CHAPTER 7

PHOTO-CATALYTIC DEGRADATION OF DYES: AN EVALUATION

Introduction

Photo-catalytic degradation of dyes or other organic pollutants is a recent research exercise intensively pursued [1-7]. Synthetic dyes are nowadays extensively used in the products like clothes, leather accessories, furniture, and plastic products. However, nearly 12% of these dyes is wasted during the dying process and ~ 20% of this wastage enters the environment [8]. Dye degradation is a process in which the large dye molecules are broken down chemically into smaller molecules. The resulting products are water, carbon dioxide, and mineral byproducts that give the original dye its color. During the dyeing process, not all of the dye molecules are used. The water waste that the industry releases contain a percentage of these dye molecules.

Heterogeneous photo-catalysis is one of the modern methods widely employed for the degradation or bleaching of the dyes [9]. The process mainly involves transfer of electrons from the valence band to the conduction band of a semiconductor surface (mostly oxides and sulfides) on illumination with appropriate wavelength of light. These generated excitons react with oxygen or water to yield superoxide anions and hydroxide radicals. These species have increased oxidizing and reducing power to degrade numerous molecules including those present in industrial dyes. The decontamination processes by these species and some other species like various forms of Fenton processes are called in scientific parlor Advanced Oxidation Process (AOP). Even though AOP is an important research area in the contemporary literature, we shall restrict only to those dye degradation processes promoted by semiconductors photo-catalytically [10-12].

It is necessary at this stage to point out the need to review this topic at this stage. The reasons include [13]:

(1) There are number of research groups working on this area and it is better to assimilate the literature at frequent periodicity

(2) Photo-catalytic degradation of pollutants is one of the methods which has some advantages including total degradation and possibly the less expensive method.

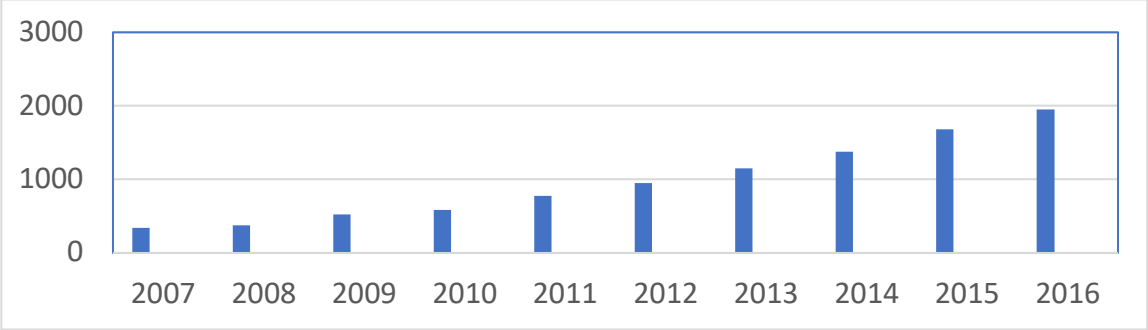
(3) The degraded components like water and carbon dioxide are non-toxic.

(4) The feasibility of degradation of any pollutant can be *a priori* decided from the numerical values of the oxidation potential of the pollutant and the reagent (like $OH^{\bullet}$ radical; standard reduction potential value is around 2 V [14]).

There are various kinds of dyes that are employed for coloring objects. These materials are classified according to the structure of the molecule component, color, the method that is adopted to apply these dyes to objects. The chromophore group attached to the dye molecule specifies the group to which the dye belongs and these can mainly be classified as acridine dyes, azo dyes, anthroquinone dyes, nitro dyes, xanthene dyes and quinine-amine dyes and so on [7]. The studies reported on photocatalytic dye degradation mainly concerned with the variables like concentration of the dye, the amount of catalyst employed, the effect of the intensity of the light irradiation and the time of irradiation and the effect of dissolved oxygen and other species. The kinetics of photocatalytic degradation of dyes are usually considered to be a pseudo first order reaction with the kinetic data fitted to the equation $-\ln (C/C_0) = kt$. The relevance of this kinetic data fit will be considered separately in a subsequent section.

Though extensive studies are reported on the photo-catalytic degradation of pollutants in water, there are certain aspects that have not yet received careful attention. The purpose of this presentation is to focus on these issues and to point out what is required in this direction. The literature in this area is increased five times or more during the last 10 years as seen from the data shown in Fig.1. It is noticed that the number of publications is doubling or more every five-year period. It is therefore natural that people attempt to review the literature at periodic intervals [5-7]. However as said earlier, the research is pursued mostly around oxides (especially TiO_2) and the variables studied are mostly the same, whether it is required or not.

Fig.1.Number of publications falling under the category of Photo-catalytic degradation of dyes (source: Web of Science)



Before we embark on the limitations of the studies so far reported, it is necessary to briefly review the available literature though not comprehensively but representatively. A few selected publications from literature are summarized in Table 1. Majority of the studies reported in literature deal with the effect on degradation activity on variables like the amount of the catalyst, the concentration of the dye employed, pH, effect of the radiation source and time of irradiation and also the effect of dissolved oxygen and others**.** The kinetics of degradation of dyes on most of the catalyst systems studied follows first order [15].

Conventional chemical, physical and biological processes have been extensively employed for treating waste water containing dye molecules. These methods have the following disadvantages like high cost, requirement of high energy, generation of secondary pollutants in the treatment process. The Advanced Oxidation Process (AOP) has received considerable attention in recent times for the decomposition of organic dyes [16].

1. The literature so far

This is an area of research which is carried out throughout the world unlike other areas of science. Research in certain areas of science is confined to certain regions of the world but degradation of dyes has been studied in almost all the countries and regions including almost all the developing countries around the world. This is reflected in the data assembled in Table 1**.** Scientifically the process involved in the degradation of dyes can be pictorially represented as shown in Fig2**.**

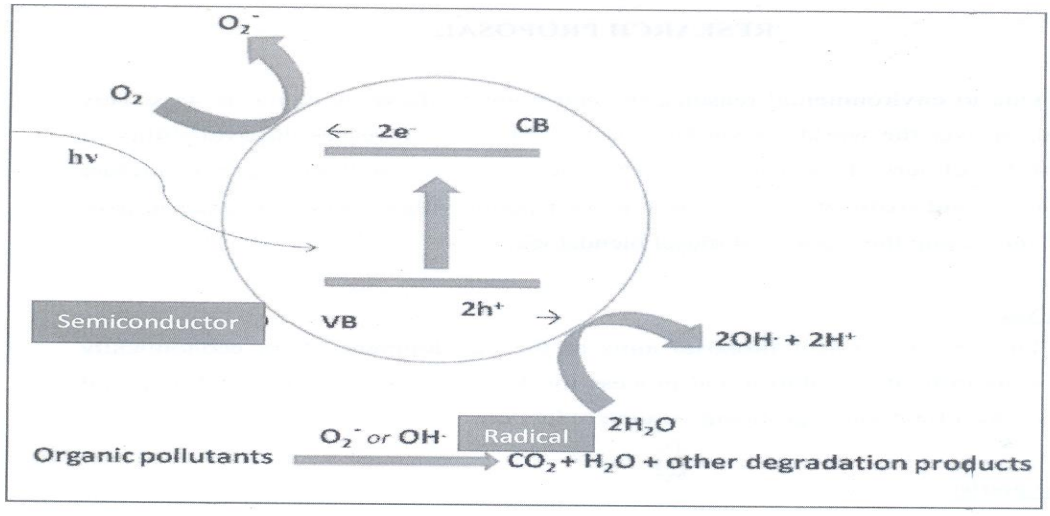


Fig.2. Pictorial representation of the process taking place in the photocatalytic degradation of dyes on semiconductor surfaces.

Most of the photocatalytic dye degradation studies reported have been with Titanium dioxide as photo-catalyst. However, the major disadvantage of TiO_2 that it absorbs only in the UV regions since it has a band gap of around 3.2 eV. Among the different phase of TiO_2, anatase form of TiO_2 is mostly employed due to its higher photon absorption characteristics. It is clear that the phase composition of TiO_2 has a role to play in degradation of dyes. Among the most prominent phases of TiO_2 namely Anatase, rutile and Boookite, the first two phases are most studied systems as seen from the data given in Table.1. The position of oxygen ions on the anatase surface exhibits a triangular arrangement which allows significant absorption of organic molecules, whereas, the orientation of titanium ions in the anatase phase creates an advantage's reaction condition with the adsorbed organic pollutants [17-24]. Interestingly, these favorable structural arrangements of oxygen and titanium ions are not present in the rutile phase. It is also believed that pure anatase phase with small proportion of rutile phase is conducive for meso-porosity and thus favourable for dye adsorption [17-28].

Mechanistically, the photon excites an electron from valence to the conduction band and the excitons (free electron in the conduction band and hole in the valence band) generate radical species which is responsible for the degradation of organic dyes to carbon dioxide and water and other degradation species.

Even though large surface area is recommended for effective dye degradation, (P-25 Degussa TiO_2 is a mixture of 80% anatase + 20% rutile phase and this combination alone makes this system active. In most of the studies this system is used as standard for comparison), dye adsorption may precede the degradation and this can affect the interpretation of the kinetics of degradation of dye. This aspect will be taken up subsequently.

Among the various waste water treatment procedures, dye removal has occupied a prominent place. Because of aesthetic and environmental concerns, the degradation of dyes in the effluent water of textile dyeing and finishing industry has been most important [29]. The semiconductors especially TiO_2 and ZnO are employed as nanorods, nano-spheres, thin porous films, nanofibers and nanowires or supported on polymeric films [30]. These systems exhibit high activity, low cost and environmentally acceptable [31-33].

Apart from TiO_2 and ZnO, various other semiconducting systems like CdS, ZrO_2 and WO_3 have been employed in the photocatalytic degradation of dyes. These studies and other reports on ternary oxides are included in Table.1. The drawback of most of these systems like TiO_2 is the high value of band gap and they require UV photon sources to be able to decolourize waste-water.

Table 1. Representative literature data on the photocatalytic degradation of dyes

Catalyst systems studied	Dyes employed	Conditions and variables studied	Reference
Graphene – gold Nano composite (GOR/Au)	Rhodamine B Methylene blue Orange H	Visible light - Rate of degradation of methylene blue is greater than Rhodamine B even though the redox potential is highest among these three dyes. Adsorption is identified as the reason	A1
Nanocrystalline anatase and rutile TiO_2	Acetophenone Nitrobenzene Methylene blue Malachite green	The activity of Anatase is higher than that observed with Rutile. The reason for this difference is not indicated in this communication	A2
TiO_2, ZnO, SnO_2	Crystal Violet Methyl Red	ZnO exhibited highest activity. Even better than Degussa P-25 and loading silver on ZnO resulted in 20% increase in photocatalytic activity	A3
Mg-TiO_2	Methyl Orange	The catalyst has better activity than the undoped TiO_2- Dye sensitization and injection of the excited electron is considered as the cause	A4
TiO_2 Impregnated ZSM-5 (TiO_2-ZSM = 0.15:1)	Reactive Black-5	This ratio system shows high adsorption capacity and degradation activity	A5
ZnO-nanoflowers	Methyl Orange Congo Red Eosin B Chicago Sky Blue	The catalyst prepared from asymmetric Zn(ii)dimeric complex showed good photocatalytic activity towards methyl Orange compared to other dyes	A6
ZnO Nano powder	Rhodamine B	95% degradation of the dye was observed under solar light irradiation	A7

TiO_2	Methyl Orange Methylene Blue	The photocatalytic activity is found to be greater in the presence of solar light than in UV.	A8
Nano-sized $GdCoO_4$	Rhodamine B Rhodamine Blue (RBL) Orange G(OG) Remazol Brilliant Blue (RBBR)	The catalyst (3nm) is more efficient than P-25. Size dependence is shown. The intermediates in both $GdCoO_4$ andP-25 are the same	A9
TiO_2	Methylene Blue Methyl Orange Congo Red	The size and Phase (Anatase) are important. Adsorption of the dye on the catalyst surface is also important (Freundlich isotherm)	A10
TiO_2	Indigo Indigo Carmine	Complete mineralization of the dyes Irradiation with visible light only produced color removal	A12
TiO_2 immobilized on polyvinyl alcohol (PVA) or polyacrylamide (PA)	Methylene Blue, Anthraquinone, Remazol Brilliant Blue R (RBBR), Reactive Orange (RO16).	TiO_2 loaded on PVA appears to be better than that loaded on PA	A11
Nanostructured TiO_2	Mono, di and tri azo class of dyes. Classes of indigoid, anthraquinone triaryl methane and xanthene dyes	Degradation depends on the chemical structure of the dye, the nature of functional groups. Mono-azo dyes degrade faster than anthraquinone dyes. Presence of nitrite group promote the degradation activity.	4
High surface area TiO_2	Methylene Blue Congo Red	Sol-gel method preparation of TiO_2 is suitable for degradation of Dyes.	2

		Freundlich Isotherm is employed.	
N-doped TiO_2	Methylene Blue Methyl Orange	Visible light source was employed and depends on nitrogen content of the catalyst	1
Nanometer sized TiO_2	Acid Orange 10(AO10) Acid Red 14 14ARI14)	The azo and sulphonate groups are determining factors for degradation	A13
SiO_2 nanoparticle dopes with Ag and Au	Methyl Red	(OH). radical produced initiates and also sustains the degradation of the dye	A14
Titanium dioxide	Emerald Green	Degradation rate constant depends on pH	A15
ZnO and TiO_2	Rhodamine B Methylene Blue Acridine Orange	ZnO dissolves as $Zn(OH)_2$ and hence shows lower activity as compared to TiO_2	A16
TiO_2 (UV/Solar/pH)	Procion Yellow	TiO_2 in presence of solar irradiation is better	A17
TiO_2	Reactive Red 2	Degradation in presence of $H2O_2$ and persulphate ion.	A18
Thermally activated ZnO	Congo Red	Pseudo second order Kinetics was observed	A19
Sol-gel TiO_2 films	Lissamine Green B	The film prepared in presence of Polyethylene glycol is better	A20
ZnO	Methylene Blue	Decoloured of actual industrial waste water	A21
Ag-TiO_2 core shell particle	Reactive Blue 220	the core shell system was better catalyst under solar light	A22
Anatase Nano-TiO_2	Reactive Blue 4 (anthraquinone dye	In presence of H_2O_2 the dye degradation increased	A23
TiO_2/ZnO Photo catalyst	Methylene Blue	ZnO appeared to be better than Pure TiO_2	A24

P160 TiO_2	Basic Yellow – 28	Better degradation in weak acidic conditions, carbonate ion increased degradation activity	A25
Ferrihydrite modified Diatomite with TiO_2 /UV	Vat Green 03	A composite catalyst with P-25 with co-adsorbent removed colour over 98%	A26
Orthorhombic WO_3	AO7 dye	Phenol, humic acid and EDTA inhibited decolouring but oxalic acid increased	A27
Fe^{3+}/C/S/-TiO_2	Mono and Di-azo dyes	Mono azo dye is better than diazo dyes. Decolurization under visible light	A28
Ni doped TiO_2	Malachite Green	Hydroxyl ion as the oxidizing species	A29
TiO_2	Solo phenyl Red 3BL	Concentration of OH^* and O^* radical determines the rate	A30
TiO_2	Mono Azo Orange 7 (AO&) Reactive Green 19 (RG19)	Mono azo dye (AO7) than the binary azo dye (RG19) under solar light	A31
TiO_2	Azo dye and disperse dye	A modelling exercise on governing parameters	A32
TiO_2	Methyl Orange Methylene Blue	Degradation under UV irradiation	A33
TiO_2 Photo-catalyst	Indigo Carmine dye	UV irradiation optimum conditions pH=4 and dye concentration 25 ppm 98% colour removal	A34
ZnO photo-catalyst	Methylene Blue	Basic solution is better.	A35
TiO_2 Photo-catalyst	Methylene Blue	Basic medium is better	A36
Carbon doped TiO_2	Amido Black-10B	Active oxygenated species is responsible for decolourization.	A37

ZnO photocatalyst	Direct Red-31 (DR-31) dye	Effect of annealing temperature (500-800C)- UV irradiation	A38
Sol-gel TiO_2 films	Methyl orange, Congo Red	TiO_2 films with dip coating with Polyethylene glycol (better) 254 UV is better than UV 365 nm	A39
Undoped and Fe doped CeO_2	Methyl Orange	1.5 % doping of Fe^{3+} was optimal	A40
Immobilized TiO_2	Methylene Blue	Deposition of Photosensitive hydroxides decreased the activity	A41
$Ni/MgFe_2O_4$	Malachite Green	Visible light active	A42
TiO_2	Methyl Orange	Superoxide anion radicalPolytetrafluoroethyle-A1 based triboelectric nanogenerator (TENG) assisted the process	A43
Crosslinked Chitosan/nano CdS	Congo Red	Acidic Medium is better, Presence of No_3^- accelerated Br^-, Cl^-, SO_4^{2-}, inhibit decolourization	A44
TiO_2/UV	Methylene Blue	Mineralization of carbon, nitrogen and Sulphur into CO_2, NH_4^+,SO_3^{2-}	A45
Cu impregnated P-25	Azo dye Orange II	Cu Impregnated TiO_2 is better than H_2O_2/UV homogeneous reaction.	A46
Ag-Ni/TiO_2 synthesized by gamma irradiation	Methyl Red	Bimetallic co-doped is better than bare TiO_2	A47
Cr doped TiO_2	Methylene Blue Congo Red	Cr doped promoted Anatase to Rutile phase transition	A48
ZnS Quantum dots doped with Au and Ag	Methylene Blue	Metal loading favours degradation; accounted in terms of increased life time of charge carriers, Opto-electronic characteristics and	A49

		isoelectric point need to be considered in proposing photo-catalyst	
Mesoporous CeO_2	Rhodamine B	Hydroxyl radicals are the active species	A50
ZnS	Rose Bengal	Hydroxyl radicals are shown as the active species	A51
C-TiO_2 films	Azorubine	Photo-degradation and adsorption effects are the reason for better decolourization	A52
La-Y/TiO_2	Methylene Blue	Optimum dose 4 g/L	A53
Ag-TiO_2	Direct Red 23	Optimum dose 3 g/L	A53
ZnO	Remazol Brilliant Blue dye (RBB)	The degradation follows first order kinetics	A54
TiO_2 Degussa P-25	2,4-dimethylphenol, 2,4-dichlorophenol, 2-chlorophenol and phenol	pH 5 was found suitable	A55
ZnO	Crystal Violet	high specific surface area (56.8 m^2/g), high crystallinity and better optical property are responsible for the better activity of ZnO nano nails.	A56
In/ZnO nano particles	Methylene Blue	In is well dispersed on ZnO	A57
TiO2 Degussa P25 and ZnO	Methylene Blue	Visible light is better and ZnO better than TiO_2	A 58
TiO_2 nano particles	Methylene Blue	Basic medium is better	A59
ZnO	Reactive Blue	Reactor design and optimum time	A60
Magnetite+H_2O_2 +UV	Methylene Blue	Process parameter optimization	A61
$Bi_{24}O_{31}Cl_{10}$	Rhodamine B	compatible energy levels and high electronic mobility	A62

BiOI	Rhodamine B anionic reactive blue KN-R	h^+ is the dominant specie for the degradation of dyes.	A63
TiO_2	Alizarin yellow	of Cl^-, SO_4^{2-} inhibit dye removal, depends on TiO_2 source	A64
TiO_2, ZnO	Polycyclic aromatic hydrocarbons (AH)	Surface to volume ratio appears to be relevant	A65
ZnS doped with Mn	Malachite green	UV/ZnS, UV/ZnS/H2O2, UV/doped ZnS systems studied	A66
TiO_2 and Cu-doped TiO_2	reactive blue 4, reactive orange 30, reactive red 120and reactive black 5	Cu-doped TiO2 nanoparticles are very effective in degrading the dye pollutants	A67
Mn_3O_4 nano particles	amido black 10B	peroxomonosulfate (PMS), peroxodisulfate (PDS) and hydrogen peroxide (HP) enhanced degradation	A68
Photo-Fenton system	Reactive orange M2R dye	Acidic pH favours, reaction mechanism is proposed	A69
TiO2 catalyst with a very low level of Pt	Phenol	Eosin Y sensitized TiO_2	A70
TiO_2	Methylene Blue	p-n junction heterostructure CuO-TiO2 enhance photoactivity	A71
TiO_2 coated Cotton fabric	amaranth dye	prepared fabric showed enhanced dye degradation capabilities	A72
titanium dioxide TiO2 and zinc phthalo cyanine (ZnPc)	4-Nitrophenol	Efficiently degrade nitrophenol	A73

Silver phosphate	Methylene Blue	visible-light-driven photodegradation of dye pollutants	A74
$CeCrO_3$	Fast Green dye	First order kinetics,	A75
ZnO	Acid Green 25	Both acidic and basic medium	A76
Anatase TiO_2	Methylene Blue Phenol	pH = 6.4 is optimum	A77
CeO_2-ZnO	Methylene Blue 4'-(1-methyl-benzimidazoyl-2)-phenylazo-2" -(8"-amino-1"-hydroxy-3",6"-disulphonic)-naphthalene acid	50-80 nm with large defects	A78
Al_2O_3-TiO_2 and ZrO_2-TiO_2 Nanocomposites	Methylene Blue Rhodamine B Methyl Orange	both the composites degrade methylene blue and rhodamine B effectively under UV-A light the photodegradation of methyl orange is slow	A79
MgO	Methylene Blue	Over 90% degradation	A80
TiO_2	Acid Orange 67	light source is UV is better in comparison to Visible.	A81
TiO_2 on Polyethylene film	Crystal Violet Methylene Blue Basic Fuchsine	Sun light degradation Undergraduate experiment	A82
Mo doped TiO_2	Toluidine blue-o	degradation of the dye follows pseudo-first order kinetics	*A83*
Copper Ferrite	Methylene blue	In Glycerol it is not effective H_2O_2 is better	A84
TiO_2 as photo-catalyst	Tatrazine (azo dye)	Influence of addition of other salts studied	A85
$Ni_{o.6}Co_{0.4}Fe_2O_4$	Congo Red	Photo-catalytic degradation maximum at pH 3	A86
Zn-TiO_2	Direct Blue 71 dye	Zn Doped system is better than bare TiO_2	A87

Ag modified ZnO	Reactive Orange *16*	Ag modified system was better than pure ZnO	A88
TiO_2	Reactive Orange 16 Dye (RO16)	Effect of the amount of TiO_2 studied	A89
ZnO-CuO	Reactive black5 (RB5)	This system is suitable technique for degradation of dyes and environmental pollution from effluents.	A90
TiO_2 on polyethylene glycol	Methyl Orange Congo Red	Under UV irradiation higher efficiency observed	A91
g-C3N4 thermally Modified with Calcium Chloride	Rhodamine B	The photo-generated hole and the superoxide radical are the main active species in the degradation process. 50 times more active than unmodified system	A92
CdO/TiO_2 coupled semiconductor	Reactive Orange 4 (RO 4)	best photocatalytic activity in the degradation of RO 4 compared with bare TiO_2	A93
ZnO	Remazol Brilliant Blue R, Remazol Black B, Reactive Blue 221 and Reactive Blue 222	A synergistic effect in the coupled TiO2-ZnO system was not observed	A94
CdS/SL g-C_3N_4) SL= Single Layer)	Rhodamine B	visible-light-responsive and environmentally friendly photo-catalyst for the degradation of dye	A95
BiOCl	Rhodamine B and other dyes	Visible light degradation may be complicated. The use of multitude of dyes is necessary	A96

		to assess the degradation activity	
Cr doped ZnS	Methyl Orange	Visible light is better than UV	A97
Nano TiO_2(C-Fe doped)	C.I. Basic blue 9, C.I. Acid orange 52	Real waste water treatment	A98
CeO_2-SnO_2	Direct Black 38	Activity is comparable with TiO_2-P25	A99
Z-scheme SnO_{2-x}/g-C_3N_4 composite	Rhodamine B	Z-scheme mechanism to enhance photo-degradation activity	A100
BiOCl-Au-CdS	Methyl Red Rhodamine B	Z-scheme BiOCl-Au-CdS exhibited excellent sunlight-driven photocatalytic activity toward the degradations of organic dyes and antibiotics	A101
TiO_2-ZnO	RB 21 dye	UV photoreactor and TiO_2 is the best	A102
CaO	indigo carmine dye	pH 9 was suitable	A103
g-C_3N_4/oxygen vacancy-rich zinc oxide	Methyl Orange	deactivated after five cycles of methyl orange degradation	A104
$CoFe_2O_4$/C_3N_4 hybrid	Rhodamine B	Typical Z-scheme system in environmental remediation	A105
α-$Bi_4V_2O_{11}$; γ-$Bi_4V_2O_{11}$	Rhodamine B Methylene Blue	Surface to Volume ratio is responsible	A106
BiVO4-rGO	Rhodamine B	Better than pure BiVO4 and P-25	A107
Flower like N-doped MoS_2	Rhodamine B	27 times better than bare MoS_2 and 7 times better than P-25	A108
$H_3PW_{12}O_{40}$/SiO_2	Rhodamine B	under simulated natural light irradiation	A109
$SrTiO_3$	Methylene Blue Rhodamine Methyl Orange	Non-selective process	A110

$CuO/Ag_3AsO_4/GO$	Phenol	Photo-stability and reusability	A111
TiO_2/diatomite	Rhodamine B, Methyl orange, Methylene blue	wastewater treatment -good photocatalytic property and reusability.	A112
Cr (VI) using Ag/TiO2	4-chlorophenol	stability and reusability of catalysts	A113
$PbCrO_4$/TiO2	Rhodamine B	good visible light-sensitive photocatalyst for removing Rh B	A114
$WO_3/SnNb_2O_6$	Rhodamine B	Z-scheme charge transfer mechanism was proposed for the elimination of organic contaminants under irradiation of visible light.	A115
ZnO	Acid Red 27	H_2O_2, $K_2S_2O_8$, $KBrO_3$ due to concentration increases the rate	A116
CuS	methylene blue, rhodamine B, eosin Y and congo red	photodegradation rates of dyes usually follow pseudo-first-order kinetics for degradation	A117
Cobalt Hexacyanoferrate (II)	Neutral Red dye	Degradation under UV light and photo-catalyst	A118
N-doped ZnO	Azure A	N-doped zinc oxide has been used as an effective catalyst for carrying out number of chemical reactions	A119
Al_2O_3-TiO_2, ZrO_2-TiO_2	methylene blue, rhodamine B	Methylene blue degradation is slow Visible light degradation of rhodamine B	A120

The percentage degradation of dyes in waste water improved with increasing intensity of exposed light. With high intensity irradiation, the recombination may not be significant, but when the intensity is low the recombination of the electron hole formed predominates. The photocatalytic activity depends on the thermal history of the semiconductor and the chemical nature of the semiconductor. The

choice of the semiconducting systems is based on parameters like physical form of the semiconductor, their stability under the reaction conditions. Environmentally acceptable, cost effectiveness, less toxicity and in all these counts titanium dioxide appears to be the best choice. Comparing various systems for use of actual waste water treatment the following order has been proposed Degusa P-25 > TiO2 (Anatase) > TiO2 (Rutile). However, the amount of catalyst employed depends on the chemical nature of the semiconductor.

The photocatalytic activity can be altered with modification of the semiconductor. The modification can be with various aims like shifting the irradiation wavelength to the visible region and also coupling semiconductors for effective use of the excited electron-hole pair. Recently g-carbon nitride (g-C_3N_4) has been modified with calcium chloride and the mechanism of degradation of Rhodamine B dye itself is modified. The proposed schematic diagram is shown in Fig.3.

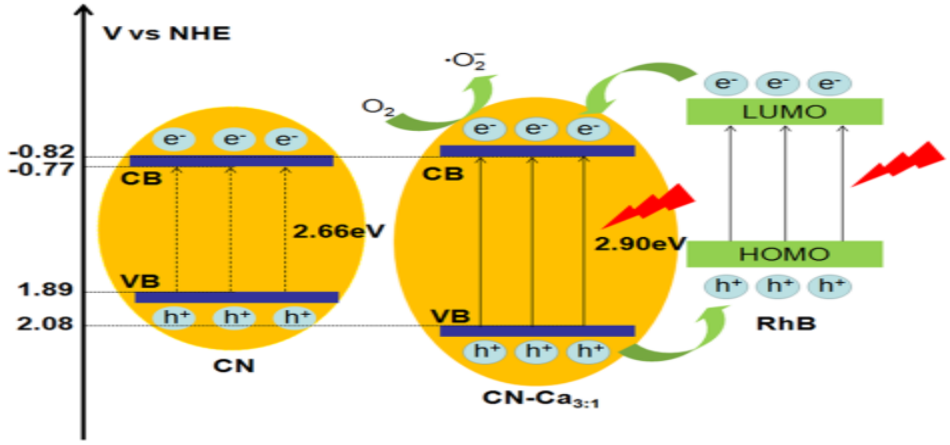


Fig.3. Energy level diagram of CN and CN modified with $CaCl_2$ and how the degradation activity of Rhodamine B is enhanced with modification of CN [reproduced from ref. A92].

The valence band level in modified system is shifted to more positive value and thus enhances the oxidation ability. Simultaneously the dye is also photoexcited and transfers the electrons to the conduction band of the modified g-C_3N_4. This route predominates when visible light is employed.

Apart from these inherent modifications to the semiconductors, (so called doping), coupling of semiconductors have also been tried for shifting the wavelength to the visible region and this is also called Z-scheme in some cases.

Mechanism of Photo-catalytic Degradation of Dyes

It has been stated that radical species generated during photoexcitation of the semiconductor is responsible for the degradation of dyes. The essential steps involved can be visualized as the following steps [34-36].

$$\text{Semiconductor} + \text{photons (hv)} \rightarrow e^- (CB) + h^+(VB) \quad (1)$$

$$h^+ + H_2O \rightarrow H^+ + OH^- \quad (2)$$

$$h^+ + OH^- \rightarrow OH\bullet \quad (3)$$

$$e^- + O_2 \rightarrow O_2\bullet \quad (4)$$

$$2e^- + O_2 + H_2O \rightarrow H_2O_2 \quad (5)$$

$$e^- + H_2O_2 \rightarrow OH\bullet + OH^- \quad (6)$$

$$\text{Organic pollutant} + OH\bullet + O_2 \rightarrow CO_2 + H_2O + \text{other degradation products} \quad (7)$$

The pictorial representation of this process is shown in Fig.2. The excited electron and hole in the semiconductor are responsible for the degradation of the dye. Variety of semiconductors have been employed and most of them are employed in the nano-state due to increased surface area and also due to favourable quantum size effect [37-40].

TiO_2 in various forms with metal and non-metal doping have been employed for the degradation of a variety of dyes owing to its stability, degradation capability, and also non-toxic nature [41,42]. However, the possible experimental variables including the wavelength of the light to be used and separation technology of the solid in treatment process restricts the employment of TiO_2 for commercial dye degradation process. More advanced level research is at present required to find suitable alternative to TiO_2 for this application. Other than TiO_2 the other system that is mostly employed is ZnO and other semiconducting oxides as stated above.

Experimental Variables Studied:

In addition to the chemical nature of the semiconductor employed, the wave length of irradiation employed based on the band gap of the semiconductor, the effect on the degradation of dyes on a number of other experimental variables have been studied. Typical semiconductors studied and the band gap values of each of them are assembled in Table.2.

Table.2. Typical Semiconductors [Refer to Table 1] used for Photo-catalytic Degradation of Dyes and the Band gap (eV) Values of these Materials.

Semiconductors studied for photodegradation of dyes	Band gap values (eV) (wavelength [nm] of irradiation)
TiO_2(Anatase form)	3.2(387)
TiO_2 (Rutile form)	3.0 (415)
TiO_2 (Brookite form)	3.14(395)
ZnO	3.36(370)
WO_3	2.76(450)
CdS	2.42(515)
CuO	1.2 (1035)
Cu_2O	2.2 (565)
MgO	5.90
Mn_3O_4	3.28(380)
ZnS	3.6(345)
CeO_2	3.19(390)
Fe_2O_3	2.3(540)
Fe_3O_4	2.25(550)
ZrO_2	3.87(320)
g-C_3N_4	2.66(465)
Ag_2O	1.4(885)
$SrTiO_3$	3.25(380)
Bi_2WO_6	3.13(395)
$BaTiO_3$	3.30
Bi_2O_3	2.80
CdO	2.20
CoO	2.01
Cr_2O_3	3.50
HgO	1.90
In_2O_3	2.80
MnO	3.60
Nb_2O_5	3.40
NiO	3.50
PbO	2.80
PdO	1.00
Sb_2O_3	3.00
SnO	4.20
SnO_2	3.50
V_2O_5	2.80

Effect of pH on the Photo-catalytic Degradation of Dyes

As seen from Table 2, each of the degradation studies is efficient at a particular pH. The reason for this observation is the change in the value of the oxidation potential (approximately 59 mV per pH) of the species involved in the experimental system studied. Since the oxidation potential of hole and reduction power of the electron generated due to irradiation are dependent on the positions of the top of the valence band and bottom of the conduction band and these are critical for the degradation of dyes on semiconducting systems employed.

The Issues on Hand

Most of the published literature covers as variables, the light source, its intensity, pH of the medium, the amount of the catalyst employed. The initial concentration of the dye taken for study, the irradiation time and the other species like oxygen present in the reaction medium. Almost all the publications have been following these variables invariably. It is recognized that the study of these variables is important for assessing the utility of this method for pollutant removal (textile dye industry) from waste water stream. The purpose of this presentation is to examine on what other aspects of these parameters can be intrinsically examined.

Kinetics of photodegradation of Dyes

Generally, the kinetics of photocatalytic degradation of organic pollutants and dyes by semiconductors have most often been treated as first order kinetics. This is most common in literature and as an example one of the recent references [15] is provided. The purpose is to analyze some of the consequences of treating the kinetic data on the removal of pollutants and other organic species especially under photo-catalytic conditions generally under first order kinetic equation. The first order kinetic equation generally employed in such circumstances [41] can be written as $- \ln (C/C_0) = kt$; where C is the concentration at any time t seconds and C_0 is the value of concentration of the species that is undergoing degradation at zero time (initial concentration taken) and k is the value of the rate constant, this may be a lumped parameter including the value of the intrinsic rate constant, adsorption equilibrium constant and so on. Typical kinetic data analyzed according to first order kinetic equation of the photo catalytic decomposition of Rhodamine B from ref 15 is given as an example.

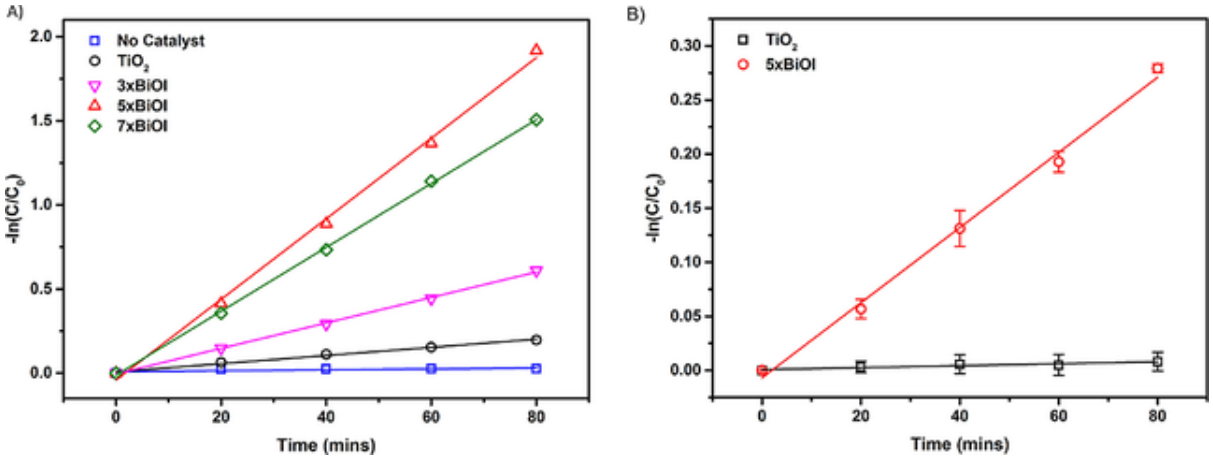


Fig 1 Photocatalytic degradation kinetics of Rhodamine B on various photo-catalysts treated according to first order kinetic equation [data reproduced from ref.15. There are any number of this kind of analysis reported in literature on photocatalytic decomposition of dyes and they are referred to in this article at other places.

The main conclusion of this study is that the inherent rate consists of the photo-catalytic and also photo-induced self-degradation of the dye follows first order kinetics. If this argument were to be accepted then the treatment of kinetic data according to first order is only grossly approximate and the apparent rate constant in the equation is only a lumped parameter consisting of mostly the value of the intrinsic rate constant and the rates of other parallel reactions that would have taken place on the surface of the catalyst and many other accompanying non-elucidated rates of degradation. Possibly, the value of the apparent rate constant cannot be taken as a measure of the activity of the catalyst for comparison since the process taking place on the two or more catalysts are not identical or not even similar. This will have serious misconceptions for comparison purposes.

In the example given, the authors report the apparent rate constant on the most active catalyst as 23.9 min^{-1} while the value of the apparent rate constant for the degradation of chlorophenol (where the photon induced degradation is assumed to be nearly negligible) is 3.47 min^{-1} which can be assumed in this case as the value of the intrinsic rate constant. May be caution has to be exercised while comparing two or more catalytic systems on the basis of the rate constant values of the kinetic data treated as first order since on all catalyst systems the reaction may not follow the same kinetics though the treatment

according to first order kinetics may apparently satisfy the first order kinetics. The statements given may be applicable to all general reactions which can involve multiple steps like preceding or succeeding surface reactions which are more often treated with first order kinetics. However, it is not our intention to make a general treatment.

Dye degradation can have many preconditions, one of them is the adsorption of the dye on the catalyst surface and this equilibrium constant should be reflected in the value of the rate constant evaluated from the data. The values of the equilibrium constants of adsorption on various catalyst surfaces can give same or different order of reactivity of adsorbents and this has to be considered while choosing the material for wastewater treatment.

The catalyst loading

Another observation invariably recorded in literature is that the rate increases with catalyst loading till certain weight and above this the rate of degradation of the dye decreases with increase in weight. This is not an unusual result since the exposed surface area of the catalyst will not be directly proportional to the amount of catalyst loaded in solution phase reactions. Since dye degradation is proportional to the amount that is adsorbed on the surface of the solid, there can be a saturation point beyond which the solid amount may not have a direct relationship to the degradation extent. In most of the studies reported the maximum amount of the solid loaded for maximum activity is 3-4 mg per liter [3] of the dye solution. This weight of the solid probably indicates the saturation limit of adsorption of the dye and possibly limits the concentration of the dye solution that can be employed for degradation and thus the industries polluting waterways must restrict their pollution limits to this level. This may be a mark for pollution control authorities to note and it must restrict pollution to this level.

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