**Photocatalytic Degradation of Dyes: An Overview**

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*Abstract*

*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. 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.*

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 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 are 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• 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 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 are 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 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 photo-catalytic 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 TiO2) and the variables studied are mainly the same, whether it is required or not.

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

Before we embark on the limitations of the studies so far reported, it is necessary to 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. TheAdvanced Oxidation Process (AOP) has received considerable attention in recent times for the decomposition of organic dyes [16].

1. **The literature so far**

This is an area of research which is carried out throughout the world unlike other areas of science. Research in particular areas of science is confined 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**.**

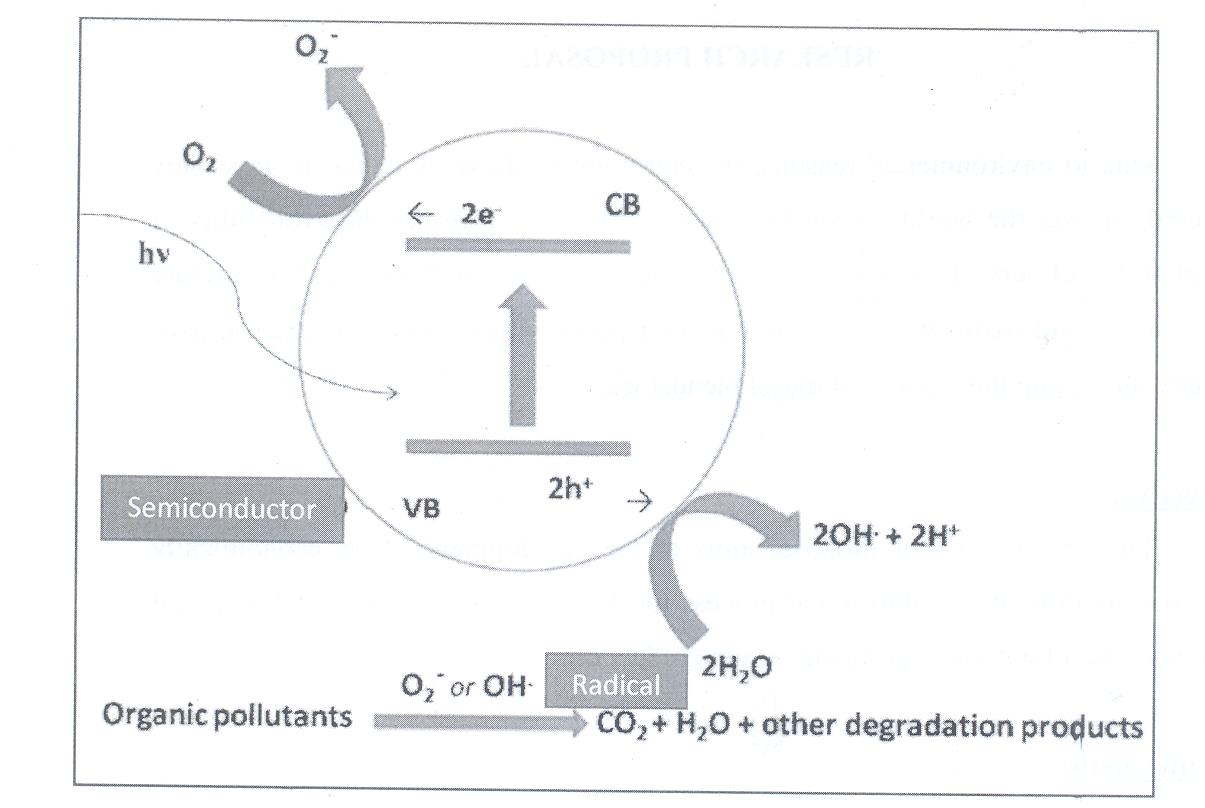


Fig.2. Pictorial representation of the process taking place in the photocatalytic degradation of dyes on semiconductor surfaces.

Most of the photocatalytic dye degradation studies reported have been with Titanium dioxide as a photocatalyst. However, the major disadvantage of TiO2 that it absorbs only in the UV region since it has a band gap of around 3.2 eV. Among the different phases of TiO2, anatase form of TiO2 is mostly employed due to its higher photon absorption characteristics. It is clear that the phase composition of TiO2 has a role to play in degradation of dyes. Among the most prominent phases of TiO2 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 [145-156].

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 TiO2, 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 [157]. The semiconductors especially TiO2 and ZnO are employed as nanorods, nanospheres, thin porous films, nanofibers and nanowires or supported on polymeric films [160]. These systems exhibit high activity, low cost and environmentally acceptable [161-163].

Apart from TiO2 and ZnO, various other semiconducting systems like CdS, ZrO2 and WO3  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 TiO2 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 K6Ta10.8O30 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)

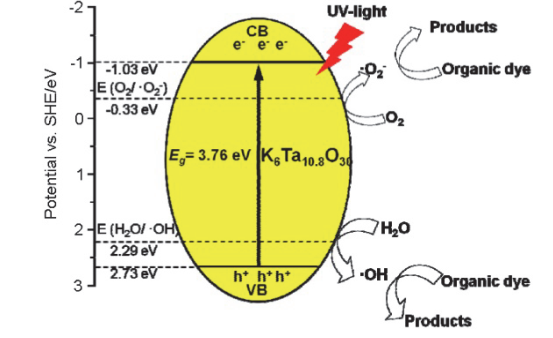


Fig 3 Representation of energy levels and species responsible for the photodegradation of dyes on typical complex oxide potassium tantalate [Reproduced from Ref.138].

Brookite is another phase of titanium dioxide which has been used as a photocatalyst for the degradation of dyes [174].

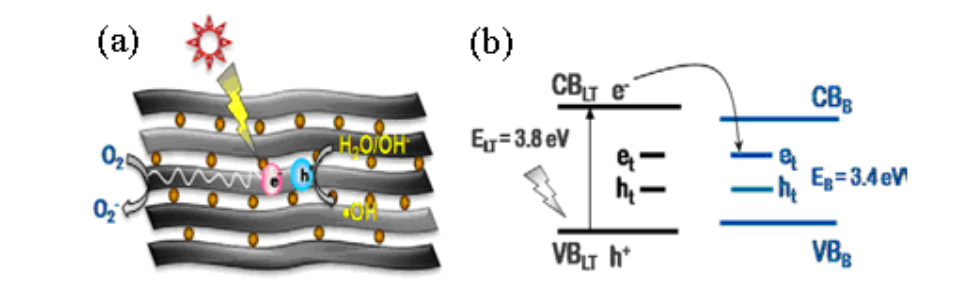


Fig.4. Diffusion behaviour of the charge carrier in layered nanosheets and (b) transport pathway of the excited electron in the mixed photo-catalysts [175].

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 various pathways in which these products are formed. These type of studies is limited in the literature [176]. 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

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

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Catalyst systems studied | Dyes employed | | Comments | Reference |
| 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. | 145 |
| Nanocrystalline anatase and rutile TiO2­ | 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 | 146 |
| TiO2, ZnO, SnO2 | Crystal Violet  Methyl Red | | ZnO shows better photoactivity than Degussa P-25 and silver deposited ZnO increases the photocatalytic activity by 20% | 147 |
| Mg2-TiO2 | Methyl Orange | | The catalyst has better activity than the un-doped TiO2- Dye sensitization and injection of the excited electron is considered as the cause | 148 |
| TiO2 Impregnated ZSM-5 (TiO2-ZSM = 0.15:1) | Reactive Black-5 | | The system shows high adsorption capacity and degradation activity. | 149 |
| 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 | 150 |
| ZnO Nano powder | Rhodamine B | | 95% degradation of the dye was observed under solar light irradiation | 151 |
| TiO2 | Methyl Orange  Methylene Blue | | The photocatalytic activity is found to be greater in the presence of solar light than in UV. | 152 |
| Nano-sized GdCoO4 | 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 GdCoO4 and P-25 are the same | 153 |
| TiO2 | 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) | 154 |
| TiO2 | Indigo  Indigo Carmine | | Complete mineralisation of the dyes  Irradiation with visible light only produced colour removal | 156 |
| TiO2 immobilised on polyvinyl alcohol (PVA) or polyacrylamide (PA) | Methylene Blue,  Anthraquinone,  Remazol Brilliant Blue R (RBBR),  Reactive Orange (RO16). | | TiO2 loaded on PVA appears to be better than that loaded on PA | 155 |
| Nanostructured TiO2 | 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 TiO2 | Methylene Blue  Congo Red | | Sol-gel method preparation of TiO2 is suitable for degradation of Dyes. Freundlich Isotherm is employed. | 2 |
| N-doped TiO2 | Methylene Blue  Methyl Orange | | Visible light source was employed and depends on nitrogen content of the catalyst | 1 |
| Nanometer sized TiO2 | Acid Orange 10(AO10)  Acid Red 14 14ARI14) | | The azo and Sulphonate groups determining factor for degradation | 157 |
| SiO2 nanoparticle doped with Ag and Au | Methyl Red | | OH radical produced initiates and also sustains the degradation of the dye | 158 |
| Titanium dioxide | Emerald Green | | Degradation rate constant depends on pH | 159 |
| ZnO and TiO2 | | Rhodamine B  Methylene Blue  Acridine Orange | ZnO dissolves as Zn(OH)2 and hence shows lower activity as compared to TiO2 | 160 |
| TiO2 (UV/Solar/pH) | | Procion Yellow | TiO2 in the presence of solar irradiation gives better degradation. | 161 |
| TiO2 | | Reactive Red 2 | The degradation in the presence of H2O2 and persulphate ion were studied. | 162 |
| Thermally activated ZnO | | Congo Red | Pseudo second order Kinetics was observed | 163 |
| Sol-gel TiO2 films | | Lissamine Green B | The TiO2 film prepared in Polyethylene glycol shows better photoactivity than the clean TiO2. | 164 |
| ZnO | | Methylene Blue | Actual industrial waste water is used for the experiments. | 165 |
| Ag-TiO2 core shell particle | | Reactive Blue 220 | The core shell system shows better photoactivity under solar light | 166 |
| Anatase Nano-TiO2 | | Reactive Blue 4 (anthraquinone dye | In the presence of externally added H2O2, the dye degradation gets increased. | 167 |
| TiO2/ZnO Photo catalyst | | Methylene Blue | ZnO appeared to be better than Pure TiO2 | 168 |
| P160 TiO2 | | C! Basic Yellow - 28 | Better degradation in weak acidic conditions, the addition of carbonate ion increased the degradation. | 169 |
| Ferrihydrite modified Diatomite with TiO2 /UV | | Vat Green 03 | A composite catalyst with P-25 with co-adsorbent removed colour over 98% | 170 |
| Orthorhombic WO3 | | AO7 dye | Phenol, humic acid and EDTA inhibited but oxalic acid increased the decolourisation of the dye. | 171 |
| Fe3+/C/S/-TiO2 | | Mono and Di-azo dyes | Mono azo dye degrades faster than diazo dyes under visible light. | 172 |
| Ni doped TiO2 | | Malachite Green | Hydroxyl ion as the oxidising species | 173 |
| TiO2 | | Solo phenyl Red 3BL | The concentration of OH\* and O\*  radical determines the degradation rate. | 174 |
| TiO2 | | Mono Azo Orange 7 (AO&)  Reactive Green 19 (RG19) | Mono azo dye (AO7) degrades faster than binary azo dye (RG19) under solar light. | 175 |
| TiO2 | | Azo dye and disperse dye | A modelling exercise on governing parameters. | 176 |
| TiO2 | | Methyl Orange  Methylene Blue | Degradation under UV irradiation | 177 |
| TiO2 Photo-catalyst | | Indigo Carmine dye | UV irradiation optimum conditions pH =4 and dye concentration 25 ppm 98% colour removal | 178 |
| ZnO photocatalyst | | Methylene Blue | The basic solution is better for the degradation reaction. | 179 |
| TiO2 Photo-catalyst | | Methylene Blue | The basic medium is better for the degradation | 180 |
| Carbon doped TiO2 | | Amido Black-10B | Active oxygenated species is responsible for decolourization. | 181 |
| ZnO photocatalyst | | Direct Red-31 (DR-31) dye | Effect of annealing temperature (500-800C)- UV irradiation | 182 |
| Sol-gel TiO2 films | | Methyl orange, Congo Red | TiO2 films with dip coating with Polyethylene glycol shows better activity in 254nm than 365 nm. | 183 |
| Undoped and Fe doped CeO2 | | Methyl Orange | 1.5 % doping of Fe3+  was optimal | 184 |
| Immobilized TiO2 | | Methylene Blue | Deposition of Photosensitive hydroxides decreased the activity | 185 |
| Ni/MgFe2O4 | | Malachite Green | Visible light active | 186 |
| TiO2 | | Methyl Orange | Superoxide anion radicalPolytetrafluoroethyle-A1 based triboelectric nanogenerator (TENG) assisted the process | 187 |
| Crosslinked Chitosan/nano CdS | | Congo Red | The degradation is better in acidic medium. The presence of NO3- accelerated, Br-, Cl- and SO42- inhibited decolourization of the dye. | 188 |
| TiO2/UV | | Methylene Blue | Mineralization of carbon, nitrogen and sulphur into CO2, NH4+, SO32- | 189 |
| Cu impregnated P-25 | | Azo dye Orange II | Cu Impregnated TiO2 is better than H2O2/UV homogeneous reaction. | 190 |
| Ag-Ni/TiO2 synthesised by gamma irradiation | | Methyl Red | Bimetallic co-doped is better than bare TiO2 | 191 |
| Cr doped TiO2 | | Methylene Blue  Congo Red | Cr doped promoted Anatase to Rutile phase transition | 192 |
| 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. | 193 |
| Mesoporous CeO2 | | Rhodamine B | Hydroxyl radicals are the active species | 194 |
| ZnS | | Rose Bengal | Hydroxyl radicals are shown as the active species | 189 |
| C-TiO2 films | | Azorubine | Photo-degradation and adsorption dual effect is the reason for better decolourization. | 195 |
| La-Y/TiO2 | | Methylene Blue | Optimum catalyst dose 4 g/L | 196 |
| Ag-TiO2­ | | Direct Red 23 | Optimum catalyst dose 3 g/L | 197 |
| ZnO | | Remazol Brilliant Blue dye (RBB) | The degradation follows first order kinetics | 198 |
| TiO2 Degussa P-25 | | 2,4-dimethylphenol, 2,4-dichlorophenol, 2-chlorophenol and phenol | pH 5 was found to be suitable for the degradation reaction. | 199 |
| ZnO | | Crystal Violet | high specific surface area (56.8 m2/g), high crystallinity and better optical property are responsible for the better activity of ZnO nanonails. | 200 |
| In/ZnO nano particles | | Methylene Blue | Indium is well dispersed on ZnO | 201 |
| TiO2 Degussa P25 and ZnO | | Methylene Blue | ZnO shows better activity in visible light than TiO2 | 202 |
| TiO2 nano particles | | Methylene Blue | Basic medium is better for the degradation | 203 |
| ZnO | | Reactive Blue | Reactor design and optimum time | 204 |
| Magnetite+H2O2+UV | | Methylene Blue | Process parameter optimization | 205 |
| Bi24O31Cl10 | | Rhodamine B | compatible energy levels and high electronic mobility | 206 |
| BiOI | | Rhodamine B  anionic reactive blue KN-R | h+ is the dominant species for the degradation of dyes. | 207 |
| TiO2 | | Alizarin yellow | The presence of Cl -, SO42- inhibits dye removal and it also depends on the TiO2 source. | 208 |
| TiO2, ZnO | | Polycyclic aromatic hydrocarbons (AH) | Surface to volume ratio appears to be relevant | 209 |
| ZnS doped with Mn | | Malachite green | UV/ZnS, UV/ZnS/H2O2, UV/doped ZnS systems studied | 210 |
| TiO2 and Cu-doped TiO2 | | reactive blue 4, reactive orange 30, reactive red 120and reactive black 5 | Cu-doped TiO2 nanoparticles are very effective in degrading the dye pollutants | 211 |
| Mn3O4 nano particles | | amido black 10B | peroxomonosulfate (PMS), peroxodisulfate (PDS) and hydrogen peroxide (HP) enhanced degradation | 212 |
| Photo-Fenton system | | Reactive orange M2R dye | Acidic pH favours, a mechanism is proposed | 213 |
| TiO2 catalyst with a shallow level of Pt | | Phenol | Eosin Y sensitised TiO2 | 214 |
| TiO2 | | Methylene Blue | p-n junction heterostructure CuO-TiO2 enhance photoactivity | 215 |
| TiO2 coated Cotton fabric | | amaranth dye | prepared fabric showed enhanced dye degradation capabilities | 216 |
| titanium dioxide TiO2 and zinc phthalo cyanine (ZnPc) | | 4-Nitrophenol | Efficiently degrade nitrophenol | 217 |
| Silver phosphate | | Methylene Blue | Visible-light-driven photodegradation of dye pollutants | 218 |
| CeCrO3 | | Fast Green dye | First order kinetics, | 219 |
| ZnO | | Acid Green 25 | Both acidic and basic medium | 220 |
| Anatase TiO2 | | Methylene Blue  Phenol | pH = 6.4 is optimum | 221 |
| CeO2-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 | 222 |
| Al2O3-TiO2 and ZrO2-TiO2 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 | 223 |
| MgO | | Methylene Blue | Over 90% degradation | 224 |
| TiO2 | | Acid Orange 67 | UV light source is better in comparison to Visible light. | 225 |
| TiO2 on Polyethylene film | | Crystal Violet  Methylene Blue  Basic Fuchsine | Sun light degradation.  Undergraduate experiment | 226 |
| Mo doped TiO2 | | Toluidine blue-o | Degradation of the dye follows pseudo-first order kinetics | *227* |
| Copper Ferrite | | Methylene blue Glycerol | Degradation of glycerol is not efficient and increased in the presence of added H2O2. | 228 |
| TiO2 as photo-catalyst | | Tartrazine (azo dye) | Influence of addition of other salts studied | 229 |
| Nio.6Co0.4Fe2O4 | | Congo Red | Photo-catalytic degradation maximum at pH 3 | 230 |
| Zn-TiO2 | | Direct Blue 71 dye | Zn Doped system is better than bare TiO2 | 103 |
| Ag modified ZnO | | Reactive Orange *16* | Ag modified system was better than pure ZnO | 104 |
| TiO2 | | **Reactive Orange 16 Dye (RO16)** | Effect of the amount of TiO2 studied | 105 |
| ZnO-CuO | | Reactive black5 (RB5) | This system is a suitable technique for degradation of dyes and environmental pollution from effluents. | 106 |
| TiO2 on polyethylene glycol | | Methyl Orange  Congo Red | Under UV irradiation higher efficiency observed | 107 |
| **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 | 108 |
| CdO/TiO2 coupled semiconductor | | Reactive Orange 4 (RO 4) | best photocatalytic activity in the degradation of RO 4 compared with bare TiO2 | 109 |
| 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 | 110 |
| CdS/SL g-C3N4) SL= Single Layer) | | Rhodamine B | visible-light-responsive and environmentally friendly photocatalyst for the degradation of dye | 111 |
| 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 | 112 |
| Cr doped ZnS | | Methyl Orange | Visible light is better than UV | 113 |
| Nano TiO2(C-Fe doped) | | C.I. Basic blue 9  C.I. Acid orange 52 | Real waste water treatment | 114 |
| CeO2-SnO2 | | Direct Black 38 | Activity is comparable with TiO2­-P25 | 115 |
| Z-scheme SnO2-x/g-C3N4 composite | | Rhodamine B | Z-scheme mechanism to enhance photo-degradation activity | 116 |
| 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 | 117 |
| TiO2-ZnO | | RB 21 dye | UV photoreactor and TiO2 is the best | 118 |
| CaO | | indigo carmine dye | pH 9 was suitable | 119 |
| g-C3N4/oxygen vacancy‐rich zinc oxide | | Methyl Orange | deactivated after five cycles of methyl orange degradation | 120 |
| CoFe2O4/C3N4 hybrid | | Rhodamine B | Typical Z-scheme system in environmental remediation | 121 |
| α-Bi4V2O11; γ-Bi4V2O11 | | Rhodamine B  Methylene Blue | Surface to Volume ratio is responsible | 122 |
| BiVO4-rGO | | Rhodamine B | Better than pure BiVO4 and P-25 | 123 |
| Flower like N-doped MoS2 | | Rhodamine B | 27 times better than bare MoS2 and 7 times better than P-25 | 124 |
| H3PW12O40/SiO2 | | Rhodamine B | under simulated natural light irradiation | 125 |
| SrTiO3 | | Methylene Blue  Rhodamine  Methyl Orange | Non-selective process | 126 |
| CuO/Ag3AsO4/GO | | Phenol | Photo-stability and reusability | 127 |
| TiO2/diatomite | | Rhodamine B, Methyl orange, Methylene blue | wastewater treatment -good photocatalytic property and reusability. | 128 |
| Cr(VI) using Ag/TiO2 | | 4-chlorophenol | stability and reusability of catalysts | 129 |
| PbCrO4/TiO2 | | Rhodamine B | good visible light-sensitive photo-catalyst for removing Rh B | 130 |
| WO3/SnNb2O6 | | Rhodamine B | Z-scheme charge transfer mechanism was proposed for the elimination of organic contaminants under irradiation of visible light. | 131 |
| ZnO | | Acid Red 27 | H2O2, K2S2O8, KBrO3 due to concentration increases the rate | 132 |
| CuS | | methylene blue, rhodamine B, eosin Y and Congo red | photodegradation rates of dyes usually follow pseudo-first-order kinetics for degradation | 133 |
| Cobalt Hexacyanoferrate(II) | | Neutral Red dye | Degradation under UV light and photo-catalyst | 134 |
| N-doped ZnO | | Azure A | N-doped zinc oxide has been used as an effective catalyst for carrying out number of chemical reactions | 135 |
| Al2O3-TiO2, ZrO2­­-TiO2 | | methylene Blue Rhodamine B | Methylene blue degradation is slow  Visible light degradation of rhodamine B | 136 |
| titanium dioxide (TiO2), zinc oxide (ZnO), stannic oxide (SnO2), zinc sulphide (ZnS), cadmium sulphide (CdS) | | Methyl Orange (MO), Rhodamine 6G (R6G | ZnO/solar light was observed to be better than ZnO/UV system | 137 |
| K6Ta10.8O30 | | ARG dye | the high photocatalytic activity of the  degradation of ARG dye under UV | 138 |
| TiO2(Brookite) | | Rhodamine | Less active than P-25 | 139 |
| TiO2 (Brookite +rutile mixture) | | Orange dye | Samples annealed at different temperatures | 140 |
|  | |  |  |  |
| Brookite nanoflowers | | Methyl Orange | More active than Anatase | 141 & 142 |
| Anatase and rich brookite rich films | | Acid orange 7  4-chlorophenol | Both exhibited same activity | 143 |
| TiO2 | | Methylene blue  Chromium (VI) | TiO2 /UV, system is very efficient compared with different natural and artificial adsorbent | 144 |

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 > TiO2 (Anatase) > TiO2 (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-C3N4) 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.

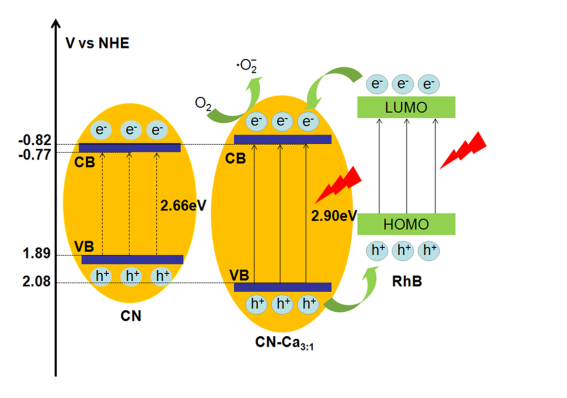


Fig.5. Energy level diagram of CN and CN modified with CaCl2 and how the degradation activity of Rhodamine B is enhanced with modification of CN [reproduced from ref. 108].

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-C3N4. 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.

* 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 [162-164]**.**

Semiconductor + photons (hᴠ) → e- (CB) + h+(VB) (1)

h+ + H2O → H+ + OH- (2)

h+ + OH- → OH• (3)

e- + O2 → O2• (4)

2e- + O2 + H2­O → H2O2 (5)

e- + H2O2  → OH•+ OH- (6)

Organic pollutant + OH•+ O2→ CO2 + H2O + 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 [165-168].

TiO2 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 [169,170]. 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 TiO2 for commercial dye degradation process. More advanced level research is at present required to find a suitable alternative to TiO2 for this application. Other than TiO2 the other system that is mostly employed is ZnO and other semiconducting oxides as stated above [171]. However, it is necessary to state the reasons for the preponderance of studies employing TiO2. 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 TiO2 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 TiO2. 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.

* 1. **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.175. 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 [176].

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) |
| TiO2(Anatase form) | 3.2(387) |
| TiO2 (Rutile form) | 3.0 (415) |
| TiO2 (Brookite form) | 3.14(395) |
| ZnO | 3.36(370) |
| WO3 | 2.76(450) |
| CdS | 2.42(515) |
| CuO | 1.2 (1035) |
| Cu2O | 2.2 (565) |
| MgO | 5.90 |
| Mn3O4 | 3.28(380) |
| ZnS | 3.6(345) |
| CeO2 | 3.19(390) |
| Fe2O3 | 2.3(540) |
| Fe3O4 | 2.25(550) |
| ZrO2 | 3.87(320) |
| g-C3N4 | 2.66(465) |
| Ag2O | 1.4(885) |
| SrTiO3 | 3.25(380) |
| Bi2WO6 | 3.13(395) |
| BaTiO­3 | 3.30(375) |
| Bi2O3 | 2.80(440) |
| CdO | 2.20(560) |
| CoO | 2.01(620) |
| Cr2O3 | 3.50(355) |
| HgO | 1.90(650) |
| In2O3 | 2.80(440) |
| MnO | 3.60(345) |
| Nb2O5 | 3.40(365) |
| NiO | 3.50(355) |
| PbO | 2.80(440) |
| PdO | 1.00(1240) |
| Sb2O3 | 3.00(415) |
| SnO | 4.20(295) |
| SnO2 | 3.50(355) |
| V2O5 | 2.80(440) |
| K6Ta10.8O30 | 3.76(330) |

* + 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.

The effect of pH on the efficiency of dye photodegradation process has to be associated with multiple roles [177]. The adsorption characteristics of the dye also change pH and the surface characteristics of the semiconductor [178]. This aspect has been already considered in detail in a publication [179]. 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 [180]. 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 [180]. Similar results have also been reported in the photo-degradation of other dyes [181-183]. 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 [184]. 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). [186]. Therefore, it is clear that the nature of the particular dye and pH have a profound effect on photocatalytic activity. [187-192]. 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 [193].

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, TiO2 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 TiO2 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.

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

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| Dye type | Light source | Photo-catalyst | pH range | Optimum pH | Ref |
| Orange G | UV | Sn/TiO2/Ac | 1.0-12.0 | 2.0 | 208 |
| Methyl Orange | UV | Pt/TiO2 | 2.5-11.0 | 2.5 | 209 |
| Orange G | Visible | N-TiO2 | 1.5-6.5 | 2.0 | 210 |
| Acid Red B | UV | Ce-TiO2 | 1.5-7.0 | 1.5 | 211 |
| Bromo-cresol purple | UV | TiO2 | 4.5 & 8.0 | 4.5 | 184 |
| Methyl Red | visible | 3%Ag+1.5%Ni-TiO2 | 3-10 | 4 | 63 |
| Methylene Blue | UV | TiO2 | 3-9 | Alkaline pH | 61 |
| Congo Red | Visible | Chitosan/CdS | 6-12 | 6 | 60 |
| Orange H | Solar | Zn-TiO2 | 3.0-10.0 | 3 | 194 |
| Malachite Green | Sun light | Ni/MgFe2O4 | 2.0-10.0 | 4 | 58 |
| Indigo Carmine | UV | TiO2 | 4.0-11.0 | 4 | 50 |
| Textile dye | UV | TiO2 | 3.0-7.0 | 5 | 48 |
| Solophenyl Red 3Bl | UV | TiO2 | 2.0-14.0 | 7 | 62 |
| Methyl Orange | UV | Fe2/C/S doped TiO2 | 2.0-12.0 | Acidic Medium | 60 |
| Acid Orange 7 | UV | WO3 | 3.0-9.0 | 3 | 43 |
| Basic Yellow 28 | UV | TiO2 | 3.0-9.0 | 5 | 41 |
| Methylene Blue | UV | TiO2ZnO | 1.0-6.0 | 2 | 40 |
| Reactive Blue 4 | UV | Anatase TiO2 | 3.0-13.0 | 3-7 | 39 |
| Methylene Blue | UV | ZnO | 2.0-11.0 | 7(minimum) | 37 |
| Congo Red | UV | ZnO | 5.0-10.0 | 8 | 35 |
| Reactive Red 2 | UV | TiO2 | 4.0-12.0 | 4-6 | 34 |
| Procion Yellow | UV | TiO2 | 2.0-10.0 | 7.8 | 33 |
| Acid Orange | UV | WO­3-TiO2 | 1.0-9.0 | 3.0 | 7, |
| Acid Yellow | UV | TiO2 | --- | 3.0 | 6 |
| Amido Black 10B | UV | TiO2 | ---- | 9.0 | 6 |
| Methyl Orange | UV | TiO2 | 2.0-10.0 | 8.0 | 24 |
| Rhodamine B | UV | ZnO | 2.0-12.0 | 12.0 | 23 |
| Methyl Orange | Visible | Mg doped TiO2 | 3.0-8.0 | -- | 20 |
| Acid Orange 10 | UV | TiO2 | 1.0-11.0 | 3.0 | 201 |
| Methyl orange, Rhodamine B | UV | ZnO | 2.0-10.0 | Basic medium | 137 |

A still more extensive compilation on the optimum pH on the photocatalytic degradation of dyes is already reported as Table.2 in the publication [203].

* 1. **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.

* + 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, 174,175 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.

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 | Ref |
| ZnO | Methyl orange (MO) | 0.1578 min-1 | 72 |
| ZnO | Congo Red (CR) | 0.1119 min-1 | 72 |
| ZnO | Direct Black DB38) | 0.0803 min-1 | 72 |
| 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 |
| TiO2 | Crystal Violet (CV) | 0.026 min-1 | 19 |
| TiO2 | Methyl Red (MR) | 0.008 min-1 | 19 |
| TiO2 | Basic Blue (BB) | 0.045 min-1 | 19 |
| SnO2 | Crystal Violet (CV) | 0.010 min-1 | 19 |
| SnO2 | Methyl Red (MR) | 0.004 min-1 | 19 |
| SnO2 | 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 | 35 |
| 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 GdCoO3 | Rhodamine B | 0.065 min-1 | 25 |
| 3 nm GdCoO3 | Rhodamine Blur | 0.078 min-1 | 25 |
| 3 nm GdCoO3 | Orange G | 0.053 min-1 | 25 |
| 3 nm GdCoO3 | Remazol Brilliant Blue | 0.019 min-1 | 25 |
| TiO2(450) | Methylene Blue | 0.0102 min-1 | 2 |
| TiO2 (450) | Congo Red | 0.0085 min-1 | 2 |
| TiO2 | Reactive Red | 0.0325 min-1 | 34 |
| ZnO | Congo Red | 0.0586 g.mg-1min-1 | 35 |
| TiO2 | Lissamine Green B | 0.0165 min+-1 | 36 |
| ZnO | Methylene Blue | 0.0135 min-1 | 37 |
| WO3 | Acid Orange 7 | 0.0225 min-1 | 43 |
| Fe3+/C/S/TiO2 | Methyl Orange | 0.01628 min-1 | 44 |
| Fe3+/C/S/TiO2 | Congo Red | 0.01533 min-1 | 44 |
| TiO2 | Carmine dye | 0.1456 min-1 | 50 |
| Chitosan/CdS | Congo Red | 0.01108 min-1 | 60 |
| ZnO | Methyl Orange | 0.00029 sec-1 | 137 |
| ZnO | Rhodamine 6G | 0.00027sec-1 | 137 |
| TiO2 | Acid Orange 10 | 0.0326 min-1 | 202 |
| TiO2 | Acid Orange 12 | 0.0269 min-1 | 202 |
| TiO2 | Acid Orange 08 | 0.0235 min-1 | 202 |
| TiO2 | Amido-black- 10B | 0.02083 min-1 | 204 |
| TiO2­ | Methyl Red | 0.0019 min-1 | 205 |
| Ag1.5Ni0.75/TiO2 | Methyl Red | 0.0077 min-1 | 205 |
| Ag1.5Ni1.5/TiO2 | Methyl Red | 0.0085 min-1 | 205 |
| Ag1.5Ni3.0/TiO2­ | Methyl Red | 0.009 min-1 | 205 |
| Ag3.0Ni1.5/TiO2 | Methyl Red | 0.0111 min-1 | 205 |
| TiO2 P25 | Organic dye | 0.003 to 0143 Min-1 | 212 |
| ZnS | Rose Bengal | ~4.51 X10-5 sec-1 | 213 |
| CeCrO3 | Fast Green | ~4.41 X 10-4 sec -1 | 214 |
| TiO2 | RG 19 | ~4.69 h-1 | 215 |
| TiO2 | AO7 | ~2.07 h-1 | 215 |
| 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 | 216 |
| 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 | 206 |

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 [41] can be written as ; where C is the concentration at any time t seconds, and C0 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.

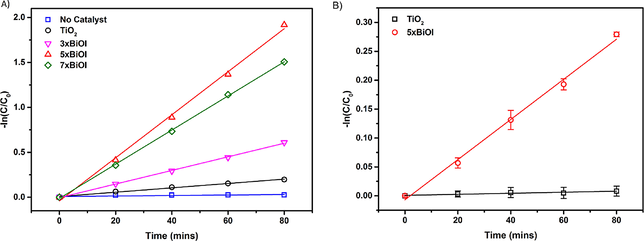


Fig 6. Photocatalytic degradation kinetics of Rhodamine B on various photo-catalysts treated according to first order kinetic equation [data reproduced from ref.15. There is any number of this kind of analysis reported in the literature on the photocatalytic decomposition of dyes, and they are referred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

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 caution has to be exercised while comparing two or more catalytic systems on the basis of the rate constant values of the kinetic data treated as first order since on all catalyst systems the reaction may not follow the same kinetics though the treatment according to first order kinetics may apparently satisfy the first order kinetics. The statements given may 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.

* + 1. **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.

* + 1. **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.

* + 1. **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 [209, 195-191]. 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 byproducts. 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.

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.

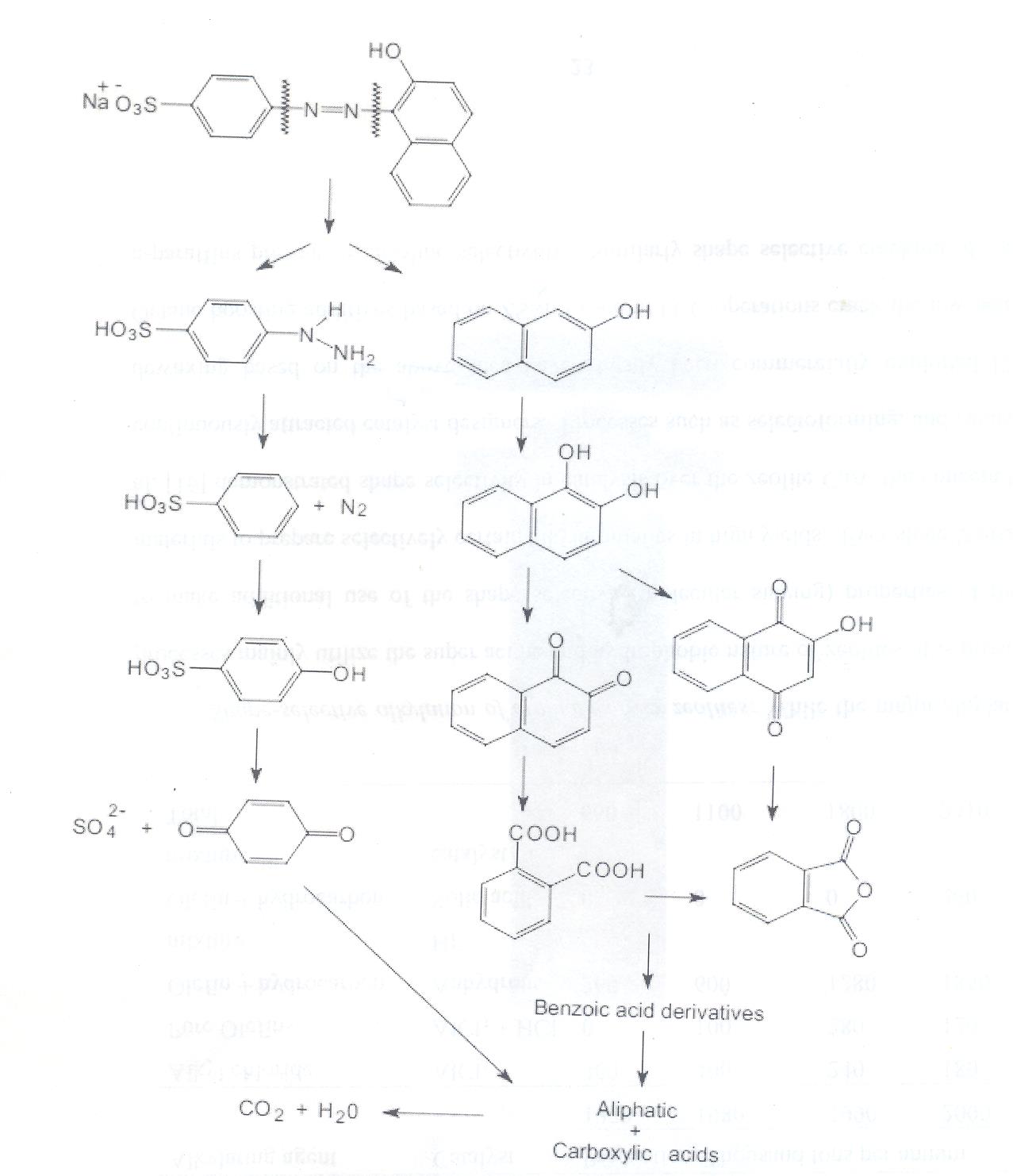


Fig.7. Possible photo-catalytic pathway for the degradation of acid orange 7 [deduced from the results reported in the publications 195-191].

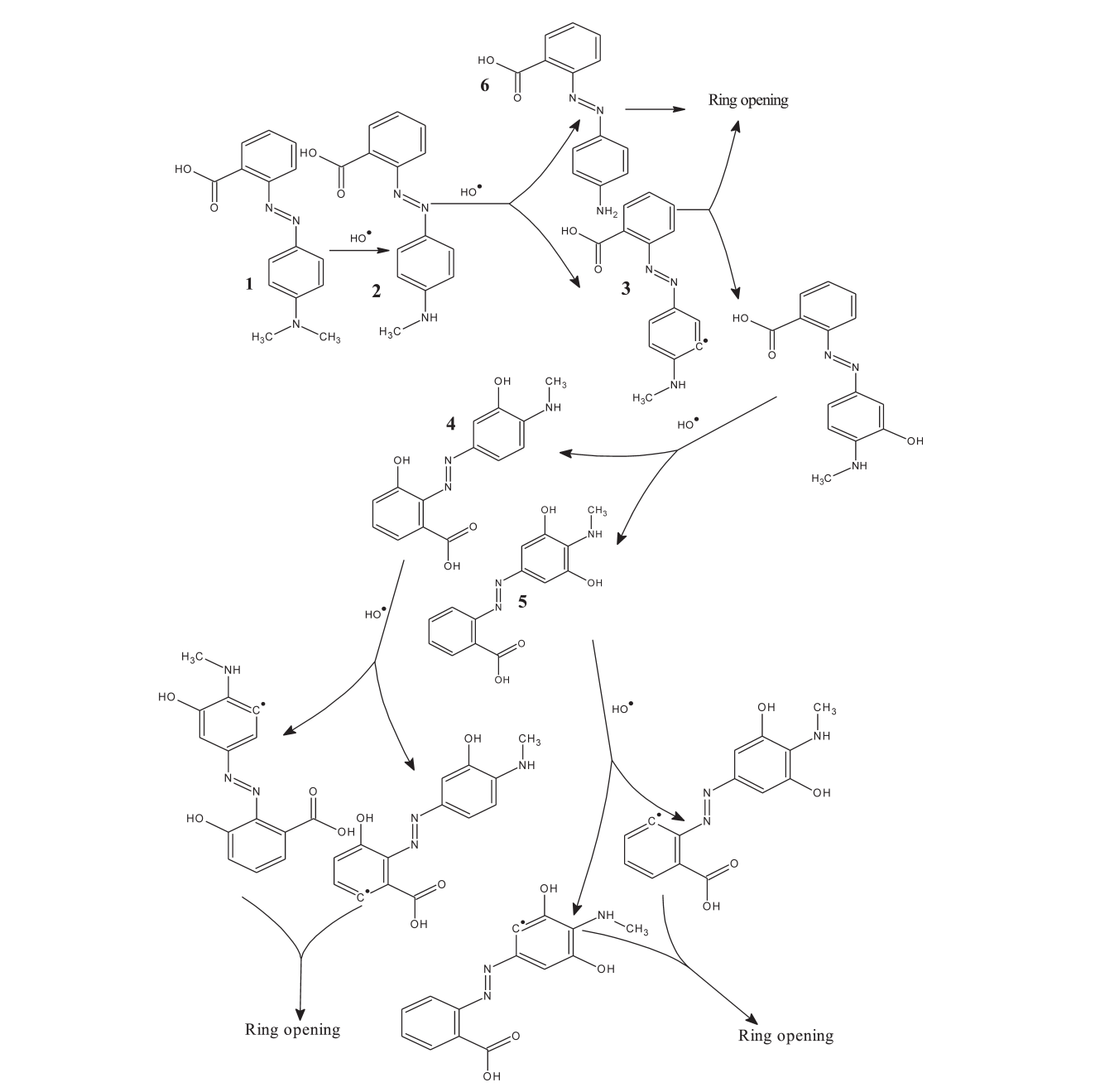
Methyl Red decomposition has been studied by Mahmoud et al. [206], and the main species responsible for this degradation is identified as superoxide anion radical (O2-•), or hydroxide radical (•OH) and the degradation route proposed by them is given in Fig.8. The possible first step can be the attack 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 byproduct. 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.

Fig.8. Mechanism of the possible routes for the photocatalytic degradation of methyl Red [Reproduced from ref 206].

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.



Fig.9. Routes of the degradation of a typical azo dye namely acid orange 7 [fig reproduced from ref.174]

* + 1. **Reactive oxygen species**

In the earlier parts, intrinsic reactive oxygen species (ROS) namely hydroxyl radical (•OH), hydrogen peroxide (H2O2), superoxide anion radical (•O2-) and singlet oxygen (1O2), 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 [209]. 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.



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

1. **Concluding Remarks**

It is true that photo-catalytic degradation of dyes has been studied throughout the world. The literature in this field is increasing steeply. 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:

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.

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