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REVIEW ARTICLE

Photocatalytic Degradation of Dyes: An Overview

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Abstract: ***Introduction:*** The photocatalytic degradation of dyes has been investigated throughout the world irrespective of the level of science in that country. The normal variables considered are the concentration of oxidising species, the concentration of the dye employed, the catalyst used and intensity and source of photons applied for degradation studies. The kinetic data obtained on the decolorization have usually been treated with pseudo first order kinetic expression even there are some exceptions.

Conclusion: This presentation addresses the limitations of the consideration of this topic under these experimental parameters and shows how the study can be directed in future.

Keywords: Dye degradation, Kinetics of degradation, Semi-conductor photo-catalysis, Mechanism of dye degradation, Reactive oxygen species, Pollution abatement

1. INTRODUCTION

Photocatalytic degradation of dyes or other organic pollutants is an intensively pursued research exercise mainly from the last quarter half of the 20th century [1-7]. Nowadays, the synthetic dyes are extensively used in products like clothes, leather accessories, furniture, and plastic products. However, during the dyeing process, nearly 12% of these dyes exclude as waste, and ~ 20% of this wastage enters to the environment [8]. In the dye degradation process, large molecules of dyes get oxidised down into smaller molecules such as water, carbon dioxide, and other mineral byproducts. As stated, the dyeing process does not utilise all the dye molecules, and consequently, a substantial amount of dyes were present in the waste water released from the industry.

Heterogeneous photocatalysis is one of the modern methods widely employed for the degradation or bleaching of the dyes [9]. The process mainly involves the transfer of electrons from the valence band to the conduction band of a semiconductor surface (mostly oxides and sulphides) on illumination with an appropriate wavelength of light. These generated excitons react with oxygen or water produces superoxide anions and hydroxide radicals. These species have the high oxidising power to degrade numerous molecules including industrial dyes. The decontamination processes by these reactive oxygen species and some other species as like various forms of Fenton processes, called in the scientific parlour as Advanced Oxidation Process (AOP). Even though AOP is an important research area in the contemporary literature, we shall restrict the discussion to the semiconductor mediated photodegradation of dyes [10-12].

At this stage, it is necessary to mention the need for a review on this topic. The reasons include the following[13];

(1) Some research groups are working in this area. Therefore, it is better to assimilate the literature at constant periodicity.

(2) Photocatalytic degradation of pollutants is one of the methods have some advantages including total deterioration of the pollutant and possibly in the less expensive method.

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

(4) The feasibility of deterioration of any pollutant can be *a priori* decided from the numerical values of the oxidation potential of the pollutant and the reagents such as $OH^{\bullet}$ radical with standard reduction potential value of around 2 V [14].

Various kinds of dyes are available in the markets as colouring objects. The classification of dye materials is according to the structure of the molecule component, colour and its method of application. The general classification of dyes evolved based on the chromophoric group in the molecular moiety as acridine dyes, azo dyes, anthraquinone dyes, nitro dyes, xanthene dyes and quinine-amine dyes and so on [7]. The studies reported on photocatalytic dye degradation are mainly concerned with the variables like the concentration of the dye, amount of photocatalyst employed, effect of the intensity of the irradiated light, time of irradiation and effect of dissolved oxygen and other species. The kinetics of photocatalytic degradation of dyes is considered to be a pseudo first order reaction with the kinetic data fitted to the equation Heterogeneous photocatalysis is one of the modern methods widely employed for the degradation or bleaching of the dyes [9]. The process mainly involves the

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transfer of electrons from the valence band to the conduction band of a semiconductor surface (mostly oxides and sulphides) on illumination with an appropriate wavelength of light. These generated excitons react with oxygen or water produces superoxide anions and hydroxide radicals. These species have the high oxidising power to degrade numerous molecules including industrial dyes. The decontamination processes by these reactive oxygen species and some other species as like various forms of Fenton processes, called in the scientific parlour as Advanced Oxidation Process (AOP). Even though AOP is an important research area in the contemporary literature, we shall restrict the discussion to the semiconductor mediated photodegradation of dyes [10-12].

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Though extensive studies are reported on the photocatalytic degradation of pollutants in water, certain aspects 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 mainly the same, whether it is required or not.

Before we embark on the limitations of the studies so far reported, it is necessary to review the available literature though not comprehensively but representatively briefly. A few publications from the literature are summarised in Table **1**. The 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, the 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].

2. THE LITERATURE SO FAR

This is an area of research which is carried out throughout the world unlike other areas of science. Research in particular areas of science is confined to ascertain regions of the world, but the 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 Fig. **2**.

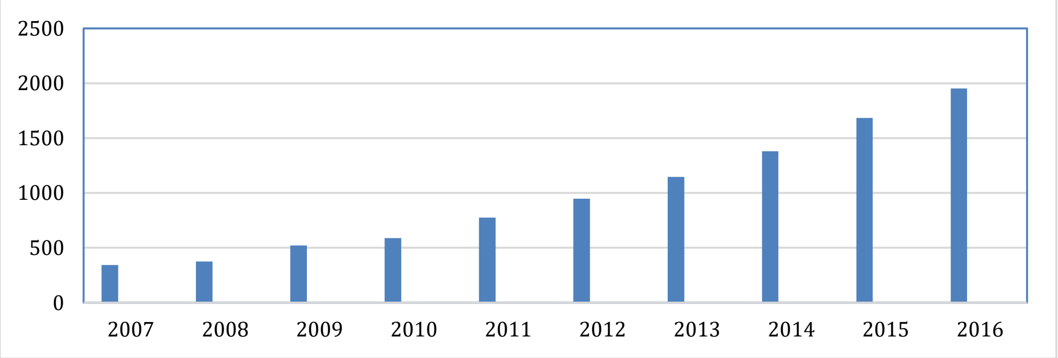

Fig. (1). Number of publications falling under the category of Photo-catalytic degradation of dyes (Source: Web of Science).

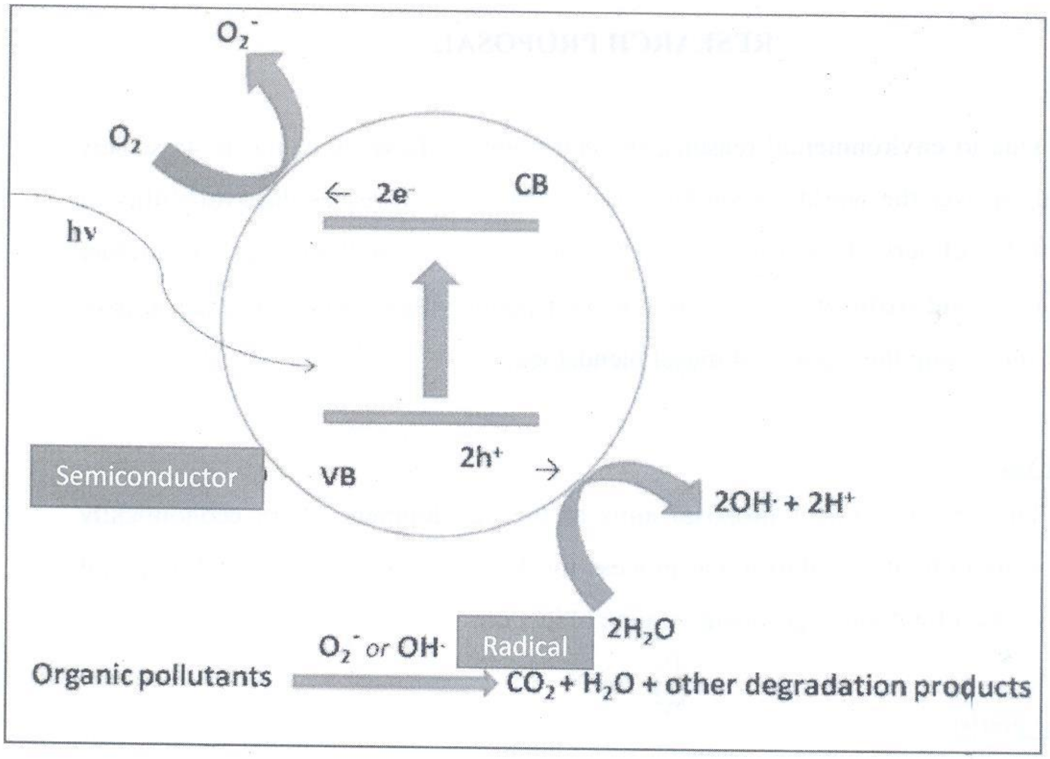

Fig. (2). Pictorial representation of the process taking place in the photocatalytic degradation of dyes on semiconductor surfaces.

Most of the photocatalytic dye degradation studies reported have been with Titanium dioxide as a photocatalyst. However, the major disadvantage of TiO_2 that it absorbs only in the UV region since it has a band gap of around 3.2 eV. Among the different phases 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 is in a triangular arrangement which allows significant absorption of organic molecules, whereas, the orientation of titanium ions in the anatase phase creates a favourable reaction condition with the absorbed organic pollutants [17-24]. Interestingly, these favourable structural arrangements of oxygen and titanium ions are not present in the rutile phase. It is also believed that pure anatase with a small proportion of rutile phase is conducive for mesoporosity and thus favourable for dye adsorption [25-36].

Mechanistically, the photon excites an electron from the valence band 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 the large surface area is recommended for the effective degradation of the dye, the 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. In the case of Degussa P-25 TiO_2, it is a mixture of 80% anatase and 20% rutile phase, and this combination alone makes this system active and in most cases used as a standard for comparison, and it is believed to be core shell model system.

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 significant [37]. The semiconductors especially TiO_2 and ZnO are employed as nanorods, nanospheres, thin porous films, nanofibers and nanowires or supported on polymeric films [40]. These systems exhibit high activity, low cost and environmentally acceptable [41-43].

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 the listing 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.

A typical pictorial representation of photodegradation of dyes on a complex photo-catalyst $K_6Ta_{10.8}O_{30}$ is shown in Fig. **3**. In general, on other layered systems and composite catalysts also the photodegradation can take place, and the pictorial representation of this process is shown in Fig. **4**(**a**) and (**b**).

Brookite is another phase of titanium dioxide which has been used as a photocatalyst for the degradation of dyes [54].

Most of the studies on the photocatalytic degradation of dyes are monitored by decolourization or Chemical Oxygen Demand (COD) measurements though it is desirable to follow the concentration of products formed and elucidate the

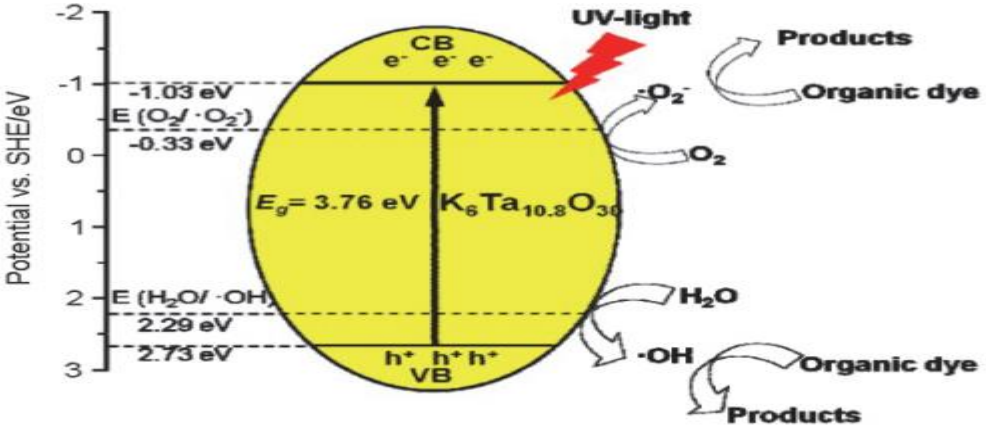

Fig. (3). Representation of energy levels and species responsible for the photodegradation of dyes on typical complex oxide potassium tantalate [Reproduced from Ref.146].

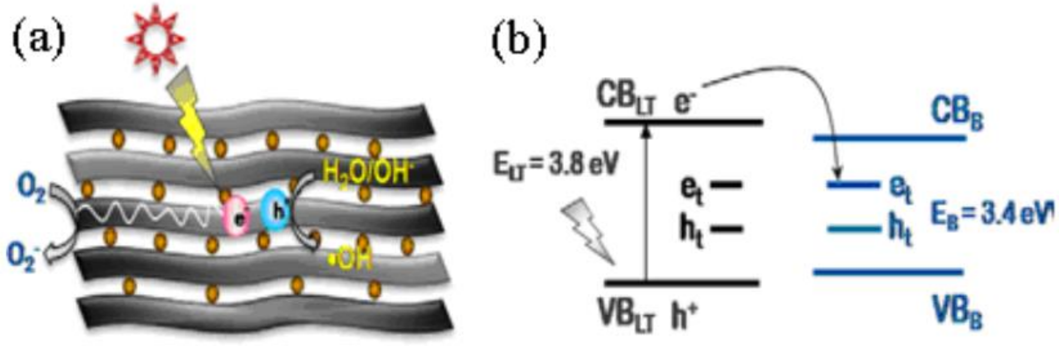

Fig. (4). Diffusion behaviour of the charge carrier in layered nanosheets and (b) transport pathway of the excited electron in the mixed photocatalysts [55].

various pathways in which these products are formed. These type of studies is limited in the literature [56]. It is essential to make sure that the degradation products are not toxic either to the material to be dyed or to living beings. The influence of parameters employed for dying process is not established as purely safe. The optimisation of parameters and identifying suitable photocatalyst may be necessary for successful implementation of this technique for purifying waste water in the dying technology

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 the physical form of the semiconductor and their stability under the reaction conditions. Environmentally acceptable, cost effectiveness, less toxicity and in all these counts titanium dioxides appears to be the common (best) choice. The following order has been proposed in most of the published literature Degussa P-25 > TiO_2 (Anatase) > TiO_2 (Rutile) for the comparison of various photocatalytic systems towards actual wastewater treatment. 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 efficient 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. **5**.

The valence band level in the 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), the coupling of semiconductors have also been tried for shifting the wavelength to the visible region, and this is known as a Z-scheme process.

2.1. 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 visualised (in a general sense) in the following steps [42-44]**.**

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

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

Catalyst Systems Studied	Dyes Employed	Comments	Refs.
Graphene – gold Nano composite (GOR/Au)	Rhodamine B Methylene blue Orange H	The rate of degradation of methylene blue is greater than Rhodamine B in the presence of visible light even though the redox potential is highest among these three dyes. Adsorption of the dye on to the surface identified as the reason for the photoactivity.	[25]
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	[26]
TiO_2, ZnO, SnO_2	Crystal Violet Methyl Red	ZnO shows better photoactivity than Degussa P-25 and silver deposited ZnO increases the photocatalytic activity by 20%	[27]
Mg^{2}-TiO_2	Methyl Orange	The catalyst has better activity than the un-doped TiO_2- Dye sensitization and injection of the excited electron is considered as the cause	[28]
TiO_2 Impregnated ZSM-5 (TiO_2-ZSM = 0.15:1)	Reactive Black-5	The system shows high adsorption capacity and degradation activity.	[29]
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	[30]
ZnO Nano powder	Rhodamine B	95% degradation of the dye was observed under solar light irradiation	[31]
TiO_2	Methyl Orange Methylene Blue	The photocatalytic activity is found to be greater in the presence of solar light than in UV.	[32]
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 $GdCoO_4$ and P-25 are the same	[33]
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)	[34]
TiO_2	Indigo Indigo Carmine	Complete mineralisation of the dyes Irradiation with visible light only produced colour removal	[36]
TiO_2 immobilised 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	[35]
Nanostructured TiO_2	Mono, di and tri azo class of dyes. Categories 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. The presence of nitrite group promotes 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. Freundlich Isotherm is employed.	[2]
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 determining factor for degradation	[37]
SiO_2 nanoparticle doped with Ag and Au	Methyl Red	OH radical produced initiates and also sustains the degradation of the dye	[38]
Titanium dioxide	Emerald Green	Degradation rate constant depends on pH	[39]
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	[40]
TiO_2 (UV/Solar/pH)	Procion Yellow	TiO_2 in the presence of solar irradiation gives better degradation.	[41]
TiO_2	Reactive Red 2	The degradation in the presence of $H2O_2$ and persulphate ion were studied.	[42]
Thermally activated ZnO	Congo Red	Pseudo second order Kinetics was observed	[43]
Sol-gel TiO_2 films	Lissamine Green B	The TiO_2 film prepared in Polyethylene glycol shows better photoactivity than the clean TiO_2.	[44]
ZnO	Methylene Blue	Actual industrial waste water is used for the experiments.	[45]
Ag-TiO_2 core shell particle	Reactive Blue 220	The core shell system shows better photoactivity under solar light	[46]
Anatase Nano-TiO_2	Reactive Blue 4 (anthraquinone dye	In the presence of externally added H_2O_2, the dye degradation gets increased.	[47]
TiO_2/ZnO Photo catalyst	Methylene Blue	ZnO appeared to be better than Pure TiO_2	[48]
P160 TiO_2	C! Basic Yellow - 28	Better degradation in weak acidic conditions, the addition of carbonate ion increased the degradation.	[49]
Ferrihydrite modified Diatomite with TiO_2 /UV	Vat Green 03	A composite catalyst with P-25 with co-adsorbent removed colour over 98%	[50]
Orthorhombic WO_3	AO7 dye	Phenol, humic acid and EDTA inhibited but oxalic acid increased the decolourisation of the dye.	[51]
Fe^{3+}/C/S/-TiO_2	Mono and Di-azo dyes	Mono azo dye degrades faster than diazo dyes under visible light.	[52]
Ni doped TiO_2	Malachite Green	Hydroxyl ion as the oxidising species	[53]
TiO_2	Solo phenyl Red 3BL	The concentration of OH^* and O^* radical determines the degradation rate.	[54]
TiO_2	Mono Azo Orange 7 (AO&) Reactive Green 19 (RG19)	Mono azo dye (AO7) degrades faster than binary azo dye (RG19) under solar light.	[55]
TiO_2	Azo dye and disperse dye	A modelling exercise on governing parameters.	[56]
TiO_2	Methyl Orange Methylene Blue	Degradation under UV irradiation	[57]
TiO_2 Photo-catalyst	Indigo Carmine dye	UV irradiation optimum conditions pH =4 and dye concentration 25 ppm 98% colour removal	[58]
ZnO photocatalyst	Methylene Blue	The basic solution is better for the degradation reaction.	[59]
TiO_2 Photo-catalyst	Methylene Blue	The basic medium is better for the degradation	[60]
Carbon doped TiO_2	Amido Black-10B	Active oxygenated species is responsible for decolourization.	[61]
ZnO photocatalyst	Direct Red-31 (DR-31) dye	Effect of annealing temperature (500-800C)- UV irradiation	[62]
Sol-gel TiO_2 films	Methyl orange, Congo Red	TiO_2 films with dip coating with Polyethylene glycol shows better activity in 254nm than 365 nm.	[63]
Undoped and Fe doped CeO_2	Methyl Orange	1.5 % doping of Fe^{3+} was optimal	[64]

Immobilized TiO_2	Methylene Blue	Deposition of Photosensitive hydroxides decreased the activity	[65]
$Ni/MgFe_2O_4$	Malachite Green	Visible light active	[66]
TiO_2	Methyl Orange	Superoxide anion radicalPolytetrafluoroethyle-A1 based triboelectric nanogenerator (TENG) assisted the process	[67]
Crosslinked Chitosan/nano CdS	Congo Red	The degradation is better in acidic medium. The presence of NO_3^- accelerated, Br^-, Cl^- and SO_4^{2-} inhibited decolourization of the dye.	[68]
TiO_2/UV	Methylene Blue	Mineralization of carbon, nitrogen and sulphur into CO_2, NH_4^+, SO_3^{2-}	[69]
Cu impregnated P-25	Azo dye Orange II	Cu Impregnated TiO_2 is better than H_2O_2/UV homogeneous reaction.	[70]
Ag-Ni/TiO_2 synthesised by gamma irradiation	Methyl Red	Bimetallic co-doped is better than bare TiO_2	[71]
Cr doped TiO_2	Methylene Blue Congo Red	Cr doped promoted Anatase to Rutile phase transition	[72]
ZnS Quantum dots doped with Au and Ag	Methylene Blue	Metal loading favours degradation; accounted in terms increased the life time of charge carriers. Up to electronic characteristics and isoelectric point need to be considered in proposing photocatalyst.	[73]
Mesoporous CeO_2	Rhodamine B	Hydroxyl radicals are the active species	[74]
ZnS	Rose Bengal	Hydroxyl radicals are shown as the active species	[69]
C-TiO_2 films	Azorubine	Photo-degradation and adsorption dual effect is the reason for better decolourization.	[75]
La-Y/TiO_2	Methylene Blue	Optimum catalyst dose 4 g/L	[76]
Ag-TiO_2	Direct Red 23	Optimum catalyst dose 3 g/L	[77]
ZnO	Remazol Brilliant Blue dye (RBB)	The degradation follows first order kinetics	[78]
TiO_2 Degussa P-25	2,4-dimethylphenol, 2,4-dichlorophenol, 2-chlorophenol and phenol	pH 5 was found to be suitable for the degradation reaction.	[79]
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 nanonails.	[80]
In/ZnO nano particles	Methylene Blue	Indium is well dispersed on ZnO	[81]
TiO2 Degussa P25 and ZnO	Methylene Blue	ZnO shows better activity in visible light than TiO_2	[82]
TiO_2 nano particles	Methylene Blue	Basic medium is better for the degradation	[83]
ZnO	Reactive Blue	Reactor design and optimum time	[84]
Magnetite+H2O2+UV	Methylene Blue	Process parameter optimization	[85]
$Bi_{24}O_{31}Cl_{10}$	Rhodamine B	compatible energy levels and high electronic mobility	[86]
BiOI	Rhodamine B anionic reactive blue KN-R	h^+ is the dominant species for the degradation of dyes.	[87]
TiO_2	Alizarin yellow	The presence of Cl^-, SO_4^{2-} inhibits dye removal and it also depends on the TiO_2 source.	[88]
TiO_2, ZnO	Polycyclic aromatic hydrocarbons (AH)	Surface to volume ratio appears to be relevant	[89]
ZnS doped with Mn	Malachite green	UV/ZnS, UV/ZnS/H_2O_2, UV/doped ZnS systems studied	[90]
TiO_2 and Cu-doped TiO_2	reactive blue 4, reactive orange 30, reactive red 120and reactive black 5	Cu-doped TiO_2 nanoparticles are very effective in degrading the dye pollutants	[91]

Mn_3O_4 nano particles	amido black 10B	peroxomonosulfate (PMS), peroxodisulfate (PDS) and hydrogen peroxide (HP) enhanced degradation	[92]
Photo-Fenton system	Reactive orange M2R dye	Acidic pH favours, a mechanism is proposed	[93]
TiO2 catalyst with a shallow level of Pt	Phenol	Eosin Y sensitised TiO_2	[94]
TiO_2	Methylene Blue	p-n junction heterostructure CuO-TiO_2 enhance photoactivity	[95]
TiO_2 coated Cotton fabric	amaranth dye	prepared fabric showed enhanced dye degradation capabilities	[96]
titanium dioxide TiO2 and zinc phthalo cyanine (ZnPc)	4-Nitrophenol	Efficiently degrade nitrophenol	[97]
Silver phosphate	Methylene Blue	Visible-light-driven photodegradation of dye pollutants	[98]
$CeCrO_3$	Fast Green dye	First order kinetics,	[99]
ZnO	Acid Green 25	Both acidic and basic medium	[100]
Anatase TiO_2	Methylene Blue Phenol	pH = 6.4 is optimum	[101]
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	[102]
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, and the photodegradation of methyl orange is found to be slow	[103]
MgO	Methylene Blue	Over 90% degradation	[104]
TiO_2	Acid Orange 67	UV light source is better in comparison to Visible light.	[105]
TiO_2 on Polyethylene film	Crystal Violet Methylene Blue Basic Fuchsine	Sun light degradation. Undergraduate experiment	[106]
Mo doped TiO_2	Toluidine blue-o	Degradation of the dye follows pseudo-first order kinetics	[107]
Copper Ferrite	Methylene blue Glycerol	Degradation of glycerol is not efficient and increased in the presence of added H_2O_2.	[108]
TiO_2 as photo-catalyst	Tartrazine (azo dye)	Influence of addition of other salts studied	[109]
$Ni_{o.6}Co_{0.4}Fe_2O_4$	Congo Red	Photo-catalytic degradation maximum at pH 3	[110]
Zn-TiO2	Direct Blue 71 dye	Zn Doped system is better than bare TiO_2	[111]
Ag modified ZnO	Reactive Orange *16*	Ag modified system was better than pure ZnO	[112]
TiO_2	**Reactive Orange 16 Dye (RO16)**	Effect of the amount of TiO_2 studied	[113]
ZnO-CuO	Reactive black5 (RB5)	This system is a suitable technique for degradation of dyes and environmental pollution from effluents.	[114]
TiO_2 on polyethylene glycol	Methyl Orange Congo Red	Under UV irradiation higher efficiency observed	[115]
g-C3N4 thermally Modified with Calcium Chloride	Rhodamine B	The photo-generated hole and the superoxide radical is the main active species in the degradation process. 50 times more active than unmodified system	[116]

CdO/TiO_2 coupled semiconductor	Reactive Orange 4 (RO 4)	best photocatalytic activity in the degradation of RO 4 compared with bare TiO_2	[117]
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	[118]
CdS/SL g-C_3N_4) SL= Single Layer)	Rhodamine B	visible-light-responsive and environmentally friendly photocatalyst for the degradation of dye	[119]
BiOCl	Rhodamine B and other dyes	Visible light degradation may be complicated. The use of multitude of dyes is necessary to assess the degradation activity	[120]
Cr doped ZnS	Methyl Orange	Visible light is better than UV	[121]
Nano TiO_2(C-Fe doped)	C.I. Basic blue 9 C.I. Acid orange 52	Real waste water treatment	[122]
CeO_2-SnO_2	Direct Black 38	Activity is comparable with TiO_2-P25	[123]
Z-scheme SnO_{2-x}/g-C_3N_4 composite	Rhodamine B	Z-scheme mechanism to enhance photo-degradation activity	[124]
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	[125]
TiO_2-ZnO	RB 21 dye	UV photoreactor and TiO_2 is the best	[126]
CaO	indigo carmine dye	pH 9 was suitable	[127]
g-C_3N_4/oxygen vacancy-rich zinc oxide	Methyl Orange	deactivated after five cycles of methyl orange degradation	[128]
$CoFe_2O_4$/C_3N_4 hybrid	Rhodamine B	Typical Z-scheme system in environmental remediation	[129]
α-$Bi_4V_2O_{11}$; γ-$Bi_4V_2O_{11}$	Rhodamine B Methylene Blue	Surface to Volume ratio is responsible	[130]
BiVO4-rGO	Rhodamine B	Better than pure BiVO4 and P-25	[131]
Flower like N-doped MoS_2	Rhodamine B	27 times better than bare MoS_2 and 7 times better than P-25	[132]
$H_3PW_{12}O_{40}$/SiO_2	Rhodamine B	under simulated natural light irradiation	[133]
$SrTiO_3$	Methylene Blue Rhodamine Methyl Orange	Non-selective process	[134]
CuO/Ag_3AsO_4/GO	Phenol	Photo-stability and reusability	[135]
TiO_2/diatomite	Rhodamine B, Methyl orange, Methylene blue	wastewater treatment -good photocatalytic property and reusability.	[136]
Cr(VI) using Ag/TiO2	4-chlorophenol	stability and reusability of catalysts	[137]
PbCrO4/TiO2	Rhodamine B	good visible light-sensitive photo-catalyst for removing Rh B	[138]
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.	[139]
ZnO	Acid Red 27	H_2O_2, $K_2S_2O_8$, $KBrO_3$ due to concentration increases the rate	[140]
CuS	methylene blue, rhodamine B, eosin Y and Congo red	photodegradation rates of dyes usually follow pseudo-first-order kinetics for degradation	[141]
Cobalt Hexacyanoferrate(II)	Neutral Red dye	Degradation under UV light and photo-catalyst	[142]
N-doped ZnO	Azure A	N-doped zinc oxide has been used as an effective catalyst for carrying	[143]

		out number of chemical reactions	
Al_2O_3-TiO_2, ZrO_2-TiO_2	methylene Blue Rhodamine B	Methylene blue degradation is slow Visible light degradation of rhodamine B	[144]
titanium dioxide (TiO_2), zinc oxide (ZnO), stannic oxide (SnO_2), zinc sulphide (ZnS), cadmium sulphide (CdS)	Methyl Orange (MO), Rhodamine 6G (R6G	ZnO/solar light was observed to be better than ZnO/UV system	[145]
$K_6Ta_{10.8}O_{30}$	ARG dye	the high photocatalytic activity of the degradation of ARG dye under UV	[146]
TiO_2(Brookite)	Rhodamine	Less active than P-25	[147]
TiO_2 (Brookite +rutile mixture)	Orange dye	Samples annealed at different temperatures	[148]
Brookite nanoflowers	Methyl Orange	More active than Anatase	[149, 150]
Anatase and rich brookite rich films	Acid orange 7 4-chlorophenol	Both exhibited same activity	[151]
TiO_2	Methylene blue Chromium (VI)	TiO2 /UV, system is very efficient compared with different natural and artificial adsorbent	[152]

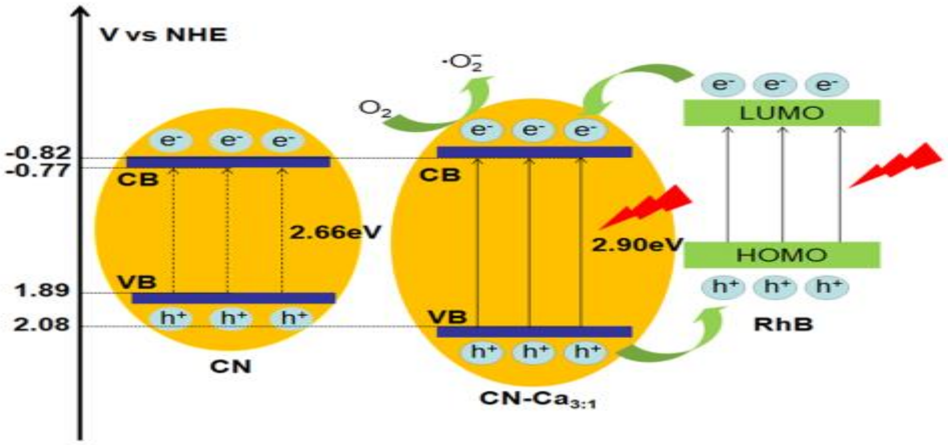

Fig. (5). Energy level diagram of CN and CN modified with $CaCl_2$ and how the degradation activity of Rhodamine B is enhanced with modification of CN [reproduced from ref. 153].

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

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

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

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

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

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

The mechanism given is a general one and depending on the experimental conditions, additional steps can be included.

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. A variety of semiconductors have been employed, and most of them are used in the nano-state due to increased surface area and also due to favourable quantum size effect [45-48].

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 [49,50]. However, the possible experimental variables including the wavelength of the light to be used and separation technology of the solid in treatment process restrict the employment of TiO_2 for commercial dye degradation process. More advanced level research is at present required to find a 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 [51]. However, it is necessary to state the reasons for the preponderance of studies employing TiO_2. Though this is an accepted observation, the reasons for this choice are not explicitly clear in the literature. It is believed that the absorption coefficient (ε) of TiO_2 is high. The scattering capacity of the semiconductor has not yet been fully taken into account though it is known that most of the surfaces depending on the value of roughness factor, the scattering intensity can vary. This may also apply to TiO_2. The value of the absorption coefficient depends on various physical properties like the surface roughness, a particle size in addition to the inherent occupancy of the valence electrons and the wave functions of the occupied states.

2.2. 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 has been studied**.** Typical semiconductors studied and the band gap values of each of them are assembled in Table.2. The photon source employed and intensity of the radiation used is not always reported or monitored. Energy efficient light emitting diodes have also been used, and these studies are reviewed in ref.55. The reaction temperature, the intensity of light and the source of the irradiation, the particle size of the catalyst used, BET-surface area of the solid catalyst used and different mineral forms of the semiconductor influence the degradation rate [56].

2.2.1. Effect of pH on the Photocatalytic Degradation of Dyes

As seen from Table **1**, 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 the 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.

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)
BaTiO3	3.30(375)
Bi_2O_3	2.80(440)
CdO	2.20(560)
CoO	2.01(620)
Cr_2O_3	3.50(355)
HgO	1.90(650)
In_2O_3	2.80(440)
MnO	3.60(345)
Nb_2O_5	3.40(365)
NiO	3.50(355)
PbO	2.80(440)
PdO	1.00(1240)
Sb_2O_3	3.00(415)
SnO	4.20(295)
SnO_2	3.50(355)
V_2O_5	2.80(440)
$K_6Ta_{10.8}O_{30}$	3.76(330)

The effect of pH on the efficiency of dye photodegradation process has to be associated with multiple roles [57]. The adsorption characteristics of the dye also change pH and the surface characteristics of the semiconductor [58]. This aspect has been already considered in detail in another publication [59]. Hydroxyl radicals can be formed by the reaction of hydroxide ions with positive holes. The positive holes are considered as the major oxidation species at low pH, whereas hydroxyl radicals are considered as the predominant species at neutral or high pH levels [60]. In alkaline solution, •OH are easier to be generated by oxidising hydroxide ions available on the semiconductor surface, thus account for the efficiency of the process is logically enhanced [60]. Similar results have also been reported in the photo-degradation of other dyes [61-63]. It has been postulated that the dyes will be charged as a function of pH and bromo-cresol purple dye degradation was better in the acidic medium than in alkaline medium. There are also views that the charged state cannot be due to change in pH [64]. The route by which photo-degradation takes place depends on the products formed as these product molecules will be adsorbed on the surface of the semiconductor surface and thereby can alter its electronic and active site configuration. It was reported that in photo-catalytic degradation the extent of adsorption on unmodified TiO2 is greater for dyes with a positive charge (cationic) than for those with a negative charge (anionic). [66]. Therefore, it is clear that the nature of the particular dye and pH have a profound effect on photocatalytic activity. [67-72]. Azo dyes are positively charged at low pH < 6.8 and higher pH, the dye is negatively charged, and so the adsorption of the dye on the semiconductor surface is affected. It is clear that the waste water treatment must take into account two factors namely the pH of the effluent is not neutral, and surface properties of the semiconductor are influenced by the mixture of substances that would have dissolved in water. The electrical double layer that will exist if charged species were to be present in solution, then this state can affect the electron hole pair separation and also the adsorption properties of the dyes on the semiconductor surface. The rate of photocatalytic degradation of dyes depends on pH and the actual value of the pH at which the rate is maximum depending on the nature of the dye. In alkaline medium, hydroxyl radical (•OH) an oxidant can be formed, thus increasing the rate of photodegradation of the dye [73].

Table 3. Data on the effect of pH on the photocatalytic degradation of dyes.

Dye type	Light source	Photo-catalyst	pH range	Optimum pH	Refs.
Orange G	UV	Sn/TiO_2/Ac	1.0-12.0	2.0	[88]
Methyl Orange	UV	Pt/TiO_2	2.5-11.0	2.5	[89]
Orange G	Visible	N-TiO_2	1.5-6.5	2.0	[90]
Acid Red B	UV	Ce-TiO_2	1.5-7.0	1.5	[91]
Bromo-cresol purple	UV	TiO_2	4.5 & 8.0	4.5	[64]
Methyl Red	visible	3%Ag+1.5%Ni-TiO_2	3-10	4	[154]
Methylene Blue	UV	TiO_2	3-9	Alkaline pH	[155]
Congo Red	Visible	Chitosan/CdS	6-12	6	[156]
Orange H	Solar	Zn-TiO_2	3.0-10.0	3	[74]
Malachite Green	Sun light	Ni/$MgFe_2O_4$	2.0-10.0	4	[157]
Indigo Carmine	UV	TiO_2	4.0-11.0	4	[158]
Textile dye	UV	TiO_2	3.0-7.0	5	[159]
Solophenyl Red 3Bl	UV	TiO_2	2.0-14.0	7	[160]
Methyl Orange	UV	Fe^2/C/S doped TiO_2	2.0-12.0	Acidic Medium	[161]
Acid Orange 7	UV	WO_3	3.0-9.0	3	[162]
Basic Yellow 28	UV	TiO_2	3.0-9.0	5	[163]
Methylene Blue	UV	TiO_2ZnO	1.0-6.0	2	[164]
Reactive Blue 4	UV	Anatase TiO_2	3.0-13.0	3-7	[165]
Methylene Blue	UV	ZnO	2.0-11.0	7(minimum)	[166]
Congo Red	UV	ZnO	5.0-10.0	8	[167]
Reactive Red 2	UV	TiO_2	4.0-12.0	4-6	[168]
Procion Yellow	UV	TiO_2	2.0-10.0	7.8	[169]
Acid Orange	UV	WO_3-TiO_2	1.0-9.0	3.0	[7]
Acid Yellow	UV	TiO_2	---	3.0	[6]
Amido Black 10B	UV	TiO_2	----	9.0	[6]
Methyl Orange	UV	TiO_2	2.0-10.0	8.0	[24]
Rhodamine B	UV	ZnO	2.0-12.0	12.0	[23]
Methyl Orange	Visible	Mg doped TiO_2	3.0-8.0	--	[20]
Acid Orange 10	UV	TiO_2	1.0-11.0	3.0	[170]
Methyl orange, Rhodamine B	UV	ZnO	2.0-10.0	Basic medium	[137]

In Table **3**, some of the specific results on pH influence on the photodegradation of various dyes are given. Therefore, it is important to study the chemical nature of the dyes to be degraded and determine the correct pH to degrade them photo-catalytically. pH variation coupled with the temperature of calcination can result in the phase changes in the semiconductor, and hence the activity also may vary with pH. It is seen from the values given in Table **3** that at acidic pH, TiO_2 degrades the dyes effectively, that means that H^+ ions are mostly adsorbed on the semiconductor and is favourable for dye degradation. This also implies that certain forms of the dye alone are preferentially photo-degraded on TiO_2 surfaces.

The effect of pH on the photodegradation of dyes has to be rationalised based on the reaction mechanism. There are three possible ways dyes can degrade as a function of pH namely (i) direct attack by hydroxyl radical (ii) direct involvement of the positive hole in the oxidation reaction (iii) direct reduction by the participation of the electron excited to the conduction band.

A still more extensive compilation on the optimum pH on the photocatalytic degradation of dyes is already reported as Table.2 in the publication [83].

2.3. 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 recognised that the study of these variables is important for assessing the utility of this method for pollutant removal (textile dye industry) from the waste water stream. The purpose of this presentation is to examine on what other aspects of these parameters can be intrinsically examined.

2.3.1. Kinetics of Photodegradation of Dyes

The kinetics of photocatalytic degradation of organic pollutants and dyes by semiconductors have been most often treated as first order kinetics. This is most common in literature, and as an example one of the recent references [15, 54,55 and many other references] is provided. In Table.4. The literature data where the kinetics of degradation of dye has been treated according to pseudo first order kinetics are summarised.

The purpose is to analyse 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 employed in such circumstances [179] can be written as $-\ln(C/C_0) = kt$; where C is the concentration at any time t seconds, and C_0 is the initial concnetration of the dye, and k is the value of the rate constant, this rate constant may be a lumped parameter including the value of the intrinsic rate constant, adsorption equilibrium constant and so on. Typical kinetic data analysed according to first order kinetic equation of the photo catalytic decomposition of Rhodamine B from ref 15 is given as an example.

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. Moreover, the apparent rate constant in the equation is a lumped parameter consisting of mostly the value of the intrinsic rate constant, 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 cau-

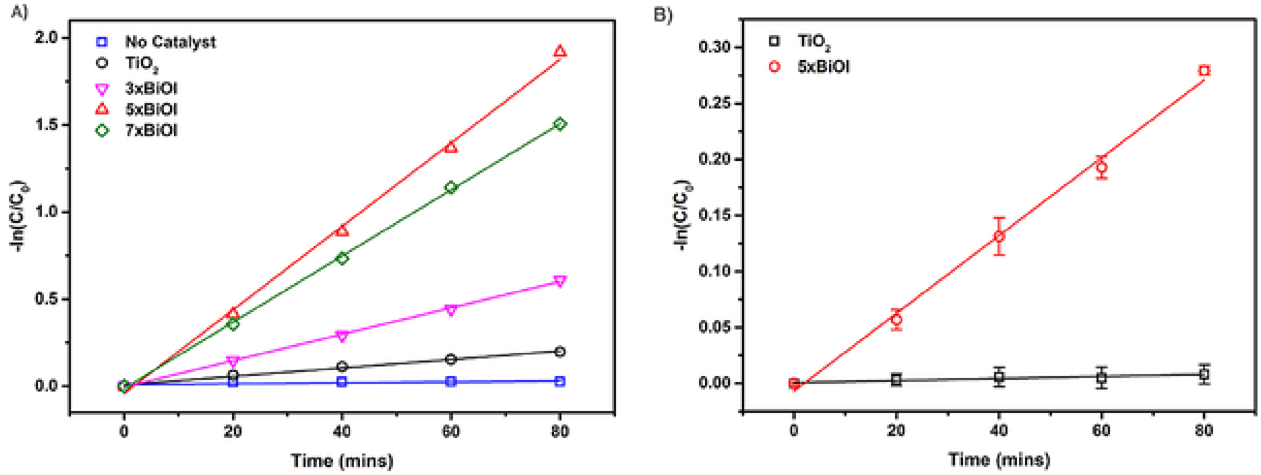

Fig. (6). Photocatalytic degradation kinetics of Rhodamine B on various photo-catalysts treated according to first order kinetic equation [data reproduced from ref.15. There is any number of this kind of analysis reported in the literature on the photocatalytic decomposition of dyes, and they are referred to in this article at other places] as an example.

Table.4. Values of first order rate constants for the photocatalytic degradation of dyes on semiconductor surfaces.

Semiconductor	Dye Degraded	Value for First Order Rate Constant	Refs.
ZnO	Methyl orange (MO)	0.1578 min^{-1}	[171]
ZnO	Congo Red (CR)	0.1119 min^{-1}	[171]
ZnO	Direct Black DB38)	0.0803 min^{-1}	[171]
ZnO	Crystal Violet (CV)	0.079 min^{-1}	[19]
ZnO	Methyl Red (MR)	0.014 min^{-1}	[19]
ZnO	Basic Blue (BB)	0.1 min^{-1}	[19]
TiO_2	Crystal Violet (CV)	0.026 min^{-1}	[19]
TiO_2	Methyl Red (MR)	0.008 min^{-1}	[19]
TiO_2	Basic Blue (BB)	0.045 min^{-1}	[19]
SnO_2	Crystal Violet (CV)	0.010 min^{-1}	[19]
SnO_2	Methyl Red (MR)	0.004 min^{-1}	[19]
SnO_2	Basic Blue (BB)	0.017 min^{-1}	[19]
Degussa P-25	Crystal Violet (CV)	0.060 min^{-1}	[19]
Degussa P-25	Methyl Red (MR)	0.012 min^{-1}	[19]
Degussa P-25	Basic Blue (BB)	0.017 min^{-1}	[167]
ZnO Nano flowers	Methyl Orange (MO)	0.05485 min^{-1}	[22]
ZnO Nano flowers	Congo Red	0.04611 min^{-1}	[22]
ZnO Nano flowers	Chicago Sky blue	0.003182 min^{-1}	[22]
ZnO Nano flowers	Eosin B	0.002884 min^{-1}	[22]
3 nm $GdCoO_3$	Rhodamine B	0.065 min^{-1}	[172]
3 nm $GdCoO_3$	Rhodamine Blur	0.078 min^{-1}	[172]
3 nm $GdCoO_3$	Orange G	0.053 min^{-1}	[172]
3 nm $GdCoO_3$	Remazol Brilliant Blue	0.019 min^{-1}	[172]
TiO_2(450)	Methylene Blue	0.0102 min^{-1}	[2]
TiO_2 (450)	Congo Red	0.0085 min^{-1}	[2]
TiO_2	Reactive Red	0.0325 min^{-1}	[168]
ZnO	Congo Red	0.0586 g.mg^{-1}min^{-1}	[167]
TiO_2	Lissamine Green B	0.0165 min+-1	[173]
ZnO	Methylene Blue	0.0135 min^{-1}	[166]
WO_3	Acid Orange 7	0.0225 min^{-1}	[174]
$Fe^{3+}/C/S/TiO_2$	Methyl Orange	0.01628 min^{-1}	[175]
$Fe^{3+}/C/S/TiO_2$	Congo Red	0.01533 min^{-1}	[176]

TiO_2	Carmine dye	0.1456 min^{-1}	[177]
Chitosan/CdS	Congo Red	0.01108 min^{-1}	[161]
ZnO	Methyl Orange	0.00029 sec^{-1}	[178]
ZnO	Rhodamine 6G	0.00027sec^{-1}	[178]
TiO_2	Acid Orange 10	0.0326 min^{-1}	[82]
TiO_2	Acid Orange 12	0.0269 min^{-1}	[82]
TiO_2	Acid Orange 08	0.0235 min^{-1}	[82]
TiO_2	Amido-black- 10B	0.02083 min^{-1}	[84]
TiO_2	Methyl Red	0.0019 min^{-1}	[85]
Ag1.5Ni0.75/TiO_2	Methyl Red	0.0077 min^{-1}	[85]
Ag1.5Ni1.5/TiO_2	Methyl Red	0.0085 min^{-1}	[85]
Ag1.5Ni3.0/TiO_2	Methyl Red	0.009 min^{-1}	[85]
Ag3.0Ni1.5/TiO_2	Methyl Red	0.0111 min^{-1}	[85]
TiO_2 P25	Organic dye	0.003 to 0143 Min^{-1}	[90]
ZnS	Rose Bengal	~4.51 X10^{-5} sec^{-1}	[91]
$CeCrO_3$	Fast Green	~4.41 X 10^{-4} sec $^{-1}$	[92]
TiO_2	RG 19	~4.69 h^{-1}	[93]
TiO_2	AO7	~2.07 h^{-1}	[93]
TiO2 0.02% Cu-doped TiO2 0.04% Cu-doped TiO2 0.06% Cu-doped TiO2 0.08% Cu-doped TiO2 0.1 % Cu-doped TiO2	Reactive Blue	0.0268 min^{-1} 0.0347 min^{-1} 0.03689 min^{-1} 0.0310 min^{-1} 0.0288 min^{-1} 0.0239 min^{-1}	[94]
Au3+-doped SiO2 Ag+-doped SiO2 Ag-deposited SiO2 Au NP-&Ag SiO2 Au NP-SiO2 NPs SiO 2 NPs.	Methyl Red	0.370 min^{-1} 0.050 min^{-1} 0.046 min^{-1} 0.037 min^{-1} 0.032 min^{-1} 0.020 min^{-1}	[86]

tion 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 apply 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 the same or different order of reactivity of adsorbents, and this has to be considered while choosing the material for wastewater treatment.

The adsorption of dyes can follow any one of the known isotherms, like Langmuir or Freundlich isotherms. The rate of decomposition of the dye depends on the adsorption equilibrium that exists on the surface and the adsorbed concentration (θ: surface coverage). Also, surface characteristics of the solid surface and the nature of the dye are the factors to be considered for adsorption. The pH of the solution also can change the surface charges and hence the adsorption of the dyes. Most of the dyes are considered as cationic or anionic, and the surface acidic or basic property will be responsible for these charged dyes. This is one aspect that has not been taken into account while treating the kinetics of photocatalytic degradation of dyes by semiconductors.

In most of the studies reported, details of adsorption of the dye and the consequences of this adsorption process on the kinetics of degradation have not been linked. This linking will be necessary for adoption of this technology for the treatment of waste water.

2.3.2. 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 because 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 g per litre [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.

2.3.3. Effect of Light Intensity and Wavelength of Irradiation

Use of solar radiation through less expensive and less hazardous, reproducible results are not assured. The effect of light intensity on the photocatalytic performance has been identified in three ranges, In the case of low intensity, the rate increases with intensity while in the intermediate intensity range the rate increases as the square root of the intensity and high intensity the rate is independent of the light intensity**.** On the whole, the rate of degradation is better when the light is from UV-Visible sources rather than solar radiation**.** Secondly, the electron hole pair formation and their recombination may be different when the UV-Visible source is employed**.** The wavelength of the light source can also affect the electron hole formation rate and their recombination.

2.3.4. The Mechanism of Dye Degradation

The degradation studies simply measure optical absorption (decolourization) or COD and thus not all information is available on the fragments and degradation products except that carbon dioxide and water are formed ultimately from the degradation process. This situation can arise because of anxiety on the removal of pollutant from water, and it is assumed that the degradation products are not harmful to living beings. The degradation scheme of a typical acid orange 7 is shown in Fig. **7**, In this case, the final product appears as carbon dioxide and water, but there are some intermediates which may participate in the reaction scheme of degradation of the dye and thus affect the overall kinetics of degradation. Among the various dyes studied, the extensively studied system is Acid Dye7 (AO 7) by some workers [89, 71-75]. A variety of degradation products has been identified, and the main ones are benzene sulphonic acid, sulphonic acid, 1,4 naphthoquinone and phthalic acid as by-products. Also, various other products have also been identified in the degradation of this dye; these include 2-naphthol, 2-hydroxy-1,4 naphthoquinone and small amounts of phthalimide, aliphatic acids like fumaric and succinic maleic and malonic acids together with other lower molecular weight products. Taking these observations, the reaction sequence for the photooxidation of AO 7 para isomer (Acid Orange 20) was proposed and is shown in Fig. **7**. This scheme is applicable only for the catalytic (TiO2) photo-degradation conditions. The main oxidising species are superoxide anion radical or hydroxyl radicals that can be formed by the participation of the exciton formed in the semiconductor photo-catalyst under irradiated conditions.

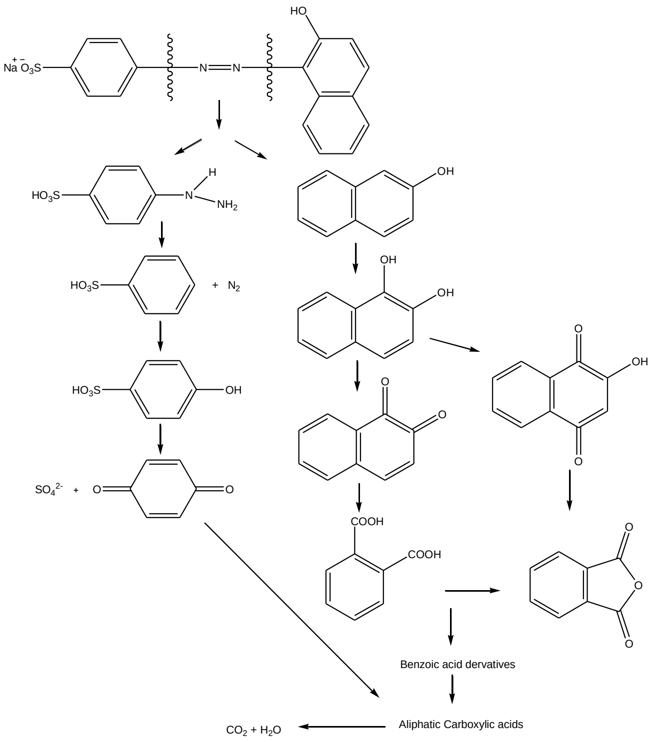

Fig. (7). Possible photo-catalytic pathway for the degradation of acid orange 7 [deduced from the results reported in the publications 71-75].

Most of the studies reported in literature either measure spectrophotometrically decolourization or COD. These are only gross measurements, and details of the degradation and the nature of degraded fragments have not been identified in most of the studies reported. Therefore, there is a need to study in detail the degradation products in the case of a number of dyes employed.

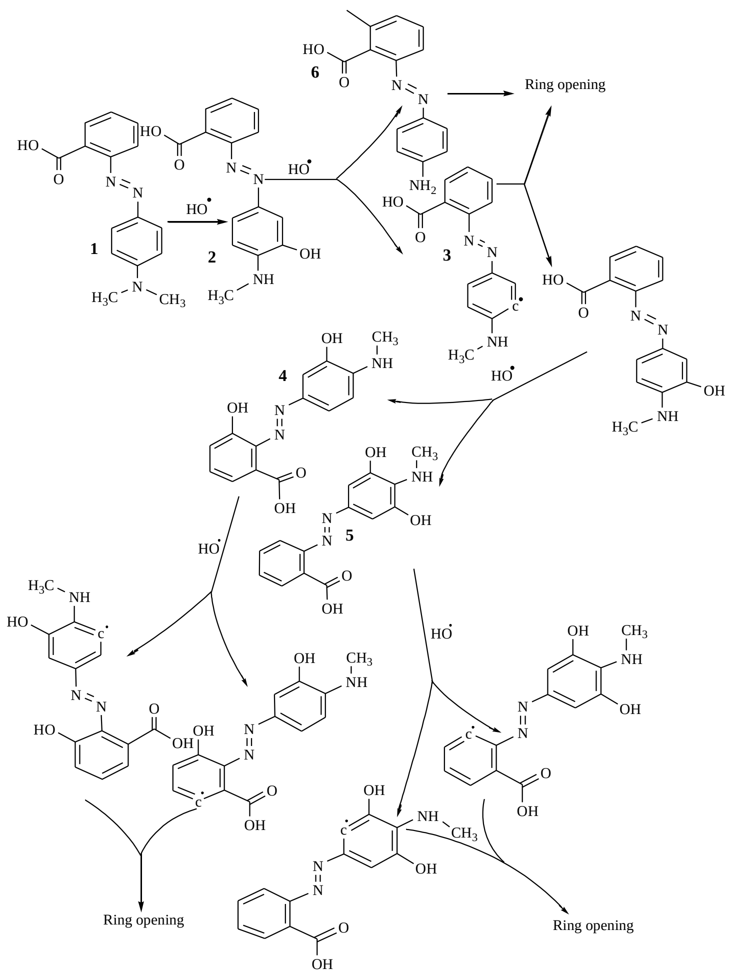

Fig. (8). Mechanism of the possible routes for the photocatalytic degradation of methyl Red [Reproduced from ref 86].

Methyl Red decomposition has been studied by Mahmoud *et al.* [86], and the main species responsible for this degradation is identified as superoxide anion radical (O_2^- •), or hydroxide radical (•OH) and the degradation route proposed by them is given in Fig. **8**. The possible first step can be the attack of the •OH radical on methyl Red which leads to the formation of a dehydrogenated radical. This intermediate can either undergo ring opening combining with ·OH, forming hydroxyl product. The intermediate might also be decomposed to form a new low molecular weight by-product. Further attacked by ·OH to form bi-hydroxyl products. The same procedure could take place until complete ring opening, and complete mineralisation occurs. The proposed sequence of steps is schematically shown in Fig. **8**.

One of the conventional azo dye is acid orange 7 whose proposed decomposition route as elucidated in literature is shown in Fig. **9**. One can see that the bond breaking either by dealkylation or hydroxylation of the dye derivatives and thus finally lead to mineralisation of the dye.

2.3.5. Reactive Oxygen Species

In the earlier parts, intrinsic reactive oxygen species (ROS) namely hydroxyl radical (•OH), hydrogen peroxide (H_2O_2), superoxide anion radical (•O^{2-}) and singlet oxygen ($^1O_2$), have been identified as the reactive oxygen species responsible for the dye degradation. The adsorbed hydroxyl radical (•OH) could be regarded as trapping holes by hydroxyl species involved in the rapid adsorption-desorption equilibrium at the semiconductor-solution interface. The trapped holes must be the dominant oxidation species because the equilibrium shifts to the adsorption side whereas •OH in solution would exert the reactivity towards the non-adsorbed reactants. The most probable routes for generating these species on semiconductor surfaces have been discussed elsewhere [89]. These authors have given the pictorial representation of the processes, and the same is reproduced in Fig. **10**.

Even though the nature of the reactive active species has been identified, their exact origin and participation in photocatalytic degradation of dyes on various semiconductors have not yet been fully elucidated. It is possible that further research in this area will throw light on this important area of research.

CONCLUDING REMARKS

It is true that photo-catalytic degradation of dyes has been studied throughout the world. This activity is intensified in the recent years [180-234]. These studies reported in literature deal with the common variables as stated above. In addition to summarising the results of these studies, this presentation focuses on certain aspects that can also be explored. These include:

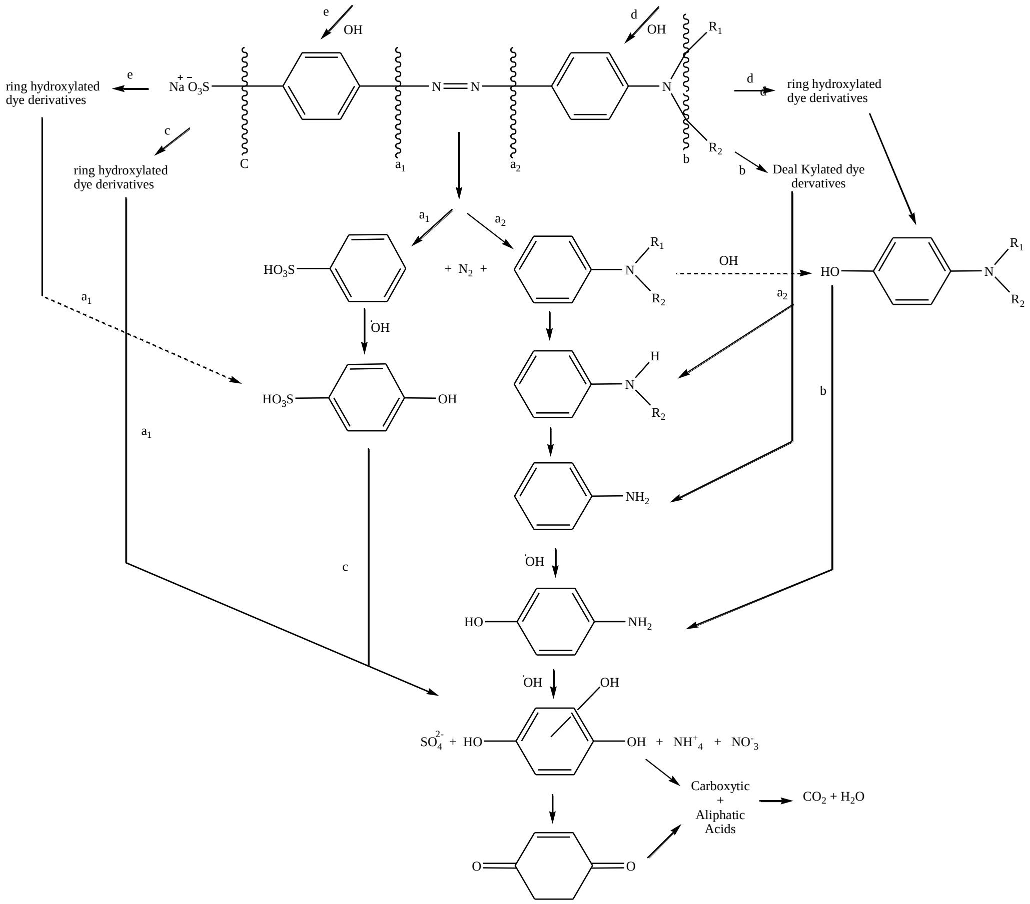

Fig. (9). Routes of the degradation of a typical azo dye namely acid orange 7 [fig reproduced from ref.54].

Fig. (10). Pictorial representation of generation of Reactive Oxygen Species on photo-catalytic semiconductor surfaces.

1. The inadequacy of treating the kinetic data in terms of pseudo-first order rate. It is necessary to take into account the prior adsorption and characteristics of this process.
2. The optimum amount of the catalyst is a natural consequence, and in this, the identification of the active sites and their number density on semiconductor surfaces can be evaluated**.**
3. The degradation of dye is dependent on the nature of the oxidising agent used, and the choice of the oxidising agent must be considered in terms of the redox potential of the species**.**

4. The pH of the medium decides which form of the dye is adsorbed on the surface and how it is degraded. The variation with pH has to be visualised in terms of the surface characteristics of the semiconductor as a function of pH.

It is concluded that the variables studied in the photocatalytic degradation of dyes are appropriate ones but the studies can extend their scope, and the interpretation can cover more global significance.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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REFERENCES

[1] Olga Sacco, Marco Stoller, Vincenzo, Vaiano, Paolo Ciambelli, Angelo Chianese, and Diana Sannino, Photocatalytic degradation of organic dyes under visible light on N-doped TiO_2 photocatalysts, International Journal of Photoenergy, 2012, pp.1-8 (2012Doi:10.1155/20121626759.

[2] M.Z.B. Mukhtish, F. Najnin, M.M. Rahman, and M.J. Uddin, Photocatalytic degradation of different dyes using TiO2 with high surface area: A kinetic study, J. Sci. Res.,2013 5(2) 301-314.

[3] Khan Mamum Reza, A S W Kurney and Fahmida Gulshan, Parameters affecting the photocatalytic degradation of dyes using TiO_2: a review, Appl. Water. Sci.,2017 7, 1569-1578, DOI:10.1007/s13201-015-0367-y.

[4] A.K. Khataee and M.B. Kasiri, Photocatalytic degradation of organic dyes in the presence of nanostructured titanium dioxide: influence of the chemical structure of dyes, Journal of Molecular Catalysis A: Chemical, 2010,328, 8-26; DOI:10.1016/j.monicata2010.05.023.

[5] U.G. Akpan and B.H. Hameed, Parameter affecting he photocatalytic degradation of dyes using TiO_2 photo-catalysts: A review, Journal of Hazardous Materials, 2009,170, 520-529; DOI:10.1016/jhazmet.3009.05.030.

[6] M.A. Rauf and S. Salman Ashraf, Fundamental Principles and application of heterogeneous photocatalytic degradation of dyes in solution, Chemical Engineering journal, 2009,151,10-18.; doi:10.1016/j.cej 2009.02.026

[7] M.A. Rauf, M.A. Meetani and S. Hisaidee, An overview on the photocatalytic degradation of azo dyes in the presence of TiO_2 doped with selective transition metals, Desalination, 2011,276,13-27;doi:10.1016/j.desal 2011.03.071.

[8] https://en.wikipedia.org/wiki/Industrial_dye_degradation.

[9] Pandit, V.K.; Arbuj, S.S.; Pandit, Y.B.; Naik, S.D.; Rane, S.B.; Mulik, U.P.; Gosavic, S.W.; Kale, B.B. Solar Light driven Dye Degradation using novel Organo–Inorganic (6,13-Pentacenequinone/TiO2) Nanocomposite". RSC Adv. 2015, 5, 10326-10331.

[10] T.M. Elmorsi, Y.M. Riyad, Z.H. Mohamed, H.M.H Abid, and E. Bary, Decolorization of mordant red 73 azo dye in water using H_2O_2/UV photo Fenton treatment, Journal of Hazardous Materials, 2010,174, 352-356.

[11] S. Gul, and O. Ozcan Yildlrln, Degradation of Reactive Red 194 and reactive yellow 145 azo dyes by O_3 and H_2O_2/UV-C process, Chemical Engineering Journal, 2009,155,684-690.

[12] F.H. AlHamedi and M.A. Rauf and S.S. Asraf, Degradation of Rhodamine B in the presence of UV/H_2O_2, Desalination 2009,239, 159-166.

[13] Y.B. Xie and X.Z. Li, Interactive oxidation of photo-electrocatalysis and electro-Fenton for azo- dye degradation using TiO_2-Ti mesh and reticulated Vitreous carbon electrode, Materials Chemistry and Physics,2006, 95,39-50.

[14] https://www.researchgate.net/post/What_is_the_Reduction_oxidation_Redox_Potential_of_Sulfate_Radicals_and_Hydroxyl_Radicals.

[15] Gylen Odling and Neil Robertson, SILAR BiOI-Sensitized TiO_2 Films for Visible-Light Photocatalytic Degradation of Rhodamine B and 4-Chlorophenol, ChemPhysChem, 2017,18, 728 – 735; DOI: 10.1002/cphc.201601417.

[16] Khan Mamun Reza, A S W Kurny and Eahmida Gulshan, Parameters affecting the photo-catalytic degradation of dyes using TiO_2: A review, Applied Water Science, 2017,7, 1569-1578.

[17] Zhigang Xiong, Li Li Zhang, Jizhen Ma and X.S. Zhao, Photocatalytic degradation of dyes over graphene-gold nanocomposites under visible light irradiation, Chem.Commun.,2010,46, 6099-6101.

[18] Rajesh J. Tayade, Praveen K. Surolia, Ramachandra G. Kulkarni and Raksh V. Jasra, Photocatalytic degradation of dyes and organic contaminants in water using nanocrystalline anatase and rutile TiO_2, Science and Technology of Advanced Materials,2007, 8, 455-462 (2007).

[19] Dnyaneshwar R. Shinde, Popat S. Tambade, Manohar G. Chaskar and Kisan M. Gadave, Photocatalytic degradation of dyes in water by analytica reagent grade photocatalysts – A comparative study, Drink.water Eng.Sci.,(under review on June2017).

[20] Balaram Kiran Avasarala, Siva Rao Tirukkovalluri and Sreeder Bojja, Magnesium doped Titania for photocatalytic degradation of dyes in visible light, Journal of Environmental and Analytical Toxicology, 2016,6,1-8.

[21] O.K.Mahadwad, P.A.Parikh, R.V. Jasra and C. Patil, Photocatalytic degradation of reactive black-5 dye using TiO_2 impregnated ZSM-5, Bulletin of Material Science,2011,34,551-556.

[22] Akbar Mohammed, Kshipra Kapoor and Shaikh M.Mobin, Improved photocatalytic degradation of organic dyes by ZnO-nanoflowers, Chemistryselect,2016, 1,3483-3490.

[23] R.Nagaraja, Nagaraju Kottam, C.R.Girija and B.M.Nagabhushana, Photocatalytic degration of Rhodamine B dye under UV/solar light using ZnO nano powder synthesized by solution combustion route, Powder Technology,2012,215-216, 91-97.

[24] Meeti Mehra and T.R.Sharma, Photo-catalytic degradation of two commercial dyes in aqueous phase using photo catalyst TiO_2, Advances in Applied Science Research,2012, 3,849-853.

[25] Mo S-D, and Ching WY. Electronic and optical properties of three phases of titanium dioxide: Rutile, anatase, and brookite. Physical Review B,1995, 51(19), 13023-32.

[26] Iskandar F, Nandiyanto ABD, Yun KM, Hogan CJ, Jr. KO, and Biswas P. Enhanced photocatalytic performance of brookite TiO2 macroporous particles prepared by spray drying with colloidal templating. Advanced Materials, 2007, 19(10), 1408–12.

[27] Bavykin DV, Friedrich JM, and Walsh FC. Protonated titanates and TiO2 nanostructured materials: Synthesis, properties, and applications. Advanced Materials 2006,18(21), 2807-24.

[28] M. Koelsch, S. Cassaignon, J.F. Guillemoles, and J.P. Jolivet.Comparison of optical and electrochemical properties of anatase and brookite TiO2 synthesized by the sol-gel method Thin Solid Films 2002,403:312–9.

[29] Morgan BJ, and Watson GW. (2010) Intrinsic n-type Defect Formation in TiO2: A Comparison of Rutile and Anatase from GGA plus U Calculations. Journal of Physical chemistry 2010,114(5), 2321-8.

[30] Qamar M, Yoon C R, Oh H J, Lee N H, Park K, and Kim D H, Preparation and photocatalytic activity of nanotubes obtained from titanium dioxide Catalysis Today, 2008, 131(1-4), 3-14.

[31] Sclafani A, and Herrmann J M. Comparison of the photoelectronic and photocatalytic activities of various anatase and rutile forms of titania in pure liquid organic phases and in aqueous solutions Journal of Physical Chemistry, 1996, 100(32), 13655-61.

[32] Bakardjieva S, Subrt J, Stengl V, Dianez M J, and Sayagues M J. Photoactivity of anatase-rutile TiO2 nanocrystalline mixtures obtained by heat treatment of homogeneously precipitated anatase. Applied catalysis B:Environmental 2005,58(3-4), 193-202.

[33] Ohno T, Tsubota T, Toyofuku M, and Inaba R. (2004) Photocatalytic activity of a TiO2 photo-catalyst doped with C4+ and S4+ ions having a rutile phase under visible light. Catalysis Letters, 2004, 98(4), 255-8.

[34] Colon G, Hidalgo MC, Munuera G, Ferino I, Cutrufello MG, and Navıo J A, Structural and surface approach to the enhanced photocatalytic activity of sulfated TiO2 photo-catalyst. Applied Catalysis B: Environmental 2006, 63(1-2), 45-59.

[35] Li H, Zhang and W, and Pan W. Enhanced photocatalytic activity of electrospun TiO2 nanofibers with optimal anatase/rutile ratio. Journal of the American Ceramic Society, 2011, 94(10), 3184-7(2011).

[36] Ohtani B, and Ogawa Y, Nishimoto S-i. Photocatalytic activity of amorphous-anatase mixture of titanium(IV) oxide particles suspended in aqueous solutions. Journal of Physical Chemistry,1997, B 101(19), 3746-52.

[37] Elahee K., Heat recovery in the textile dyeing and finishing industry: lessons from developing economies Journal of Energy in Southern Africa, 2010,21(3), 9-15 (2010).

[38] Singh P, Mondal K, and Sharma A. Reusable electro-spun mesoporous ZnO nanofiber mats for photocatalytic degradation of polycyclic aromatic hydrocarbon dyes in wastewater. Journal of Colloid and Interface Science, 2013,394, 208-15.

[39] Hoffmann M R, Martin S T, Choi W, and Bahnemannt D W. Environmental Applications of Semiconductor Photo catalysis. Chemical Reviews,1995, 95(1), 69-96.

[40] Meng Z, and Juan Z. Wastewater treatment by photocatalytic oxidation of nano-ZnO. Global Environmental Policy in Japan,2008, 12, 1-9.

[41] Hernandez-Alonso MD, Fresno F, Suareza S, and Coronado JM. Development of alternative photo catalysts to TiO2: Challenges and opportunities. Energy & Environmental Science,2009, 2(12), 1231-57.

[42] Mills, A., Davies,R.H., and Worsley, D., Water Purification by semiconductor photocatalysis, Chemical Society of Reviews,1993, 22(6),417-25.

[43] Hashimoto,k., Irie,H., and Fujishima, A., TiO_2 Photcatalysis: A historical overview future prospects, Japanese Journal of Applied Physics, 2005, 44(12),8269-8285.

[44] Neppolian, B., Sakthivel,S., Arabindoo,B., Palanichamy, M.,and Murugesan,V., Degradation of textile dye by solar light using TiO_2 and ZnO photocatalysts, Journal of Environmental science and Health Part A., Toxic/Hazardous Substances and Environmental Engineering, 1999,34(9),1829-1838.

[45] Ye, M., Zhang,Q., Hu,Y., Ge,J., Lu,Z,and He,L., Magnetically recoverable core shell nanocomposites with enhanced photocatalytic activity, Chemistry – a European Journal, 2010, 16(21), 6243-6250.

[46] Colmenares, J.C., Luque, R., Campelo,J.M., Colmenares,F., Karpinski,Z., and Romero, A.A., Nanostructured photocatalysts and their applications in the photocatalytic transformation of lignocellulosic biomass: an Overview, Materials, 2009,2(4),2228-2258.

[47] Anpo,M., Shima,T., Kodama,S., and Kubokawa,Y., Photocatalytic hydrogenation of propyne with water on small particle titania: size quantization effects and reaction intermediates, Journal of physical Chemistry, 1987,91(16),4305-4310.

[48] Lin,H., Huang C.P., Li,W., Ni,C., Shah,S.I., and Tseng, Y-H, Size dependency of nanocrystalline TiO_2 on its optical property and photocatalytic reactivity exemplified by 2-chlorophenol, Applied Catalysis B:Environmental,2006, 68(1-2),1-11.

[49] Reza Sarkhanpour, Omid Tavakoli, Samira Ghiyasi, Mohammad Reza Saeb, and Rafael Borja, Photocatalytic Degradation of a Chemical Industry Wastewater: Search for Higher Efficiency, Journal of Residuals Science & Technology, 2017, 14, 44-58; doi: 10.14355/jrst.2017.1404.006.

[50] Anila Ajmal, Imran Majeed, Riffat Naseem Malik, Hicham Idriss and Muhammad Amtiaz Nadeem, Principles and mechanisms of photocatalytic dye degradation on TiO_2 based photo-catalysts: a comparative overview, RSC Advances, 2014, 4,37003-37026. DOI: 10.1039/C4RA06658H

[51] Tesfay W. Gebreslassie1, Manjunatha Pattabi and Rani M. Pattabi, Review on the Photocatalytic Degradation of Dyes and Antibacterial Activities of Pure and Doped-ZnO, International Journal of Science and Research,2015, 4(5), 2252-2264.

[52] Agatino Di Paola, Marianna Bellardita and Leonardo Palmisano, Brookite, the Least Known TiO2 Photo-catalyst, *Catalysts, 2013, 3*, 36-73; doi:10.3390/catal3010036.

[53] Nguyen-Phan, T.D., Kim,E.J., Hahn,S.H., Kim,W.-J., and Shin, E.W., Synthesis of hierarchical rose bridal bouquet- and humming-top-like Tio_2 nanostructures and their shape dependent degradation efficiency of dye, Journal or Colloid Interface Science, 2011,356, 138-144.

[54] Ioannis K. Konstantinou and Triantafyllos A. Albanis, TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations; A review, Applied Catalysis B: Environmental 2004, 49, 1–14.

[55] Wan-Kuen Jo and Rajesh.J.Tayade, Recent developments in photocatalytic dye degradation upon irradiation with energy-efficient light emitting diodes Chinese Journal of Catalysis,2014 35, 1781–1792.

[56] Khan Mamun Reza, ASW Kurny and Fahmida Gulshan, Parameters affecting the photocatalytic degradation of dyes using TiO_2: a review, Applied water Science,2017, 7(4),1569-1578.

[57] I.K. Konstantinou, and T.A. Albanis, TiO2-assisted photocatalytic degradation of azo dyes in aqueous solution: kinetic and mechanistic investigations—A review, Appl. Catal. B: Environ.2004, 49, 1–14.

[58] M.A. Fox, and M.T. Dulay, Heterogeneous photocatalysis, Chem. Rev. 1993,93, 341.

[59] D.W. Bahnemann, J. Cunningham, M.A. Fox, E. Pelizzetti, P. Pichat, and N. Serpone, in: R.G. Zepp, G.R. Heltz, D.G. Crosby (Eds.), Aquatic Surface Photochemistry, Lewis Publishers, Boca Raton, 1994, p. 261.

[60] S. Tunesi, and M. Anderson, Influence of chemisorption on the photodecomposition of salicylic acid and related compounds using suspended titania ceramic membranes, J. Phys. Chem. 1991,95,3399–3405.

[61] W.Z. Tang and H. An, UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions, Chemosphere 1995,31,4158–4170.

[62] C. Guillard, J. Disdier, C. Monnet, J. Dussaud, and S. Malato, J. Blanco, M.I. Maldonado, and J.M. Herrmann, Solar efficiency of a new deposited titania photo-catalyst: chlorophenol, pesticide and dye removal applications, Applied Catalysis. B: Environmentol. 2003, 46 (2), 319–332. [63] L.B. Reutergarth and M. Iangpashuk, Photocatalytic decolorization of reactive azo dye: a comparison between TiO2 and CdS photo-catalysts, Chemosphere 1997,35,585–596.

[64] W. Baran, A. Makowski, and W. Wardas, The effect of UV radiation absorption of cationic and anionic dye solutions on their photocatalytic degradation in the presence of TiO2, Dyes Pigm.2008, 76, 226–230.

[65] K.-H. Wang, Y.-H. Hsieh, C.-H. Wu, and C.-Y. Chang, The pH and anion effects on the heterogeneous photocatalytic degradation of o-methylbenzoic acid in TiO_2 aqueous suspension, Chemosphere,2000, 40,389–394.

[66] W. Baran, A. Makowski, and W. Wardas, The influence of FeCl3 on the photocatalytic degradation of dissolved azo dyes in aqueous TiO2 suspensions, Chemosphere 2003, 53,87–95.

[67] W.Z. Tang, and H. An, UV/TiO2 photocatalytic oxidation of commercial dyes in aqueous solutions, Chemosphere 1995, 31,4158–4170

[68] W.Z. Tang, and H. An, Photocatalytic degradation kinetics and mechanism of acid blue 40 by TiO2/UV in aqueous solution, Chemosphere, 1995,31,4171–4183

[69] I.A. Alaton, and I.A. Balcioglu, Photochemical and heterogeneous photocatalytic degradation of waste vinylsulphone dyes: a case study with hydrolyzed Reactive Black 5, J. Photochem. Photobiol. A: Chem.2001, 141,247–254. [70] D. Grosse, and N. Lewis, Handbook on Advanced Photochemical Oxidation Processes, Center for Environmental Research Information, National Risk Management Research Laboratory, Office of Research and Development, US,EPA, Cincinnati, USA, 1998.

[71] I. Poulios, and I. Aetopoulou, Photocatalytic degradation of the textile dye Reactive Orange 16 in the presence of TiO2 suspensions, Environ. Technol. 1999,20, 479–487.

[72] I. Poulios, A. Avrans, E. Rekliti, and A. Zouboulis, Photocatalytic oxidation of Auramine O in the presence of semiconducting oxides, J. Chem. Biotechnol.2000, 75, 205–212.

[73] T.Zhang, T.Oyama, S.Horikoshi, H.Hidaka, J.Zhao and N.Serpone, Photocatalyzed N-demethylation and degradation of methylene blue in titania dispersions exposed to concentrated sunlight, solar energy Materials Solar cells, 2001,73,287-303.

[74] Y. Zhiyong, M. Bensimon, V. Sarria, I. Stolitchnov, W. Jardim, D. Laub, E. Mielczarski, J. Mielczarski, L. Kiwi-Minsker, and J. Kiwi,

ZnSO4–TiO2 doped catalyst with higher activity in photocatalytic processes, Appl. Catal. B: Environ. 2007,76,185–195.

[75] C.Galindo, P.Jacques and A.Kalt, chemosphere, 2001, 45,997.

[76] M.Stylide, D.I.Kondarides and X.E.Verykios, Applied catalysis B Environmental,2003, 40,271.

[77] J.Bandara, J.A.Mielczarski and J.Kiwi, Langmuir, 1999,15,7680.

[78] K.Venodogopal, D.Wynkoop and P.Kamat, Environ.Sci.Technol.,1996, 30,1660.

[79] C.Bauer, P.Jacques and A.Kalt,J.Photochem. photobiol. A.Chem., 2001,140, 87.

[80] Xiaoqing chen, Zhansheng Wu, Dandan Liu and Zhenzhen Gao, Preparation of ZnO photocatalyst for the efficient and rapid photocatalytic degration of azo dyes, Nanoscale Research letters, 2017,12,143.

[81] S.A.Abo-Farha, Photocatalytic degradtion of monoazo and diazo dyes in waster water on nanometer sized TiO_2, researcher,2010, 2(7),1-20.

[82] A.R.Khataee, M.N.Pons and O.Zahraa, Photocatalytic degradation of three azo dyes using immobilized TiO_2 nanoparticles on glass plates activated by UV light irradiation: Influence of dye molecular structure, Journal of Hazardous Materials, 2009, 168, 451-457.

[83] Saber Ahmed, M.G.Rasul, Wayde n.Martens, Richard Brown and M.A.Hashib,Advances in Heterogeneous photocatalytic degradation of phenols and Dyes in wastewater: A reivew, Water, Air Soil Pollutant,2011, 215,3-29.

[84] E K Kirupavasam and G.Allen Ganana Raj, Photocatalytic Degradation of Amido black-10B Catalyzed by Carbon Doped TiO2 Photocatalyst, International Journal of Green Chemistry and Bioprocess,2012, 2(3),20-25.

[85] Vo Thi Thu Nhu, Do QuangMinh, Nguyen Ngoc Duy, Nguyen QuocHien, Photocatalytic Degradation of Azo Dye (Methyl Red) In Water under Visible Light Using AgNi/TiO2 Sythesized by γ - Irradiation Method, International Journal of Environment, Agriculture and Biotechnology (IJEAB),2017,2(1),529-538.

[86] M.A. Mahmoud, A. Poncheri, Y. Badr and M.G. Abd El Wahed, Photocatalytic degradation of methyl red dye, South African Journal of Science 2009,105,299-203.

[87] Ioannis K.Konstantinou and Triantafyllos A.Albanis, TiO_2 assisted photocatalytic degradation of azo dyes in aqueous solution: Kinetics and mechanistic investigations A review, Applied Catalysis B.Environmental, 2004, 49,1-14.

[88] J. Sun, X. Wang, J. Sun, R. Sun, S. Sun and L. Qiao, Photocatalytic degradation and kinetics of Orange G using nano-sized Sn(IV)/TiO2/AC photocatalyst, J. Mol.Catal. A: Chem. 2006, 260, 241–246.

[89] M. Huang, C. Xu, Z. Wu, Y. Huang, J. Lin, J. Wu, Photocatalytic discolourization of methyl orange solution by Pt modified TiO2 loaded on natural zeolite, Dyes Pigm. 2008,2, 327–334.

[90] J. Sun, L. Qiao, S. Sun, G. Wang, Photocatalytic degradation of Orange G on nitrogen-doped TiO2 catalysts under visible light and sunlight irradiation, J. Hazard. Mater.2008, 155, 312–319.

[91] C.-H. Wei, X.-H. Tang, J.-R. Liang, S. Tan, Preparation, characterization and photocatalytic activity of boron- and cerium-co-doped TiO2, J. Environ. Sci. 2007, 19, 90–96.

[92] Guettai, N and Amar H.A., Photocatalyti oxidation of methyl orange in presence of titanium dioxide in aqueous suspension Part II Kinetic study, Desalination, 2005, 185, 439-448.

[93] Shweta Sharma, Rakshit Ameta, R.K.Malkani and Suresh C.Ameta, Photocatalytic degradation of Rose Bengal using semiconducting zinc sulphide as the photocatalyst, J.Serbian chemical Society, 2013, 78(6),897-905.

[94] Indu Bhati, Pinki B Punjabi and suresh C Ameta, photocatalytic degradation of fast green using nanosized $CeCrO_3$, Macedonian Journal of Chemistry and Chemical Engineering, 2010, 29(2), 195-202.

[95] Ohm-Mar Min, Li-Ngee Ho, Soon-An Ong and Yee-Shian Wong, Comparison between the photocatalytic degradation of single and binary azo dyes in TiO2 suspensions under solar light irradiation, Journal of water Reuse and Desalination, 2015,579-591.

[96] P. Dharmarajan, A. Sabastiyan M. Yosuva Suvaikin, S.Titus and C.Muthukumar, Photocatalytic Degradation of Reactive Dyes in Effluents Employing Copper Doped Titanium Dioxide Nanocrystals and Direct Sunlight, Chemical Science Transactions,2013, 2(4),1450-1458.

[97] Yoshio Nosaka and Atsuko Y. Nosaka, Generation and Detection of Reactive Oxygen Species in Photo-catalysis, Chemical reviews (2017).

[*98*] Tiantian Wu, Yanping Liang and Fangyuan Deng, Study on the Degradation of Dye Pollutants Over Silver Phosphate Photocatalyst, International Conference on Advances in Energy, Environment and Chemical Engineering (AEECE-2015).

[99] Indu Bhati, Pinki B. Punjabi, and Suresh C. Ameta, Photocatalytic degradation of fast green using nonosized $CeCrO_3$, Macedonian Journal of Chemistry and Chemical Engineering. 2010, Vol. 29, No. 2, pp. 195–202.

[100] Mohamed A. Salem, Shaban Y. Shaban and Sherin. M. Ismail, Photocatalytic Degradation of Acid Green 25 using ZnO and Natural Sunlight, International Journal of Emerging Technology and Advanced Engineering, 2015, 5(3), 439-443.

[101] Kamila Bubacz, Julia Choina, Diana Dolat, Antoni W. Morawski, Methylene Blue and Phenol Photocatalytic Degradation on Nanoparticles of Anatase TiO2, Polish Journal of Envirometal Studies,2010,19 (4) 685-691.

[102] Gabriela Antoaneta Apostolescu, Corina Cernatescu, Claudia Cobzaru, Ramona Elena Tataru-Farmus, Nicolae Apostolescu, Studies on the photocatalytic degradation of organic dyes using CeO_2 – ZnO mixed oxides, Environmental Engineering and Management Journal, 2015,14(2), 415-420.

[103] C. Karunakaran, P. Magesan, P. Gomathisankar, P. Vinayagamoorthy, "Photocatalytic Degradation of Dyes by Al_2O_3-TiO_2 and ZrO_2-TiO_2 Nanocomposites", Materials Science Forum, 2013,Vol. 734, 325-333.

[104] Zainab Raheem and Ahmed M. Hameed, Photocatalytic Degradation for Methylene Blue Dye Using Magnesium Oxide, International Journal of Basic and Applied Science, 2015,4(1),81-83.

[105] Rachita Mehta and Menka Surana, Photodegradation of Dye Acid Orange 67 by Titanium Dioxide in the Presence of Visible Light and UV Light, Research Reviews, 2013,2(2), 1216.

[106] *https://www.rit.edu/affiliate/nysp2i/sites/rit.edu./12rdsc09_report_cuny-csi.pdf.*

[107] Rakshit Ameta, Sanyogita Sharma, Shweta Sharma and Yogesh Gorana, Visible Light Induced Photocatalytic Degradation of Toluidine Blue-O by using Molybdenum Doped Titanium Dioxide, European Journal of Advances in Engineering and Technology, 2015,2(8), 95-99.

[108] Lum Sin Wan, A Study into photocatalytic degradation of methylene blue and glycerol aqueous solution over copper ferrite catalyst, Bachelor degree thesis, Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia, Pahang, (2015).

[109] Valentine Rupa,A., Manikandan, D., Divakar,d., Revathis, S., Leena Preethi, M., Esther Shanthi, K., and Sivakumar, T., Photocatalytic degradation of tetrezine dye using TiO_2 catalyst: Salt effect and kinetic studies, Indian Journal of Chemical Technology, 2007,14(1) 71-78.

[110] Narde SB, Lanjewar RB, Gadegone SM, Lanjewar MR, Photocatalytic Degradation of Azo Dye Congo Red Using Ni0.6Co0.4Fe2o4 as Photocatalyst, Der Pharma Chemica, 2017,9(7),115-120.

[111] Zahra Minaii Zangi, Hossein Ganjidoust and Bita Ayati, Analysis of photocatalytic degradation of azo dyes under sunlight with response surface method, *Desalination and Water Treatment,* 2017,63, 262–274.

[112] Bojana Simovic´, Dejan Poleti2, Aleksandar Golubovic´, Aleksandar Matkovic´, Maja Šcepanovi, Biljana Babic´, and Goran Brankovic, Enhanced photocatalytic degradation of RO16 dye using Ag modified ZnO nano-powders prepared by the solvothermal method, Processing and Application of Ceramics 2017,11 [1] 27–38.

[113] Khaled Mezughi, Chedly Tizaoui, and Ma'an Fahmi Alkhatib, Effect of TiO2 Concentration on Photocatalytic Degradation of Reactive Orange 16 Dye (RO16), *Advances in Environmental Biology, 2014, 8,(3), 692 – 695.*

[114] Salehi Kamal, Maleki Afshin, Shahmoradi Behzad, Mansouri Borhan, and Gharibi Fardin, Investigation of photocatalytic degradation of reactive black 5 dye using ZnO-CuO nano-composite, Zanki Journal of Medical Sciences,2014, 15(46)66-74.

[115] Veronika Marinovic, Davor Ljubas, Lidija Curkovic, Effects of concentration and UV radiation wavelengths on photolytic and photocatalytic degradation of azo dyes aqueous solutions by sol-gel

TiO2 films, The Holistic Approach to Environment, 2017,7, 1, 3-14.

[116] Xiaozhou Long, Tingnan Yan, Tianjiao Hu, Xianghui Gong, Huaming Li, and Zengyong Chu, Enhanced Photo-catalysis of g-C3N4 Thermally Modifed with Calcium Chloride, Catalysis Letters, 2017,147, 1922-1930. DOI 10.1007/s10562-017-2099-0.

[117] P.Dhatshanamurthi, B.Subash and M.Shanthi, Investigation on UV-A light photocatalytic degradation of an azo dye in the presence of CdO/TiO_2 coupled semiconductor, Materials Science in Semiconductor Processing, 2015,35,22-29.

[118] Cresus V.D. Gouvea, Fernandes Wypych, Sandra G.Moraes, Padricio Peralta-Zamora, Semiconductor-Assisted Photo-catalytic Degradation of Reactive Dyes in Aqueous Solution,Chemosphere, 2000,40(4), 433-440.

[119] Xinshan Rong, Fengxian, Hao Zhao, Jie Yan, Xiaolu Zhu and Dongya Yang, Fabrication of Single-Layer Graphitic Carbon Nitride and Coupled Systems for the Photo-catalytic Degradation of Dyes under Visible-Light Irradiation, Eur. J. Inorg. Chem.,2015, 1359–1367.

[120] Malka Rochkind, Sagi Pasternak and Yaron Paz, Using dyes for evaluating photo-catalytic Properties: A critical Review, Molecules, 2015,20,88-110; doi:10.3390/molecules20010088.

[121] Alemseged Eyasu, O.P.Yadav, and R.K.Bachheti, Photo-catalytic degradation of methyl orange dye using Cr-doped ZnS nanoparticles under visible radiation, International Journal of chemtech Research, 2013,5(4), 1452-1461.

[122] Raji, Jeevitha, Palanivelu, Kandasamy, Semiconductor coupled solar photo-Fenton`s treatment of dyes and textile effluent, Advances in Environmental research, 2016,5(1) 61-77.

[123] Edson Luiz Foletto, Suellen Battiston, Gabriela Carvalho Collazzo, Mariana Moro Bassaco and Marcio Antonio Mazutti, Degradation of Leather dye using CeO_2-SnO_2 nanocomposite as photocatalyst under sunlight, water Air Soil pollutant,2012, 223, 5773-5779.

[124] Yiming He, Lihong Zhang, Maohong Fan, Xiaoxing Wang, Mikel L.Walbridge, Qingyan Nong, Ying Wu, Leihong Zhao, Z-scheme SnO_{2-x}/g-C_3N_4 composite as an efficient photo-catalyst for dye degradation and Photocatalytic CO_2 reduction, Solar Energy Materials and solar cells, 2015,137, 175-184.

[125] Qiaoying Li, Zhipeng Guan, Di Wu, Xiuge Zhao, Shenyuan Bao, Baozhu Tian and Jinlong Zhang, Z-Scheme BiOCl-Au-CdS Heterostructure with Enhanced Sunlight-Driven Photocatalytic Activity in Degrading Water Dyes and Antibiotics, *ACS Sustainable Chemistry Engineering, June (2017).* **DOI:** 10.1021/acssuschemeng.7b01157.

[126] Julie M.Pardiwala, Femina J.Patel and Sanjay S.Patel, Photocatalytic degradation of RB21 dye by TiO_2 and ZnO under natural sunlight: Microwave Irradiation and UV reactor, International Journal of Advanced Research in Engineering and Technology,2017,8(1), 8-16.

[127] Kirana Devarahosahalli Veeranna, Madhu Theeta Lakshamaiah, and Ramesh Thimmasandra Narayan, Photocatalytic Degradation of Indigo Carmine Dye Using Calcium Oxide, International Journal of Photochemistry, Volume 2014 (2014), Article ID 530570, 6 pages, http://dx.doi.org/10.1155/2014/530570.

[128] Yanan Liu, Ruixia Wang, Zhengkun Yang, Hong Du, Yifan Jiang, Congcong Shen, Kuang Liang, Anwu Xu, Enhanced visible-light photocatalytic activity of Z-scheme graphitic carbon nitride/oxygen vacancy-rich zinc oxide hybrid photocatalysts, Chinese Journal of Catalysis 2015,36, 2135–2144.

[129] Yunjin Yao, Guodong Wu, Fang Lu, Shaobin Wang, Yi Hu, Jie Zhang, Wanzheng Huang, and Fengyu Wei, Enhanced photo-Fenton-like process over Z-scheme $CoFe_2O_4$/g-C_3N_4 Heterostructures under natural indoor light, Environmental Science and Pollution Research, 2016,23 (21), 21833–21845.

[130] Surender Kumar and Sahare, P.D, Photocatalytic acitivity of bismuth vanadate for the degradation of organic compounds, *NANO, 2013,* 08, 1350007. https://doi.org/10.1142/S1793292013500070.

[131] Shimin Xiong, Tianhui Wu, Zihong Fan, Deqiang Zhao, Mao Du, and Xuan Xu, Preparation of a Leaf-Like BiVO4-Reduced Graphene Oxide Composite and Its Photocatalytic Activity, Journal of Nanomaterials, 2017, Article ID 3475248, 12 pages, https://doi.org/10.1155/2017/3475248.

[132] Peitao Liu, Yonggang Liu, Weichun Ye, Ji Ma and Daqiang Gao, Flower-like N-doped MoS_2 for photocatalytic degradation of RhB by visible light irradiation, Nanotechnology 2016, 27 225403 (8pp).

[133] Shuijin Yang, Yongkui Huang, Yunzhi Wang Yun Yang, Mingbo Xu and Guohong wang, Photocatalytic Degradation of Rhodamine B with H3PW12O40/SiO2 Sensitized by H2O2, International Journal of Photoenergy (2012). DOI: 10.1155/2012/927132.

[134] Luís F da Silva, Osmando F Lopes, Vagner R de Mendonça, Kele T G Carvalho, Elson Longo, Caue Ribeiro, Valmor R Mastelaro, An Understanding of the Photocatalytic Properties and Pollutant Degradation Mechanism of SrTiO3 Nanoparticles, *Photochemistry and Photobiology, 2016, 92 (3): 371-8.*

[135] Md.Rakbuddin, Subrata Mandal, Rajkumar Ananthakrishnan, A novel ternary CuO decorated Ag_3AsO_4/GO hybrid as a z-scheme photocatalyst for enhanced degradation of phenol under visible light, New Journal of Chemistry, 2017,41, 1380-1389.

[136] Guangxin Zhang, Bin Wang, Zhiming Sun, Shuilin Zheng and Shushu Liu, A comparative study of different diatomite-supported TiO_2 composites and their photocatalytic performance for dye degradation, Journal of Desalination and Water Treatment, 2016,57, (37).

[137] Yeoseon Choi, Min Seok Koo, Alok D. Bokare, Dong-hyo Kim, Detlef W. Bahnemann, and Wonyong Choi, Sequential Process Combination of Photocatalytic Oxidation and Dark Reduction for the Removal of Organic Pollutants and Cr(VI) using Ag/TiO2, Environmental Science Technology, 2017,51, 3973-3981.

[138] Z. M. Abou-Gamra, M. A. Ahmed, and M. A. Hamza, Investigation of commercial PbCrO4/TiO2 for photodegradation of rhodamine B in aqueous solution by visible light, Nanotechnology for Environmental Engineering, 2017, 12, DOI: 10.1007/s41204-017-0024-9.

[139] Ma,X., Ma,W., Jiang,D., Li,D., Meng,S., and Chen, M., Construction of novel $WO_3/SnNb_2O_6$ hybrid nanosheet heterojunctions as efficient z-scheme photo-catalysts for pollutant degradation, Journal of Colloid and Interface Sciene, 2017,506, 93-101. doi:10.1016/j.jcis.2017.07.017.

[140] M.Shanthi and V.Kuzhalosai, Photo-catalytic degradation of an azo dye acid Red 27 in aqueous solution using nano ZnO, Indian Journal of Chemistry, 2012,51A, 428-434.

[141] Dasari Ayodhya, M. Venkaresham, A. Santoshi Kumar, G. Bhagayanth Reddy, D. Ramakrishna and G.Veerabhadram, Photocatalytic degradation of dye pollutants under solar, visible and UV lights using green synthesized CuS nano-particles, Journal of Experimental Nanoscience,2016, 11 (6) 418-432.

[142] Omprakash Sharma and Mohan Kumar Sharma, Use Of Cobalt Hexacyanoferrate(II) Semiconductor In Photocatalytic Degradation Of Neutral Red Dye, International Journal of ChemTech Research, 2013,5(4),1615-1622.

[143] Priya Rathore, Rakshit Ameta and Sanyogita Sharma, Photocatalytic Degradation of Azure A Using N-doped Zinc Oxide, Journal of Textile Science and Technology, 2015,1, 118-126.

[144] C. Karunakaran, P. Magesan, P. Gomathisankar and P. Vinayagamoorthy, "Photocatalytic Degradation of Dyes by Al_2O_3-TiO_2 and ZrO_2-TiO_2 Nanocomposites", Materials Science Forum, 2013,Vol. 734, pp. 325-333,.

[145] S.K.Kansal, M.Singh and D.Sud, Studies on photodegradation of two commercial dyes in aquesous phase using different photocatalysts, Journal of Hazardous Materials, 2007,141(3) 581-590.

[146] Junting Wang, Chun Xiao, Xiaoyong Wu, and Gaoke Zhang, Potassium Tantalate $K_6Ta_{10.8}O_{30}$ with Tungsten Bronze Structure and Its Photocatalytic Property, Chinese Journal of Chemistry, 2017,35(2), 189-195.

[147] Xie, J.; Lü, X.; Liu, J.; Shu, H. Brookite titania photocatalytic nanomaterials: Synthesis, properties, and applications. *Pure Appl. Chem*. 2009, *81*, 2407–2415.

[148] Štengl, V and Králová, D., Photoactivity of brookite–rutile TiO2 nanocrystalline mixtures obtained by heat treatment of hydrothermally prepared brookite. *Mater. Chem. Phys*. 2011, *129*, 794–801.

[149] Zhao, B.; Chen, F.; Huang, Q.; Zhang, J. Brookite TiO2 nanoflowers. *Chem. Commun*. 2009, 5115–5117.

[150] Zhao, B.; Chen, F.; Jiao, Y.; Zhang, J. Phase transition and morphological evolution of titania/titanate nanomaterials under alkalescent hydrothermal treatment. *J. Mater. Chem*. 2010, *20*, 7990–7997.

[151] Shibata, T.; Irie, H.; Ohmori, M.; Nakajima, A.; Watanabe, T.; Hashimoto, K. Comparison of photochemical properties of brookite

and anatase TiO2 films. *Phys. Chem. Chem. Phys*. 2004, *6*, 1359–1362.

[152] V. S. Shrivastava, Photocatalytic degradation of Methylene blue dye and Chromium metal from wastewater using nanocrystalline TiO2 Semiconductor, Archives of Applied Science Research, 2012,4 (3),1244-1254.

[153] Kunal Mondal and Ashutosh Sharma, Photocatalytic Oxidation of Pollutant Dyes in Wastewater by TiO$_2$ and ZnO nono-materials, A Mini-review, www.nasi.org.in/Nano/3%20-20Ashutosh% *20Sharma.pdf*

[154] Vo Thi Thu Nhu, Do Quang Minh, Nguyen Ngoe Duy and Nguyen Quoc Hien, Photocatalytic degradation of Azo dye (methyl Red) in water under visible light using Ag-Ni/TiO$_2$ synthesized by γ-Irradiation method, International Journal of Environment Agriculture and Biotechnology, 2017, 2 (1), 529-538.

[155] Ammar Houas, Hinda Lachheb, Mohamed Ksibi, Elimame Elaloui, Chantal Guilard, Jean-Marie Herrmann, Photocatalytic degradation pathway of methylene blue in water, Applied Catalysis, B. Environmental, 2001, 3 145-157.

[156] Huayue Zhu, Ru Jiang, Ling Xiao, Yuhua Chang, Yujiang Guan, Xiaodong Li, and Guangming Zeng, Photocatalytic decolorization and degradation of Congo Red on innovative crosslinked chitosan/nano CdS composite catalyst under visible light irradiation, Journal of Hazardous Materials, 2009,169, 933-940.

[157] A.Abilarasu, T.Somanathan, A.Saravanan, V.Saravanan and P.Rajkumar, Enhanced photo-catalytic degradation of malachite green on spinel ferrite(nickel/magnesium ferrite) under direct sunlight, International Journal of Pharma and Bio-Sciences,2016, 7(4),93-99.

[158] Ahmed Hassan Ali, Study on the photocatalytic degradation of Indigo Carmine dye by TIO$_2$ photo-catalyst, Journal of Kerbala University, 2013,11(2)145-153.

[159] Sayed Mohammad Bagner Hosseini, Narges Falish and Sayed Javid Royaee, Optimization of photocatalytic degradation of real textile dye house wastewater by response surface methodology, Water Science and Technology, (2016).

[160] N.Divya, A.Bansal and A.K.Jana, Photocatalytic degradation of azo dye orange II in aqueous solutions using copper impregnated titania, International Journal of Environmental Science and Technology, 2013,10, 1265-1274.

[161] Pankaj Chowdhury, Jesus Moreira, Hassan Gomaa and Ajay K. Ray. "Visible-solar-light-driven photocatalytic degradation of phenol with dye-sensitized TiO2: parametric and kinetic study" Industrial & Engineering Chemistry Research, 2012, Vol. 51 Iss. 12. Available at: http://works.bepress.com/pankaj_chowdhury_western_university/6/

[162] Azita Mohagheghian, Seyydeh-Amene Karimi, Jae-Kyu Yang, and Mehdi Shirzad Siboni, Photocatalytic degradation of a textile dye by Illuminated Tungsten oxide nano powder, Journal of Advanced Oxidation Technology,2015, 18 (1) 61-68.

[163] Veljko Djokic, Jelena Vujovic, Aleksandar Marinkovic,Rada Petrovic, Djordje Janackovic, Antonije Onjia, and Dusanijin, A study of the photocatalytic degradation of the textile dye C1 Basic Yellow 28 in water using a P160 TiO$_2$ based catalyst, Journal of the Serbian Chemical Society,2012,77(12), 1747-1757.

[164] N.P.Mohabansi, V.B.Patil and N.Yenkie, A comparative study on Photodegradation of Methylene blue dye effluent by advanced oxidation process by using TiO$_2$/ZnO photocatalyst, Rasayan Journal Chemistry,2011,4(4),814-819.

[165] Emy Marlina Samsudin, Sze Nee Guh, Ta Young Wu, Tan Tong Ling, Sharifati Bee Abd Hamid and JoonChingJean, Evaluation on the photocatalytic degradation activity of reactive Blue-4 using Pure anatase Nano-TiO$_2$, Sains Malaysiana 2015,44(7),1014-1019

[166] Susheela Bai Gajbhiye, Photocataltic degradation study of methylene blue solution and its application to dye industry effluent, International Journal of Modern Engineering Research, 2012,2(3), 1204-1208.

[167] Tapas Kumar Roy and Naba Kumar Mondal, Photocatalytic degradation of congo red dye on thermally activated Zinc Oxide, International Journal of Scientific Research and environmental Science, 2014, 2 (12)457-469.

[168] M.V. Shankar, B.Neppolian. S.Sakthivel, Banumadhi Arabindoo. M.Palaniswamy and V.Murugesan, Kinetics of photocatalytic degradation of textile dye reactive Red 2, Indian Journal of Engineering and Material Scince, 2001,8, 104-109.

[169] Chhoyu Ram, Ravi Kant Pareek and Varinder Singh, Photocatalytic degradation of textile dye using Titanium dioxide nanocatalyst, International Journal of Theroetical and applied Sciences, 2012, 4(2) 82-88.

[170] S.K.Kansal, M.Singh and D.Sud, Studies on photodegradation of two commercial dyes in aquesous phase using different photocatalysts, Journal of Hazardous Materials, 2007,141(3) 581-590.

[171] Nirmalya Tripathy, Rafiq Ahmad, Jeong Eun Song, Hyun Park, and Gilson Khang, ZnO nanonails for photocatalytic degradation of crystal violet dye under UV irradiation, AIMS Materials Science, 2017, 4(1) 267-276; doi:10.3934/matersci.2017.1.267.

[172] Partha Mahata, T. Aarthi, Gridhar Madras and Srinivasan Natarajan, Photocatalytic degradation of Dyes and Organics with nanosized GdCoO$_4$, Journal of Physical Chemistry C, 2007,111, 1665-1674.

[173] Lidija Curkovic, Davor Ljubas, Suzana Segota, Ivana Bacic, Photocatalytic degradation of Lissminw Green B dye by using Nanostructured Sol-gel TiO$_2$ films, Journal of Alloys and Compounds,2015, 604, 308-316.

[174] Azita Mohagheghian, Seyydeh-Amene Karimi, Jae-Kyu Yang, and Mehdi Shirzad Siboni, Photocatalytic degradation of a textile dye by Illuminated Tungsten oxide nano powder, Journal of Advanced Oxidation Technology,2015, 18 (1) 61-68.

[175] William Wilson Anku, Samuel-Osei-Bonsu Oppong, Sudheesh Kumar Shukla and Poomani Penny Govender, Comparative photocatalytic degradation of Mono-azo and diazo dyes under simulated visible light using Fe^{3+}/C/S doped TiO$_2$ nano particles, Acta Chimica Slovakia, 2016, 63, 380-391.

[176] Valentine Rupa,A., Manikandan, D., Divakar,d., Revathis, S., Leena Preethi, M., Esther Shanthi, K., and Sivakumar, T., Photocatalytic degradation of tetrezine dye using TiO$_2$ catalyst: Salt effect and kinetic studies, Indian Journal of Chemical Technology, 2007,14(1) 71-78.

[177] Ahmed Hassan Ali, Study on the photocatalytic degradation of Indigo Carmine dye by TIO$_2$ photo-catalyst, Journal of Kerbala University, 2013,11(2)145-153-178]

[178] S.K.Kansal, M.Singh and D.Sud, Studies on photodegradation of two commercial dyes in aqueous phase using different photocatalysts, Journal of Hazardous Materials, 2007,141(3) 581-590.

[179] Veljko Djokic, Jelena Vujovic, Aleksandar Marinkovic,Rada Petrovic, Djordje Janackovic, Antonije Onjia, and Dusanijin, A study of the photocatalytic degradation of the textile dye C1 Basic Yellow 28 in water using a P160 TiO$_2$ based catalyst, Journal of the Serbian Chemical Society,2012,77(12), 1747-1757.

[180] Jan Sima and Pavel Hasal, Photocatalytic Degradation of Textile Dyes in a TiO$_2$/UV system, Chemical Engineering Transactions, 2013,32, 79-84.

[181] Manon Vautier, Chantal Guillard and Jean-Marie Herrman, Photocatalytic Degradation of Dyes in Water: Case study of Indigo and Indigo Carmine, Journal of Catalysis,2001, 201,46-59.

[182] S.A. Abo-Farha, Photocatalytic degradation of Monoazo and Diazo dyes in wastewater on Nanometer-sized, Researcher,2010, 2(7) 1-20.

[183] M.A. Mahmoud, A.Poncheri, Y. Badr and M.G. Abd El Wahed, Photocatalytic degradation of methyl red dye, Aouth African Journal of Science, 2009,105, 299-303.

[184] Morteza Montazerozohori, Masoud Nasr-Esfahani and Shiva Joohari, Environment Protection Engineering, 2012,38,45-55.

[185] M. Amini and.M. Ashrati, Photocatalytic degradation of some organic dyes under solar light irradiation using TiO$_2$ and ZnO nanoparticles, Nano.Chem.Res., 2016,1 (1) 79-86.

[186] Ankita Khanna and Vidya K Shetty, Solar light induced photocatalytic degradation of Reactive Blue 220 (RB—220) dye with highly efficient Ag@TiO$_2$ core shell nanoparticles: A comparison with UV photo-catalysts, Solar Energy, 2014,99,67-76.

[187] W.Rezig and M.Hadjel, Photocatalytic degradation of Vat Green 03 textile dye using the ferrihydrite-modified Diatomite with TiO$_2$/UV process, Oriental Journal of Chemistry, 2014, 30(3),993-1007.

[188] Khushnuma Parveen and Ritu Vyas, Photocatalytic degradation of Non-Biodegradable Malachite Green dye by Ni-Doped Titanium dioxide, Journal of Current Chemical and Pharmaceutical Science, 2016,6(4) 53-62.

[189] A.Bonkhennoufu, M.Bouhelassa and Z.Zoulalidian, Photocatalytic degradation of Solo phenyl Red 3 BL an aqueous suspension of Ti-

tanium Dioxide, Journal of Advanced Chemical Engineering,2011, 1, 1-8.

[190] Ohm-Mar Min, Li-Ngee Ho, Soon-An Ong and Yee-Shian Wong, Comparison between the photocatalytic degradation of single and binary azo dyes in TIO_2 suspensions under solar light irradiation, Journal of Water Reuse and Desalination, 13 pages (2015).

[191] Nyabaro Obed Mainya, Patrick Tum and Titus M Muthoka, Photodegradation and adsorption of methyl orange and Methylene Blue dyes on TiO_2, International journal of Science and Research, 2015,4(4)3185-3189.

[192] S.K.Pinky, Ferdush Ara,A.S.W Kurny, Fahmida Gulshan, Photo degradation of industrial dye using ZnO as photo catalyst, International Journal of Innovative Research in Science, Engineering ad Technology, 2015, 4 (10) 9986-9992.

[193] Aghareed M.Tayeb and Dina S.Hussein, Synthesis of TiO_2 nanoparticles and their photo catalytic activity for methylene Blue, American Journal of Nanomaterials, 2015,3(2) 57-63.

[194] E.K.Kirupavasam and G.Allen Gnana Raj, Photocatalytic degradation of amido black-10B catalyzed by carbon doped TiO_2 photocatalyst, International Journal of Green Chemistry and Bioprocess, 2012,2(3)20-25.

[195] Neha Verma, Sunik Bhatia and R.K.Bedi, Effect of annealing temperature on ZnO nano particles and its applications for photocatalytic degradation of DR-31 dye, International Journal of Pure and Applied physics, 2017,13(1)118-122.

[196] Veronika Marinovic, Davor Ljubas and Lidija Curkovic, Effects of concentration and UV radiation wavelengths on photolytic and photo-catalytic degradation of azo dyes aqueous solution by sol-gel TiO_2 films, The Holistic Approach to Environment, 2017, 7,3-14.

[197] D.Channei, B.Inceesungvorn, N.Wetchakun, S.Ukritnukun, A.Nattestad, J.Chen, and S.Phanichphant, Photo-catalytic degradation of methyl orange by CeO_2 and Fe-doped CeO_2 films under visible light irradiation, AP energy conference Proceedings, (2014).

[198] Siew-Teng Ong, Wai-Sim Cheong, and Yung-Tse Hung, Photodegradation of commercial dye, methylene blue using immobilized TiO_2, 4th International conference on Chemical, Biological and Environmental Engineering, IPCBEE, 2012, 43,109-113.

[199] Yuanjie Su, Ya Yang, Hulin Zhang, Yannan Xie, Zhiming Wu, Yadong Jiang, Naoki Fukata, Yoshio Bando and Zhong Lin Wang, Enhanced Photodegradation of methyl orange with TiO_2 nanoparticles using a triboelectric nanogenerator, Nanotechnolgy, 2013,24, 1-6.

[200] Pei Wen Koh, Mohd Hayrie Mohd Hatta, Stew Teng Ong, Leny Yuliati and Siew Ling Lee, Photocatalytic degradation of photosensitizing and non-photosensitizing dyes over chromium doped titania photo-catalysts under visible light, Journal of photochemistry and Photobiology: A Chemistry, 2017, 332, 215-223.

[201] Metwally Madkour and Fakhreia Al Sagheer, Au/ZnS and Ag/ZnS nano heterostructures as regenerated nano photo-catalysts for photo-catalytic degradation of organic dyes, Optical Materials Express, 2017,7, 158-169.

[202] Subas K Muduli, Songling Wang, Shi Chen, Chin Fan Ng, Cheng Hon Alfred Huan, Tze Chen Sum, and Han Sen Soo, Mesoporous Cerium oxide nano spheres for the visible light driven photocatalytic degradation of dyes, Beilstein Journal of Nanotechnology, 2014,5, 517 523.

[203] Shweta Sharma, Rakshit Ameta, R.K.Malkani and Suresh C.Ameta, Photo-catalytic degradation of Rose Bengal using semiconducting Zinc Sulphide as the photo-catalyst, Journal of the Serbian Chemical Society, 2013,78, 897-905.

[204] Jatinder Kumar and Ajay Bansal, Dual effect of photo-catalysis and adsorption in degradation of Azorubine dye using nano-sized TiO_2 and activated carbon immobilized with different techniques, International Journal of Chemtech Research, 2010, 2(3),1537-1543.

[205] Muhammad Umar and Hamidi Abdul Aziz, Photocatalytic degradation of organic pollutants in water, Environmental Science," Organic Pollutants Monitoring Risk and Treatment", book edited by M. Nageeb Rashed, 2013 and other systems referred to in Table 2 in this chapter 8 of this book.

[206] Abrar M. Algubil, Enas M. Alrobay and Ayad F. Alkaim, Photocatalytic degradation of Remazol Brilliant Blue dye by ZnO/UV process, International Journal of chemical Sciences, 2015, 13(2), 911-921.

[207] Raquel Cruz, Laura Hinojosa Reyes, Jorge L. Guzmán-Mar, Juan Manuel Peralta-Hernández and Aracely Hernández-Ramírez, Photocatalytic degradation of phenolic compounds contained in the effluent of a dye manufacturing Industry, Sustainable Environmental Research, 2011,21(5), 307 -312.

[208] E.S.Baeissa, Photocatalytic degradation of methylene blue dye under visible light irradiation usin In/ZnO nanocomposites, Frontiers in Nanoscience and Nanotechnology, 2016, 2 (5) 1-5.

[209] Ouarda Brahmia, Photocatalytic Degradation of a Textile Dye under UV and Solar Light Irradiation Using TiO2 and ZnO nanoparticles, International Journal of Advances in Chemical Engineering and Biological Sciences (IJACEBS),2016, 3, (2), 225-227; ISSN 2349-1507 EISSN 2349-1515.

[210] Aghareed M. Tayeb, Dina S. Hussein, Synthesis of TiO2 Nanoparticles and Their Photocatalytic Activity for Methylene Blue, American Journal of Nanomaterials,2015,3,(2), 57-63.

[211] Loum Janani, Kanwezi Henry, and Kamalha Edwine, Optimization of photocatalytic degradation of reactive blue dye using zinc oxide catalyst, International Journal of Research and Review,2015, 2(6)343-347.

[212] Khan M. Reza, Asw Kurny, and Fahmida Gulshan, Photocatalytic Degradation of Methylene Blue by Magnetite+H_2O_2+UV Process, International Journal of Environmental Science and Development,2016, 7(5),325-329.

[213] Liang Wang1, Jun Shang1, Weichang Hao, Shiqi Jiang, Shiheng Huang, Tianmin Wang, Ziqi Sun, Yi Du, Shixue Dou, Tengfeng Xie, Dejun Wang and& Jiaou Wang, A dye-sensitized visible light photocatalyst, Science Reports (2014) DOI: 10.1038/srep07384.

[214] F U Dawei, Xie Ruyi, Zhang Linping, Xu Hong, Zhong Yi, Sui Xiafeng and Mao Zhiping, Preparation of Hallow spherical Bismuth oxyiodide and its adsorption and Photocatalytic degradation of dyes, Chinese Journal of Applied Chemistry, 2017,34(5), 590-596.

[215] S.Aliouche, K.Djebbar, R.Zouaghi and T.Sehili, Photocatalytic degradation of yellow Alizarin Azo Dye in the presence of TiO_2 suspension, Sciences & Tecnhologie, A; No.39 June 2014, pp.23-30.

[216] Jyoti Tolia, Mousumi Chakraborty and Z.Murthy, Photocatalytic degradation of malachite green dye using doped and undoped ZnS nanoparticles, Polish Journal of Chemical Technology, 2012,14(2)16-21 (2012).

[217] P. Dharmarajan, A.Sabastiyan, M.Yosuva Suvaikin, S.Titurs and C.Muthukumar, Photocatalytic Degradation of Reactive Dyes in Effluents Employing Copper Doped Titanium Dioxide Nanocrystals and Direct Sunlight, Chemical Science Transactions, 2013, 2(4),1450-1458.

[218] K. Govindan, H.T. Chandran, M. Raja, S.U.Maheswari, and Murali Rangarajan, "Electron scavenger-assisted photocatalytic degradation of amido black 10B dye with Mn_3O_4 nanotubes: A response surface methodology study with central composite design", Journal of Photochemistry and Photobiology A: Chemistry, 2017,Vol. 341, pp. 146-156.

[219] S.Harikengaram, M.Robinson, A.Chellamani, Homogeneous Photocatalytic Degradation of Reactive Orange M2R Dye in Aqueous Medium, Journal of Environmental Nanotechnology, 2017,3(2), 1-8.

[220] S.N.Muhith, B.D.Choudhury, M.T.Uddin and M.A.Islam, Study of Photo-catalysts for the Treatment of Dye-Contaminated Wastewater, International Journal of Integrated Sciences & Technology, 2016, 2, 19-23.

[221] Jatinder Kumar, and Ajay Bansal, Photocatalytic degradation of amaranth dye in aqueous solution using sol-gel coated cotton fabric, Proceedings of the World Congress on Engineering and Computer Science 2010 Vol II, WCECS 2010, October 20-22, 2010, San Francisco, USA.

[222] Houda Ben Yahia Smida1 and Bassem Jamoussi, Degradation of Nitroaromatic Pollutant by Titanium dioxide/Zinc Phthalocyanine: Study of the Influencing Factors, IOSR Journal of Applied Chemistry (IOSR-JAC),2012,2(3)11-17.

[223] Tiantian Wu, Yanping Liang and Fangyuan Deng, Study on the Degradation of Dye Pollutants Over Silver Phosphate Photocatalyst, International Conference on Advances in Energy, Environment and Chemical Engineering (AEECE-2015).

[224] Indu Bhati, Pinki B. Punjabi, and Suresh C. Ameta, Photocatalytic degradation of fast green using nonosized $CeCrO_3$, Macedonian Journal of Chemistry and Chemical Engineering. 2010, Vol. 29, No. 2, pp. 195–202.

[225] Mohamed A. Salem, Shaban Y. Shaban and Sherin. M. Ismail, Photocatalytic Degradation of Acid Green 25 using ZnO and Natu-

ral Sunlight, International Journal of Emerging Technology and Advanced Engineering, 2015, 5(3), 439-443.

[226] Kamila Bubacz, Julia Choina, Diana Dolat, Antoni W. Morawski, Methylene Blue and Phenol Photocatalytic Degradation on Nanoparticles of Anatase TiO_2, Polish Journal of Envirometal Studies, 2010,19 (4) 685-691.

[227] Gabriela Antoaneta Apostolescu, Corina Cernatescu, Claudia Cobzaru, Ramona Elena Tataru-Farmus, Nicolae Apostolescu, Studies on the photocatalytic degradation of organic dyes using CeO_2–ZnO mixed oxides, Environmental Engineering and Management Journal,2015,14(2), 415-420.

[228] C. Karunakaran, P. Magesan, P. Gomathisankar, P. Vinayagamoorthy, "Photocatalytic Degradation of Dyes by Al_2O_3-TiO_2 and ZrO_2-TiO_2 Nanocomposites", Materials Science Forum, 2013,Vol. 734, 325-333.

[229] Zainab Raheem and Ahmed M. Hameed, Photocatalytic Degradation for Methylene Blue Dye Using Magnesium Oxide, International Journal of Basic and Applied Science, 2015,4(1),81-83.

[230] Rachita Mehta and Menka Surana, Photodegradation of Dye Acid Orange 67 by Titanium Dioxide in the Presence of Visible Light and UV Light, Research Reviews, 2013,2(2), 1216.

[231] *https://www.rit.edu/affiliate/nysp2i/sites/rit.edu./12rdsc09_report_cuny-csi.pdf.*

[232] Rakshit Ameta, Sanyogita Sharma, Shweta Sharma and Yogesh Gorana, Visible Light Induced Photocatalytic Degradation of Toluidine Blue-O by using Molybdenum Doped Titanium Dioxide, European Journal of Advances in Engineering and Technology, 2015,2(8), 95-99.

[233] Lum Sin Wan, A Study into photocatalytic degradation of methylene blue and glycerol aqueous solution over copper ferrite catalyst, Bachelor degree thesis, Faculty of Chemical & Natural Resources Engineering, Universiti Malaysia, Pahang, (2015).

[234] Narde SB, Lanjewar RB, Gadegone SM, Lanjewar MR, Photocatalytic Degradation of Azo Dye Congo Red Using Ni0.6Co0.4Fe2o4 as Photocatalyst, Der Pharma Chemica, 2017,9(7),115-120.