

Chapter 1

Introduction

1.1 Introduction

Water contamination is caused by various sources such as industrial effluents, chemical spills, domestic consumes and agricultural runoff. These effluents released into the rivers are highly contaminated and pose a potential environmental pollution (Qamar, et al., 2005). Color is usually the first contaminant to be recognized in wastewater which generated by using synthetic dyes in the industrials. Considering both discharged volumes and effluent composition, the wastewater generated by the textile industry is rated as one of the most polluting among all industry sectors. With the great variety of fibers, dyes, process aids and finishing products in use, the textile industry generated wastewater of great chemical complexity, diversity and volume (Bizani, et al., 2006). Synthetic dyes are extensively used in the textile industries because of their simple dyeing procedure and good stability during washing process. Over 10,000 dyes with an annual production over 7×10^5 metric ton worldwide are commercially available and it is estimated that approximately 15% of the dyestuffs are lost in the industrial effluents during manufacturing and processing operations. Synthetic dyes, classified by their chromophores, have different and stable chemical structures to meet various coloring requirements (Toor, et al., 2006). When, the release of this colored wastewater in the eco-system is a dramatic source of aesthetic pollution, eutrophication, and perturbation in aquatic life. The toxicity of wastewater with aquatic life is shown in Figure 1. Therefore, the removal of colored wastewater is a necessary before being released into the environment (Senthikumaar, et al., 2005).

Traditional techniques used for color removal are filtration, activated carbon (charcoal), and coagulation. Each method has few advantages and disadvantages. For example, the use of charcoal is technically easy but has high waste disposal cost. Coagulation using alums, ferric salts or limes is a low cost process, but all these methods have a major disadvantage of simply transferring the pollutants from

one phase to another phase rather than destroying them and sometime the by-products may be more toxic than the dye itself. Biological treatment is a proven method and cost effective. However, it has been reported that majority of dyes are adsorbed on the sludge and very long degraded times, due to the biorecalcitrant nature of these dyes molecules. This leads to a search for highly effective method to degrade the dye into environmentally compatible products (Toor, et al., 2006).



Figure 1 The toxicity of wastewater with aquatic life
(<http://teenet.chiangmai.ac.th>)

In recent years, attention has been focused on heterogeneous photocatalysis for the treatment of recalcitrant chemical present in the wastewater. Among these heterogeneous photocatalysis in the presence of irradiated semiconductors, TiO_2 has been successfully used to decolorize and mineralize many organic pollutants including several dyes and their intermediates present in aqueous systems using both artificial light and under sunlight using solar technology (Muruganandham, et al., 2005). TiO_2 is the most widely used photocatalyst because of its good activity, chemical stability, commercial availability and inexpensiveness. It is generally used as a photocatalyst for environmental applications such as air purification, water disinfection, hazardous waste remediation and water purification (Nagaveni, et al., 2004).

However, the application of powdered TiO_2 in wastewater treatment is limited since a post-treatment separation is required to recover the catalyst. Mobile photocatalyst powder is also not applicable for air purification, as it may contribute to respirable particles that cause adverse human health problems (Yu, et al., 2005). In order to avoid the use of photocatalyst powders, efforts have been made to coat TiO_2 thin films on various substrates such as glass (Losito, et al., 2005), ITO glass (Sankapal, et al., 2005), plastics (Kwon, et al., 2004) and polymers (Yang, et al., 2006), but these substrates are expensive and limited for the applications. TiO_2 thin films have been prepared by various techniques such as chemical vapor deposition (Ding, et al., 2001), spray pyrolysis deposition (Weng, et al., 2005), flame synthesis (Partsinis, et al., 1996), sol-gel dip coating (Sen, et al., 2005) and so on. However, the above methods have some disadvantages for industrial, need more expensive equipment and complex procedures. Therefore, a simple, less expensive and effective method for the preparation of TiO_2 films on the substrate is investigated.

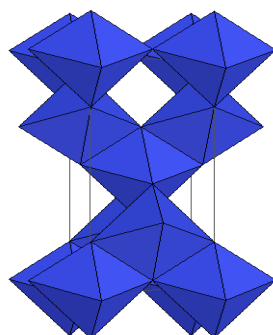
This work presents a simple, less expensive and effective method for the preparation of immobilized TiO_2 (Immo- TiO_2) films on the rubber substrate by direct mixing of commercial TiO_2 powders with latex and distilled water. The rubber strikes our interest because of its versatility in daily life, available locally, and to the best of our knowledge has never been used as a substrate for TiO_2 coating. We hope this should have potential applications in environmental business. The effect of various parameters such as amount of distilled water, latex and commercial TiO_2 powders were studied to optimize the preparation of Immo- TiO_2 thin films for maximum photocatalytic degradation of methylene blue (MB) dye in aqueous solutions under UV light irradiation. Furthermore, the effect of pH, initial concentration of MB solution, and UV light intensity were studied on the photocatalytic degradation of Immo- TiO_2 films for direct application of water purification.

1.2 Review of Literatures

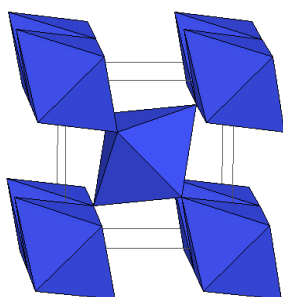
Titanium dioxide (TiO_2) or titania is a polymorphic compound, having three polymorphous structures: anatase, brookite, and rutile. These polymorphic forms of titanium dioxide are shown in Figure 2. Both anatase and rutile are tetragonal,

whereas brookite is orthorhombic. In all three oxide modifications, each titanium atom is coordinated to six almost equidistant oxygen atoms, and each oxygen atom to three titanium atoms (Clark, et al., 1968). In the case of anatase, the TiO_6 octahedron is slightly distorted, with two Ti-O bonds slightly greater than the other four, and with some of the O-Ti-O bond angles deviating from 90° . The distortion is greater in anatase than rutile. The structures of anatase and rutile crystals have been described frequently in terms of chains of TiO_6 octahedral having common edges. Two or four edges are shared in rutile and anatase, respectively. The third form of titanium dioxide; brookite, the interatomic distances and the O-Ti-O bond angles are similar to those of rutile and anatase. The essential difference is that there are six different Ti-O bonds ranging from 1.87 to 2.04 Å. Accordingly, there are 12 different O-Ti-O bond angles ranging from 77° to 105° . Brookite is formed by joining together the distorted TiO_6 octahedral sharing three edges. All three oxide modifications are birefringent; anatase is uniaxial negative, brookite is biaxial positive and rutile is uniaxial positive.

(a) Anatase



(b) Rutile



(c) Brookite

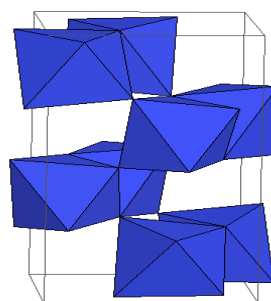


Figure 2 Crystal structures of TiO_2 ; (a) Anatase, (b) Rutile, and (c) Brookite

(<http://ruby.colorado.edu>)

Titanium dioxide occurs primarily in three different forms: anatase, rutile, and brookite. The most common are anatase and rutile, since brookite is rather unstable. The brookite type cannot be used in industries because of its instability at room temperature. The anatase type has high photocatalytic due to appropriate energy gap, heat resistant, and photostability. It also has advantage for purification environmental applications such as air purification, deodorization, soil proof, sterilization, and water purification. The rutile type used as a white pigments and outdoor applicability because of its good light resistance, high refractive index, and can be applied to surfaces by the use of adsorption technology without advanced skills or sophisticated equipment.

In industry, it is well known that TiO_2 pigments are produced by the older sulfate or newer chloride processes. The economics of the two processes are very much dependent upon the raw material available. The starting materials for TiO_2 production are ilmenite and titaniferous slag in the case of the sulfate process (Figure 3) and leucoxene, rutile, synthetic rutile, and in the future possibly also anatase, for the chloride process (Figure 4) (Büchner, et al., 1989).

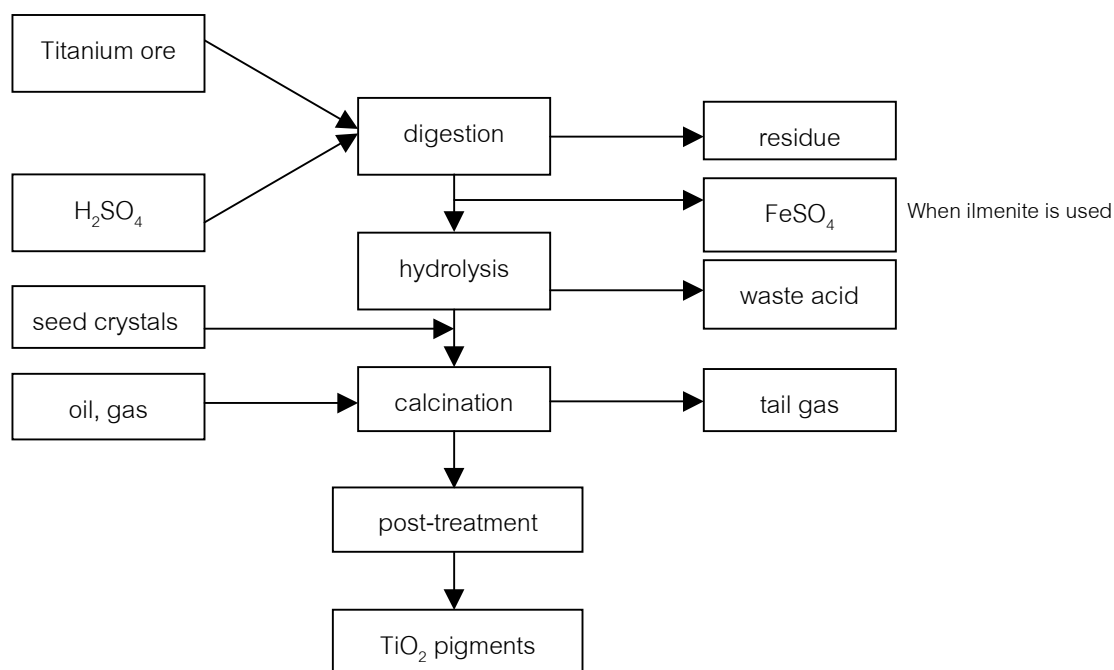


Figure 3 TiO_2 pigment manufactured by the sulfate process
(Büchner, et al., 1989 : 526)

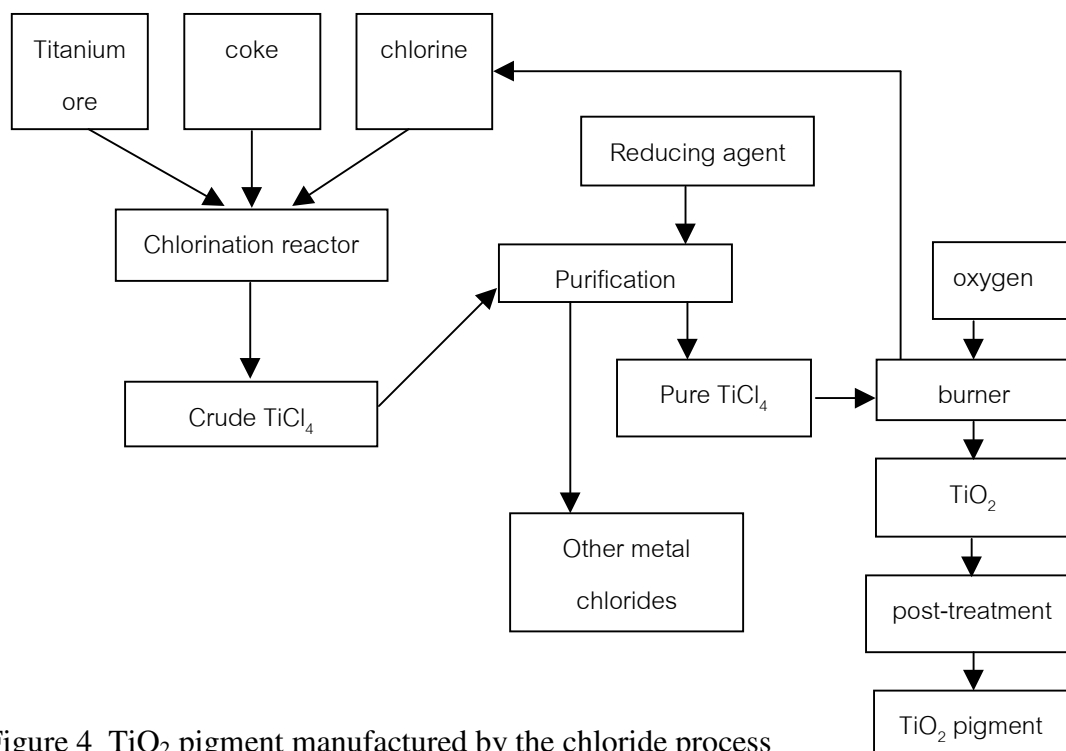


Figure 4 TiO₂ pigment manufactured by the chloride process
(Büchner, et al., 1989 : 528)

The sulfate process was the first commercial scale technology used to convert ilmenite to TiO₂. The process started from digestion the finely ground raw materials in an exothermic reaction with concentrated sulfuric acid, the digested cake dissolved in cold water and the residue separated off. To prevent their precipitation during the subsequent hydrolysis the Fe (III) ions are reduced to Fe (II) by adding a Ti (III) solution. Upon evaporation of the solution, the large quantities of iron (II) sulfate heptahydrate are produced, when ilmenite is used, and crystallizes out. The titanium oxysulfate is then hydrolyzed to titanium oxyhydrate by heating the clear solution with steam at 95-110°C. TiO₂ seed crystals are added or formed before hydrolysis to ensure yields of 93-96 % TiO₂ and to obtain a hydrolysis product which yields the optimum particle size of ca. 0.2 μm upon firing. Diluted sulfuric acid remains as “waste acid”. The hydrolysis product is washed, treated with a Ti (III) solution to remove adsorbed heavy metal ions (Fe, Cr, Mn, V) and calcined at temperature between 800-1,000°C. Anatase or rutile pigments can be produced in the calcination process depending upon the choice of additives, which determine the characteristics of the product. TiO₂

obtained in this way usually has the structure of anatase since the sulfate ions stabilize this modification which could not be removed during the process of washing, and it would benefit to the formation of anatase and the transformation temperature must take place at high temperature (about 1,000°C) to obtain rutile TiO₂ (Yang, et al., 2002).

The newer chloride process offers tighter product control, less labor intensive, avoids the iron sulfate waste problem and, at larger scales, is cheaper to operate. Currently about 60 % of 4 million ton of pigment produced worldwide is produced by this process. This process required the ilmenite to be processed to the rutile form (i.e. removal of the iron component to yield crude titanium dioxide (synthetic rutile)). The chloride process started from the reaction of chlorine with synthetic rutile to form raw titanium tetrachloride which is then mixed with reducing agent to convert impurities such as vanadium oxychloride, iron chloride to lower oxidation state compounds. It is then distilled yielding titanium tetrachloride in almost any required purity. Finally, it is combusted with pure oxygen to TiO₂ and chlorine, which is reused in the chlorination. Usually, TiO₂ prepared from this process has the mixture structure of anatase and rutile with the average diameter about 20 nm. For instance, the typical commercial formed TiO₂ (anatase) made by Degussa, contains about 25 % rutile.

Titanium dioxide is extensively used as a white permanent pigment with good covering power in paint, paper, printing ink, plastic, polymer and cosmetic products. Paints made with titanium dioxide are excellent reflectors of infrared radiation and are used in exterior paints. It is also used as strengthening filler in paper and cement. Recently, there has been increasing interest in application of nanocrystalline materials for catalyst, supports, ceramics, inorganic membranes, gas sensing, water purification, and solar energy conversion. Furthermore, photocatalysis of nanocrystalline titanium dioxide has a great many advantage on waste water treatment such as high catalysis efficiency, energy saving, no pollution, etc. and can degrade all kinds of organic pollutants from water effectively. All of those merits make photocatalysis of water treatment and it is supposed to be used widely in the future (Baolong, et al., 2003).

Coloration is a key factor in the commercial success of textile products, particularly those with high fashion content, especially garments, furnishings and upholstery. The business generated by the dye industry over the last two years was approximately US\$ 22 billion, and constituted a total employment of about 1.45 million people. Excluding fluorescent brighteners, the dye consumption per capita is approximately 150 g per year, serving an average consumption of textile fiber of about 14 kg per year per inhabitant. Despite, the high economic importance of the textile industry in the world, this industry is responsible for over 7×10^5 metric ton of about 10,000 different types of dyes on pigments produced each year. During dye use among the several industries responsible for pollution of the aquatic ecosystems, the textile dyeing and printing industries are major players, around a half of a ton of these dyestuffs are lost per day to the environment. Approximately 200 L of water is required, for every kilogram of finished cotton fabric. The reactions necessary to fix these dyes to the fibers are not very efficient. Therefore, residual dyes, several types of chemicals and salts are dumped into the water and are discharged in the wastewater system. At least 15% of those not used dyes might enter the environment through effluents from wastewater treatment plants (Carneiro, et al., 2004).

Removal of color in wastewater generated by the textile industries is an issue of discussion and regulation all over the world. Among the relative dyes, the textile azo dyes with synthetic intermediates as contaminant and its degradation products have undoubtedly attracted the most attention with regard to high environmental impact, because of their widespread use, their potentiality to form toxic aromatic products (carcinogenicity and mutagenicity properties) and their low removal rate during primary and secondary treatment. They represent about 50% of the worldwide production and correspond to an important source of contamination considering that a significant part of the synthetic textile dyes are lost in waste streams during manufacturing or processing operations. Therefore it is important to develop effective wastewater remediation technologies for these compounds.

Various chemical and physical treatment processes are currently proposed for these dyes. These largely fall into the categories of direct precipitation or elimination by adsorption, flocculation, membrane separation, coagulation and chlorination. These methods have been largely incomplete and ineffective because the

problem is not completely resolved, being required further treatment. A number of biological processes, such as sequenced anaerobic / aerobic digestion, have been proposed in the treatment of textile wastewater, but they are limited due to the fact that many of the dyes are xenobiotic and non-biodegradable. Alternative methods based on advanced oxidation processes combining ultraviolet irradiation and oxidative agents for dye treatment have been also investigated, but the presence of intermediates arising from the photodegradation reaction could be more harmful than the pollutant itself.

In recent years attention has been focused on heterogeneous photocatalysis for the treatment of recalcitrant chemical present in the wastewater. Among these heterogeneous photocatalysis in the presence of irradiated semiconductors (TiO_2 , WO_3 , SnO_2 , ZnO , CdS , and others), TiO_2 has been successfully used to decolorize and mineralize many organic pollutants including several dyes and their intermediates present in aqueous systems using both artificial light and under sunlight using solar technology (Muruganandham, et al., 2005). TiO_2 is the most widely used photocatalyst because of its good activity, chemical stability, commercial availability and inexpensiveness. It is generally used as a photocatalyst for environmental applications such as air purification, water disinfection, hazardous waste remediation and water purification (Nagaveni, et al., 2004).

The efficiency of advanced oxidation processes for degradation of recalcitrant compounds has been extensively documented. Photochemical processes are used to degrade toxic organic compounds to CO_2 and H_2O without the use of additional chemical oxidants, because the degradation is assisted by high concentrations of hydroxyl radicals (OH^\bullet) generated in the process. In this case, the photoexcitation of TiO_2 particles promotes an electron from the valence band to the conduction band, generating an electron/hole pair. Both reductive and oxidative processes can occur at or near the surface of the photoexcited TiO_2 particle. In general, oxygen is used to scavenge the conduction band electron, producing a superoxide anion radical ($\text{O}_2^{\bullet-}$), effectively preventing electron/hole recombination, and prolonging the lifetime of the hole. The photogenerated hole has the potential to oxidize several substrates by electron transfer. In aqueous solutions, oxidation of water to hydroxyl radical by the photogenerated hole appears to be the predominant pathway. Hydroxyl radicals and, to a lesser extent, superoxide anion can act as oxidants,

ultimately leading to the mineralization of organic compounds (Gome de Moraes, et al., 2000).

The mineralization of most of the organic pollutants could be degraded following the usually proposed mechanism (Equations.1-9); for the heterogeneous photocatalytic oxidation processes as shown in Figure 5.

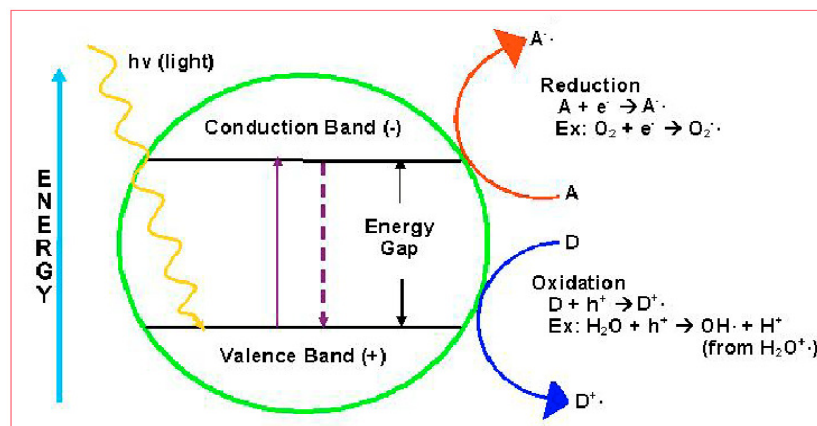


Figure 5 The heterogeneous photocatalytic oxidation processes of titanium dioxide photocatalyst (<http://dev.nsta.org>)

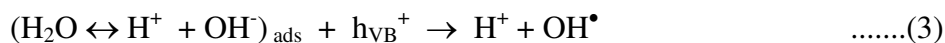
1. Absorption of efficient photons ($h\nu > E_g = 3.2 \text{ eV}$) by titania



2. Oxygen ionosorption (first step of oxygen reduction; oxygen's oxidation state changes from 0 to -1/2)



3. Neutralization of OH^- groups by photoholes which produces OH^\bullet radicals



4. Neutralization of $\text{O}_2^{\bullet-}$ by protons



5. Transient hydrogen peroxide formation and dismutation of oxygen



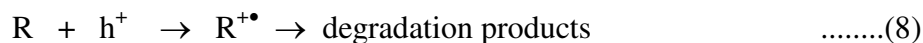
6. Decomposition of H_2O_2 and second reduction of oxygen



7. Oxidation of the organic reactant via successive attacks by OH[•] radicals



8. Direct oxidation by reaction with holes



As an example of the last process, holes can react directly with carboxylic acid generating CO₂



In most cases, the degradation is conducted for dissolved compounds in water with UV-illuminated titania. The possible extents of the technique concern the irradiation source and the physical state of the pollutant. Recently, some works have reported the degradation of organic dyes induced by visible light by photosensitization. The interest is to use solar visible light which is free and inexhaustible (Houas, et al., 2001).

In the present work, it was attempted to establish the degradation of a dye present in colored aqueous effluents from textile industries. The model dye chosen was methylene blue (MB).

Methylene blue, MB, is a brightly colored blue cationic thiazine dye, with λ_{max} values at 665, 614 and 292 nm. The uses of MB include being an antidote for cyanide poisoning in humans, antiseptic in veterinary medicine and, most commonly, in vitro diagnostic in biology, cytology, hematology and histology. The structure of methylene blue shows in Figure 6.

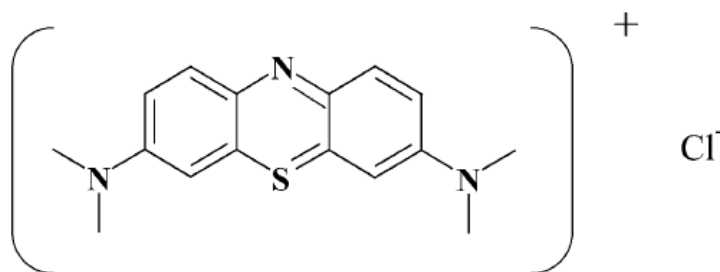


Figure 6 The structure of methylene blue (Mills, et al., 1999)

The doubly reduced form of MB, leuco-methylene blue, i.e., LMB, is colourless (typically, $\lambda_{\max} = 256$ nm) and stable in de-aerated aqueous solutions. The singly reduced form of MB, the semi-reduced radical, $\text{MB}^{\bullet-}$, is pale yellow ($\lambda_{\max} = 420$ nm) and readily disproportionates ($k = 3 \times 10^9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) to form MB and LMB, i.e.,

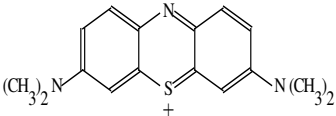
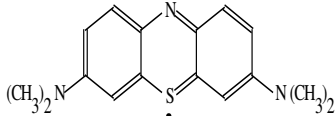
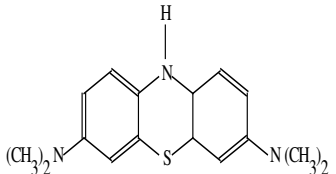
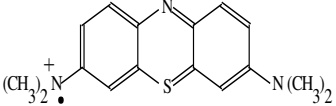


Less research has been conducted into the oxidised form of MB, i.e., $\text{MB}^{\bullet+}$, $\lambda_{\max} = 520$ nm, which appears to be quite stable and it easily reduced back to MB in acidic solution, but decomposes irreversibly in slightly alkaline (pH = 9.1) solution. MB readily forms dimers in aqueous solution, i.e.,



A typical value for K_D , the equilibrium constant associated with the dimerisation process, is $3970 \text{ dm}^3 \text{ mol}^{-1}$. The structures of most of the methylene blue-type compounds highlighted above are illustrated in Table 1 along with the associated pKa and redox potential data.

Table 1 Structure and UV-Vis absorption characteristics of methylene blue and its common reduced and oxidised forms (Mills, et al., 1999)

Species / Structure	Abbreviation	pK _a	E ⁰ vs. NHE (V)	λ _{max}	Other properties
<p>Methylene blue</p> 	MB	0		660, 614, 292	K _D = 3970 dm ³ mol ⁻¹
<p>Semi-reduced methylene blue</p> 	MB ^{°·}	-3, 2, 9	(MB/MB ^{°·}) = -0.23	420	Readily disproportionates to form MB and LMB
<p>Leuco methylene blue</p> 	LMB	4, 5, 5.8	(MB/LMB) = - 0.011 (pH7) and 0.532 (pH0)	256	
<p>Oxidised methylene blue</p> 	MB ^{°+}		(MB ^{°+} /MB) = 1.08	520	Stable in acid (pH 1) and unstable at pH 9

The photochemistry of MB has been widely studied. MB remains a popular dye sensitizer in photochemistry especially in the areas of singlet oxygen production and reductive electron transfer. The wide and varied use of MB in photochemistry is attributable to its relatively long-lived, triplet state, $\tau_T = 450 \mu\text{s}$, with its high probability of formation, $\phi_T = 0.52$, large energy (1.44 eV above the ground state) and high triplet oxidation potential $E^0(\text{MBT} / \text{MB}^{\bullet+}) = 1.21 \text{ V}$ versus NHE. The major photophysical and redox characteristics of MB are summarized in Table 2 (Mills, et al., 1999).

Table 2 Photophysical properties of methylene blue (Mills et al., 1999)

	Singlet: MB ¹	Triplet: MB ³
ϕ_T	-	0.52
E (excited state) (kJ mol ⁻¹)	180	138
τ	30-390 ps	450 μs
ϕ (fluorescence)	0.04	-
E^0 (excited state/ MB ^{•+}) vs. NHE (V)	1.60	1.21

Given the well-established photochemical activity of MB, initially it might appear surprising to note that MB has often been used as a reactant in semiconductor photocatalysis. This surprise may well increase when it is realized that the semiconductor most often employed in such studies is TiO₂, a UV absorber. However, a brief inspection of the UV-Vis absorption spectra of MB, illustrated in Figure 7 (solid line), reveal that MB absorbs a little light between 300 and 400 nm. The latter wavelength region is usually the region of illumination in TiO₂-sensitized semiconductor photocatalysis, since most UV irradiation sources used in such work are designed to emit light of $\lambda < 400 \text{ nm}$, and most of the glassware used is Pyrex, which cuts off at 300-310 nm. To emphasize the latter point a little further, the relative emission intensity versus λ profile for one of the most common light sources in use in semiconductor photocatalysis, the blacklight bulb ($\lambda_{\text{max}}(\text{emission}) = 355 \text{ nm}$), is also

illustrated in Figure 7 (dotted line). A brief inspection of the two spectra in Figure 7 reveals a marked lack of overlaps (Mills, et al., 1999).

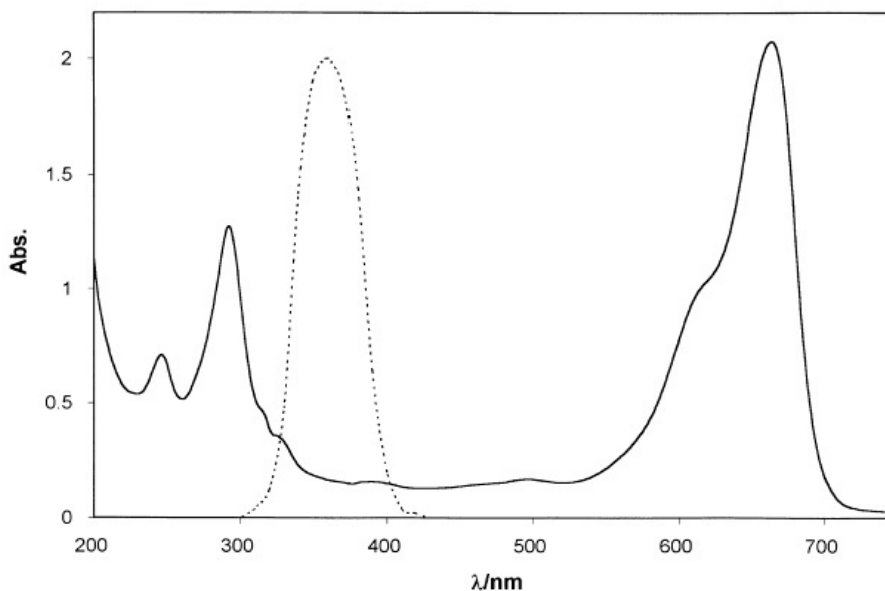


Figure 7 UV-Vis absorption spectrum of MB aqueous solution (solid line) and the relative emitted light intensity (dotted line) for 8W blacklight bulb (Mills, et al., 1999)

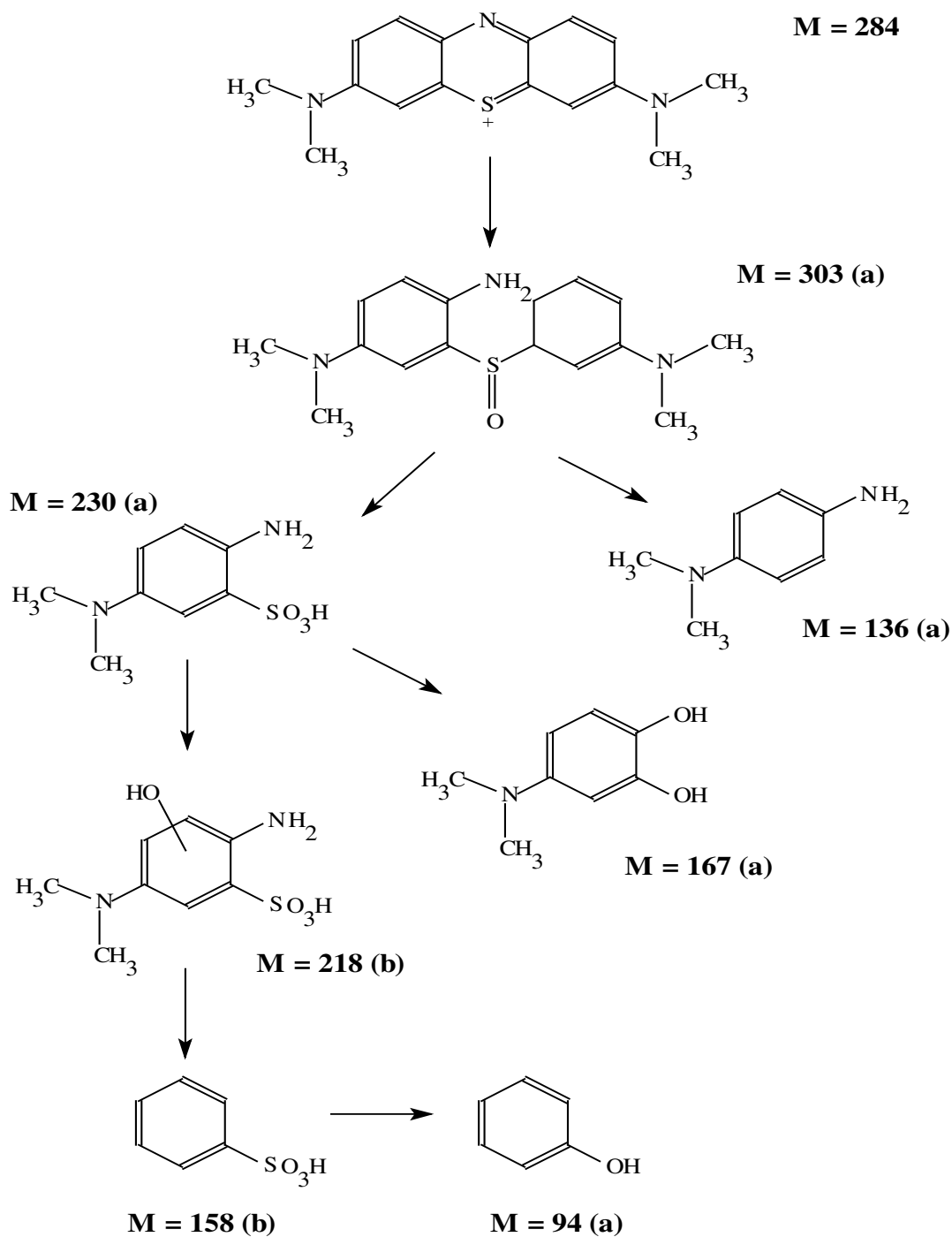
Many studies for photocatalytic degradation of MB, others textile dyes and pollutants by TiO_2 powder in aqueous suspension are as follows.

Xu, et al., (1999) synthesized ultrafine TiO_2 particles by sol-gel method and studied the influence of particle size of TiO_2 on the photocatalytic degradation of methylene blue (MB) in aqueous solution. The results suggested that the adsorption rate and adsorbability of MB on suspended TiO_2 particles increased as the particle sizes of TiO_2 decreased. Photocatalytic activity of TiO_2 also increased as the particle sizes of TiO_2 became smaller, especially when the particle size is less than 30 nm. The half-life of the photocatalytic degradation of MB also decreased as the particle sizes of TiO_2 decreased. The first order reaction rate constant for photocatalytic degradation of MB increased as particle size of TiO_2 decreased. The initial degradation rate of MB in a suspended model was higher than that of a fixed-bed model. This will overcome the

difficulty of preparation of ultrafine TiO_2 particles. The industrialization of the TiO_2 suspended-type photoreactor will be easier once the problem of separation of fine TiO_2 particles is solved. The application of the ceramic membrane for this problem is now in progress and will be published.

Ding, et al., (2000) prepared a series of TiO_2 samples with different anatase-to-rutile ratios, and studied the roles of the two crystallite phase of TiO_2 on the photocatalytic activity in oxidation of phenol in aqueous solution. High dispersion of nanometer-size anatase in the silica matrix and the possible bonding of Si-O-Ti in $\text{SiO}_2/\text{TiO}_2$ interface were found to stabilize the crystallite transformation from anatase to rutile. The temperature for this transformation was 1200°C for the $\text{SiO}_2/\text{TiO}_2$ sample, much higher than 700°C for Degussa P25 TiO_2 . It is shown that samples with higher anatase-to-rutile ratios have higher activities for phenol degradation. However, the activity did not totally disappear after a complete crystallite transformation for P25 TiO_2 samples, indicating some activity of the rutile phase. Furthermore, the activity for the $\text{SiO}_2/\text{TiO}_2$ samples after calcinations decreased significantly even though the amount of anatase did not change much. The activity of the same samples with different anatase-to-rutile ratios is more related to the amount of the surface-adsorbed water and hydroxyl groups and surface area, leading to the decrease in activity.

Houas, et al., (2001) investigated the TiO_2/UV photocatalytic degradation of MB in aqueous solution. In addition to a prompt removal of the color, TiO_2/UV -based photocatalysis was simultaneously able to oxidize the dye, with an almost complete mineralization of carbon and of nitrogen and sulfur heteroatoms into CO_2 , NH_4^+ , NO_3^- and SO_4^{2-} , respectively. A detailed degradation pathway has been determined by a careful identification of intermediate products, shown in Figure 8, in particular aromatics, whose successive hydroxylation lead to the aromatic ring opening. It can be concluded that photocatalysis can decontaminate colored used waters. Photocatalysis appears as the only sub-discipline of heterogeneous catalysis, which is able to convert organic pollutants to CO_2 in water without heating nor using high pressure of oxygen nor requiring chemical reactants or additives. These results suggest that TiO_2/UV photocatalysis may be envisaged as a method for treatment of diluted wastewater in textile industries.



(a) detected by GC/MS (extraction of ions)

(b) detected by LC/MS

Figure 8 Photocatalytic degradation pathway of methylene blue (Houas, et al., 2001)

Ranjit, et al., (2001) investigated the photocatalytic degradation of salicylic acid and *t*-cinnamic acid in aqueous suspensions of lanthanide oxide (Eu^{3+} , Pr^{3+} , Yb^{3+}) doped TiO_2 photocatalysts. Complete mineralization has been achieved in the case of lanthanide oxide doped TiO_2 photocatalysts. The equilibrium dark adsorption of salicylic acid and *t*-cinnamic acid is *ca.* three times and two times higher, respectively, on the lanthanide oxide modified TiO_2 photocatalysts as compared to the non-modified TiO_2 catalyst. The enhanced degradation is attributed to the formation of the Lewis acid-base complex between the lanthanide ion and the substrates at the photocatalyst surface.

Chatterjee, et al., (2002) investigated the visible light assisted degradation of aromatics, viz phenol, chlorophenol, 1,2-dichloroethane, trichloroethylene and surfactants, viz cetyl pyridinium chloride (CPC; cationic), sodium dodecylbenzene sulfonate (DBS; anionic) and neutral Triton-100 in air equilibrated aqueous mixtures has been achieved on the surface of TiO_2 semiconductor modified with methylene blue (MB) and rhodamine B (RB). Under 5 h of irradiation with a 150 W xenon lamp, over 40-75% degradation of pollutants to degrade on non-conducting Al_2O_3 surface essentially suggests the role of semiconducting TiO_2 photocatalyst in the photochemical process. A working mechanism involving excitation of surface adsorbed dye, followed by injection into the TiO_2 conduction band and formation of reactive $\text{O}_2^{\bullet-}/\text{HO}_2^{\bullet}$ radicals is proposed for the degradation of organic to carbon dioxide.

Chiang, et al., (2002) synthesized copper (II) oxide loaded onto the surface of Degussa P25 TiO_2 particles by photodecomposition. The doped sample was subsequently utilized as the photocatalyst for cyanide oxidation. The copper content on the TiO_2 surface was varied from 0.05 to 10.0 wt.% of Cu. It was found that nanosized CuO deposited were present on the surface of TiO_2 . Modifying TiO_2 with CuO changed the optical properties of TiO_2 and the onset of absorption was red shifted. The photocatalytic activity of the CuO loaded TiO_2 was measured to determine their ability to oxidize cyanide. It was found that the rate of photooxidation of cyanide assisted with the doped catalyst was improved slightly at 0.10 wt.% of Cu. Any further increase of the copper dopant concentration decreased the oxidation rate remarkably. The decrease in the activity was explained in terms of the competition reaction of Cu (II)

cyanide complex ions for surface hydroxyl radical. In all cases cyanide was being oxidized to cyanate, the end product of cyanide photooxidation.

Stylidi, et al., (2003) investigated the photocatalytic degradation of Acid Orange 7 (AO-7) in aqueous TiO₂ suspensions with the use of a solar light simulating source. The photoreaction was followed by monitoring the degradation of the dye and the formation of intermediates and final products, as a function of time of irradiation, both in solution and on the photocatalyst surface. It has been found that the process leads to decolorization and, eventually, to complete mineralization of the dye solution. Evolution of intermediates and final products on both the photocatalyst surface and the solution has been monitored with a variety of techniques, which enable the identification of the reaction pathway, from adsorption of the dye molecule on the photocatalyst surface, to the formation of final products. AO-7 adsorbs on the photocatalyst surface via the oxygen of its hydrazone form and the two oxygen atoms of the sulfonate group. Interaction with solar light results, initially, in cleavage of the dye molecule in the vicinity of the azo bond and the formation of molecules containing naphthalene- and benzene- type rings. This step, which takes place, to a significant extent, via the photosensitized mechanism, results in decolorization of the solution but is not accompanied by significant decrease of the COD.

Tsuji, et al., (2003) reported that the modification of rutile TiO₂ by Ag negative-ion implantation found Ag nanoparticles formed in the surface layer of rutile. The photocatalytic efficiencies for Ag-implanted titania were evaluated by means of decolorization of methylene blue solution under fluorescent light. Ag-implanted rutile after annealing at 500 °C showed the better photocatalytic efficiency 2.2 times higher than that of unimplanted rutile titania. In the evaluation under fluorescent light through UV-cut filters, the Ag-implanted rutile showed 6.7 times better efficiency.

Matsuo, et al., (2004) examined the defect of simply adsorbed Sm, Eu, and Yb ions on TiO₂ (Ln/TiO₂) and Fe ions adsorbed onto TiO₂ (Fe/TiO₂) from the photocatalytic decomposition of adenosine 5'-triphosphate (ATP) as an anionic substance, 2-propanol as a neutral substance, and methylene blue (MB) as a cationic substance. The amount of ATP disappearing in 40 min of reaction in the presence of Ln/TiO₂ increase in the order: Ln-Sm < Eu < Yb. For 2-propanol, the photocatalytic activity of Ln/TiO₂ catalyst were similar to that of unmodified TiO₂ (u-TiO₂) catalyst.

For MB, the photocatalytic activities of Ln/TiO₂ catalyst were less than that of u-TiO₂ catalyst. By contrast, Fe/TiO₂ catalyst was excellent in photocatalytic decomposition of ATP, 2-propanol and MB. The photocatalytic activity of Yb/TiO₂-C calcined at 500°C for 1 h decreased for ATP, slightly decreased for 2-propanol, and increased for MB compared with Yb/TiO₂. Photocatalytic activity of Fe/TiO₂-C for ATP, 2-propanol and MB were all less than that of Fe/TiO₂. Since EXAFS revealed that the coordination structure around Yb (III) ions on the surface of TiO₂ in Yb/TiO₂ was like a hydrated structure including chloride ions, and that in Yb/TiO₂-C was like an oxide structure, the difference in photodegradation between Fe/TiO₂ and Fe/TiO₂-C is believed to be a result of the coordination structure around Fe (III) ions on the surface of TiO₂. These facts together suggest that the selectivity of photocatalytic decomposition for target substances can be controlled and is a combination of the properties of adsorbed metal ions (e.g. ionic radius, d-electron or f-electron, redox potential) and the coordination structure of their ions on the surface of TiO₂. In the present study, Sm/TiO₂, Eu/TiO₂, and Yb/TiO₂ are more selective toward anionic substances than Fe/TiO₂, which is excellent for decomposition of ionic and neutral substances.

Nagaveni, et al., (2004) investigated the solar photocatalytic degradation of various dyes such as methylene blue (MB), remazol brill blue R (RBBR) and orange G (GG) over combustion synthesized nano TiO₂ and the activity was compared with that of commercial Degussa P-25 TiO₂ under similar conditions. The effect of catalyst loading, initial concentration of the dye and the deactivation studies of the catalysts were also investigated. The catalyst was characterized by techniques like X-ray diffraction (XRD), gravimetric-differential thermal analysis (TG-DTA), BET, IR and UV absorption. The initial degradation rates with combustion synthesized nano TiO₂ was 20 times higher for RBBR, 4 times higher for MB and 1.6 times higher for OG, compared to Degussa P-25 TiO₂. The enhanced photocatalytic of combustion synthesized catalyst is attributed to the crystallinity, nano-size, large amount of surface hydroxyl species and reduced band-gap.

Sung-Suh, et al., (2004) examined the photocatalytic degradation of the rhodamine B (RB) dye in aqueous suspensions of TiO₂ and Ag-deposited TiO₂ nanoparticles under visible and UV light irradiation. The Ag deposits significantly

enhanced the RB photodegradation under visible light irradiation whereas the RB photodegradation under UV irradiation was slightly enhanced. The significant enhancement in the Ag-TiO₂ photoactivity under visible light irradiation can be ascribed to simultaneous effect of Ag deposits by both acting as electron traps and enhancing the RB adsorption on the Ag-TiO₂ surface.

Wu, et al., (2004) synthesized vanadium doped TiO₂ catalysts by sol-gel method. The results show that the increase of vanadium doping promoted the particle growth, and enhanced red-shift in the UV-Vis absorption spectra. The photocatalytic activity was evaluated by the degradation of crystal violet (CV) and methylene blue (MB) under visible light irradiation. The degradation rate of CV and MB on V-doped TiO₂ were higher than those of pure TiO₂.

Faisal, et al., (2005) investigated the photocatalytic degradation of two selected dyes, such as Acridine Orange (1) and Ethidium Bromide (2) in aqueous suspension of titanium dioxide (TiO₂) under a variety of conditions, which is essential form application point of view. The degradation was monitored by measuring the change in substrate concentration as a function of irradiation time employing UV spectroscopy analysis technique. The degradation was studied using different parameters such as type of TiO₂, reaction pH, catalyst concentration, substrate concentration and in the presence of different electron acceptors such as hydrogen peroxide (H₂O₂), potassium bromate (KBrO₃) and ammonium persulphate (NH₄)₂S₂O₈) beside air. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst, Degussa P25, was found to be more efficient for the photocatalytic degradation of dye derivative (1) and (2). The dye derivative (1) was found to degrade faster as compared to the dye derivative (2).

Muruganandham, et al., (2005) investigated the photocatalytic decolourization and degradation of an azo dye Reactive Yellow 14 (RY14) in aqueous solution with TiO₂-P25 (Degussa) as photocatalyst in slurry using solar light. The study on the effect of various photocatalysts on the decolourization and degradation reveals the following order of reactivity: ZnO > TiO₂-P25 > TiO₂ (anatase). CdS, Fe₂O₃ and SnO₂ have negligible activity on RY14 decolourization and degradation. The effects of various parameters such as catalyst loading and initial dye concentration play an important role affecting the reaction rate on the decolourization and

degradation. A study on the effect of electron acceptors on photooxidant reveals that both decolourization and degradation increase in the presence H_2O_2 , $(\text{NH}_4)_2\text{S}_2\text{O}_8$ and KBrO_3 to certain dosage beyond which the enhancement effect is negligible. Addition of dye assisting chemical such as CO_3^{2-} and Cl^- inhibits the dye removal rate.

Qamar, et al., (2005) investigated the photocatalytic degradation of two selected dye derivatives, chromotrope 2B (1) and amido black 10B (2) in aqueous suspension of titanium dioxide under a variety of conditions which is essential from an application point of view. The degradation was monitored by measuring the change in substrate concentration as a function of irradiation time employing UV spectroscopic analysis. In these studies, a number of by products were formed during the photooxidation process which could potentially be harmful to the environment, therefore, they studied the mineralization of the pollutants by measuring the total organic carbon (TOC) as a function of irradiation time. The degradation was studied using different parameters such as type of TiO_2 , reaction pH, catalyst concentration, substrate concentration and in the presence of different electron acceptors such as hydrogen peroxide (H_2O_2), potassium bromate (KBrO_3) and ammonium persulphate ($(\text{NH}_4)_2\text{S}_2\text{O}_8$) besides molecule oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient as compared with other catalysts. The dye derivative (1) was found to be degraded faster than the dye derivative (2).

Sameiro, et al., (2005) investigated the photocatalytic degradation of the commercial azo dye *C.I. Reactive Orange 4* in its reactive and hydrolysed, using commercial samples of TiO_2 as a photocatalyst. With UV light, aqueous solutions containing only dye and no dyebath additives are decolourized slightly more rapidly with Riedel-de-Haen TiO_2 than with Degussa P-25 TiO_2 . The rate of decolourization increases markedly with increasing pH. Sunlight is also very effective as a light source. On the other hand, comparison experiments involving UV irradiation of hydrolysed and unhydrolysed *Reactive orange 4* in a simulated spent dyebath showed Degussa P-25 TiO_2 to be significantly the more efficient catalyst, giving more than 90% decolourization after 20 min.

Senthilkumaar, et al., (2005) prepared nanocrystalline pure anatase titania by sol-gel process at room temperature followed by ultrasonication (Ti-US). The photocatalytic activity of Ti-US has been evaluated by the degradation of textile dye, Methylene Blue in the presence and absence of common inorganic salts (NO_3^- , $\text{C}_2\text{O}_4^{2-}$, SO_4^{2-} , and citrate). It was observed that, in the presence of anions, the degradation of the dye increase significantly. The photocatalytic rate of methylene blue increased in the presence of hydrogen peroxide (H_2O_2). The dependence of photodegradation of the dye rate on various parameters such as dye concentration, photocatalyst concentration and pH were also observed. The photodegradation rate follows first order kinetic. H_2O_2 and UV light have a negligible effect in absence of Ti-US catalyst.

Senthilkumaar, et al., (2005) prepared nanostructured TiO_2 ultrafine powder (Ti-SG) 100% anatase phase by sol-gel method was used as a photocatalyst in the decomposition reaction of a basic dye, Crystal Violet (CV) in water under UV light irradiation. Optimization of the photocatalyst performance as a function of irradiation time, catalyst concentration and solution pH was performed. The extent of the photooxidation or –reduction of CV was discussed in terms of Langmuir-Hinshelwood model. Results also indicated that the proper addition of H_2O_2 cold improves the degradation rate, but excess H_2O_2 quenched the formation of OH^\bullet . From the experimental results, sol-gel derived TiO_2 (Ti-SG) showed higher photocatalytic activity than commercially available TiO_2 (Degussa P-25) for the degradation of CV.

Bizani, et al., (2006) investigated the photocatalytic degradation of two commercial azo dyes in the presence of TiO_2 suspensions as photocatalyst. The degradation of the dyes follows pseudo-first order kinetics according to Langmuir-Hinshelwood model. Under the certain experimental conditions, in the presence of TiO_2 P-25 decolourization is achieved within 100 min of illumination, while in the presence TiO_2 Hombikat UV-100 complete color disappearance is accomplished in less than 50 min of light exposure. Parameters, such as concentration of the catalyst or initial pH value play an important role affecting the reaction rate. The mineralization of the two dyes was determined by measuring the dissolved organic carbon of the dye solutions and by evaluating toxicity. Although DOC was almost 80% removed after 5 h of illumination, the toxicity of the solution is slightly decreased in the presence of the

catalyst and the oxidant, but the intermediate degradation products seem to be more toxic than the initial compound. The application of the TiO₂ photocatalytic method to real wastewater proved to be efficient in decolorizing the wastewater (complete decolourization within 6 h of illumination) and it achieved partial DOC and toxicity removal (29% DOC and 35% toxicity removal for a 6 h illumination period).

Silva, et al., (2006) investigated the degradation of three commercially available textile azo dyes, Solophenyl Green BLE 155% (SG), Erionyl Red B (ER) and Chromotrope 2R (C2R) by using photochemical and photocatalytic process under UV irradiation. The adequacy of each process depends on the concentration of dye. At low dye concentration, the neat photochemical degradation is very efficient. The photocatalytic process, using either slurry of Degussa P-25 TiO₂ or a biphasic mixture of TiO₂ and activated carbon (AC), more effectively bleaches heavier colored solutions. The heterogeneous photocatalytic regime was characterized in terms of catalyst load, TiO₂ to AC mass ratio, initial dye concentration and oxygen partial pressure. The efficiency of the different photo-induced degradation process was evaluated in terms of apparent rate constants, mineralization degrees and initial quantum yields. Overall, the results revealed the superiority of photocatalytic process over neat photolysis and the advantage of using a suspension of TiO₂+AC mixture instead of TiO₂ alone.

Toor, et al., (2006) investigated the adsorption and photocatalytic degradation of diazo Direct Yellow 12 (Chrysophenine G), commonly used as a cotton, paper and leather in aqueous suspension of semiconductor oxide TiO₂ as photocatalyst in a non- concentrating shallow pond slurry type reactor under UV light. The adsorption of dye on the semiconductor shows a strong dependence on the pH and follows a Langmuir adsorption model. The studies include dark adsorption experiments at different pH conditions and their effect on initial rate of photocatalytic degradation. The photodegradation of dye on the semiconductor shows dependence effects of initial concentration of dye, catalyst loading, pH and addition of oxidant. The disappearance of the organic molecule follows approximately a pseudo-first kinetic order according to the Langmuir-Hinshelwood model. COD analysis of the dye under optimum conditions showed 94 % reductions in COD after 2.5 h and complete decolourization as determined by UV-vis analysis was achieved in 1.5 h.

However, the application of powdered TiO_2 in wastewater treatment is limited since a post - treatment separation is required to recover the catalyst. Mobile photocatalyst powder is also not applicable for air purification, as it may contribute to respirable particles that cause adverse human health problems. In order to avoid the use of photocatalyst powders, efforts have been made to coat TiO_2 thin films on various substrates such as glass, ITO glass, plastics, polymers and so on. The TiO_2 thin films grown on various substrates promise to have a high commercial potential in the environmental applications such as self-cleaning, anti-bacterial and wastewater purification containment. TiO_2 thin films have been prepared by various techniques such as chemical vapor deposition, spray pyrolysis deposition, flame synthesis, sol-gel dip coating, sputtering and so on.

There are many studies for photocatalytic degradation of MB, others textile dyes, and pollutants by TiO_2 thin films as follows.

Herrmann, et al., (1997) synthesized TiO_2 and Ag-TiO_2 catalysts supported thin layer by a dip-coating procedure on quartz substrate. The resulting materials were characterized by SEM/EDX, XRD, XPS and UV-Vis absorption spectroscopy. The immobilized catalysts were tested in the photocatalytic degradation of malic acid. For this reaction, the presence of metallic silver does not produce an intrinsic increase in photocatalytic activity in comparison with pure titania. The apparent increase observed in activity is principally due to the increase in the exposed surface due to the textural characteristics of the Ag-TiO_2 layer in comparison with TiO_2 . In addition, a previous treatment of the deposited Ag-TiO_2 samples under UV light just after calcinations induces a slightly higher photocatalytic activity, whatever the expression chosen for it. This has to be ascribed to a partial photoreduction of Ag^+ ions into Ag^0 atoms, which can agglomerate, as small metallic clusters identical to those found in photographic process. Metallic silver in low amounts can play a favourable role by attracting electrons, thus helping the electron-hole pair separation and preventing the electron-hole recombination. The improvement in quartz-deposited titania by addition of Ag^+ ions and UV pretreatment is about 12%. A careful comparison of the photocatalytic activity of supported titania samples with bulk TiO_2

Degussa P-25 shows a decrease in activity. This effect should be compensated by the benefit of avoiding filtration of small particles.

Wang, et al., (1998) presented the results the photocatalytic experiment involving a series of semiconductor oxide thin films mixed with TiO_2 and WO_3 , immobilized on glass plates by reactive sputtering method. The degradation was carried out in dyeing wastewater to investigate the effect of film structure and semiconductor properties on photocatalyst. The film structure and properties were studied by means of TEM and UV transmission spectra. The efficiency of photocatalytic degradation is enhanced with the increase of crystalline content in thin films. Comparison experiment between the TiO_2 thin film and Degussa P25 (TiO_2) powder shows that the TiO_2 thin film has better destruction effect than the powder, due to its unique microstructure. This kind of immobilized photocatalyst achieves good experimental results in treating Rhodamine B dyeing wastewater. This implies that immobilized photocatalyst has wide application prospect in water purification.

Byun, et al., (2000) prepared TiO_2 thin films on window glass substrates by chemical vapor deposition (CVD). Anatase-structured TiO_2 thin films were deposited on window glass by CVD and the photocatalytic dissociation rates of benzene were studied. TiO_2 thin films deposited on glass exhibited the higher degree of (112)-preferred orientation with increasing deposition temperature. The (112)-preferred orientation of TiO_2 thin film resulted in a columnar structure with a larger surface area for benzene dissociation. Obviously, benzene dissociation rate was maximum when the degree of the (112) preferential orientation was maximum. It is clear that the thin film TiO_2 should be controlled to exhibit the preferred orientation for optimum photocatalytic reaction rate. CVD method is an alternative for the deposition of the photocatalytic TiO_2 .

Dumitriu, et al., (2000) prepared TiO_2 thin films by direct current (DC) reactive sputtering, using various kinds of supports such as glass, silicon, alumina and glass coated with indium tin oxide. The photocatalytic properties of the samples were tested on the degradation of phenol. The best efficiency with respect to phenol mineralization was obtained for simple preparation using an Ar- H_2O mixture as the reactive gas. Indium tin oxide supports provide the most efficient thin films. The

catalytic efficiency per unit area of the sputtered films is at least one order of magnitude better than that of $50 \text{ m}^2\text{g}^{-1}$, reference TiO_2 powder.

Ding, et al., (2001) investigated coating TiO_2 onto three difference activated carbon (AC), γ - alumina (Al_2O_3) and silica gel (SiO_2) by chemical vapor deposition (CVD) method. It was found that introducing water vapor during CVD or adsorbing before CVD was crucial to obtain anatase TiO_2 on the surface of the particle supports. Among the three types of material supports, silica gel was the best for coating anatase TiO_2 by CVD and $\text{TiO}_2/\text{SiO}_2$ showed the highest activity in the photocatalytic degradation of phenol in water due to higher surface hydroxyl groups and macropore surface area.

Michael, et al., (2002) prepared TiO_2 thin film photo-semiconductor electrodes by chemical vapor deposition (CVD) and compared for the photocatalytic (PC) and photoelectrocatalytic (PEC) degradation of 4-chlorophenol (4-CP) in aqueous solution. The efficiency of PC degradation of 4-CP were low, but were found to be improved significantly by PEC with an applied potential. The effect of the film properties, particularly film thickness and crystalline form, on degradation rate by PEC was studied. For films deposited at 370° and 400°C it was suggested that differences in behavior could be related to depletion layer widths.

Arabarzis, et al., (2003) investigated nanocrystalline titania thin film photocatalysts by gold deposition via electron beam evaporation, with an attempt to study decomposition reaction rate of industrial water pollutants. The materials were characterized and their photocatalytic activity was tested for methyl orange photodegradation. The surface deposition of gold particles improves the photocatalytic efficiency of the titania films by the synergetic action on the charge separation process onto the semiconductor. The most advantageous surface concentration of gold particles in the composite Au/TiO_2 photocatalyst was found to be $0.8 \mu\text{g cm}^{-2}$, leading to a two times faster degradation of methyl orange with respect to the rate obtained with the original TiO_2 material. Higher surface loading result in an efficiency decrease and this can be understood in terms of an optimum gold particle size and surface characteristics as well as the semiconductor availability for light absorption and pollutant adsorption. The improvement in the photocatalytic efficiency of titania films by gold ions deposition is more than 100%. This enhancement is attributed to the action of Au

particles, which play a key role by attracting conduction band photoelectron and preventing electron-hole recombination.

Kwon, et al., (2004) prepared titanium dioxide nano-crystalline thin films on glass, polycarbonate and aluminum via a sol-gel process using different alkoxide precursors. All specimens exhibited nano-sized (< 10 nm) crystals of the anatase phase with very tiny amount of brookite phase. The surface morphology of the thin film was influenced by the nature of the substrate. As the thickness of the film increased, the effect of the substrate diminished in terms of photocatalytic decomposition of methylene blue solution. Surface morphology and thereby photocatalytic reactivity of the TiO_2 thin films can be tailored by proper heat treatment. The maximum photocatalytic decomposition of methylene blue solution was a heat treatment at 400°C , which was ascribed to the enlarged surface area upon morphological change of the surface.

Losito, et al., (2005) investigated the X-ray photoelectron spectroscopy for the analytical characterization of composite titanium dioxide-poly(vinylidene fluoride); (TiO_2 -PVDF) films developed for applications in the photocatalytic degradation of pollutants. The composite was deposited on glass substrates by casting or spin coating from TiO_2 -PVDF suspensions in dimethylformamide (DMF). XPS data on the TiO_2 -PVDF surface composition were used to optimize preparation conditions in terms of titanium dioxide surface amount and film stability. The use of spin-coating deposition and the increase of TiO_2 amount in the DMF suspensions were found to improve the titanium dioxide surface content, although high TiO_2 /PVDF ratios led to film instability. TiO_2 -PVDF films were also used in preliminary photocatalytic degradation tests on isoproturon, a phenylurea herbicide, under solar UV irradiation; the results were compared to direct photolysis to evaluate the catalytic efficiency of immobilized TiO_2 and the role played by the PVDF film during the degradation process.

Wang, et al., (2005) prepared multi-walled carbon nanotubes (MWNT) and TiO_2 composite catalysts by a modified sol-gel method. The nanoscaled composite materials were extensively characterized by TG, N_2 adsorption-desorption isotherm, XRD, SEM, EDX, TEM and UV-vis spectra. The photocatalytic degradation of phenol was performed under visible light irradiation on these catalysts. An optimum of

synergetic effect on photocatalytic activity was observed for a weight ratio MWNT/TiO₂ equal to 20% with an increase in the first order rate constant by factor of 4.1. The synergetic effect, induced by a strong interphase between MWNT and TiO₂, was discussed in terms of different role played by MWNT in the composite catalysts.

Yuan, et al., (2005) investigated the photocatalytic degradation of methylene blue (MB) in aqueous solution by using TiO₂ immobilized on activated carbon fibers (ACFs). The TiO₂ and ACF combination (TiO₂/ACF) was prepared by using epoxy as the precursor of the link between TiO₂ and ACFs, followed by calcinations at 460°C in a N₂ atmosphere. The TiO₂/ACF composite prepared was easier to handle than the original TiO₂ powder in suspension. More significantly, the TiO₂/ACF composite can be used repeatedly without a decline in photodegradation ability. After six cycles, the amount of MB removal for the TiO₂/ACF composite was slightly higher than that for fresh P-25 TiO₂ in suspension. Through measurement of chemical oxygen demand in the solution and the concentration of ammonium generated during degradation of MB, it was confirmed that MB molecules are mineralized instead of adsorbed by ACFs.

Zainal, et al., (2005) investigated the photodegradation of various dyes in aqueous solution by using glass coated titanium dioxide thin film as photocatalyst. Photodegradation process of methylene blue (MB), methyl orange (MO), indigo carmine (IC), Chicago sky blue 6B (CSB) and mixed of the four mentioned single dye were reported. As each photodegradation system is pH dependent, the photodegradation experiment was carried out in each dye photodegradation reactive pH range about at 28°C. The dyes removal efficiency was studied and compared using UV-vis spectrophotometer analysis. The total removal of each dye was: methylene blue (90.3%), methyl orange (98.5%), indigo carmine (92.4%), Chicago sky blue 6B (60.3%) and mixed dyes (70.1%), respectively.

Ge, et al., (2006) prepared anatase TiO₂ thin films on glass slide substrates via a sol-gel method from refluxed sol (RS) containing anatase TiO₂ crystals at low temperature of 100°C. The influences of various refluxing time on crystallinity, morphology and size of the RS sol and dried TiO₂ films particles were discussed. These samples were characterized by infrared absorption spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission-scanning

electron microscopy (FE-SEM) and UV-vis absorption spectroscopy (UV-vis). The photocatalytic activities of the TiO₂ thin films were assessed by the degradation of methyl orange in aqueous solution. The results indicated that titania films thus obtained transparent and their maximal light transmittance exceeded 80% under visible region. The TiO₂ thin films prepared from RS-6 sol showed the highest photocatalytic activity, when the calcinations temperature is higher than 300°C. The degradation of methyl orange of RS-6 thin films reached 99% after being irradiated for 120 min, the results suggested that the TiO₂ thin films prepared from RS sol exhibited high photoactivities.

Yang, et al., (2006) developed dip-coating process for TiO₂ thin film on polymer substrates (acrylonitrile-butadiene-styrene polymer: ABS, polystyrene: PS). At first, a monodispersed and transparent TiO₂ nano-sol solution was prepared by the controlled hydrolysis of titanium iso-propoxide in the presence of acetylacetone and nitric acid catalyst at 80°C. Powder X-ray diffraction patterns of the dried particles are indicative of crystalline TiO₂ with anatase-type structure. According to the XRD and transmission electron microscopy (TEM) studies, the mean particle size was estimated to be ca. 5 nm. The transparent thin films on ABS and PS substrates were fabricated by dip-coating process by changing the processing variables, such as the number of dip-coating and TiO₂ concentration in nano-sol solution. Scanning electron microscopy (SEM) analysis for the thin film samples reveals that the acetylacetone-modified TiO₂ nano-sol particles are effective for enhancing the interfacial adherence between films and polymeric substrates compared to the unmodified one. Photocatalytic degradation of methylene blue (MB) on the TiO₂ thin films showed complete decomposition after 180 min under UV light irradiation.

Yu, et al., (2006) prepared Fe-doped TiO₂ thin films *in situ* on stainless steel substrates by liquid phase deposition, followed by calcinations at various temperatures. It was found that some Fe³⁺ ions were *in situ* doped into the TiO₂ thin films. At 400°C, the film became photoactive due to the formation of anatase phase. At 500°C, the film showed the highest photocatalytic activity due to an optimal Fe³⁺ ion concentration in the film. At 900°C, the photocatalytic activity of the films decreased significantly due to the further increase of Fe³⁺ ion concentration, the formation of rutile phase and the sintering and growth of TiO₂ crystallites.

Zhang, et al., (2006) prepared titanium dioxide thin film supported on glass containing 0.1, 0.5 and 0.8 wt.% of platinum-dopant by the microemulsion templating. The results films had an average size of TiO₂ nanoparticles of 15-20 nm with a narrow size distribution and a mesoporous film structure. The thin films prepared showed a TiO₂ anatase structure and shifted the UV-vis absorption to visible light region. The Pt-modified TiO₂ thin films possessed the higher photocatalytic activity than that of TiO₂ thin films alone for the photodegradation of the methyl orange dye in the visible light range.

Ge, et al., (2007) synthesized novel InVO₄-TiO₂ thin films by introducing nano InVO₂ into the TiO₂ thin films via a sol-gel method. The photocatalytic efficiency of InVO₄-TiO₂ thin films was investigated by photodegrading of methyl orange in aqueous solution under visible light irradiation. A wide range of characterization techniques, such as X-ray diffraction (XRD), transmission electron microscopy (TEM), field emission-scanning electron microscopy (FE-SEM) and UV-vis absorption spectroscopy (UV-vis), were applied to characterized the obtained thin films. The results indicated that the InVO₄-TiO₂ thin films consist of uniform anatase TiO₂ crystals of 70-80 nm with highly dispersed orthorhombic InVO₄ nanocrystals. The decoloration of methyl orange results illustrated that the InVO₄-TiO₂ thin films with 0.5 wt.% InVO₄ showed the best photoactivities under visible light irradiation, the decoloration rate reached 32.5% after irradiated for 15 h. The InVO₄-TiO₂ thin films exhibited photoactivity under visible light after doped InVO₄ in the TiO₂ films.

Habibi, et al., (2007) investigated the photocatalytic degradation of a non-biodegradable azo dye called (C.I. Direct 80, Red Sulphonyl 3BL) using TiO₂ thin films in aqueous solution under irradiation of a mercury lamp Philips (UV-C) light source. The effect of operational parameters, i.e., annealing temperature of thin film, substrate nature on which TiO₂ films were deposited, film thickness, pH of the solution dye concentration and irradiation time on the degradation rate of azo dye aqueous solutions was examined. Results show that the employment of efficient photocatalyst and the selection of optimal operational parameters lead to complete decolorization. The best conditions for maximum photocatalytic degradation were found to be pH 1 at 5 ppm concentration of dye over TiO₂ thin films deposited on glass substrate coated with indium-tin oxide having 350 nm thicknesses annealed at 550°C.

TiO₂ films can be prepared by various techniques, but the above methods have some disadvantages such as sol-gel dip coating, spray coating or spin coating methods have been the most commonly employed methods for the deposition of anatase-structured photocatalytic TiO₂ thin films, but these methods require the post-annealing process for the crystallization into anatase structure. Whereas, chemical vapor deposition (CVD), spray pyrolysis deposition and flame synthesis have some disadvantages for industrial, need more expensive equipment and complex procedures. Therefore, a simple, less expensive and more effective method for the preparation of TiO₂ films on the substrate is investigated.

This work presents a simple, less expensive but more effective method for the preparation of immobilized TiO₂ (Immo-TiO₂) films on the rubber substrate by direct mixing of commercial TiO₂ powders (anatase; Carlo Erba, Italy and Degussa P25; Degussa AG, Germany) with latex (60%HA) and distilled water. The rubber strikes our interest because of its versatility in daily life, available, and has never been used as a substrate for TiO₂ coating, we hope this should have a potential application in environmental business. The surface morphology and cross section of all Immo-TiO₂ films were observed by using scanning electron microscopy (SEM). The X-ray diffraction (XRD) used to study crystalline phase identification and confirms structures of some Immo-TiO₂ film samples. The effect of various parameters such as amount of distilled water, latex and commercial TiO₂ powders were studied to optimize the preparation of Immo-TiO₂ films for maximum photocatalytic degradation of methylene blue (MB) dye in aqueous solutions under UV light irradiation, and comparing with original commercial TiO₂ powders. Furthermore, the effect of pH, initial concentration of MB solution, and intensity of UV light (from blacklight lamps) were studied on the photocatalytic degradation of MB by Immo-TiO₂ films in order to find direct application in water purification.

1.3 Objectives

- 1.3.1 To study the optimum conditions for preparing immobilized TiO₂ films on the rubber substrate by direct mixing of commercial TiO₂ powders (anatase; Carlo Erba, Italy and Degussa P25; Degussa AG, Germany) with latex (60% HA) and distilled water.
- 1.3.2 To study the surface morphology and photocatalytic activity of these Immobilized TiO₂ films, and compare with original commercial TiO₂ powder catalysts under the same conditions.
- 1.3.3 To study the effect of pH, initial concentration of MB solution and the intensity of UV light on the photocatalytic degradation of the Immo-TiO₂ films.