania at the interface.

Conclusion

Owing to its many advantages mainly involving most stable and active naturally occurring photocatalyst, TiO₂ is, so far, seen as the best catalytic material for degradation of various contaminants and sustainable environmental remediation technology. It has been widely employed in dye photodegradation studies. Photodegradation of industrial dyes using improved TiO₂ has presented a somewhat promising and effective treatment technology. However, in order to overcome constraint such as sensitivity towards operational parameters *i.e.* pH, temperature, catalyst dose, amount of dye, inability for high photon efficiency

to utilize wider solar spectra, and separation after treatment inhibits the ability of TiO₂ from its real time application on a vast scale. Therefore, more advanced level research studies are needed to address TiO₂ shortfalls or to formulate potential alternative for TiO₂.

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