CHAPTER (2)

2. THEORETICAL PART

2.1. Wastewater[3, 4]

Water resource is one of the most important resources for human being, as well as animals and plants in the world. With the rapid development of science and technology, many industries such as chemical, petrochemical, pharmaceutical, mining, semiconductor and microelectronics are set up worldwide. Each of these industries requires large quantity of water for processing and water discharged from these industries is contaminated with toxic organic pollutants. Wastewater is the combination of liquid or water carried wastes originating in the sanitary conveniences of dwellings, commercial or industrial facilities and institutions, in addition to any groundwater, surface water and storm water that may be present. Untreated wastewater generally contains high level of organic material, numerous pathogenic microorganisms, as well as nutrients and toxic compounds. It thus entails environmentally and health hazards, and consequently, must immediately be conveyed away from its generation sources and treated appropriately before final disposal. The ultimate goal of wastewater management is the protection of the environment in a manner commensurate with public health and socio-economic concern. To overcome the water pollution problems, and to meet stringent environmental regulations, scientist and researchers have been focusing on the development of new or improvement of existing water purification process.

2.2. Characteristics of textile wastewater [3]

Textile waste water contains strong color due to including a large variety of dyes and chemicals additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical compositions.

Main polluting textile wastewater came from dyeing and finishing processes. These processes require the input of wide range of chemicals and dyestuffs, which generally are organic compounds of compels structure. Because all of them are not contained in the final product, they became waste and caused disposal problems. Major pollutants in textile wastewater are high

suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble substances. The large pH swing in the textile wastewater (can changed from 2 to over 12) is another strong negative point. This variation is primarily caused by different kinds of dyestuff used in the dying process. Some characteristics of textile wastewater is shown in Table 2.1[5]

Table 2.1 characteristics of textile wastewater

pH	7-9
BOD	80-6000 mg/l
COD	150-12000 mg/l
TDS	2900-3100 mg/l
TSS	15-8000 mg/l
Chloride	1000-1600 mg/l
TKN	70-80 mg/l

2.2.1. History of Dyes [6]

In 1771, Woulfe prepared picric acid by the action of nitric acid on indigo and showed that it dyed silk in bright yellow shades. Laurent in 1842 converted phenol into picric acid. An 18 year old chemistry student William H.Perkin working in August Wilhelm von Hofmann's laboratory in London attempted to synthesize quinine and instead discovered how to make mauveine, a purple dye. Perkin was experimenting with a compound called aniline in a possible first step in the pathway to quinine. He obtained a black tarry mess, but when he removed it from the flask with alcohol he observed a purple color in the dilute solution. When he dipped a piece of silk into this mixture, the silk was dyed reddish purple. Through the help of his father, Perkin started a factory for making synthetic mauveine near London, 1957, this way the first synthetic dye to be manufactured.

Faraday discovered benzene in 1825 and Hoffmann isolated it from coalter in 1845. By 1869 kekule established the structure of benzene. It paved the way for the systematic study of aromatic compound. During last 125 years synthetic dyes have been prepared in bewildering number and variety. At least 7500 dyes are recognized now and thousand of patents have been granted in

various countries for the synthesis and application of dyes. Reports of new dyes are published every two weeks in the possibilities of further synthesis are unlimited.

2.2.2. Classes of Dyes

All aromatic compounds absorb electromagnetic energy but only those that absorb light wavelengths in the visible range (350 -700nm) are colored. Dye contain chromophores, delocalized electron system with conjugated double bonds and auxochromes, electron withdrawing or electron donating substituents that cause or intensity the color of the chromophore by altering the overall energy of the electron system. Visual chromophers are –C=C–; –C=N–C=O; –N=N–; $–NO_2$ and quinoid rings visual auxochromes are $–NH_2$, –COOH, $–SO_3H$ and –OH. Based on chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Azo (monoazo, diaazo, triazo, polyazo), anthraquinone , phthalocyanine and triarylmethane dyes are quantitatively the most important gruops. Other groups are triarylmethane , indigoid , azine , oxazine, thiazine,xanthene, nitro, nitrose, methine, thiazole, indamine, indophenol, lactone, aminoketone and hydroxyketone dyes and dyes of undetermined structure (stilbene and sulphur dyes). The vast array of commercial colorants is classified in terms of color, structure and application method in the color index (C.I), which is edited since 1924 (and revised every three months) by the society of dyers and colorists and the American Association of Textile Chemists and Colorist. Each different dye is given a C.I. generic name determines by its application characteristics and its color. The color index discerns is different application classes:

2.2.2.1. Acid dyes

The largest class of dyes in the color index is referred to as Acid dyes (~2300 different acid dyes listed, ~40 % of them are in current production). Acid dyes are anionic compounds that are mainly used for dyeing nitrogen -containing fabrics like wool, polyamide, silk and modified acryl. They bind to the cationic NH_4^+ ions of those fibers. Most acid dyes are azo (yellow to red, or a broader range colors in case of metal complex azo dyes), anthraquinone or triarylmethane (blue and green) compounds. The adjective 'acid' refers to the pH in acid dye baths rather than to the present of acid groups (sulponate, carboxyl) in the molecular structure of these dyes. The ionic bonding between the dye and the fiber is the result of reaction of the amino groups on the

fiber with acid groups on the dye. Generally the fastness of this dye depends on the rate with which the dye can diffuse through the fiber under the conditions of washing. Metal complex (cobalt or chromium) acid dyes are used mainly on wool for improved fastness.

2.2.2.2. Reactive dyes

Reactive dyes are dyes with reactive groups that form covalent bonds with OH-, NH-, or SH groups in fibers (cotton, wool , silk , nylon). The reactive group is often a heterocyclic aromatic ring substituted with chloride or fluoride, e.g. dichlorotriazine. Another Common reactive group is vinyl sulphone. The principal chemical classes of reactive dyes are azo, triphendioxazine, phthalocyanine, formazan, and anthraquinone. The use of reactive dyes has increased ever since their introduction in 1956, especially in industrialized countries. In the color index, the reactive dyes from the second largest dye class with respect to the amount of active entries: about 600 of the ~1050.

2.2.2.3. Direct dyes

Direct dyes are relatively large molecules with high affinity for especially cellulose fibers. Van der waals forces make them bind to the fiber. Direct dyes are mostly azo dyes with more than one azo bond or phthalocyanine, stilbene or oxazine compounds. Direct dyes are water-soluble anionic dyes, but are not classified as acid dyes because the acid groups are not the means of attachment to the fiber. The solubility of the dye in the dye bath is often reduced by adding common salt or Glauber's salt. In the color index, the direct dyes from the second largest dye class with respect to the amount of different dyes: About 1600 direct dyes are listed but only ~30% of them are in current production.

2.2.2.4. Basic (Cationic) dyes

Basic dyes are cationic compounds that are used for dyeing acid- group containing fibers, usually synthetic fibers like modified polyacryl. They are water-soluble and produce colored cations in solution. They are mostly amino and substituted amino compounds soluble in acid and made insoluble by the solution being made basic. They bind to the acid groups of the fibers. Most basic dyes are diarylmethane, triarylmethane, anthraquinone or azo compounds. Basic dyes represent ~5% of all dyes listed in the color index.

2.2.2.5. Mordant dyes

Mordent dyes are fixed to fabric by the addition of a mordant, a chemical that combines with the dye and the fiber. The fiber is first treated with an aluminum, chromium and iron salt and then contacted with a lake forming dye (azo and anthraquinone derivatives). Though mordant dyeing is probably one of the oldest ways of dyeing, the use of mordant dyes is gradually decreasing: only ~23% of the ~600 different mordant dyes listed in the color index are in current production. They are used with wool, leather, and silk, paper and modified cellulose fibers. Most mordant dyes are azo, oxazine or triarylmethane compounds. The mordants are usually dichromate or chromium complexes.

2.2.2.6. Azo Dyes

It is the largest group of dyes, with -N=N- as a chromophore, in an aromatic system. They are produced on textile fibers (usually cotton, rayon and polyester) by diazotization of primary aromatic amine in an acidic solution by using nitrous acid in the present of ice. The diazo compound so formed is coupled with a suitable component such as an aromatic amine, nepthol or other phenolic substance to form an azo compound. Depending upon the number of azo groups present they are called as monoazo, diazo, triazo, tetrakisazo and polyazo dyes. All types of azo dyes amount to over one thousand commercially most important class of synthetic coloring compound. It has wide variety of application.

2.2.2.7. Disperse dyes

Disperse dyes are scarcely soluble dyes that penetrate synthetic fibers (cellulose acetate, polyester, polyamide, acryl, etc.). Disperse dyes are applied as very finely divided materials which are adsorbed onto the fibers with which they then form a solid solution. This diffusion requires swelling of the fiber, either due to high temperatures (>120 ^{o}C) or with the help of chemical softeners. Dying takes place in dye baths with fine disperse solutions of these dyes. Disperse dyes from the third largest group of dyes in the color index: about 1400 different. compounds are listed, of which ~40% is currently produced. They are usually small azo or nitro compounds (yellow to red), anthraquinones (blue and green) or metal complex azo compounds (all colors).

2.2.2.8. Pigment dyes

Pigment dyes (i.e. organic pigments) represent a small but increasing fraction of the pigments, the most widely applied group of colorants. About 25% of all commercial dye names listed in the color index are pigment dyes but these ~ 6900 product names stand for less than 800 different dyes. These insoluble, non-ionic compounds or insoluble salts retain their crystalline or particulate structure throughout their application. Pigment dyeing is achieved from a dispersed aqueous solution and therefore requires the use of dispersing agents. Pigments are usually used together with thickeners in print pastes for printing diverse fabrics. Most pigment dyes are azo compounds (yellow, orange and red) or metal complex phthalocyanines (blue and green). Also anthraquinone and quinacridone pigment dyes are applied.

2.2.2.9. Vat dyes

The vat dyes are insoluble complex polycyclic molecules based on the quinone structure (keto-forms) that are particularly and widely used for dyeing cellulose fibers. The dyeing method is based on the solubility of vat dyes in their reduced (leuco) form. Reduced with sodium dithionite, the soluble leuco vat dyes impregnate the fabric. Next, oxidation is applied to bring back the dye in its insoluble form. Almost all vat dyes are anthraquinones or indigoids. Indigo itself is a very old example of a vat dye, with about 5000 years of application history. 'Vat' refers to the vats that were used for the reduction of indigo plants through fermentation.

2.2.2.10. Anionic dyes and ingrain dyes

Azoic dyes and Ingrain dyes (naphthol dyes) are the insoluble products of a reaction between a coupling component (usually naphthols, phenols or acetoacetylamides; listed in the color index as C.I. azoic coupling components) and a diazotised aromatic amine (listed in the color index as C.I. azoic diazo components). This reaction is carried out on the fiber. All naphthol dyes are azo compounds.

2.2.2.11. Sulphur dyes

Sulphur dyes are complex polymeric aromatics with heterocyclic S-containing rings. Though representing about 15% of the global dye production, sulphur dyes are not so much used in Western Europe. The actual structures of sulfur dyes are largely unknown although it is

considered that they possess sulfur-containing heterocyclic rings. Dyeing with sulphur dyes involves reduction and oxidation, comparable to vat dyeing. They are mainly used for dyeing cellulose fibers.

2.2.2.12. Solvent dyes

Solvent dyes (lysochromes) are non-ionic dyes that are water-insoluble but soluble in alcohols, chlorinated hydrocarbons, or liquid ammonia. They are used for dyeing substrates in which they can dissolve, e.g. plastics, varnish, ink, waxes and fats. They are not often used for textile – processing but their use is increasing. Most solvent dyes are diazo compounds that underwent some molecular rearrangement. Also triarylmethane, anthraquinone and phthalocyanine solvent dyes are applied.

2.2.2.13. Fluorescent brighteners

Fluorescent brighteners (or bluing agent) mask the yellowish tint of natural fibers by absorbing ultraviolet light and weakly emitting visible blue. They are not dyes in the usual sense because they lack intense color. These compounds are added to soaps and detergents to produce greater brilliance in laundry washings. Based on chemical structure, several different classes of fluorescent brighteners are discerned: stilbene derivatives, coumarin derivatives, pyrazolines, 1,2-ethene derivatives naphthalimides and aromatic or heterocyclic ring structures. Many fluorescent brighteners contain triazinyl units and water solubilising groups.

2.2.2.14. Metal complex dyes

Among acid and reactive dyes, many Metal complex dyes can be found (not listed as a separate category in the color index). These are strong complexes of one metal atom (usually chromium, copper, cobalt or nickel) and one or two dye molecules, respectively 1: 1 and 1: 2 metal complex dyes. Metal complex dyes are usually azo compounds. About 1/6 of all azo dyes listed in the color index are metal complexes but also phthalocyanine metal complex dyes are applied.

2.2.3. Chemical properties of dyes

A dye is used to impart color to materials of which it becomes an integral part. An aromatic ring structure coupled with a side chain is usually required for resonance and thus to impart color. Resonance structure that causes displacement or appearance of absorption bands in the visible spectrum of chemical structure with color has been accomplished in the synthesis of dye using a chromogen chromophore with auxochrome. Chromogen is the aromatic structure containing benzene, naphthalene, or anathracene rings. Chromophore group is a color giver and represented by the following radicals, which from the chemical basis of classification of dyes when coupled with chromogene: azo(–N=N–); carbonyl (=C=O), carbon (=C=C=); carbon-nitrogen (>C=NH or –CH=N) or –CH=N–) ; nitroso (–NO or N–OH) ; nitro (–NO_2 or =NO-OH) ; sulfur (>C=S and other carbon sulfur group)

The chromogen-chromophore structure is often not sufficient to impart solubility and causes adherence of dye to fiber. The auxochrome or bounding affinity, and sulfonic radicals or their derivatives. Electrophilic aromatic substitution (EAS) is an organic reaction in which an atom, usually hydrogen, in an aromatic system is replaced by an electrophilie. The most important reaction of this type that take place aromatic nitrogen, aromatic halogenations, aromatic sulfonation, and acylation and alkylating Friedel-craft reactions.The principal problem to overcome in aromatic degradation is the chemical stability of the aromatic ring.

2.2.4. Treatment of wastewater containing dyes

Wastewaters from various industries, factories, laboratories, etc. are serious problems to the environment. The discharged wastes containing dyes are toxic to microorganisms, aquatic life and human beings [7]. These deleterious effects of chemicals on the earth ecosystems are a cause for serious concern. Several of these chemicals such as azo dyes, herbicides, and pesticides are actually present in rivers and lakes, and are in part suspected of being endocrine-disrupting chemicals (EDCs) [8–11]

Textile dyes and other industrial dyestuffs constitute one of the largest groups of organic compounds that represent an increasing environmental danger [12]. About 1–20% of the total world production of dyes is lost during the dyeing process and is released in the textile effluents

[13]. The release of those colored wastewaters in the environment is a considerable source of non-aesthetic pollution and eutrophication and can originate dangerous byproducts through oxidation, hydrolysis, or other chemical reactions taking place in the wastewater phase. It must be noted that dyes can present toxic effects and reduce light penetration in contaminated waters [14].

Degradation of dyes in industrial wastewaters has therefore received increasing attention and some methods of remediation have been proffered. These methods are shown in Figure 2.1. Traditional physical techniques (adsorption on activated carbon, ultrafiltration, reverse osmosis, coagulation by chemical agents, ion exchange on synthetic adsorbent resins, etc.) have been used for the removal of dye pollutants [12–15]. These methods only succeed in transferring organic compounds from water to another phase, thus creating secondary pollution. This will require a further treatment of solid-wastes and regeneration of the adsorbent which will add more cost to the process. Microbiological or enzymatic decomposition [16], biodegradation [17], ozonation [18], and advanced oxidation processes such as Fenton and photo-Fenton catalytic reactions [12–19], H_2O_2/UV processes [20] have also been used for dyes removal from wastewaters. The traditional wastewater treatment technologies have proven to be markedly ineffective for handling wastewater of synthetic textile dyes because of the chemical stability of these pollutants, and went further to verify that 11 out of 18 azo dyes selected for their investigations passed through the activated sludge process practically untreated [21]. Most textile dyes are photo-catalytically stable and refractory towards chemical oxidation [22], and these characteristics render them resistant towards decolorization by conventional biochemical and physico-chemical methods. All the aforementioned processes have a wide range of their deficiencies in the removal of dyes from wastewaters.

A relatively new class of technologies, mentioned as Advanced Oxidation Process (AOPs), evolved from research works has been considered to overcome many limitations of traditional wastewater treatment process.

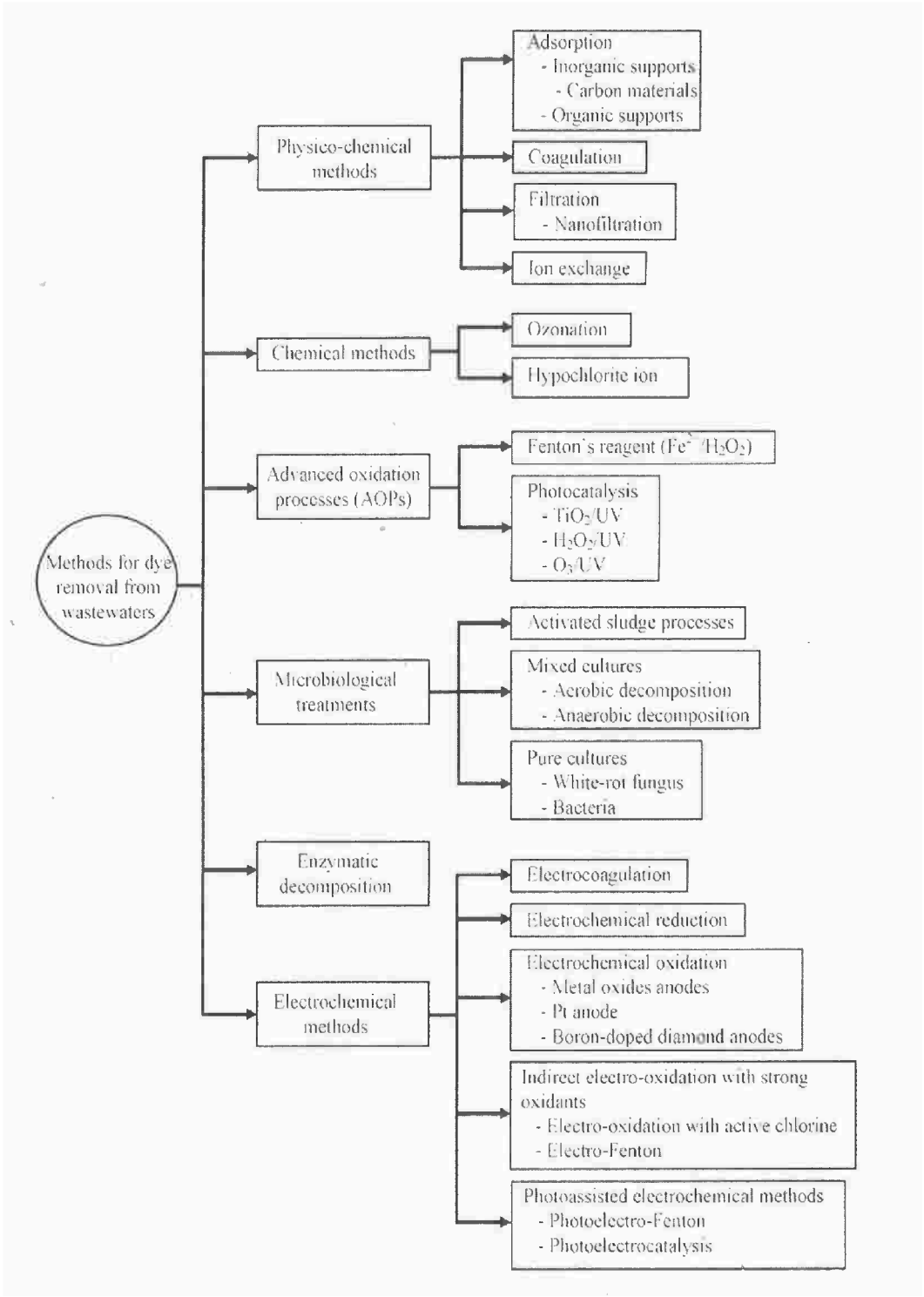

Figure 2.1: Main methods used for removal of organic dyes from wastewater

2.3. Advanced Oxidation Processes (AOPs) [23, 24]

Advanced oxidation processes (AOPs) are alternative techniques of destruction of harmful organic pollutants from wastewaters. These AOPs include H_2O_2/UV, O_3/UV, H_2O_2/O_3/UV, TiO_2/UV and vacuum ultra-violet (VUV) process, Fenton's.

AOPs have been applied for destructing hazardous organic chemicals in water, destroys the contaminants through an oxidative breakdown initiated by a powerful oxidizing species such as hydroxyl radicals which are the most powerful oxidizing species after fluorine.

AOPs can be applied to many processes involving contaminated industrial wastewater, groundwater, drinking water and process water. Many applications have been for groundwater remediation and the removal of volatile and semi-volatile organic compounds such as chlorinated alkenes, ethers, chlorinated alkanes and pesticides. AOPs are also applied for the treatment of industrial wastewater and removal of phenolic compounds, COD, dyes, cyanides and ketones. These compounds are commonly encountered in wastewater generated from various industries such as the explosives, resins, wood preservation, textile, aerospace, and electronic industries.

Among the AOPs, heterogeneous photocatalysis has appeared as the most promising destructive technology. Recent studies [17, 25–31] have been devoted to the use of photocatalysis in the removal of dyes from wastewaters, particularly, because of the ability of this method to completely mineralize the target pollutants [32]. In most cases the degradation is conducted for dissolved compounds in water with UV-illuminated TiO_2 powder.

2.3.1 Photocatalysis for Wastewater Treatment [33, 34]

Photocatalysis differs from other AOPs because it employs low energy UV light and reusable catalysts, and it does not require addition of any other strong oxidants. In addition, photocatalysis can also use sunlight since about 5% of the solar spectrum reaching the earth is in the UV wavelength range. The advantages of photocatalysis over other conventional methods can be summarized as follows:

1. Almost all organic pollutants including hydroxyl radical resistant, such as carbon tetrachloride, in wastewater can be mineralized.

2. This process is known as green technology because degradation products (carbon dioxide, water and mineral acids) are environmentally harmless.
3. Atmospheric oxygen is used as oxidant and no other oxidant is required.
4. The photocatalysts are cheap, non-toxic, stable, biologically and chemically inert, insoluble under most conditions and reusable.
5. Low energy UV light is used for photocatalyst activation and even solar light can be used.
6. Economically it is comparable with activated carbon adsorption method for intermediate and large capacities.

2.3.1.1. Principles of photocatalysis

The term photocatalysis consists of combination of photochemistry and catalysis which implies that light and catalyst are necessary to promote a chemical reaction [35]. Photocatalysis is defined as a change in the rate of chemical reactions or their generation under the action of light in the presence of substances -called photocatalysts- that absorb light and are involved in the chemical transformations of the reaction participants [36]. The definition of a photocatalyst is: A substance that is able to produce, by absorption of light, chemical transformations of the reaction participants, repeatedly coming with them into the intermediate chemical interactions and regenerating its chemical composition after each cycle of such interactions [36–39]. The main difference of photocatalytic reaction with the conventional catalytic reaction is that catalyst is activated by light other than by heat [40].

In general, photocatalytic process can be classified as homogeneous and heterogeneous photocatalysis based on the difference in phases of catalyst and the reacting species. In homogeneous photocatalysis, a powerful UV lamp is used to illuminate the contaminated water in the presence of Fe^{3+}, O_3, or H_2O_2 which act as a catalyst and the reaction take place in the bulk solution. On the other hand, heterogeneous photocatalysis can be defined as catalytic process during which one or more reaction steps occur by means of generation of electron-hole pairs by suitable light on the surface of the solid semiconductor materials. The distribution and utilization of light energy due to the presence of solid catalyst material in liquid or gaseous mixtures makes this process more complex compared with homogeneous process[40].

2.3.1.2 Semiconductors and band gap energy [41, 42]

Semiconductor materials are particularly useful for photocatalytic process because of a favorable combination of electronic structure, light adsorption properties, charge transport characteristics and lift time of excited state. As semiconductor has specific electronic structure of a filled valence band and an empty conduction band, it can be used as photocatalyst. The valence band is the band made up of the completely occupied molecular orbital, low in energy. On the other hand, the conduction band is the band of the molecular orbital that are high in energy, sufficient to make the electrons free to move from atom to atom under the influence of applied energy. The energy gap between the conduction band and the valence band is called band gap energy, E_{bg}. It requires applied energy to promote electron from valence band to conduction band, and since the band gap energy is different for different semiconductors, the required energy is also different for different semiconductors.

When a photon with sufficient energy activates the semiconductor, electron jumps from the filled lower energy valence band to higher energy empty conduction band. Since the conduction band is only partially filled, the electron can move freely through the semiconductor lattice. On the other hand, the resulting vacancy of the electron in the newly partially filled valence band is also free to move. The vacancy or absence of an electron is usually referred to hole and it is designated by h_{vb+}. The process of generation of electron and hole in the conduction and valence band of the semiconductor is shown in Figure 2.2.

Knowing the band gap energy of a particular semiconductor, the required threshold wavelength of light source can be easily calculated by a simple equation (1.1).

$$\lambda_{bg}(nm) = 1240/E_{bg}\,(eV) \qquad (1.1)$$

The wavelength of light source should be equal or less than the threshold wavelength of that corresponding semiconductor to activate it. It is seen from equation (1.1) that lower band gap energy of semiconductor is preferable as it can be activated by higher wavelength visible light, which exhibits low energy.

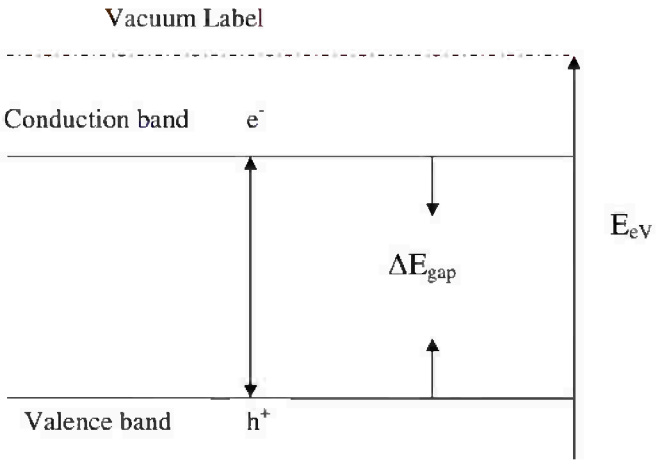

Figure 2.2: Photogeneration of electron-hole pairs

2.3.1.3. Mechanism of photocatalysis

In heterogeneous photocatalysis, a redox reaction is mediated by a photocatalyst, which plays an important role in this reaction. As semiconductor has specific electronic structure of a filled valence band and an empty conduction band, it can be used as photocatalyst. The energy gap between the conduction band and valence band is called band gap energy [42].Activation of a semiconductor photocatalyst could be achieved through the absorption of a photon of ultraviolet light with energy equal or higher than the band gap energy which results in the promotion of an electron, e^-, from the valence band into the conduction band; at the same time, a hole, h^+, is generated in the valence band [43].

Once excitation of the semiconductor occurs across the band gap, there is a sufficient lifetime, in the nanosecond regime, for the created electron-hole pair to undergo charge transfer to adsorbed species on the semiconductor surface from solution or gas phase contact. If the semiconductor remains intact and the charge transfer to the adsorbed species is continuous and exothermic, the process is termed heterogeneous photocatalysis. The concentration of electron-hole pairs in a semiconductor particle is dependent on the intensity of the incident light and the semiconductor's electronic characteristics that prevent them from recombining. Figure 2.3 shows the excitation of an electron from the valence band to the conduction band initiated by light absorption with energy equal to or greater than the band gap of the semiconductor. The photo induced electron transfer to adsorbed organic species or to the solvent results from migration of electrons and

holes to the semiconductor surface. The electron transfer process is more efficient if the species are pre adsorbed on the surface [44].While at the surface the semiconductor can donate electrons to reduce an electron acceptor (usually oxygen in an aerated solution) (pathway C); in turn, a hole can migrate to the surface where an electron from a donor species can combine with the surface hole oxidizing the donor species (pathway D). The probability and rate of the charge transfer processes for electrons and holes depends on the respective positions of the band edges for the conduction and valence bands and the redox potential levels of the adsorbate species. In competition with charge transfer to adsorbed species is electron and hole recombination. Recombination of the separated electron and hole can occur in the volume of the semiconductor particle (pathway B) or on the surface (pathway A) with the release of heat. In classical heterogeneous photocatalytic process, the reaction itself occurs in the adsorbed phase and the overall process can be decomposed into following steps [45–47].

1) Transfer of reactants from the bulk of fluid to the exterior surface of the catalyst;

2) Transfer of reactants from the external surface of the catalyst into its pore structure;

3) Adsorption of at least one of the reactants;

4) Reaction in the adsorbed phase;

5) Desorption of the products;

6) Transfer of products out of the pore structure to the exterior of the catalyst surface;

7) Transfer of products from the external surface of the catalyst to the bulk of the fluid.

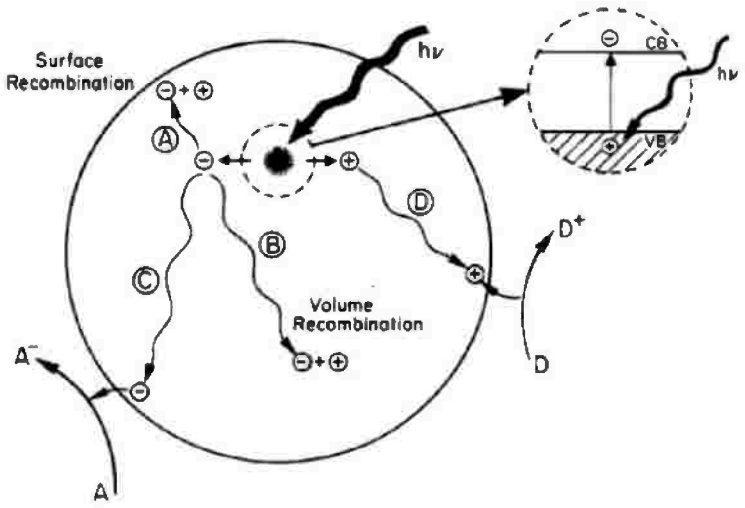

Figure 2.3: Schematic photo excitation in a solid semiconductor

2.3.1.4. Photocatalyst Material[44, 48–51]

There are many semiconductors especially as metal oxides and sulfides such as TiO_2, ZnO, ZnS, WO_3, CdS, Fe_2O_3, etc. which are commercially available and investigated in the literature in photocatalytic process. The band gap energies of several semiconductor photocatalysts are listed in Table 2.2. Of all the semiconductors tested in laboratory, TiO_2 has been proven to be the most suitable for widespread environmental applications [52–54].

Table 2.2 Band gap energy of semiconductor photocatalysts

Semiconductor	Band gap (eV)	Wavelength (nm)	Energy (kcal/mol)
SnO_2	3.8	326	87.7
ZnS	3.6	344	83.1
ZnO	3.2	388	73.8
WO_3	3.2	388	73.8
TiO_2	3.2	388	73.8
$SrTiO_3$	3.2	388	73.8
SiC	3.0	413	69.2
CdS	2.5	496	57.5
Fe_2O_3	2.3	539	53.1
GaP	2.25	551	51.9
CdSe	1.7	730	39.2

One of the most active fields of research in heterogeneous photocatalysis using semiconductor particles is the development of a system capable of using natural sunlight to degrade a large number of organic and inorganic contaminants in wastewater. The overall photocatalytic activity of a particular semiconductor system for the stated purpose is measured by several factors including the stability of the semiconductor under illumination, the efficiency of the photocatalytic process, the selectivity of the products, and the wavelength range response. Although several photocatalysts such as CdS have band gap energy small enough to receive excitation in the visible region of the solar spectrum, but are usually unstable and photo degrade with time. On the other hand, TiO_2 is a quite stable photocatalyst, but since the band gap is large (E_{bg}= 3.2 eV) it is only active in the ultraviolet region which is < 10% of the overall solar intensity. The limitations of a particular semiconductor as a photocatalyst for a particular use can be surmounted by modifying the surface of the semiconductor. To date, three benefits of modifications to photocatalytic semiconductor systems have been studied:[55]

(1) Inhibiting recombination by increasing the charge separation and therefore the efficiency of the photocatalytic process;

(2) Increasing the wavelength response range (i.e. excitation of wide band gap semiconductors by visible light); and

(3) Changing the selectivity or yield of a particular product.

These modifications include:

1) **Doping** [56]

Research into photocatalyst doping has spanned several decades. Usually doping involves the use of metals or non-metals and is designed to extend the photocatalytic activity of a semiconductor lower energy excitation. Technically, doping is the introduction of foreign elements into the parent photocatalyst without giving rise to new crystallographic forms, phases or structures and the aims are to enhance the net separation of photo generated charges and thereby efficiently harness the wide visible-light component of about 43% in the solar spectrum as opposed to the narrow ultraviolet component of 5%. It is thus an area of increasing research activity in photocatalysis.

2) Composite photocatalyst [57]

It is possible to create coupled colloidal structures, in which illumination of one semiconductor produces a response in the other semiconductor at the interface between them [54]. Coupled semiconductor photocatalysts exhibit very high photocatalytic activity for both gas and liquid phase reactions by increasing the charge separation and extending the energy range of photo excitation. The geometry of particles, surface texture, and particle size play a significant role in inter-particle electron transfer. Appropriate placement of the individual semiconductors and optimal thickness of the covering semiconductor are crucial for efficient charge separation.

There has been much interest in coupling different semiconductor particles with TiO_2, with coupled samples such as TiO_2-CdS, Bi_2S_3-TiO_2, TiO_2-WO_3, TiO_2-SnO_2, TiO_2-MoO_3, and TiO_2-Fe_2O_3 being reported. The coupled structure that has received the most attention is that consisting of CdS and TiO_2 colloidal particles [4].

3) Dye sensitization [55]

Surface sensitization of a wide band gap semiconductor photocatalyst such as TiO_2 via chemisorbed or physisorbed dyes can increase the efficiency of the excitation process and expand the wavelength range of excitation for the photocatalyst. This occurs through excitation of the sensitizer followed by charge transfer to the semiconductor.

Charge carriers can form in semiconductor particles by exciting a dye attached to the surface of the photocatalyst. The excited state can inject either a hole, or more commonly, an electron to the particle. Highly efficient charge injection is observed when a monolayer of a dye is dispersed on a photocatalyst with a high surface area. This sensitization increases the range of wavelength response of the photocatalyst, which is very important for photocatalyst to operate under natural sunlight. Photosensitization of semiconductors by various dyes has been monitored by nanosecond and pico-second flash photolysis as well as femto-second spectroscopy. The electron injection and back electron-transfer rates from the dye to the photocatalyst depend upon the nature of the dye molecules, properties of the TiO_2 nanoparticles and the interactions between the dye and nanoparticles

2.3.1.5. TiO_2 vs. other materials as a photocatalyst

The primary criteria for an efficient semiconductor photocatalyst is that the redox potential of the charge couple, i.e., e^-/h^+, lies within the band gap domain of the photocatalyst .According to thermodynamics, in order to photo oxidize a chemical species, the potential of the valence band of the semiconductor must be more positive than the oxidation potential of the chemical species and to photo-reduce a chemical species, the potential of the conduction band of the semiconductor must be more negative than the reduction potential of the chemical species. For a semiconductor, in order to be active as a catalyst for photocatalytic reactions, the redox potential of the photo induced valence band hole must be sufficiently positive to generate absorbed $OH^{\bullet}$ radical, which can subsequently oxidize the organic pollutants, and the redox potential of the photo generated conduction band electron must be sufficiently negative to be able to reduce absorbed O_2 to superoxide [58, 59].

In view of the utilization of energy (solar or UV light), semiconductors with lower band gap energy are more desired; however, the low band gap semiconductors usually suffer from serious stability problems [43, 57].To be a good photocatalyst, some basic requirements must be met:

1) photoactive; 2) able to utilize visible and/or near UV light; 3) biologically and chemically inert; 4) photo stable; 5) inexpensive [60].

Numerous researchers have worked on different semiconductor materials, and examples include metal oxides like WO_3, ZnO, CeO_2, Nb_2O_3, Fe_2O_3, SnO_2 and TiO_2 etc, and also chalcogenides like ZnS, CdTe, ZnSe, CdSe, etc and reported so far, few of them are appropriate for efficient photocatalytic reaction of a wide range of organic contaminants and TiO_2 has proven to be the most suitable for widespread environmental applications [61].Studies [56, 62, 63, 60, 64, 65] showed that interest in photocatalysis has also centered on ZnO, which has similar energy characteristic to TiO_2. They report that ZnO however suffers from photo-corrosion problems upon excitation in solution with respect to inappropriate dissolution to yield $Zn(OH)_2$ on the ZnO particle surface and thus leading to catalyst inactivation over time [66–68]. Although WO_3 can be activated in the visible light up to 500 nm but it is generally less photocatalytically active than TiO_2 [69, 70]. Hematite (α-Fe_2O_3) is also absorptive in the visible range (absorption onset = 560 nm) but shows much lower photocatalytic activity than does TiO_2 [71]. Although CdS exhibits not as photoactive

as TiO_2, it has been extensively studied because of its spectral response to longer wavelength in the solar spectrum. However its usage is limited due to photo-corrosion [72, 73].The photocatalytic activity of ZnS has not received as much attention as TiO_2 because of its generally poor catalytic efficiency and photo-instability.

Titanium dioxide was found to be one of the most promising semiconducting metal oxides because of its properties. It is the most researched semiconductor material because of the following properties[74, 75]

a) It is photo-stable
b) Photo-active
c) Relatively non toxic
d) Chemically and biologically inert
e) Its super hydrophilicity
f) Antimicrobial action

But the only disadvantage of TiO_2 that it is activated under ultraviolet light which limits the application of TiO_2 as a photocatalyst with visible light [58, 76].

2.3.1.6. Crystal structure of TiO_2

TiO_2 belongs to the family of transition metal oxides. There are four commonly known polymorphs of TiO_2 found in nature: anatase (tetragonal), brookite (orthorhombic), rutile (tetragonal), and TiO_2 (B) (monoclinic) [59]. Besides these polymorphs, two additional high-pressure forms have been synthesized from the rutile phase. These are TiO_2 (II) with a PbO_2 structure and TiO_2 (H) with a hollandite structure[77, 78]. Only the crystal structures (Table 2.3) and properties of the rutile, anatase and brookite polymorphs are considered [77–81].

Table 2.3 crystal structure data for TiO_2

Properties	Rutile	Anatase	Brookite
Crystal structure	Tetragonal	Tetragonal	Orthorhombic
Lattice constant (Å)	a = 4.5936 c =2.9587	a = 3.784 c = 9.515	a = 9.184 b = 5.447 c = 5.154
Band gap energy(eV)	3.2	3.02	2.96
Molecule (cell)	2	2	4
Volume/ molecule ($Å^3$)	31.2160	34.061	32.172
Density (g cm^{-3})	4.13	3.79	3.99
Ti–O bond length (Å)	1.949 (4) 1.980 (2)	1.937(4) 1.965(2)	1.87–2.04
O–Ti–O bond angle	81.2°–90.0°	77.7°–92.6°	77.0°–105°

2.3.1.6.1. Rutile

Rutile TiO_2 has a tetragonal structure and contains 6 atoms per unit cell (Figure 2.4). The TiO_6 octahedron is slightly distorted [81–83]. The rutile phase is stable at most temperatures and pressures up to 60 kbar, where TiO_2 (II) becomes the thermodynamically favorable phase [84]. It was found that anatase and brookite structures transformed to the rutile phase after reaching a certain particle size, with the rutile phase becoming more stable than anatase for particle sizes greater than 14 nm. Once the rutile phase formed, it grew much faster than the anatase. The activity of the rutile phase as a photocatalyst is generally very poor [85]. However, the rutile phase can be active or inactive, depending on its preparation conditions [86].

2.3.1.6.2. Anatase

Anatase TiO_2 also has a tetragonal structure but the distortion of the TiO_6 octahedron is slightly larger for the anatase phase [55, 87], as depicted in Figure 2.4. It was found that the anatase phase is more stable than the rutile at 0 K, but the energy difference between these two phases is small

(~2 to 10 kJ/mol) [87]. The anatase structure is preferred over other polymorphs for solar cell applications because of its higher electron mobility, low dielectric constant and lower density [58]. The increased photo reactivity is because of the slightly higher Fermi level, lower capacity to adsorb oxygen and higher degree of hydroxylation in the anatase phase [88]

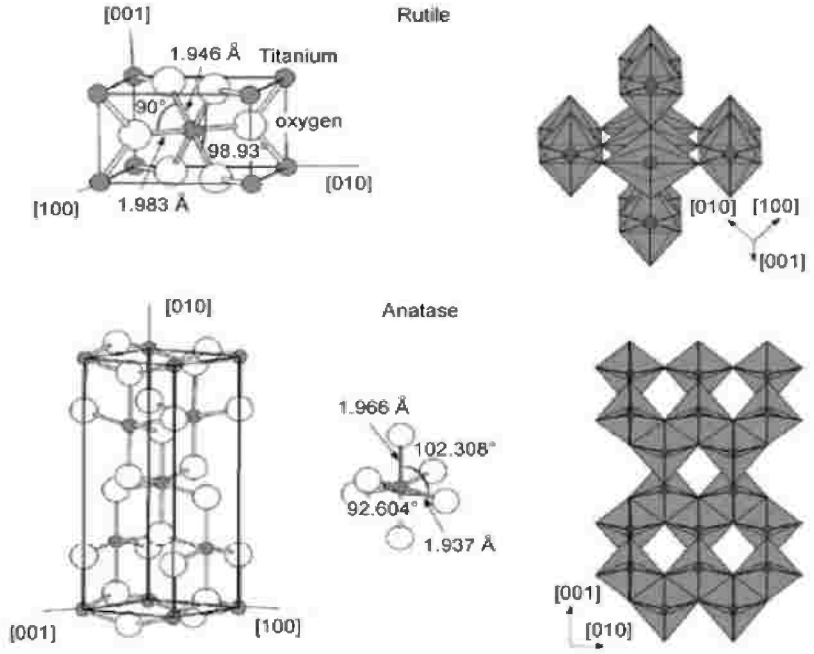

Figure 2.4: Crystal structure of rutile and anatase phases of TiO_2

2.3.1.6.3. Brookite:

Brookite TiO_2 belongs to the orthorhombic crystal system. Its unit cell is composed of 8 formula units of TiO_2 and is formed by edge-sharing TiO_6 octahedra (Figure 2.5). It is more complicated, has a larger cell volume and is also the least dense of the 3 forms and is not often used for experimental investigations [82].

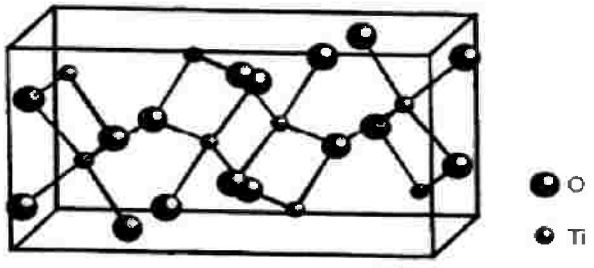

Figure 2.5: Lattice structure of brookite TiO_2

Both anatase and rutile structures have been most used in practical work as brookite is rarer and more difficult to prepare [89, 90]. Anatase and brookite both transformed to rutile upon heating at temperature between 450 ^{o}C and 1200 ^{o}C [91].This transformation is dependent on several parameters such as initial particle size, initial phase, dopant concentration, reaction atmosphere and temperature [92, 93]. There are several factors in determining important properties in the performance of TiO_2 for applications such as particle size, crystallinity and the morphology [94–96].

Although rutile has a lower band gap (anatase: 3.2 eV, rutile: 3.0 eV), anatase shows a higher photocatalytic activity in the oxidation of organic pollutants [97, 98]. A precise reason for anatase's better photocatalytic activity has not been documented, but an explanation may be found in anatase's conduction band energy (E_{cb}). Figure 2.6 shows anatase's E_{cb} to be 0.2 V more negative than rutile's Ecb which allows for a more favorable reduction of O_2 to over a wide pH range [98].

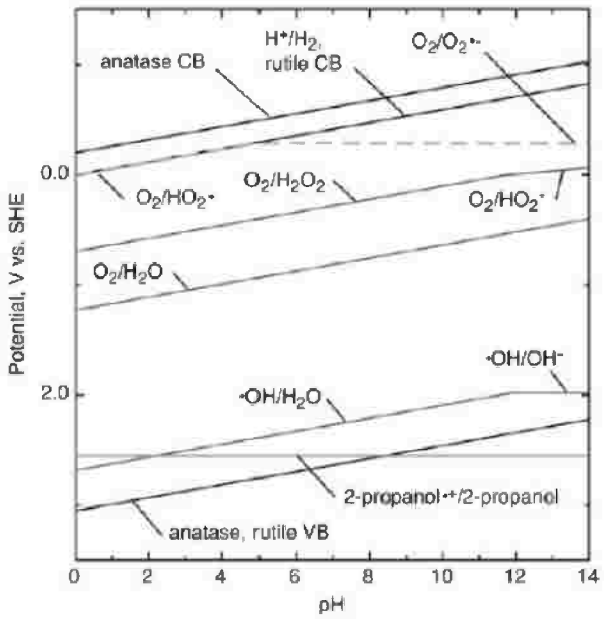

Figure 2.6: TiO_2 energy bands and corresponding potential differences of redox reactions occurring on the TiO_2 surface as function of pH

2.3.1.7. Applications of TiO_2 in various fields [59]

Due to non-toxic, easily available, inexpensive, biologically and chemically inert and stable to photo and chemical corrosion, TiO_2 is used in various fields as shown in Figure 2.7

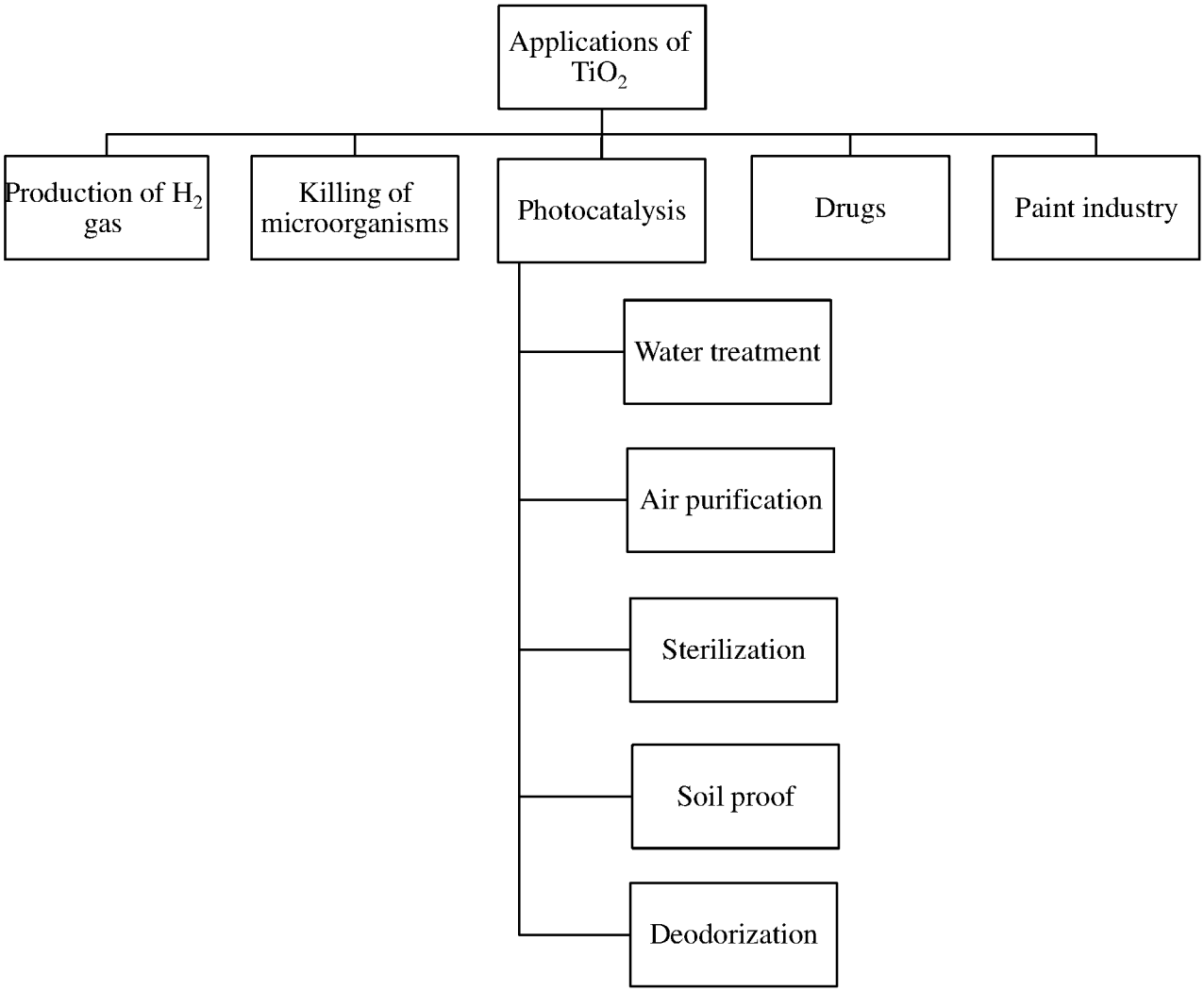

Figure 2.7: Applications of TiO_2 and photocatalysis in various fields.

2.4. Immobilization of TiO_2

In current reactor designs either a TiO_2 slurry or immobilized film is used. In the slurry reactors, suspended TiO_2 nano-particles can have a high surface to volume ratio. However, the suspended particles contaminate the yield and need to be removed. This is more difficult for smaller particles as they stay suspended in water easily, clog filter membranes and penetrate filter materials [99]. Removal of the catalyst from the reaction mixture is an additional step in the process that increases its costs.

Different researchers have tried to avoid the filtering process and to increase catalyst durability by immobilizing TiO_2 on solid supports as bound particles or thin films. However, the photocatalytic activity of immobilized films is often lower due to a lower surface area to volume ratio and mass transfer limitations [100].

A good photo-catalyst material should in general have the following attributes: [101, 102]

- The material should be transparent or at least allow some UV radiation to pass through it
- Be chemically inert or non-reactive to the pollutant molecules, its intermediates and the surrounding aqueous system
- The material should sufficiently bond either physically or chemically to the TiO_2 without reducing the reactivity of titanium dioxide
- The material should have a high surface area and a strong adsorption affinity towards the pollutants to be degraded
- The material should allow for fast and easy photo-catalyst recovery and re-use with or without regeneration.

Many substrates have already been proposed as catalyst supports for the photo-degradation of water contaminants. Most of these supports are based on SiO_2, either as a glass reactor wall or in the form of sand and silica gel. Glass beads, glass tubes, fiberglass, woven mesh, steel mesh, quartz, stainless steel, aluminum, metal fibers, and many types of plastics and ceramics such as alumina have also been tried as support material [103, 104].Glass possess an advantage as a catalyst support because of its transparency to UV light in photocatalytic applications [105].

2.4.1. Attributes of glass as a support material

Use of glass substrate as a support for titanium dioxide photo-catalyst has the following advantages;

(1) Glass is affordable and recyclable

(2) The main constituent of glass is SiO_2 which is abundant in nature

(3) It presents a surface for catalyst support

(4) It is transparent to the UV radiation required to activate TiO_2

(5) Silicon dioxide is a good adsorbent.

The above mentioned attributes are the reasons why a glass substrate was chosen as the support material for TiO_2 photo-catalyst.

2.4.2. Techniques of immobilizations

To deposit the titanium dioxide on the substrate, different techniques may be utilized. The Sol-Gel method has been extensively reported as low cost and easy. This method involves a colloidal suspension of the TiO_2 particles. In the process the suspension is converted to a viscous gel and finally to a solid material. Sol-Gel shows good adherence to the substrate because of oxygen bridges that are formed during heating of the precursor (such as titanium tetrachloride). Dip or spread coating can be used to coat the substrate [106]. Dip coating results in a thin and controllable layer while spread coating may be used to attain a thicker layer.

Another easy and reproducible technique is the use of Previously Made Titania Powder (PMTP). Unlike the Sol-Gel method which uses a precursor, commercially available Titania powder such is used and mixed with a solvent. Coating may be done by different methods such as pipetting and spin coating. After sintering at high temperature (400-600 °C) the film will adhere to the substrate [107].

Chemical vapor deposition (CVD) covers a lot of different processes that differ by type of precursor, type of support, uniformity of the film and reaction conditions. The method generally

involves exposing the substrate to a volatile gaseous phase precursor in an inert, high temperature and pressure environment. The precursor will decompose at the surface, forming the TiO_2 film. This method can coat a substrate of any shape. Other deposition techniques include sputtering, thermal treatment and electrophorectic deposition [101, 107].

2.5. Kinetics of decolorization of Methylene blue on TiO_2[108]

2.5.1. Determination of the reaction order

2.5.1.1. Pseudo-first-order kinetic model (Lagergren's rate equation)

In this model, the kinetic rate in differential form and its analytical solution can be expressed as

$$\frac{dq_t}{dt} = k(q_e - q_t)$$

$$\log(q_e - q_t) = \log(q_e) - \frac{k}{2.303} t$$

Where

q_e and q_t are the solid-phase concentration at equilibrium and at time (t), respectively. Here, k is the reaction constant in s^{-1}.

2.5.2. Pseudo second-order kinetic model

In this model, the kinetic rate in differential form and its analytical solution can be expressed as

$$\frac{dq_t}{dt} = k(q_e - q_t)^2$$

$$\frac{t}{q_t} = \frac{1}{kq_e^2} + \frac{1}{q_e} t$$

Where q_e and q_t are the solid-phase concentration at equilibrium and at time t, respectively. Here, the units of k are g/(mol s) provided that q is in mol/g.

2.6. Literature survey

Joshi, K. M. et al [109] studied the photocatalytic degradation of methylene blue using nano sized TiO_2 and ZnO. The TiO_2 and ZnO can totally remove methylene blue dye. The effect of various process parameters like initial concentration, contact time, dose of catalyst and pH on the extent of removal of dye by photocatalysis in presence of TiO_2 and ZnO was studied. The results showed that the percentage of dye removal increases with increase in contact time. The optimum contact time was fixed at 180 minutes for both nanomaterials. The results of this study reveal that the dyes could be removed by semiconducting nanomaterials assisted photocatalytic degradation. The semiconducting materials were analyzed by XRD and SEM before and after degradation of methylene blue.

Houas, A. et al [110] investigated The photocatalytic degradation of methylene blue (MB) in aqueous heterogeneous suspensions of TiO_2/UV. 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 hetero-atoms 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, in particular aromatics, whose successive hydroxylations lead to the aromatic ring opening. These results suggest that TiO_2/UV photocatalysis may be envisaged as a method for treatment of diluted waste waters in textile industries.

Ramaswamy, V. et al [111] prepared Nanocrystalline particles of pure anatase titania by two different methods. One is the sol–gel method at ambient temperature using ultrasonication (TiO_2-SG-US) and conventional stirring method (TiO_2-SG-S) and the other by surfactant assisted hydrothermal synthesis (TiO_2-HT). More uniform distribution/dispersion of the nanoparticles (SEM), marginally higher surface area, better thermal stability and phase purity are some of the advantages of preparation of nanocrystalline titania by sol gel ultrasonication method and hydrothermal synthesis method. The behavior of anatase titania in photocatalytic decomposition of methylene blue in aqueous medium was studied as a function of the method of preparation and the crystallite size. The nanoparticles prepared by ultrasonication method were more effective than both, the sample prepared by conventional stirring method and commercial Degussa P-25. The higher photocatalytic activity of TiO_2-SG-US is attributed to the more uniform size of the particles as compared to TiO_2-SG-S samples. Both TEM and XRD data on TiO_2-HT samples

reveal a uniform and nanocrystalline TiO_2 particles, which showed photocatalytic activity in both UV and visible region although brookite phase was also present.

Salehi, M. et al [112] study the degradation of methylene blue as a dye in the presence of TiO_2 nano-powders using photolysis and sonolysis systems separately and simultaneously. Effect of different parameters such as catalyst dosage, initial concentration of dye, UV power, pH and type of catalyst on the removal efficiency was ascertained. The results showed that basic pH is proper for the photocatalytic removal of the dye. Furthermore higher UV power and lower initial concentration of dye leads to higher removal percent. Moreover TiO_2 showed more photocatalytic activity than ZnO in the nano-powder form. The experimental kinetic data followed the pseudo-first order model in both photocatalytic and sono-photocatalytic processes but the rate constant of sono-photocatalysis is higher than it at photocatalysis process. Finally the reaction order of the rate law respect to nano-catalyst dosage in photocatalysis process is obtained 1.45. High activation energy of this process shows its high sensitivity to temperature

Gajbhiye, S. Bai [1] studied the use of Zinc oxide (ZnO) in the photocatalytic decolorization and degradation study of a dye namely, methylene blue (MB). The effect of the various rate determining parameters like initial dye concentration, catalyst loading, pH of the medium, temperature of the dye solution on the photo degradation of MB were studied in detail. The various thermodynamic and kinetic parameters of the process were evaluated. The MB degradation and its reaction kinetics analysis were utilized in the photocatalytic treatment of an actual effluent collected from an industry manufacturing intermediates for dyes. It revealed that the effluent could be effectively decolorized and degraded by photocatalytic method, without generation of any hazardous wastes or by-products as evident from the considerable reduction in chemical oxygen demand (COD) values.

Chakrabarti, S. et al [25] found that Semiconductor photocatalysis often leads to partial or complete mineralization of organic pollutants. Upon irradiation with UV/visible light, semiconductors catalyze redox reactions in presence of air/O_2 and water. the potential of a common semiconductor, ZnO, has been explored as an effective catalyst for the photo degradation of two model dyes: Methylene Blue and Eosin Y. A 16 W lamp was the source of UV-radiation in a batch reactor. The effects of process parameters like, catalyst loading, initial dye concentration, airflow rate, UV-radiation intensity, and pH on the extent of photo

degradation have been investigated. Substantial reduction of COD, besides removal of colour, was also achieved. A rate equation for the degradation based on Langmuir–Hinshelwood model has been proposed.

AMETA, A. et al [113] studied the Photocatalytic degradation of methylene blue over ferric tungstate in presence of light. The progress of the reaction was monitored spectrophotometrically. The effect of some parameters affecting the rate of reaction, such as pH, dye concentration, amount of semiconductor, light intensity, etc. has been studied. Kinetic studies show that this reaction follows pseudo-first order kinetics. A tentative mechanism for photocatalytic degradation of methylene blue has also been proposed.

Sleiman, M.et al [17] carried out the photocatalytic degradation of an azo dye Metanil Yellow in aqueous solution using TiO_2 as photocatalyst under UV irradiation. The decolorization and degradation kinetics were investigated and both followed a pseudo first order kinetic according to Langmuir– Hinshelwood model. Using HPLC/DAD and GC/MS analyses, more than 10 major reaction intermediates were identified and a tentative degradation pathway was proposed. Furthermore, ion chromatography (IC) and TOC measurements revealed a complete mineralization of Metanil Yellow into CO_2, N_2, H_2O and inorganic ions (NH_4^+, NO_3^- and SO_4^{-2}).

Coleman, H. M. et al [8] found that Micro-molar concentrations of aqueous 17-b-oestradiol were 98% destroyed in 3.5 h by photocatalysis over the titanium dioxide powder immobilized on Ti-6Al-4V alloy. The concentration of oestradiol was determined by HPLC with fluorescence detection. The degradation kinetics were fitted to a Langmuir–Hinshelwood model with k(S) = 4.4×10^{-2} mmol dm^{-3} min^{-1} and K(S) = 0.347 dm^3 $mmol^{-1}$. The pseudo-first-order rate constant (1.57×10^{-2} min^{-1}) was in line with the 50% degradation time of 40 min. The apparent quantum yield per electron was $\varphi e0$ = 0.41%. The effect of pH on the initial rate of degradation was similar to that reported for phenol

Mehra, M. [114] studied the photo catalytic degradation of methyl orange and methylene blue by heterogeneous photo catalytic process using TiO_2 as semi conductor. An attempt has been made to study the effect of process parameters viz. → concentration of dye and pH on photo catalytic degradation of methyl orange and methylene blue. The experiments were carried out by the irradiating the aqueous solution of dyes containing photo catalyst with UV and solar light. The

rate of decolorization was estimated from residual concentration spectrophotometrically. The % reduction of methyl orange and methylene blue was estimated under UV / solar system.

Bubacz, K. et al [2] prepared a photocatalyst by treating the commercial amorphous anatase titanium dioxide with ammonia water. During the preparation of photocatalytic material the optimal conditions of the separation operation were found. The photocatalyst was characterized by UV/VIS-DR, FTIR-DR, and XRD techniques, and high-resolution transmission electron microscopy (HR-TEM). According to the XRD method, the mean crystalline size of TiO_2 was 12.7-13 nm. The particulates were characterized using a particle size analyzer (mean size 195.7 nm). TEM studies presented the morphology of the sample. The photocatalytic activity of the photocatalyst was determined on the basis of the decomposition rate of phenol and azo-dye (methylene blue) under UV irradiation. The pH effects on the photocatalytic degradation were investigated. The degree of the dye and phenol removal in the solutions was measured by UV/VIS spectroscopy and a TOC analyzer. The decomposition of methylene blue increased along with an increase of pH value, whereas the activity of the prepared photocatalyst toward phenol degradation was the highest at pH=6.5. TOC disappearance in solutions of both organic compounds during photocatalytic reaction corresponded to their decrease of concentration, but with a little delay

Subrata Naskar et al [115] studied the immobilization of Degussa TiO_2 nanoparticles on a foamed polyethylene by thermal bonding to produce a stable catalyst sheet containing 0.7 mg TiO_2 cm^{-2} and retaining 40–50% of active surface area of the particles. On such a catalyst sheet, exposed to radiation of a 125 W mercury vapour lamp, decomposition of about 0.3 mg of methylene blue (MB) is obtained per cm^2 in 1 h at ambient temperature from an aqueous solution of 200 ppm MB. The rate data fit well to classical Langmuir—Hinshelwood (L—H) rate form. This rate form also results from mechanisms based on the assumption of hydroxyl radical formation on the irradiated catalyst and a reaction between the hydroxyl radical and the organic dye molecule, either or none of them being adsorbed on the catalyst surface. An activation energy of 14.5 kcal mol^{-1} is obtained for the photocatalytic decomposition of methylene blue following the L—H rate laws.

Arbuj, S. S. et al [116] prepared TiO_2 nanoparticles by the thermal decomposition of titanium tetraisopropoxide (TTIP) using a tubular electric furnace at various synthesis temperatures (700–1300 °C) and TTIP heating temperatures (80–110 °C). The photocatalytic activity of the resulting TiO_2 nanoparticles was examined by measuring the rate of methylene blue decomposition. The TiO_2 nanoparticles were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET) measurements and transmission electron microscopy (TEM). The crystallite size and crystallinity increased with increasing synthesis temperature and TTIP heating temperature. A TTIP heating temperature and synthesis temperature of 95 °C and 900 °C, respectively, were found to be the optimal synthesis conditions. The primary particle diameter obtained under optimum synthesis conditions was considerably smaller than the commercial photocatalyst (Degussa, P25). The specific surface areas were more than 134.4 $m^2\ g^{-1}$. Under the optimal conditions, the photocatalytic activity for methylene blue was higher than that of the commercial photocatalyst

J. Antonio, R. M et al [117] prepared ZnO thin films by electrodeposition and the response surface methodology (RSM) was applied to evaluate the effect of variables such as: concentration of methylene blue dye (MB), pH and air flow involved on the photocatalytic degradation of methylene blue. The results showed that the RSM is a suitable technique to determine the operating conditions favorable for the degradation of MB within a determined range of study.

M. Barjasteh-Moghaddam et al [118] studied the photocatalytic degradation of methylene blue (MB) on ZnS nanoparticles, prepared in aqueous solution of a room-temperature ionic liquid (RTIL), was studied and the results were compared with commercial ZnS. Influence of various operational parameters such as calcination temperature, catalyst weight, pH of solution, and initial concentration of MB on the photo degradation reaction was investigated to achieve maximum degradation efficiency. The optimum value of pH and catalyst dose was found to be 9.5 and 0.6 g l^{-1}. It was demonstrated that the photo degradation of MB follows a pseudo first-order kinetic. At optimized conditions, the rate constant of the reaction on ZnS nanoparticles prepared in aqueous solution of the RTIL is about five and four times greater than the prepared sample in water and commercial ZnS, respectively.

Shrivastava, V. S. [119] studied the removal of dye methylene blue(MB) and metal chromium Cr (VI) by considering influent concentration, loading of photocatalyst, pH and contact time as

operating variables. The percentage removal of dye MB and Cr(VI) increase with increase in contact time. The optimum contact time was fixed at 180 minutes for TiO_2. The results of this study reveal that the dyes could be removed by semiconducting nanomaterials assisted photocatalytic degradation. The kinetics studies of experimental data were analyzed using the pseudo first order kinetics of Lagergren and Pseudo second order model to determine adsorption rate constant. The semiconducting nano materials were characterized by EDX, XRD and SEM for determining the contents and the size of particles.

Mohabansi, N. et al [120] studied the irradiation of aqueous solution of methylene blue (MB) dye in presence of photo catalyst & UV light were carried out in the batch photo reactor. Titanium dioxide (TiO_2) & zinc oxide (ZnO) were used as photo catalyst for the study. The rate decolorization was estimated from residual concentration spectrophotometrically. Effects of some operating parameters such as the initial PH, H_2O_2/COD ratio, & the amounts of catalyst on the degradation of the dyes were investigated. Results show that ZnO is a better alternative photo catalyst compared to TiO_2 in terms of percentage degradation of MB. The maximum decolorizing efficiency was occurred in less than 90min with 50mg/750ml of ZnO catalyst dose.

Wu, C.-H. et al [121] examined the photocatalytic behavior of methylene blue (MB) on titania-dispersed bamboo charcoals, prepared by sol–gel method combined with chemical-wet impregnation. The experimental results of nitrogen adsorption showed that specific surface area of the TiO_2-charcoals was found to increase with TiO_2 loading, whereas their mean pore sizes exhibited a decreasing trend. It can be suggested that TiO_2 nanoparticles were mostly coated on the charcoal surface and partially deposited in the mouth of pore channels. Our preparation technique for the heterogeneous catalysts improves the dispersed degree of TiO_2catalyst, which shows a better photocatalytic performance than pure TiO_2 aggregation. A linearity relationship between the overall photocatalytic efficiency and the TiO_2 loading reflected that each titania particle behaves as identical photocatalytic reactivity. The liquid-phase photocatalytic behavior of the heterogeneous catalysts can be well described by Elovich kinetic model.

Chin Mei Ling et al [122] studied the synthesis and immobilization of TiO_2 thin film photocatalyst on glass reactor tube using sol–gel method. The synthesized TiO_2 coating was transparent, which enabled the penetration of ultra-violet (UV) light to the catalyst surface. Two photocatalytic

reactors with different operating modes were tested: (a) tubular photocatalytic reactor with re-circulation mode and (b) batch photocatalytic reactor. A new proposed TiO_2 synthesized film formulation of 1 titanium isopropoxide: 8 isopropanol: 3 acetyl acetone: 1.1 H_2O: 0.05 acetic acid (in molar ratio) gave excellent photocatalytic activity for degradation of phenol and methylene blue dye present in the water. The half-life time, $t_{1/2}$ of photocatalytic degradation of phenol was 56 min at the initial phenol concentration of 1000 μM in the batch reactor. In the tubular photocatalytic reactor, 5 re-circulation passes with residence time of 2.2 min (single pass) degraded 50% of 40-μM methylene blue dye. Initial phenol concentration, presence of hydrogen peroxide, presence of air bubbling and stirring speed as the process variables were studied in the batch reactor. Initial methylene blue concentration, pH value, light intensity and reaction temperature were studied as the process variables in the tubular reactor. The synthesized TiO_2 thin film was characterized using SEM, XRD and EDX analysis. A comparative performance between the synthesized TiO_2 thin film and commercial TiO_2 particles (99% anatase) was evaluated under the same experimental conditions. The TiO_2 film was equally active as the TiO_2 powder catalyst.

Kasanen, J. et al [123] found that A multilayer photocatalytic TiO_2 coating on a high-density polyethylene (HDPE) disk to degrade aqueous methylene blue in a batch reactor study. The TiO_2 coating was fabricated by a low-temperature method using polyurethane resin (PU) as a barrier layer for HDPE and as a binding agent for two TiO_2 layers. Adequate adhesion between the HDPE substrate and PU barrier in aqueous environment was ensured with an oxygen plasma treatment. The photocatalytic effect of immersed TiO_2 coating on the degradation of methylene blue in aqueous solution was monitored by UV–vis spectrometry as a function of UV-illumination time. Samples were allowed to adsorb methylene blue in the dark for 1 h before the UV-degradation experiments were started. The percentages of methylene blue degraded during 6 h UV illumination ($\lambda = 365$ nm) varied from 80% to 92%. The degradation followed pseudo-first order reaction kinetics, and the observed rate constants (k_{obs}) were between 0.27 and 0.43 h^{-1}.

Kuo, W. S et al [124] studied a photocatalytic decolorization system equipped with immobilized TiO_2 and illuminated by solar light was used to remove the color of wastewater. To examine the decoloring efficiency of this system, photocatalytic decolorization of an organic dye such as

methylene blue was studied as an example. The effects of light source, pH, as well as the initial concentration of dye were also investigated. It was observed that the solution of methylene blue could be almost completely decolorized by the solar light/TiO_2 film process while there was about 50% color remaining with solar irradiation only. In addition, it was found that the decoloring efficiency of solution was higher with solar light irradiation than with artificial UV light irradiation, even though the artificial UV light source supplied higher UV intensity at 254 nm. The color removal rate of methylene blue with solar light irradiation was almost twice that of artificial UV light irradiation. This phenomena was mainly attributed to that some visible light range of solar light was useful for exciting the methylene blue molecules adsorbed on TiO_2 film, leading to a photosensitization process undergoing and decoloring efficiency promoted. This solar-assisted photocatalytic device showed potential application for decoloring organic dyes in wastewater.