Chapter 3
Recent Developments in Photocatalytic Techniques of Dye Degradation in Effluents

Barkha Tiwari and Hui Joon Park

Abstract In this chapter, we describe how a new trend of materials "nano" and its composites preferential grown as different sizes of small crystallites of structures using varied synthesis routes for photocatalytic dye degradation. Here, we will discuss about the different synthesis methods "traditional and trending" for the purification of water by degradation of dyes using photocatalytic techniques. To support the main outline of this chapter, we have supported various characterizations done to confirm the presence of nanomaterials like XRD for its crystal structure, SEM/TEM for morphology and XPS for elemental analysis; confirming with some functional groups using FTIR and Raman analysis. The modulation of parameters for the purification of water/effluents is pivotal in such work. So, we have compared the new novel techniques and materials trending all over research community as compared to the conventional ones. Certain nanomaterials synthesized are even doped with metals like rare-earth ions and transition metal ions to bring an effective output when illuminated to UV or visible light. Photocatalytic degradation has grown in last 20 years because of the impurities added to water bodies as source from industries and sewage, mainly comprising of waste like chemical dyes. This has paved way for lot of research in the fields of materials science, chemistry, environmental science and energy. Majorly synthetic dyes used in clothes, plastic, leather and other accessories are biggest motif behind this research. Our aim in this chapter is to summarize the whole scenario in compact but covering all relevant information. Usually, the procedure for photocatalytic dye degradation is step-wise process, involving choice of catalyst, concentration of dyes, light illumination and time taken for degradation of dye. Time taken for degradation of dye and choice of materials are inter-related, however efficiency of catalyst for certain dyes is better than other dyes. To make it clearer we will first give a brief introduction on the dyes, photocatalysis process, materials used as catalysts and purification.

Keywords Photocatalysis · Dye degradation · Advanced oxidation

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3.1 Introduction

From the last 20 years, the on-going trend in the field of photocatalytic degradation of dyes has increased relatively and gradually showing pace in its extensive usage; synthetic dyes are most prominently used in textile and plastic industries. As, it has become a major issue of textile, leather and plastic industries that the waste "effluents" generated are polluting the water bodies (Sacco et al. 2012; Mukhtish et al. 2013; Khan et al. 2017a; Khataee et al. 2010; Akpan and Hameed; Rauf and Salman). Most of the dyeing process effluents enter our environment in a large amount, approximately 20%; thus, hampering our natural resources (Rauf et al. 2011). So, to easily remove this issue, one such method adapts to tackle it involves the degradation of dyes. Where large molecules of dyes are oxidized down into smaller molecules like water, carbon dioxide, hydrogen and other by-products. But we are still struggling to find way to completely utilize all the dye molecules for degradation, as most of it released in water remains unused; making it difficult for researchers.

New modern methods now revolve around heterogenous photocatalysis for the dye's degradation; hetero here means more than one material. Spintronics of the charge carriers or the charge dipole at different energy levels gives rise to its transfer from the valence band to the conduction band when illuminated by light of particular wavelength (occurs in semiconducting material oxides) (Pandit et al. 2015). The exciting electrons generated at the energy levels react with the water molecules or oxygen molecules thus producing hydroxide radicals and oxide anions. Such high oxidizing species have better efficiency to degrade n number of molecules; effluents of industries and others. Advanced Oxidation Process (AOP) is well known type of Fenton processes in the scientific world which is actually the decontamination process using reactive oxygen species and other molecular species. So, advanced Oxidation Process has become an important research area in the common history of photocatalytic degradation but in this chapter, we will limit our discussions to the semiconducting medium types of catalysts (Elmorsi et al. 2010; Gul and Yildlrln 2009; AlHamedi et al. 2009).

It is compulsory at this stage to detail about the demand of this topic as a review. Some of the cause for this to happen have been listed below (Xie and Li 2006):

1. Several groups in the field of science and technology are working and collaborating in this realm. So, it's good to compile the complete literature and its ongoing trend at uniform recurring.
2. This method which is known for its various advantages over the years has major benefits using it in a bigger realm; as it is economically plausible thus making the photocatalytic procedure of degradation of dyes as demanding research.
3. The by-products evolved after degradation are mostly non-toxic components like oxygen, carbon dioxide and water.
4. The efficiency of degradation of the pollutants could be priorly calculated using the reagents like the hydroxide (OH group) to the potential applied for reduction of the pollutant and numerical counts of the pollutant's oxidation potential (Odling and Robertson 2017).

Variety of chemical dyes are used in coloring things in the industries and markets for our daily necessities. These dye materials have been classified in accordance with its molecular structures, optical properties, color, wavelength and applications. Major difference in dyes is done through its chromophoric group (having colour) in the molecular species such as azo dyes, nitro dyes, quinine-amine dyes, acridine dyes, xanthene dyes, anthraquinone dyes and so on (Rauf et al. 2011). The photocatalytic dye degradation studies reported mainly dealing with the variables such as the number of catalysts used, intensity of the light irradiated, concentration of dye, time taken for effect to occur when irradiated by light evolving oxygen and other species. The pseudo first order reaction with kinetic data fitting to the equation $-\ln(C/C0) = kt$ is nothing but the kinetics of photocatalytic degradation of dyes. The importance of kinetic data fit has been shown separately in other sub-section.

Although humongous studies have been reported for degradation of dyes using photocatalytic technique but still there are several areas which have not been attentively checked. Now we will point out those issues lying in this field that need to be tackled. As the Fig. 3.1 shows in the bar graph that there is a sharp increase of research in the field of catalysis in the last 15 years; five times in the 10 years of span thus the publication number have risen double in last 5 years (Akpan and Hameed; Rauf and Salman; Rauf et al. 2011). As we have told in the outline of this chapter that mostly research done in this area are metal oxides or its composites (hybrid) varying the crystallites size to tune the overall performance. Before we start with the ongoing trends in the research of photocatalysis and its limitations, we would briefly illustrate about the literature (comprehensive history).

We have tried to summarize some of the important research done in the field of photocatalysis in the last few years in Table 3.1. Most of the research works that have been reported in literature state the degradation effect of dyes that depends on variety of stuff like concentration of dye, amount of catalyst taken, pH of solution, time taken for light illumination, source of illumination etc. The first order system is followed in the study of the kinetics of photocatalytic dye degradation (Khan et al. 2017b).

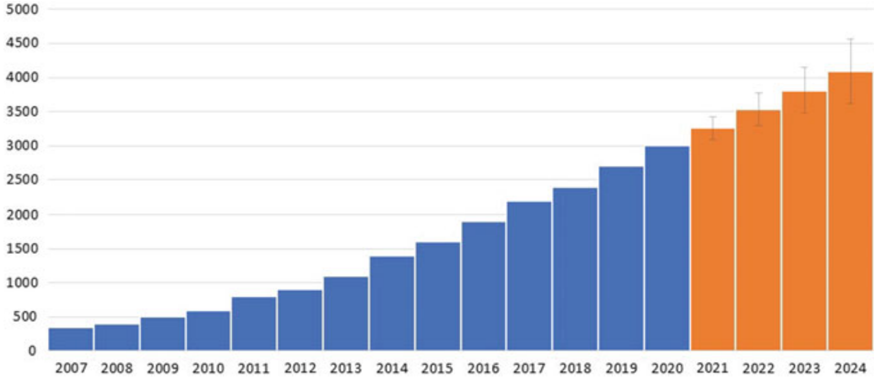

Fig. 3.1 Number of publications versus year plot (*Source* web of science)

Table 3.1 Brief comparative research history data on the degradation of dyes

Catalyst systems studied	Dyes employed	Comments	References
N-doped TiO_2	Methylene blue, Methyl orange	Depends on illuminated visible light and nitrogen content in catalyst	Sacco et al. (2012)
High surface area TiO_2	Methylene blue, Congo red	Sol–gel method preparation of TiO_2	Mukhtish et al. (2013)
Nanostructured TiO_2	Mono, di and tri-azo class of dyes	Degradation depends on the chemical structure of dye	Khan et al. (2017a)
Graphene-nanogold composite	Methyl blue, Rhodamine B	Methylene blue has better efficiency as compared to Rhodamine B when illuminated by visible light	Khataee et al. (2010)
Nano TiO_2 (anatase and rutile)	Methylene blue, Nitrobenzene, Acetophenone	Anatase shows better performance as compared to rutile	Akpan and Hameed
TiO_2, ZnO, SnO_2	Crystal violet, Methyl red	ZnO shows better performance	Rauf and Salman
Mg-TiO_2	Methyl orange	This catalyst has better efficiency in comparison to un-doped TiO_2	Rauf et al. (2011)
ZnO nanoflowers	Congo red, Methyl orange	New photocatalyst synthesized of ZnO showing better results for methyl orange	Pandit et al. (2015)
ZnO nanopowder	Rhodamine B	95% dye degraded under sun light	Elmorsi et al. (2010)
TiO_2	Congo red, Methyl orange, Methylene blue	Anatase phase of TiO_2 was dependent on its size and adsorption of catalyst	AlHamedi et al. (2009)
TiO_2	Indigo carmine, Indigo	Visible light was used as source of light	Xie and Li (2006)
Immobilized TiO_2 on polyvinyl alcohol and polyacrylamide	Reactive orange, Methylene blue	On PVA trapped TiO_2 showed better result than polyvinyl alcohol	Odling and Robertson (2017)

(continued)

Table 3.1 (continued)

Catalyst systems studied	Dyes employed	Comments	References
Nano-TiO_2	Acidic red, Acidic orange	Sulphonate and azo groups shows degradation	Khan et al. (2017b)
Ag, Au doped SiO_2 nanoparticles	Methyl red	Hydroxide radicals help in dye degradation	Xiong et al. (2010)
TiO_2	Emerald green	pH effects the dye degradation	Rajesh et al. (2007)
(Solar, pH, UV) TiO_2	Procyon yellow	Solar light initiates dye degradation in TiO_2	Avasarala et al. (2016)
TiO_2	Reactive red	H_2O_2 and sulphates were studied	Mahadwad et al. (2011)
Thermally activated ZnO	Congo red	Second order kinetics	Mohammed et al. (2016)
Sol–gel TiO_2	Lissamine green B	Thin film of TiO_2 showed better result	Nagaraja et al. (2012)
Ag-TiO_2 core–shell structures	Reactive blue 220	Core–shell shows good dye degradation under solar light	Mo and Ching (1995)
Nano-TiO_2 Anatase	Reactive blue 4	In the presence of H_2O_2, dye degradation is increased	Iakandar et al. (2007)
TiO_2/ZnO	Methylene blue	ZnO shows better performance	Bavykin et al. (2006)
P160-TiO_2	Yellow-28	Presence of carbonate ions increased the performance	Koelsch et al. (2002)
Orthorhombic WO_3	AO7 dye	Oxalic acid initiates reaction	Morgan and Watson (2010)
Ni doped TiO_2	Malachite green	Oxidizing species used are hydroxyl ions	Qamar et al. (2008)
TiO_2	Solo phenyl red 3BL	Concentration of hydroxide and oxygen ions determine rate of degradation	Sclafani and Herrmann (1996)
TiO_2	Reactive green 19, Azo orange	Azo orange has better efficiency as compared to reactive green under sunlight	Bakardiieva et al. (2005)
TiO_2	Disperse and azo dyes	Tuning parameters	Ohno et al. (2004)

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Table 3.1 (continued)

Catalyst systems studied	Dyes employed	Comments	References
TiO_2	Carmine indigo	UV light, pH = 4	Li (2011)
ZnO	Methylene blue,	Basic solution has better performed	Ohtani et al. (1997)
Carbon-TiO_2	Amido black	Activated O_2 ions are responsible for degradation	Singh et al. (2013)
ZnO	Direct red-31	UV irradiation and annealing temperature (500–800 °C)	Hoffman et al. (1995)
Sol–gel TiO_2 thin films	Congo red, methyl orange	Dip coated TiO_2 showed better performance	Meng and Juan (2008)
Undoped and Fe doped CeO_2	Methyl orange	1.5% doping of Fe in Titanium dioxide showed better dye degradation	Hernandez-Alonso et al. (2009)
Immobilized TiO_2	Methylene blue	Deposition of photosensitive layer decreases the performance	Mills et al. (1993)
Ni-$MgFe_2O_4$	Malachite green	Depends on illuminated visible light	Hashimoto et al. (2005)
UV-TiO_2	Methylene blue	Mineralization of sulphur, carbon and nitrogen	Ye et al. (2010)
Cu doped P-25	Azo dye orange	It is better than H_2O_2/UV reaction	Colmenares et al. (2009)
Ag–Ni TiO_2	Methyl red	Doped is better than undoped TiO_2	Anpo et al. (1987)
Cr doped TiO_2	Congo red, Methylene blue	Anatase to rutile phase transition	Lin et al. (2006)
Au and Ag doped ZnS quantum dots	Methylene blue	Loading of metals favors better performance	Sarkhanpour et al. (2017)
Mesoporous CeO_2	Rhodamine B	Hydroxyl groups are active species	Ajmal et al. (2014)
ZnS	Rose Bengal	OH^- groups show the result	Tesfay et al. (2015)

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Table 3.1 (continued)

Catalyst systems studied	Dyes employed	Comments	References
Films of C-TiO_2	Azorubine	Photocatalytic reaction and absorption of catalyst effect performance	Paola et al. (2013)
La-Y/TiO_2	Methylene blue	4 g/L catalyst	Nguyen-Phan et al. (2011)
Ag-TiO_2	Direct red 23	3 g/L catalyst	Ioannis and Triatafyllos (2004)
ZnO	RBB dye	1st order kinetics	Kurny and Fahmida (2017)
ZnO	Crystal violet	Better optical property, high crystallinity, high surface area is responsible for good dye degradation	Fox and Dulay (1993)
In/ZnO nanoparticles	Methylene blue	Indium is well dispersed on ZnO	Tunesi and Anderson (1991)
TiO_2-P25-ZnO	Methylene blue	ZnO has better result in visible light as compared to TiO_2	Tang and An (1995)
TiO_2 nanoparticles	Methylene blue	Basic medium is better for degradation	Guillard et al. (2003)
ZnO	Indigo carmine, Indigo	Visible light was used as source of light	Reutergarth and Iangpashuk (1997)
BiOI	Reactive orange, Methylene blue	On PVA trapped TiO_2 showed better result than polyvinyl alcohol	Baran et al. (2008)
TiO_2	Acidic red, Acidic orange	Sulphonate and azo groups show degradation	Wang et al. (2000)
ZnO, TiO_2	Methyl red	Hydroxide radicals help in dye degradation	Baran et al. (2003)
ZnS doped with Mn	Emerald green	pH effects the dye degradation	Tang and An (1995)
Undoped and Cu doped TiO_2	Methylene orange, Rhodamine B	ZnO shows lower performance	Alaton and Balcioglu (2001)
Mn_3O_4 nanoparticles	Procyon yellow	Solar light initiates dye degradation in TiO_2	Poulios and Aetopoulou (1999)

(continued)

Table 3.1 (continued)

Catalyst systems studied	Dyes employed	Comments	References
TiO_2 with Pt	Reactive red	H_2O_2 and sulphates were studied	Poulios et al. (2000)
TiO_2	Congo red	Second order kinetics	Zhang et al. (2001)
TiO_2 coated cotton fabric	Lissamine green B	Thin film of TiO_2 showed better result	Zhiyong et al. (2007)
Silver phosphate	Methylene blue	Industrial waste water is used	Bauer et al. (2001)
$CeCrO_3$	Reactive blue 220	Core–shell shows good dye degradation under solar light	Xiaoqing et al. (2017)
ZnO	Reactive blue 4	In the presence of H_2O_2, dye degradation is increased	Abo-Farha (2010)
CeO_2-ZnO	Yellow-28	Presence of carbonate ions increased the performance	Saber et al. (2011)
MgO	Methylene blue	90% degradation	Kirupavasam and Allen (2012)
TiO_2	Acid orange	UV light source as better effect than visible light	Quang et al. (2017)
TiO_2 on polyethylene film	Crystal violet, Methylene blue	Solar light dye decolorization	Mahmoud et al. (2009)
Mo doped TiO_2	Toluidine blue-o	Pseudo first kinetics	Sun et al. (2006)
Copper ferrite	Glycerol, Methylene blue	Glycerol degradation is not good until H_2O_2 is added	Huang et al. (2008)
TiO_2	Tartrazine	Influence of other salts	Sun et al. (2008)
Zn-TiO_2	Direct blue 71	Zn doped has better performance over undoped	Wei et al. (2007)
Ag-ZnO	Reactive orange 16	Ag doped is better than undoped	Guettai and Amar (2005)
TiO_2	Reactive orange 16	Shows good performance	Sharma et al. (2013)
ZnO-CuO	Reactive black 5	It is good for reduction of effluents in environment	Bhati et al. (2010)

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Table 3.1 (continued)

Catalyst systems studied	Dyes employed	Comments	References
TiO_2 on polyethylene glycol	Congo red, Methylene orange	UV light high efficiency	Min et al. (2015)
g-C_3N_4 and CaCl	Rhodamine B	Modified system is 50 times better than bare system	Dharmarajan et al. (2013)
CdO/TiO_2	Reactive orange 4	UV irradiation and annealing temperature (500–800 °C)	Nosaka and Nosaka (2017)
ZnO	Reactive blue	Photocatalytic performance good in coupled TiO_2-ZnO	Salem et al. (2015)
BiOCl	Methyl orange	Visible light degradation	Bubacz et al. (2010)
ZnS-Cr doped	Methyl orange	Visible light is better than UV	Salem et al. (2015)
Nano-TiO_2 (C-fe doped)	Basic blue 9	Waste water usage	Bubacz et al. (2010)
CeO_2-SnO_2	Direct black 32	Activity is comparable with TiO_2-P25	Raheem and Hameed (2015)
TiO_2-ZnO	RB 21 dye	UV photoreactor and TiO_2	Mehta and Surana (2013)
CaO	Indigo carmine dye	pH 9 was suitable	Ameta et al. (2015)
$SrTiO_3$	Methyl orange, Methylene blue	Non-selective process	Rupa et al. (2015)
CuO/Ag_3AsO_4/GO	Phenol	Photosensitivity	Narde et al. (2017)
TiO_2/diatomite	Rhodamine B, Methylene blue, Methyl orange	Waste water treatment	Zangi et al. (2017)
$PbCrO_4$	Rhodamine B	Visible light sensitive	Simovic et al. (2017)
ZnO	Acid red 27	Photocatalytic reaction and absorption of catalyst effect performance	Mezughi et al. (2014)

(continued)

Table 3.1 (continued)

Catalyst systems studied	Dyes employed	Comments	References
CuS	Methylene blue, Rhodamine B, Congo red	Pseudo first order kinetics	Kamal et al. (2014)
N-doped ZnO	Azure A	Effective for number of reactions	Marinovic et al. (2017)
TiO_2 (brookite)	Rhodamine	1st order kinetics	Long et al. (2017)
TiO_2 (brookite + rutile)	Orange dye	Annealed at varied temperatures for good result	Dhatshabamurthi et al. (2015)
g-CN	Methylene blue	g-CN under UV is much more efficient	Tiwari and Ram (2019)

Traditional wet chemical, physical and bio-friendly synthesis routes have been used extensively for dye degradation present in effluents. These synthesis processes have shown certain disadvantages like high energy, high cost, by-products formed end up in other types of secondary pollutants. Therefore, Advanced Oxidation Process i.e., AOP has gained considerable notice for the degradation of such harmful dyes in recent trends (Xiong et al. 2010).

3.2 Literature

This is one of the research fields that is done all over the world when compared with other research areas. To validate more about our above point that the research in this particular area "photocatalytic degradation" has always been in trend since more than 10 years as compared to other realms of science and technology; we have shown it in Table 3.1. The pictorial representation of dye degradation phenomena happening in the spintronic level of molecules is clearly shown in Fig. 3.2. The most common of all materials used for the degradation of dyes as photocatalysts is titanium dioxide. But unfortunately, the main flaws of using titanium dioxide (TiO_2) are its wide bandgap i.e., 3.2 eV. Out of all the crystal phases of TiO_2, in reports it is researched that the anatase gives better performance in dye degradation in photocatalysis due to its high absorption intensity for photons. This shows that the crystal phase in TiO_2 plays a major role for dyes degradation (Rajesh et al. 2007; Dnyaneshwar 2017; Avasarala et al. 2016; Mahadwad et al. 2011; Mohammed et al. 2016; Nagaraja et al. 2012; Mehra and Sharma 2012).

Out of the three most prominent phases of titanium dioxide such as anatase, rutile and brookite; anatase and rutile phases have been studied more as shown in Table 3.1. The oxygen ions positioned in the anatase crystal structure of TiO_2 is in such an

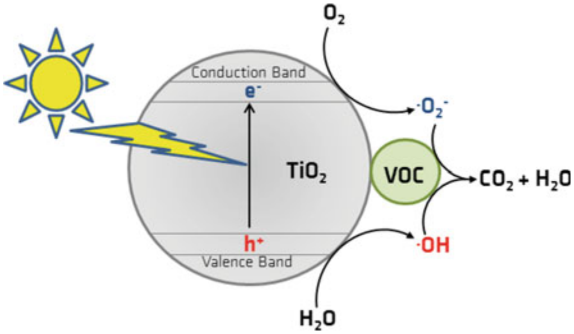


Fig. 3.2 Photocatalytic degradation of dyes in semiconducting materials (ref. Birte et al. (2017))

arrangement that allows maximum absorption of organic pollutants, even the orientation of titanium ions creates a condition favorable for reaction condition with those absorbed dyes (Mo and Ching 1995; Iakandar et al. 2007; Bavykin et al. 2006). But unfortunately, such beneficial crystal structural arrangements of molecules are not present in rutile phase of titanium dioxide. As reviewed, the researchers have found out that the pure form of anatase with small percent of rutile phase is more conductive for porosity and favoring better dye degradation. Spintronically, the charge carriers are excited by illumination of light thus hovering from lower energy level “valence band” to higher energy levels “conduction band” thus creating electron–hole pair, this generates radical ions which are an important reason for the degradation of dyes into water, carbon dioxide and some other species (Koelsch et al. 2002; Morgan and Watson 2010; Qamar et al. 2008; Sclafani and Herrmann 1996; Bakardiieva et al. 2005; Ohno et al. 2004; Colon et al. 2006; Li 2011; Ohtani et al. 1997).

For the dyes degradation using photocatalytic effect needs a material “catalyst” with larger surface area to have good adsorption of the effluents waste thus increasing the kinetics of the reaction. It will be considered slowly. In the standard P-25 TiO_2, which is the mixture of 20% rutile and 80% anatase phase, making the overall material as a core–shell system with high productivity and active in most of the cases, that’s the reason it is used as standard material in comparison. For the treatment of effluents, various ways have been tried in history but dye removal using photodegradation has implied a pivotal role. Due to environmental and aesthetic concerns, the dye degradation from the waste in water bodies of industries like textiles, leather, plastic, etc. played a significant role (Elahee 2010). Metal oxides like ZnO and TiO_2 have been used in nanospheres, nanorods, thin films, nanowires and nanofibers on a polymeric matrix; they have high performance, low price and eco-friendly. There are other semiconducting materials too like CdS, WO_3, ZrO_2, etc. for the dye degradation under light irradiation; these materials are already included in Table 3.1. The cons of such materials like titanium dioxide are that it has got high band gap, and need UV light illumination to degrade the dye in effluents. To give a clear picture of photodegradation of dyes, Fig. 3.3. Typically, some other materials and their composites show such photodegradation which is shown in Fig. 3.4a, b using pictorial presentation. Brookite has also been served for photocatalysis phenomena in dye degradation as

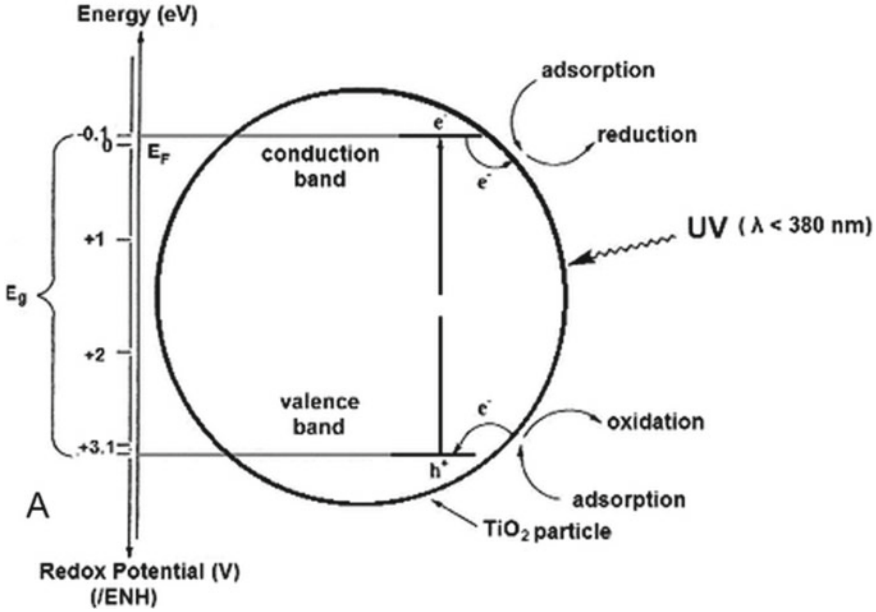


Fig. 3.3 Energy band diagram of photocatalytic degradation of dyes in semiconducting materials (ref. Elena et al. (2017))

one of the phases of titanium dioxide. Commonly, the studies carried out on photocatalytic dye degradation as checked by chemical oxygen demand measurements. Still, it is said to check the product concentration while formation and clear various routes through which these products are formed. There has always been a limitation to using such studies in large scale as it is important to see if the degradation material products are non-toxic to living beings and environment (Singh et al. 2013; Hoffman et al. 1995; Meng and Juan 2008; Hernandez-Alonso et al. 2009; Mills et al. 1993; Hashimoto et al. 2005). Optimization of parameters is pivotal as like the choice of photocatalyst material for successful technique implementation in purifying effluents in this new trending technology. So, the trend in this field has shown that with increase in light intensity of irradiating source, the degradation of dyes percent can also be increased. High value of irradiation light, more will be the recombination (electron–hole pairs) and vice-versa.

The photocatalytic response mainly depends on the chemical nature and annealing temperature of the semiconductor. Most of our choices of semiconducting materials and its crystal structures are based on several parameters like the physical form of the semiconductor and its stability under adverse the conditions of chemical reactions (Neppolian et al. 1999; Ye et al. 2010; Colmenares et al. 2009; Anpo et al. 1987; Lin et al. 2006; Sarkhanpour et al. 2017; Ajmal et al. 2014). Environmentally friendly, low cost or economically viable, less toxic are pivotal characteristics for good photocatalytic materials and out of this titanium dioxide has been reported and

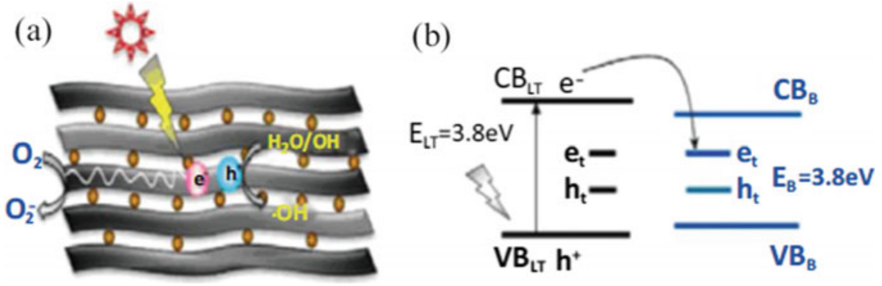


Fig. 3.4 **a** Diffusion behavior of charge carriers in layered nanosheets and **b** transport pathway of the excited electron in the mixed photocatalyst (ref. Thuy-Duong Nguyen et al. (2011))

most trending material of all in this area of research. As the last research has been drafted and reviewed, it is seen that the standard material for comparison of photocatalytic performance of any new material is compared with P-25 TiO_2 (anatase has performance better than rutile but less than standard material). Although, various parameters are optimized to get best result but the amount of photocatalyst material has been used mainly depends on the chemical behavior of the semiconducting property of it; thus, photocatalytic reaction has been easily tuned with certain modifications in literature (Tesfay et al. 2015; Paola et al. 2013; Nguyen-Phan et al. 2011). The changes have been done with various levels like modulating wavelengths of light, and spin-energy level coupling in semiconduction for efficient usage of the charge pair or e^- hole pair. Recently a new trend has emerged in materials used as catalysts for dye degradation using photocatalysis phenomena i.e., use of graphitic carbon nitride (g-C_3N_4) as shown in Fig. 3.5. The V.B. level (valence band level) in the system could be shifted to better value which enhances the oxidation ability.

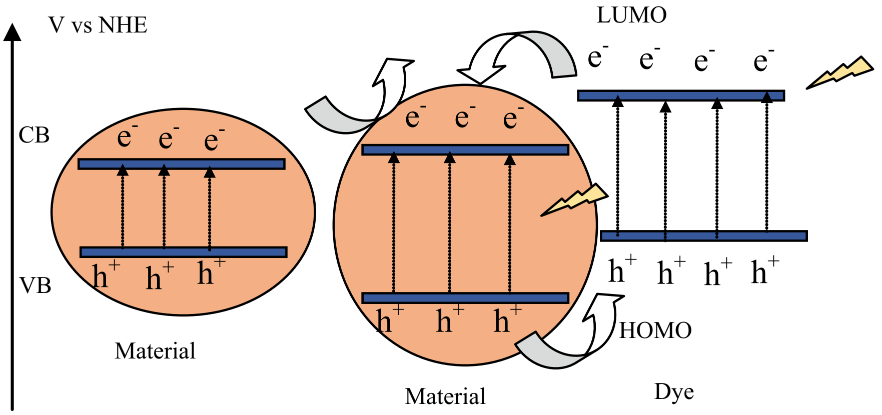


Fig. 3.5 Band diagram (discrete energy levels) of carbon nitride (CN) and CN-Ca for degrading dye

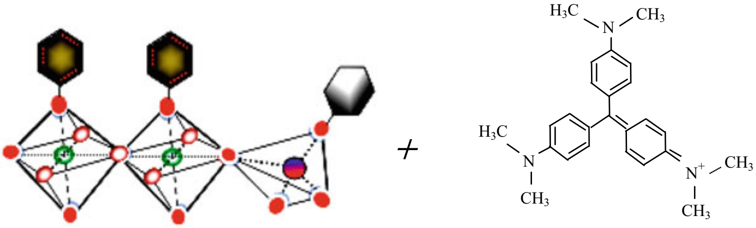
Simultaneously, using the photoexcitation in the dye degradation, the transfer of electrons to the higher energy levels i.e., conduction band. This is predominant in the presence of visible light. Other than this many researchers have tried doping the semiconductor catalysts for better in large realm of wavelengths and degradation performance (Ioannis and Triatafyllos 2004; Kurny and Fahmida 2017; Fox and Dulay 1993).

3.3 Photocatalytic Dye Degradation Chemical Phenomena in Core–Shell

Due to progressively increasing textiles, paper and other coloring industries around the world, the residues sank out of them are a major issue of chemical pollutants/hazards of damaging our routine life-cycle by contaminating water bodies and badly affecting the living beings (both aquatic and non-aquatic). Color dyes have been classified into various classes in the literature, which are often non-biodegradable of a source of badly affecting our eco-system of a green nature. Out of all this, a crystal violet (CV) dye is one of the cationic dyes being used in inks that is majorly polluting our green nature throughout the globe. To control an environmental pollution, it is thus highly required to degrade it (before it is damped as a waste in nature) in an ecofriendly method, such as its photocatalytic degradation in a water host, which is the mostly easily available in plenty in the nature. Usually, a CV dye strongly absorbs visible light with absorption maximum lying at 570 or 590 nm, which can be explored in degrading it using a suitable photocatalyst, for example, C-$CaIn_2O_4$ we synthesized in small core–shell crystallites in this work. As a result, in this investigation, we analyze how a CV dye can be degraded using a core–shell C-$CaIn_2O_4$ as a photocatalyst as follows (Tiwari et al. 2018).

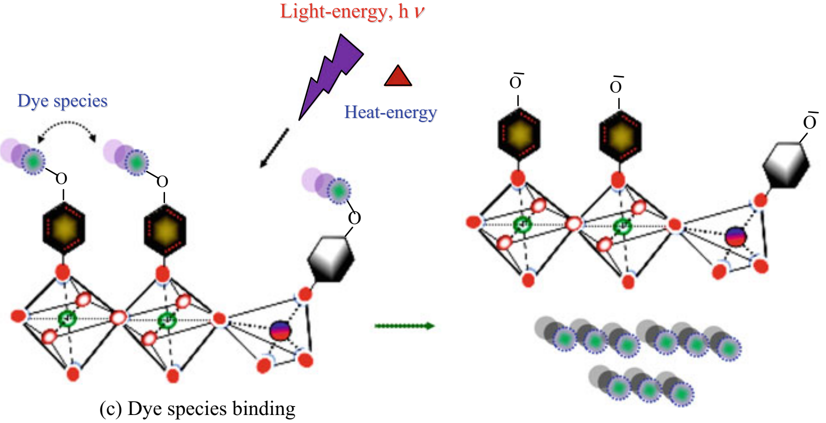
A photocatalytic experiment was carried out under UV irradiation (24 W power, 400 lx intensity, 300–420 nm range with its average peak position lying at λ_{max} = 365 nm) of a CV dye (5×10^{-5} ML^{-1} concentration in water) charged on a sample C-$CaIn_2O_4$ in water while stirring. Typically, a 1.0 gL^{-1} of a C-$CaIn_2O_4$ sample was dispersed in each solution to let the pollutant adsorb over its surfaces to the equilibrium in a deep dark for a sufficient time-period of 30 min. Then, the sample was degraded in parts by irradiating for equal intervals of 15 min followed by centrifuged at 6000 rpm for 5 min to separate the dye from the C-$CaIn_2O_4$ catalyst. Recovered solutions in this way were studied in terms of UV–visible absorption spectra to determine any residual dye left-out after degradation in the solutions. An average of three consecutive measurements was used in analyzing the degradation process and its kinetic parameters. A good catalyst offers its photocatalytic features in four major factors (i) how it uploads a given pollutant in a liquid carrier, (ii) how the uploaded species absorb light in a wide band, (iii) how the "$e^- - h^+$" ion pairs decouple in transient interfaces formed on the catalyst by irradiating so obtained sample and (iv) how degraded species after the reaction ultimately get separated from the dye and disperse back into the solution of a reservoir. Small C-$CaIn_2O_4$ core-shells and tiny pores of a sample we used here promptly adsorb a dye over large surfaces having large charge carriers. The whole reaction process occurs in successive steps that can be put in a simple model reaction scheme as follows. Model molecular diagrams given in Fig. 3.6 describe how (a) core–shell C-$CaIn_2O_4$ crystallites uploads (b) a crystal violet dye (when adding in a solution) on (c) its reactive C-sp^2 modified surfaces so that the dye degrades thereon in a light induced reaction and (d) ultimately the degraded dye species segregate and disperse into the solution as a separate phase (Tiwari and Ram 2019).

As a result, as soon as the dye degrades in this process it proportionally loses its absorbance of its characteristic light absorption band as shown in Fig. 3.7. In this figure, only selective absorption bands, which were recorded in a regular interval of 30 min of UV-irradiating (over 300–420 nm wavelengths) an as-prepared C-$CaIn_2O_4$ sample-1 dispersed along with a CV dye in water, are compiled in order to determine how the irradiation causing the dye to be progressively degrading over a time scale, which is prolonged up to 240 min in a continuous UV irradiation. No any measurable degradation appears in absence of any UV–visible light in a complete dark medium ensuring that it is only the UV-irradiation that it leads the dye to degrade on the $CaIn_2O_4$ sample-1 in the photocatalytic reactions with its reactive surfaces. The reaction is mostly complete in a 240 min of a regular irradiation after which only a



(a) C-$CaIn_2O_4$

(b) Crystal violet dye



(c) Dye species binding On C-$CaIn_2O_4$

(d) Degraded dye species

Fig. 3.6 Catalytic performance of **a** C-$CaIn_2O_4$ in (**b**, **c**) adsorbed dye degradation and **d** removing a crystal violet dye on irradiating UV-light (115)

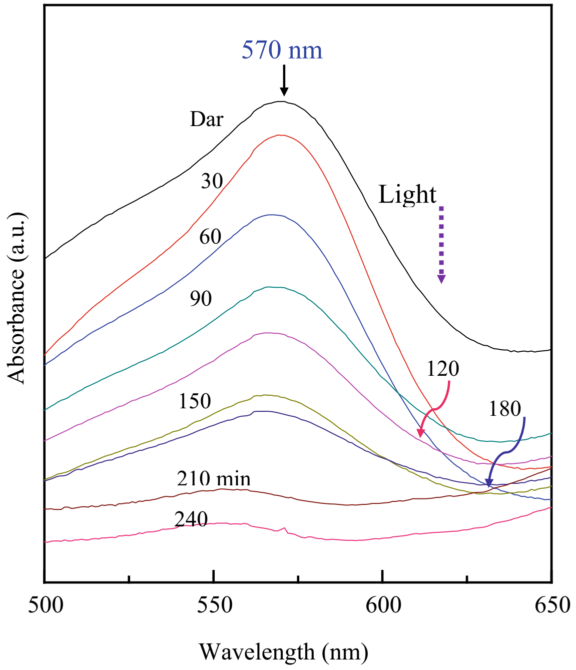


Fig. 3.7 Light-absorption by the dye adsorbed over C-CaIn$_2$O$_4$ core-shells in a catalytic reaction when irradiated by a UV-light

small residual absorption band lasts and it does not change any more (Mills et al. 1993; Hashimoto et al. 2005; Neppolian et al. 1999).

$$\text{Semiconductor} + \text{photons } (h\nu) \rightarrow e^-(\text{CB})$$
$$+\, h^+(\text{VB})\ (1)\ h^+ + H_2O \rightarrow H^+ + OH^-$$
$$h^+ + OH^- + OH$$
$$e^- + O_2 \rightarrow O_2$$
$$2e^- + O_2 + H_2O \rightarrow H_2O_2$$
$$e^- + H_2O_2 \rightarrow OH + OH^-$$
$$\text{Organic pollutant} + OH + O_2 \rightarrow CO_2 + H_2O + \text{other degradation products}$$

As usual, excited photons in the UV-irradiation lead to excite an electron from the valence band to the conduction band, leaving behind a hole “h$^+$” in the valence band in a decoupled “e$^-$ – h$^+$” ion-pair. These holes could readily oxidize the donor dye molecules so as to promptly react with H$_2$O forming refined hydroxyl species (Ye et al. 2010; Colmenares et al. 2009; Anpo et al. 1987; Lin et al. 2006). We optimized adsorption of the dye on the different C-CaIn$_2$O$_4$ samples-1, 2, 3 dispersed in water in a fixed volume in a completely dark room in terms of its absorbance in its characteristic light-absorption band. Both as-prepared and annealed C-CaIn$_2$O$_4$ samples readily adsorb the CV dye on its multiple surfaces of small core–shell crystallites. A dispersion of the dye on C-CaIn$_2$O$_4$ in water has been equilibrated in its maximum adsorption on its surfaces over an extended exposure time to nearly 90 min

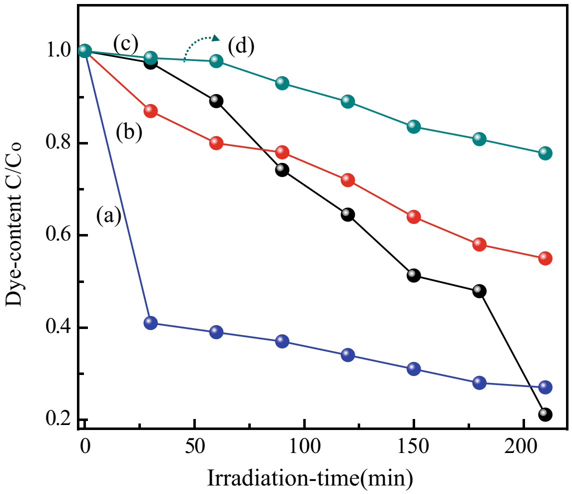


Fig. 3.8 Photocatalytic degradation of the CV dye using **a** the as-prepared and annealed C-$CaIn_2O_4$ powders at **b** 400 °C and **c** 600 °C for 2 h in air, and **d** a standard P25-TiO_2 powder dispersed in water by irradiating over UV–light

until it becomes stable. As soon as the adsorption completed and the final sample becomes stable in absorbing light, we started measuring its degradation by irradiating it by UV-light over predetermined intervals of time of 30 min as shown in the so obtained results, which are plotted in Fig. 3.8. Here, C_0 (which is proportional to the maximum absorbance in the dye in the sample) describes an initial dye concentration before any irradiation and C/C_0 is its normalized residual value after a photocatalytic degradation performed in this experiment. To find out a critical extent of a recurring degradation achieved in this experiment, the intermediate samples were centrifuged at 6000 rpm for 10 min in which so far degraded dye desorbs off the catalyst and disperses in the water.

In the plot in Fig. 3.8a, as the UV-light irradiating time $t \rightarrow 25$ min, the CV dye in sample-1 is decayed rapidly till a minimum $C/C_o \cong 40\%$. A nearly four times larger dye lasts in Fig. 3.8d in decaying much slowly in a standard P25-TiO_2. A reasonably large porosity of ultrafine pores and a reasonably thick C-sp^2 surface layer in this sample-1 promptly favor its catalytic features. A reasonably larger degradation rate constant $k = 0.065\ \text{min}^{-1}$ (against $0.013\ \text{min}^{-1}$ in the P25-TiO_2) thus prolongs in a pseudo first order reaction in a non-linear regression of $\ln(C/C_o) = -kt$ over t as plotted in Fig. 3.9a for this sample. Other samples involve much lower k-values as can be determined assuming linear plots in Fig. 5.9b, c. Further, the degradation plots in Fig. 3.10 describe a non-linear degradation of the CV dye (a) before and (b) after dispersing in a photocatalytic C-$CaIn_2O_4$ sample-3 in water and irradiating over UV-light. In a degradation plot made in Fig. 3.10a, a bare CV dye hardly degrades up to 12% in a very slowly reaction with H_2O molecules by UV irradiation when dispersed in water. This result clearly shows a crucial role a photocatalyst is playing in degrading it reasonably faster as observed in this experiment in the presence of a photocatalyst of a C-$CaIn_2O_4$ sample.

Further, in absence of an irradiation, the dye dispersed in a catalytic sample-3 decays much slowly (hardly by nearly up to 25%) in a marked microscopic effect of a light induced photochemical reaction in this example. A maximum of 81% degradation efficiency, $\eta = (C_0 - C_\infty)\ \mathrm{C_0}^{-1}$, of degrading a CV-dye thus has been observed in our photocatalytic C-$\mathrm{CaIn_2O_4}$ sample-3 in water after a long exposure of UV irradiation up to 210 min. Here, $C = C_\infty$ as $t \rightarrow \infty$ (taken as 210 min of the degradation reaction) has been used according to the degradation plots given in Fig. 3.8. Nevertheless, an as-prepared C-$\mathrm{CaIn_2O_4}$ sample-1 serves to be a faster photocatalyst in degrading the CV-dye over early periods, $t \leq 60$ min, of the UV irradiation in the present experiments. An annealed C-$\mathrm{CaIn_2O_4}$ sample-2 at 400 °C for 2 h in air exhibits a reasonably lower $\eta = 40\%$ in accounts of its enhanced electrical conductivity on forming highly regular and stable conductive C-sp^2 surface channels (of a critical $\delta = 1$–2 nm thickness of a conjoint network of a surface layer) as will be described in the following section in this chapter. In this case, a decoupled "e$^-$ – h$^+$" ion-pair mostly takes part in the electrical conduction rather than in a desired photocatalytic degradation in this experiment. A standard P25-$\mathrm{TiO_2}$ photocatalyst as used over here yields a still inferior $\eta = 20\%$ in degrading a CV-dye in water in the present experimental conductions.

A bar chart given in Fig. 3.11 compares η-values observed in selective samples studied in this work. A few other authors have studied photocatalytic properties of pure and C-sp^2 modified $\mathrm{CaIn_2O_4}$ in degrading crystal violet dye dispersed in water and in visible irradiations, with similar degradation results of $\eta \leq 80$ values. Also in these experiments, a surface C-sp^2 modified $\mathrm{CaIn_2O_4}$ had duly improved photocatalytic properties according to its local structure.

3.4 Optimization of Variables in Photocatalysis of Dye Degradation

In this we have explained that while optimization of dye degradation chemical phenomena, we not just check chemical synthesis methods for the materials employed but even the wavelength of light used as source for the energy bandgap of semiconducting materials. So, the dye degradation has effects of several variables used in experiment that can be varied and optimized for best result. We have tried to give collective bandgap information on the last 20 years and ongoing semiconducting materials in Table 3.2. Unfortunately, most of the time researchers don't report the light source intensity and it's monitoring; LEDs having good energy efficiency have also been employed, temperature of chemical reaction, light intensity, source of light and the catalyst particles size, surface area of catalyst and varied forms of materials affecting the dye degradation rate.

Table 3.2 Trending material semiconductors (Table 3.1 as reference) that are used for dye degradation with band gap values in eV

Semiconducting materials for dye degradation	Band gap (eV)
TiO_2–Anatase	3.2
TiO_2–Rutile	3.0
TiO_2–Brookite	3.14
ZnO	3.36
WO_3	2.76
CdS	2.42
CuO	1.2
Cu_2O	2.2
MgO	5.9
Mn_3O_4	3.28
CeO_2	3.6
Fe_2O_3	3.19
Fe_3O_4	2.3
ZrO_2	2.25
g-C_3N_4	2.661
Ag_2O	1.4
$SrTiO_3$	3.25
Bi_2WO_6	3.13
$BaTiO_3$	3.302
Bi_2O_3	2.8
CdO	2.2
CoO	2.01
Cr_2O_3	3.5
HgO	1.9
In_2O_3	2.8
MnO	3.6
Nb_2O_3	3.4
NiO	3.5
PbO_2	2.8
PbO	1
Sb_2O_3	3
SnO	4.2
SnO_2	3.5
V_2O_5	2.8
$K_6Ta_{10.8}O_{30}$	3.76

3.4.1 pH Variable Effect on the Dye's Degradation Chemical Phenomena

As shown in Table 3.1, that we have mentioned so beautifully about materials and its dye degradation phenomena is dependent on pH value. The change in oxidation potential as per pH values for the molecular species used in the chemical solution for dye degradation is on pivotal observation. As the hole oxidation potential and electron reduction power that is generated when light is irradiated on the semiconducting catalysts for dye degradation are even dependent on the positions of the high energy level of the valence band and low energy level of conduction band. Thus, pH has greater effect even when adsorption of dye is done on the photocatalyst materials, a change in pH and surface characteristics is noticed. OH^- ions (hydroxyl groups) could be easily formed in these reactions by hydroxide ions having positive holes. At neutral of high pH values, the majorly considered species are hydroxyl radicals whereas the holes (positive charges) are predominantly considered at low values of pH. OH^- ions are produced easier in the alkaline solution by oxidizing the hydroxide species available at the surface of semiconducting materials, thus count to increase in efficiency of dye degradation; mostly dyes have similar behavior like this. According to trends in this research field, dyes have been considered as a function of pH like bromo-cresol purple dye degrade better in acidic medium than in alkaline medium. The synthesis methods for the photo-degradation depends on the formation of products on the way molecules of dyes get adsorbed to the surface of catalysts, thus altering electronic properties.

It has been researched by the scientific teams that in dye degradation using photocatalytic technique the advent of adsorption on unmodified TiO_2 shows better for cationic dyes with positive charges than anionic dyes with negative charges. Therefore, explicitly the behavior of a dye and its pH give a huge impact on photocatalytic reaction efficiency. Azo dyes are cationic dyes having positive charge with low pH of around 6.8 and at higher pH value it gives anionic charges (negatively charged), hence effecting the adsorption of dye on the surface of materials. Lucidly, the effluents treatment should take into consideration two important points that are:

1. pH of the waste should not be neutral
2. Surface behavior of semiconducting materials gets influenced by the substances that will be mixed inside the water.

The dyes adsorbed on the semiconducting materials surface and the electron and hole charge pair separation state which will happen when electrical double layer forms due to charged species. The rate at which dye degrades in the photocatalysis phenomena mostly depends on pH of that dye and the reaction rate for that particular dye is maximum on the nature of pH, whether its acid or alkaline. Like OH^- radicals are formed in alkaline medium that increases the reaction rate of catalysis for dye degradation. We have given trends in materials for dye degradation showing influence of pH value of solution in Table 3.3. So, it is pivotal for us to understand the chemical behavior of these dyes and pH value for proper degradation using photocatalysis. As

Table 3.3 Collective data of the dye's degradation on varied effect of pH

Type of dye	Source of irradiation	Photo-catalyst	pH range	Optimum pH	Ref
Amido black 10B	UV	TiO_2	–	9.0	Sacco et al. (2012)
Acid Yellow	UV	TiO_2	–	3.0	Sacco et al. (2012)
Acid Orange	UV	WO_3-TiO_2	1.0–9.0	3.0	Mukhtish et al. (2013)
Methyl Orange	UV	TiO_2	2.0–10.0	8.0	Khan et al. (2017a)
Rhodamine B	UV	ZnO	2.0–12.0	12.0	Khataee et al. (2010)
Methyl Orange	Visible	Mg doped TiO_2	3.0–8.0	– -	Akpan and Hameed
Bromo-cresol Purple	UV	TiO_2	4.5 & 8.0	4.5	Rauf and Salman
Orange G	UV	Ac/TiO_2/ Sn	1.0–2.0	2.0	Rauf et al. (2011)
Methyl Orange	UV	Pt/TiO_2	2.5–11.0	2.5	Pandit et al. (2015)
Orange G	Visible	N-TiO_2	1.5–6.5	2.0	Elmorsi et al. (2010)
Acid Red B	UV	Ce-TiO_2	1.5–7.0	1.5	Gul and Yildlrln (2009)
Orange H	Solar	Zn-TiO_2	3.0–10.0	3.0	AlHamedi et al. (2009)
Methyl Red	Visible	1.5%Ni-3.0%Ag-TiO_2	3.0–10.0	4.0	Xie and Li (2006)
Methylene B	UV	N-TiO_2	3.0–9.0	Alkaline	Odling and Robertson (2017)
Congo Red	Visible	Chitosan/CdS	6.0–12.0	6.0	Khan et al. (2017b)
Malachite Green	Sun light	Ni/$MgFe_2O_4$	2.5–10.0	4.0	Xiong et al. (2010)
Indigo Carmine	UV	TiO_2	4.0–11.0	4.0	Rajesh et al. (2007)
Textile dye	UV	TiO_2	3.0–7.0	5.0	Dnyaneshwar (2017)
Solophenyl Red 3BI	UV	TiO_2	2.0–14.0	7.0	Avasarala et al. (2016)

(continued)

Table 3.3 (continued)

Type of dye	Source of irradiation	Photo-catalyst	pH range	Optimum pH	Ref
Methyl Orange	UV	Fe2/C/S dopedTiO_2	2.0–12.0	Acidic medium	Mahadwad et al. (2011)
Acid Orange 7	UV	WO_3	3.0–9.0	3.0	Mohammed et al. (2016)
Basic Yellow 28	Sun light	TiO_2	3.0–9.0	5.0	Nagaraja et al. (2012)
Methylene blue	UV	ZnO-TiO_2	1.0–6.0	2.0	Mehra and Sharma (2012)
Reactive Blue 4	UV	Anatase-TiO_2	3.0–13.0	3.0–7.0	Mo and Ching (1995)
Methylene blue	UV	ZnO	2.0–11.0	7.0	Iakandar et al. (2007)
Congo Red	UV	ZnO	5.0–10.0	8.0	Bavykin et al. (2006)
Reactive Red 2	UV	TiO_2	4.0–12.0	4.0–6.0	Koelsch et al. (2002)
Procion Yellow	UV	TiO_2	2.0–10.0	7.8	Morgan and Watson (2010)
Acid Orange 10	UV	TiO_2	1.0–11.0	3.0	Qamar et al. (2008)
Methyl Orange	UV	ZnO	2.0–10.0	Basic medium	Sclafani and Herrmann (1996)

we change the annealing temperatures, pH value varies thus changing the phase or crystal structure of the semiconducting materials. As compared with few examples given in Table 3.3 that TiO_2 degrades faster with good efficiency when at acidic medium. Hence, it degrades the chemically toxic dyes by absorbing H^+ ions on the surface of semiconducting materials; ultimately giving a new trend for wide range of dyes degraded alone with a single material. Based on the mechanism of chemical reaction, effects of pH on the dye degradation should be rationalized. Possibly, there are only 3 ways through which dyes can photocatalytically degraded in relation to pH value:

i. Involvement of positive charges “holes” directly in the oxidation reaction
ii. Hydroxyl species are directly attacked
iii. When electrons are excited to the higher energy bands (conduction bands) get directly reduced.

A detailed collection of the optimized values of pH for different photocatalysts and varied dyes is given in Table 3.2 with references.

3.4.2 Issues Still to Be Handled with New Trends

In the research literature most of the covered portions of this field as variables; source of light for dye degradation, its light intensity, the quantity and concentration of catalyst used, pH of the solution medium, initial dye concentration used for the detailed study of its degradation, time taken for irradiation in the whole dye degradation along with other cations present in the chemical reaction medium. Since ages, literature shows that research community has been following these variables avidly. So, it is considered that it is important to study these variables for getting the correct information for the effluents treatment using photocatalytic phenomenon in the dye industries like textile, paint and plastic. The main purpose of this chapter is to briefly compile and present all the past and ongoing trends in photocatalytic dye degradation for the waste treatment "effluents" and cleaning water bodies that are getting polluted by the industries, considering all parameters.

3.4.2.1 Kinetics of Dye Degradation

The kinetics of dye degradation using photocatalytic phenomenon by these semiconducting catalysts have been mostly using the first order kinetics. In Table 3.4, we have clearly given detailed information of so many catalysts used in past and present that are trending for dye degradation with references along with its kinetic value "first order rate constant value". The purpose of this analysis is to determine some of the outcomes of treating these first order kinetic data in the degradation of the dye "pollutants" and other toxic effluents in the form of molecular species under the irradiation of light and semiconducting catalysts. The equation used for the first order kinetic in these chemical reaction phenomena could be written as

$$-\ln(C/C_o) = kt;$$

where C is quoted as the concentration, at t time in seconds, C_o is the initial dye concentration and k represents the rate constant value, and adsorption constant, so on. Typical data of kinetic analysis is given for C-$\mathrm{CaIn_2O_4}$ in Fig. 3.9 for dye degradation using photocatalytic phenomenon. This study could be concluded with pivotal points that the innate rate of catalytic reaction is source dependent and self-degradation in first order kinetics (Gouvea et al. 2000; Rong et al. 2015; Rochkind et al. 2014; Eyasu et al. 2013; Raji and Palanivelu 2016; Foletto et al. 2012; He et al. 2015). The lucid rate constant in the kinetic equation is a lumped parameter mostly consisting of those rates constant value, the other parallel chemical reaction rates that took place over semiconducting catalyst surface and several other unclear rates of dye degradation. So, the rate constant for catalytic reaction cannot be taken as a lucid measure for comparing this process that is taking place between two or more catalysts that are not similar; it will have some very serious misconceptions when doing comparative study. In these examples given in Table 3.4, the researchers have reported the chemical

Table 3.4 First order rate constant values for dyes degraded when adsorbed on photocatalyst

Photocatalyst	Dye	First order rate constant value	References
ZnO	Crystal Violet	0.079 min^{-1}	Rauf and Salman
ZnO	Methyl Red	0.014 min^{-1}	Rauf and Salman
ZnO	Basic Blue	0.1 min^{-1}	Rauf and Salman
TiO_2	Crystal Violet	0.026 min^{-1}	Rauf and Salman
TiO_2	Methyl Red	0.008 min^{-1}	Rauf and Salman
TiO_2	Basic Blue	0.045 min^{-1}	Rauf and Salman
SnO_2	Crystal Violet	0.010 min^{-1}	Rauf and Salman
SnO_2	Methyl Red	0.004 min^{-1}	Rauf and Salman
SnO_2	Basic Blue	0.017 min^{-1}	Rauf and Salman
ZnO nanoflowers	Methyl Orange	0.05485 min^{-1}	Pandit et al. (2015)
ZnO nanoflowers	Congo Red	0.04611 min^{-1}	Pandit et al. (2015)
ZnO nanoflowers	Chicago Sky Blue	0.003182 min^{-1}	Pandit et al. (2015)
ZnO nanoflowers	Eosin B	0.002884 min^{-1}	Pandit et al. (2015)
TiO_2	Congo Red	0.0102 min^{-1}	Mukhtish et al. (2013)
TiO_2	Methylene Blue	0.0085 min^{-1}	Mukhtish et al. (2013)
TiO_2	Acid Orange 10	0.0326 min^{-1}	Quang et al. (2017)
TiO_2	Acid Orange 12	0.0269 min^{-1}	Quang et al. (2017)
TiO_2	Acid Orange 8	0.0235 min^{-1}	Quang et al. (2017)
TiO_2	Amido Black 10B	0.02083 min^{-1}	Singh et al. (2013)
TiO_2	Methyl Red	0.0019 min^{-1}	Anpo et al. (1987)
1.5Ag–0.75Ni/TiO_2	Methyl Red	0.0085 min^{-1}	Anpo et al. (1987)
1.5Ag–1.5Ni/TiO_2	Methyl Red	0.0326 min^{-1}	Anpo et al. (1987)
1.5Ag–3.0Ni/TiO_2	Methyl Red	0.0269 min^{-1}	Anpo et al. (1987)
3.0Ag–1.5Ni/TiO_2	Methyl Red	0.0235 min^{-1}	Anpo et al. (1987)
P25-TiO_2	Amido Black 10B	0.02083 min^{-1}	Singh et al. (2013)
ZnO	Rose Bengal	~4.5 × 10^{-5} s^{-1}	Abo-Farha (2010)
$CeCrO_3$	Fast Green	~4.4 × 10^{-4} s^{-1}	Xiaoqing et al. (2017)
TiO_2	RG 19	~4.69 h^{-1}	Quang et al. (2017)
TiO_2	AO 7	~ 2.07 h^{-1}	Quang et al. (2017)
P-25 TiO_2	Crystal Violet	0.060 min^{-1}	Rauf and Salman
P-25 TiO_2	Methyl Red	0.012 min^{-1}	Rauf and Salman
P-25 TiO_2	Basic Blue	0.017 min^{-1}	Gul and Yildlrln (2009)
ZnO	Methyl Orange	0.00029 min^{-1}	Dnyaneshwar (2017)

(continued)

Table 3.4 (continued)

Photocatalyst	Dye	First order rate constant value	References
ZnO	Rhodamine 6G	0.00027 min^{-1}	Dnyaneshwar (2017)
WO_3	Acid Orange 7	0.0225 min^{-1}	Morgan and Watson (2010)
TiO_2	Carmine dye	0.1456 min^{-1}	Li (2011)
TiO_2	Lissamine Green B	0.0165 min^{-1}	Zhiyong et al. (2007)
ZnO	Methylene Blue	0.0135 min^{-1}	Abo-Farha (2010)
TiO_2	Reactive Red	0.0325 min^{-1}	Min et al. (2015)
ZnO	Congo Red	0.0586 min^{-1}	Mezughi et al. (2014)

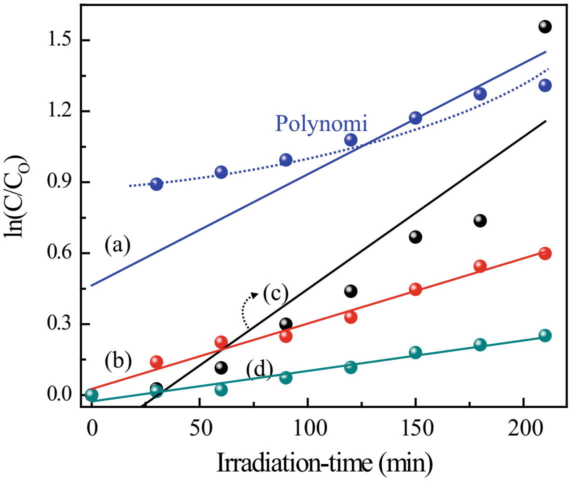


Fig. 3.9 The ln(C/C_0) versus t plots of a photocatalytic degradation of the CV dye using **a** the as-prepared and annealed C-$CaIn_2O_4$ at **b** 400 °C and **c** 600 °C for 2 h in air, and **d** a standard P25-TiO_2 powder dispersed in water by irradiating over UV–light

kinetic rate constant for the best catalyst as around 24 min^{-1} whereas the value for the degradation of chlorophenol rate constant of around 3.47 min^{-1} (here photon irradiated degradation is not present) (Li et al. 2017; Paridwala et al. 2017; Liu et al. 2015, 2016; Kumar and Sahare 2013).

Some of the precautions have been exercised when comparing two or more semiconducting catalytic system phenomenon on the basis of the chemical kinetic constant rate values when used first order for catalysts reactions when dye gets adsorbed on the surface following its degradation. This may apply to certain reactions generally involving multiple steps that may succeed or precede the surface chemical reactions that are sometimes taken as first order reaction kinetics. Degradation of dye can foster several preconditions, out of which one is the adsorption of dyes on the surface of semiconducting catalyst surface and the equilibrium constant must be shown in the rate constant value calculated in data collected. There are so many preconditions that have been reported for the dye degradation, like the surface adsorption

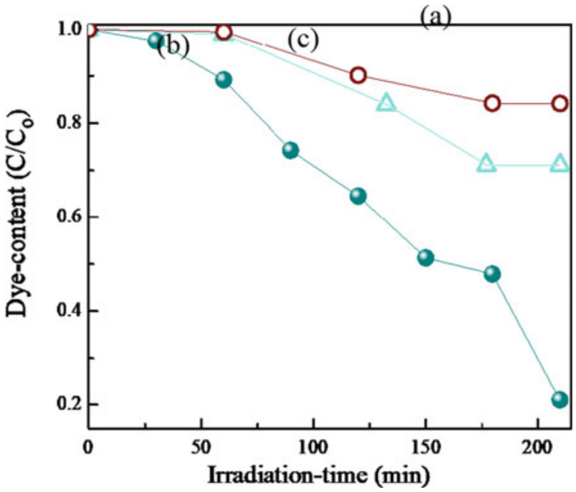


Fig. 3.10 A degradation of the CV-dye **a** before and **b** after dispersing in a photocatalytic C-$CaIn_2O_4$ sample-3 in water by irradiating over UV-light, with **c** degradation of sample (**b**) in absence of any irradiation

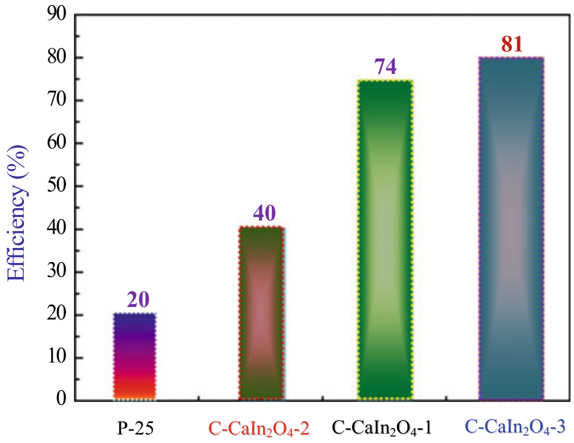


Fig. 3.11 A comparison of efficiencies of photocatalytic degradation of a CV dye in different catalysts dispersed in water and irradiating over UV-light

of organic dyes on catalyst and rate constant value. The surface values are capable of giving different orders of reactivity for adsorbents, and it should be considered when choosing the materials for treatment of effluents. BET adsorption isotherms are very famous Brunauer, Emmett, Teller isotherms as shown in Fig. 3.12 for determining surface area of the catalyst using adsorption curve; Table 3.5 shows the reported surface areas and pore sizes of annealed samples of core–shell C-$CaIn_2O_4$ nanostructures (*This is one of my recent works*). Keeping in mind the surface characteristics of these catalysts and nature of organic dyes have always been considered in this research field, not just this but even pH can change the surface charge carriers thus effecting the adsorption of dyes. Dyes are mostly chosen with surface as acidic or basic characteristics, showing anionic or cationic property in charged dyes. This

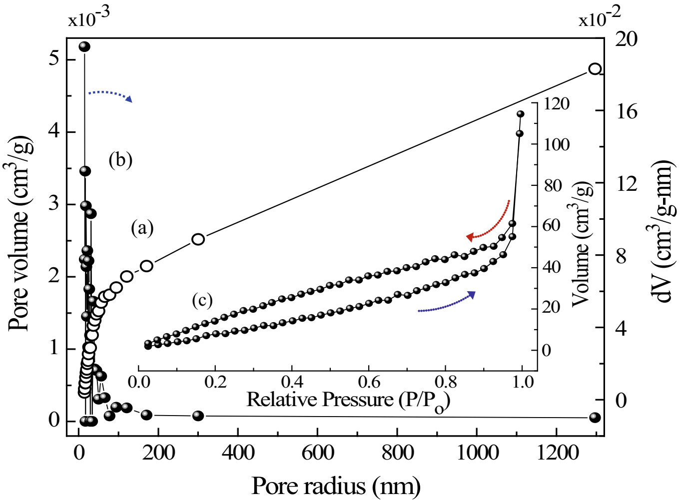


Fig. 3.12 **a** Commutative V_c and **b** its derivative plotted over r-values a C-$CaIn_2O_4$ sample, with **c** N_2 adsorption–desorption isotherms

Table 3.5 Surface area and pore size obtained for the as-prepared and annealed C-$CaIn_2O_4$ samples using the BET analysis

S. No	Sample	Surface area ($m^{2-}g^{-1}$)	Pore radius (nm)
1	As-prepared	22.312	1.5
2	Annealed at 400 °C for 2 h in air	26.526	1.5
3	Annealed at 600 °C For 2 h in air	47.996	1.5

aspect has not yet been tackled when treating the chemical kinetics of photocatalytic dye degradation on semiconducting materials. In recent studies, the details on adsorption of dyes and its consequences on the kinetic behavior of dye degradation have not been touched or linked yet; this comparison will benefit for future.

3.4.2.2 Loading of Semiconducting Catalyst

Some of the observations that have been checked and recorded in the recent trends of photocatalytic degradation of dyes is that as the weight of dyes load increases, the overall efficiency to degrade dye via adsorption on the catalyst surface decreases. So, it’s not an easy one to find out as the surface area exposed to dye adsorption of the catalyst will sometimes not be equivalent to quantity of catalyst present in the solution. The saturation point for dye adsorption on the surface of the semiconducting catalyst is also checked, as beyond certain extent of limit it will stop the photocatalytic phenomenon; most of the research studies report only few kg of around 3–4 g per liter of dye in solution. Industries should now put a control on the effluents that are possibly destroying water bodies and environment, as already mentioned that the weight extent of dye adsorption on the surface of catalyst is still an ongoing limitation. This could be marked as the control of pollution and effluents by the authorities for our environmental safety and protection.

3.4.2.3 Light Wavelength and Its Intensity of Irradiation Effect

The usage of solar light radiation has always been less expensive and less toxic to our lives and environment. The effect of photo light irradiation on the chemical photocatalytic phenomenon has been demonstrated in three ranges:

i. At low intensity, the rate of reaction increases with the light irradiation
ii. At medium and high intensities, the kinetic rate is not dependent on the light intensity.

Overall, the degradation rate for UV–visible light as a source of irradiation is better than the solar light radiation. Secondly, the charge pairs i.e., electron–hole formation & its recombination would be differently done under UV–visible light source. Thus, light wavelength is another major point in affecting the charge pair formation and recombination rate.

3.4.2.4 Dye Degradation Mechanism

Photocatalyst is one of the best methods that can be applied for several applications for example, organic pollutants degradation from wastewater, production of hydrogen gas, purifying of air and other antibacterial activity. In 1972, Fujishima and Honda discovered the beginning of a new era in heterogeneous photocatalysis as a photocatalytic splitting of water on a TiO_2 electrode as noticeable by the phenomena. The wavelength or light (photon) energy and the catalyst are main characteristics on which photocatalytic reaction are dependent. In general, as a catalyst which performs as sensitizer especially, semiconducting materials due to their electronic structure for the irradiation of light stimulated redox process, which is defined by a filled valence band and a vacant conduction band as shown in Fig. 3.13.

When photons in terms of the light energy falls (or interacts) on the surface of a material of energy of incident radiation if equivalent or more than the bandgap energy of the semiconducting material, the electrons present in valence band are excited to the conduction band of the semiconductor. Holes would be charges left in the valence band; these holes can oxidize donor molecules and react with water molecules to generate hydroxyl radicals. The conduction band electrons react with dissolved oxygen species to form superoxide ions. These electrons induce the redox reactions. These holes and electrons could undergo successive oxidation and reduction reactions with any species, which might be adsorbed on the surface of the semiconductor to give

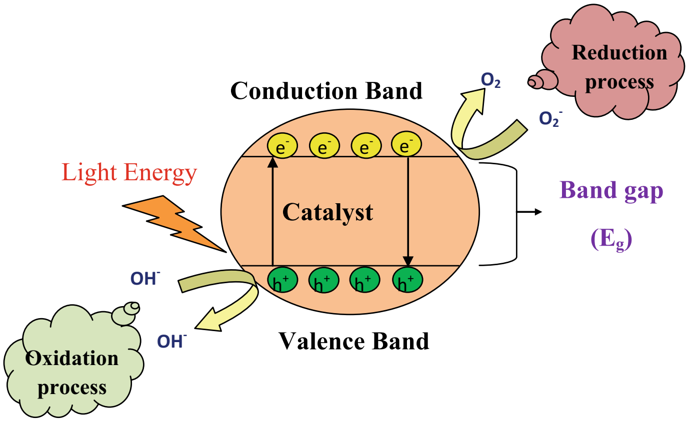


Fig. 3.13 Schematic representation of semiconductor photocatalytic mechanism

the necessary products. The photocatalytic performance of C-$CaIn_2O_4$ powders (as-prepared and annealed at 400 and 600 °C) were studied along with the benchmark Degussa P25 TiO_2 powder by considering crystal violet (CV) as the target dye. Photocatalytic studies were done under UV (24 W, intensity 400 lx, $\lambda < 400$ nm) irradiation at the sample surface under stirring condition.

Aqueous solutions of crystal violet with a concentration 5×10^{-5} M with a photocatalyst loading of 1 g/L were taken. The dispersions were equilibrated for dye adsorption on the photocatalyst surface for 30 min. During the degradation period, the dispersions were collected at regular intervals of thirty minutes in case of UV light irradiation as shown in Fig. 3.14. To note down the extent of the degradation, the samples were centrifuged at 6000 rpm for 10 min to collect the so far degraded dye solution. Absorption spectra of all the collected dye solutions were taken using Perkin-Elmer UV–visible spectrophotometer Lambda 750.

3.5 Summary

In this chapter, we clearly explained the recent developments in the photocatalytic performance of different semiconducting materials for varied dyes that have been thoroughly studied by researchers in terms of optimized parameters like, pH, concentration of solution, quantity of catalyst employed, cationic and anionic form of dye, bandgap of semiconducting materials and source of light. The research in this field has increased immensely in recent years and is only going to grow as trend says. The reports of these studies mentioned in our literature mainly deal with some common variables as given above. In end the summarization of the results in this detailed study, this work deals with several aspects which we can explore in following way:

1. Insufficiently treating the chemical kinetic information collected in terms of the pseudo first order reaction rate. Hence, we have to priorly take in consideration the adsorption characteristics in this phenomenon.

Fig. 3.14 Setup of photocatalytic mechanism

2. The natural effect in this research is the adequate quantity of catalyst, and identification of those active sites and surface area number density that will be adsorbed on the surface of semiconductor.
3. The dye degradation is partially or sometimes completely dependent on the behavior of oxidizing agent that has been incorporated; choice of oxidizing agent is under our control for the redox potential of the species.
4. The dye adsorption on the semiconducting surface decides that whether the pH of the solution is acidic or basic; thus, the process of degradation gets clear. This variation in pH was been demonstrated for the semiconducting surface in response to the pH value.

We can conclude in the end of this book chapter, that all studies done in this photocatalytic field of dye degradation for waste water treatment or effluents treatment could be appropriately be extended to other detailed studies in future thus covering more economical and global significances.

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