SONOPHOTOCATALYTIC DEGRADATION OF ALIZARIN RED: REACTIVE DYE OVER SLURRY TITANIUM DIOXIDE

A Thesis
Submitted in partial fulfillment of the requirements
For the award of degree of
MASTER OF ENGINEERING
In
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Submitted By:	**Under Supervision Of:**
Partibha Sangwan	**Er. Anoop Verma**
60701004	

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DEPARTMENT OF BIO-TECHNOLOGY AND ENVIRONMENTAL SCIENCES
Thapar University
Patiala-147004

Certificate

I hereby certify that the work that is being presented in the thesis entitled "Sonophotocatalytic degradation of Alizarin Red dye: reactive dye over slurry titanium dioxide", submitted by Partibha Sangwan in partial fulfillment of the requirements for the award of the degree of Master of Technology submitted in Department of Biotechnology and Environmental Sciences, Thapar University, Patiala is an authentic record of my own work carried under the supervision of Er. Anoop Verma. The report has not been submitted for the award of any other degree or certificate in this or any other University or Institute.

Partibha

Partibha Sangwan

This is to certify that the above statement made by the candidate is correct and true to the best of my knowledge.

03/07/09

Er. Anoop Verma
Lecturer, DBTES,
TU, Patiala.

Department of Biotechnology and Environmental Sciences
Thapar University
Patiala.

Countersigned by
(Head)
Department of Biotech and Environ. Sciences
Thapar University
Patiala.

08/07/2009

RK Sharma 13/7/09

(Dean)
Academic Affairs
Thapar University
Patiala.

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Partibha Sangwan

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ABSTRACT

The release of dyes into the receiving water bodies is deleterious, not only because of their color, but also because they are not easily degraded by aerobic bacteria and forms toxic compounds under the action of anaerobic bacteria. Therefore, it becomes imperative to completely degrade these organic compounds before their discharge. Such pollutants cannot be completely degraded by well established techniques like coagulation, flocculation, precipitation, adsorption, membrane separation, aerobic biological treatment. The incapability of conventional wastewater treatment methods to effectively remove such pollutants leads to explore the new, efficient and cost effective treatment systems. In order to meet stringent environmental regulations, the latest development is the oxidation of these biorecalcitrant organic compounds. These radicals have high oxidizing power superior to other usual oxidants and results in complete degradation. The methods are called advanced oxidation processes (AOP's),which are characterized by production of the hydroxyl radical (OH) as a primary oxidant. Examples of AOP's include the use of (H_2O_2/UV), semiconductor photocatalysis, ozonolysis and ultrasonic irradiation (sonolysis), (ultrasound/O3) as important segmental or parallel processes and are found to enhance OH radical production leading to higher oxidation rates and organic matter mineralization. In this work, we investigated the Photocatalytic oxidative degradation and discoloration of various reactive dyes and dye intermediates using light (UV/visible)/semiconductor catalyst by optimizing the operational parameters to ensure the rapid and complete transformation of the toxic organic compounds to benign chemicals. Also the simultaneous sonochemical effect along with photochemical oxidation process (light/semiconductor/ultrasound) is used which leads to faster destruction rate.

The scope of this project is to see Sonophotocatalysis as a viable treatment option in case of dyes. Titanium dioxide was used as Photocatalyst. Experiments were performed in slurry mode in both UV and solar light at optimized condition. The degradation of wastewater has been investigated in terms of reduction in Conc. Various process parameters like catalyst dose, pH, concentration of oxidant, initially pollutant concentration were varied and their effects have been analyzed. In this case the catalyst concentration was optimized at .1g/200ml, pH at 4.8 and oxidant concentration at 3ml/200ml of the sample.

The results obtained were quit appreciable as it reduced COD from 280 to 40 mg/l, BOD from 125 to 40 mg/l.

The results of Sonophotocatalytic degradation of dyes showed that it could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater. The investigations demonstrate the importance of selecting the optimal degradation parameters for practical applications of this operation.

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CHAPTER 1

INTRODUCTION

1.1 Review

Water, water everywhere but just a little that is clean! Water, pre-requisite for life and key resource of humanity is in abundance on our earth. When Neil Armstrong saw the Earth from the Moon, it appeared blue! This is because water covers more than two-thirds of the Earth's surface. **Goate P.R., et al.,(2004).** However, 97.5% is salt water .Of remaining 2.5% is fresh water, 70% is frozen, and rest is present as soil moisture or subterranean inaccessible aquifers. Thus only 1% of the fresh water resources are readily available for use **WHO (2002).** Comprising over 70% of the Earth's surface, water is undoubtedly the most precious natural resource that exists on our planet as shown by **Fig.1**. Without the seemingly invaluable compound comprised of hydrogen and oxygen, life on Earth would be non-existent: it is essential for everything on our planet to grow and prosper. Although we as humans recognize this fact, we disregard it by polluting our rivers, lakes, and oceans. Subsequently, we are slowly but surely harming our planet to the point where organisms are dying at a very alarming rate. In addition to innocent organisms dying off, our drinking water has become greatly affected as is our ability to use water for recreational purposes. In order to combat water pollution, we must understand the problems and become part of the solution.

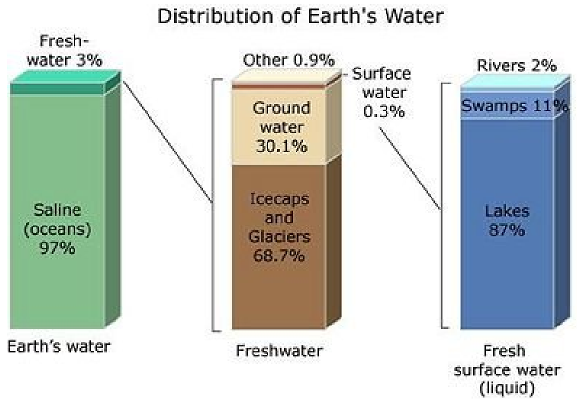


Fig -1 Showing distribution of water on earth

Water is basic requirement in all industrial processes, domestic and commercial activities, so the waste water generated from different activities contains various contaminants which are harmful for both flora and fauna existing on this planet. The industrial processes mainly pharmaceutical , textile pesticide and other organic chemical manufacturing industries generates waste water containing phenolic compounds and various dyes. These effluents are intensely colored and are contaminated with high concentration of organic compounds such as suspended and dissolved salts and many other recalcitrant compounds. **Mahamuni N.N.,et al., (2005).**

1.2 Waste Water

Wastewater is water that has been used for some purpose and is deemed unfit for further use. In fact, wastewater can be used for secondary purposes in most cases. Also, efficient use of water reduces the amount of wastewater generated.

Wastewater is used water. It includes substances such as human waste, food scraps, oils, soaps and chemicals. In homes, this includes water from sinks, showers, bathtubs, toilets, washing machines and dishwashers. Businesses and industries also contribute their share of used water that must be cleaned.

Wastewater also includes storm runoff. Although some people assume that the rain that runs down the street during a storm is fairly clean, it isn't. Harmful substances that wash off roads, parking lots, and rooftops can harm our rivers and lakes.

1.2 Common organic waste water pollutants

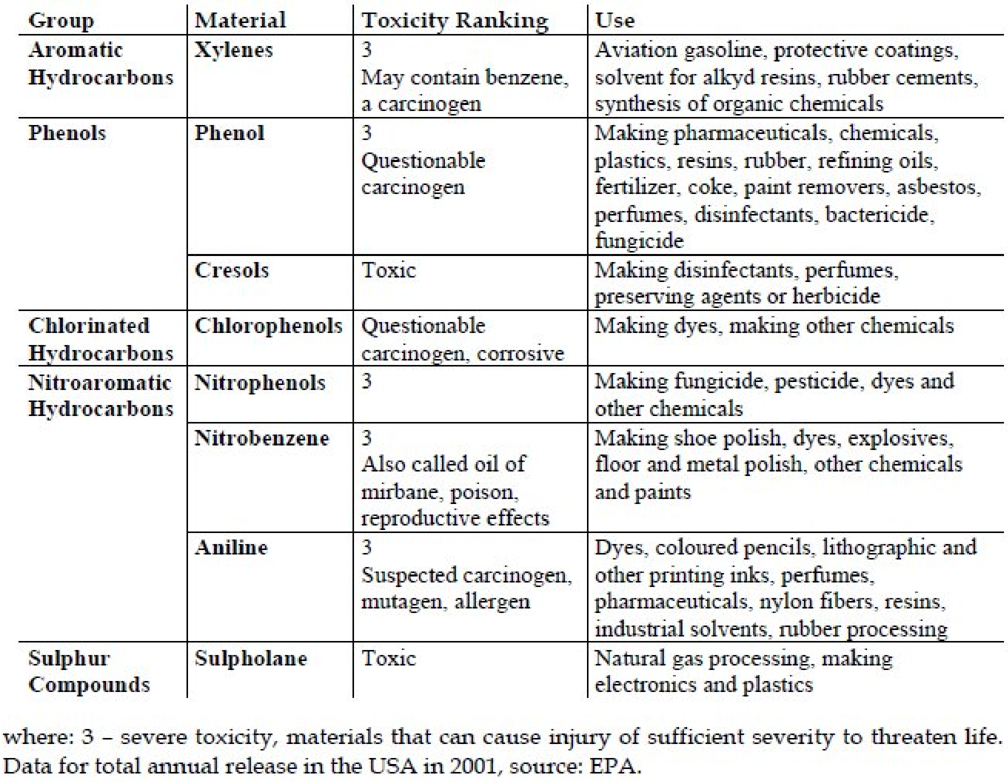
Now days, there exists strong environmental concern on a large no. of organic pollutants coming from wide range of sources, which may enter in waste water, for example, identified over 137 organic compounds in the influent of the municipal wastewater plants in Stockholm. Many of these pollutants are totally artificial organic compounds, being products of an increasingly inventive chemical industry.

The potential (long term) and actual (short term) impact of each of these xenobiotic compounds, however, is extremely difficult to predict or assess.

The following classifications of organic water pollutants can be established:

- -TCE (trichloro ethylene), Chloroform, Carbon Tetrachloride;
- -Herbicides, Pesticides;

- -and Oil and Grease, PAHs (Poly aromatic hydrocarbons), Hydrocarbons.



Group	Material	Toxicity Ranking	Use
Aromatic Hydrocarbons	Xylenes	3 May contain benzene, a carcinogen	Aviation gasoline, protective coatings, solvent for alkyd resins, rubber cements, synthesis of organic chemicals
Phenols	Phenol	3 Questionable carcinogen	Making pharmaceuticals, chemicals, plastics, resins, rubber, refining oils, fertilizer, coke, paint removers, asbestos, perfumes, disinfectants, bactericide, fungicide
	Cresols	Toxic	Making disinfectants, perfumes, preserving agents or herbicide
Chlorinated Hydrocarbons	Chlorophenols	Questionable carcinogen, corrosive	Making dyes, making other chemicals
Nitroaromatic Hydrocarbons	Nitrophenols	3	Making fungicide, pesticide, dyes and other chemicals
	Nitrobenzene	3 Also called oil of mirbane, poison, reproductive effects	Making shoe polish, dyes, explosives, floor and metal polish, other chemicals and paints
	Aniline	3 Suspected carcinogen, mutagen, allergen	Dyes, coloured pencils, lithographic and other printing inks, perfumes, pharmaceuticals, nylon fibers, resins, industrial solvents, rubber processing
Sulphur Compounds	Sulpholane	Toxic	Natural gas processing, making electronics and plastics

where: 3 – severe toxicity, materials that can cause injury of sufficient severity to threaten life.
Data for total annual release in the USA in 2001, source: EPA.

Table 1.1 Use and hazard ranking information for chemicals (Sax & Lewis, 1992).

1.4 Photocatalysis in water treatment

The presence of harmful organic compounds in water supplies and in the discharge of wastewater from chemical industries, power plants, landfills, and agricultural sources is a topic of global concern. Traditional water treatment processes include filtration and flocculation, biological treatment, thermal and catalytic oxidation, and chemical treatment using chlorine, potassium permanganate, ozone, hydrogen peroxide and high-energy ultraviolet light **Legrini et al.,(1993).** All these water treatment processes, currently in use, have limitations of their own and none is cost-effective: (i) Phase transfer methods remove unwanted organic pollutants from wastewater, but they do not eliminate the pollutants entirely; (ii) Cost of biological treatment is low, however, some of the toxic compounds present are found to be lethal for microorganisms intended to degrade them, and there is a class of non-biodegradable organic products noted as biorecalcitrant organic compounds; (iii) While chemical treatments based on aqueous phase hydroxyl radical chemistry are powerful to oxidize toxic organic compounds present in water, these processes either use high-energy ultraviolet light or strong chemical oxidants of hazardous and therefore, undesirable nature **Mills et al., (1993).** Moreover, several intermediates, which are more hazardous, are formed in these processes, and because of very low efficiencies, overall treatment cost becomes high if destruction of intermediates and complete mineralization are to be achieved, especially for treating dilute wastewater streams **Ollis et al.,(1989).** 1 Heterogeneous photocatalysis on metal oxide semiconductor particles is an advanced oxidation technology (AOT), which has been shown to be an effective means of removing organic pollutants from water streams. Compared with traditional oxidation processes, heterogeneous photocatalysis has the following advantages **Hoffmann et al.,(1995).**

i. It utilizes low-energy ultraviolet light with semiconductors acting as Photocatalyst and leads to complete mineralization of pollutants to environmentally harmless compounds.
ii. The Photocatalytic reactions allow thermodynamically unfavorable reactions to occur and allow destruction of non-biodegradable refractory contaminants.
iii. While catalytic processes normally require high temperature or high pressure, Photocatalytic oxidation is a promising technique for many purposes due to its ability to operate at or slightly above ambient conditions.

However, the rate of the Photocatalytic reaction is determined by the illuminated surface area of photo catalysts, light irradiance, reactants adsorption rate, and the properties of photo catalysts. Generally, the rate is not significantly great due to the low photo efficiency. Thus commercialization of Photocatalytic processes is still in its infancy.

Reactor design can alleviate some of the problems and increase the efficiency of the photo catalyzed process. However, there are four main barriers to scale-up of Photocatalytic reactors. Firstly, the efficient exposure of the catalyst to light in a large scale reactor poses a challenge. Secondly, the illuminated catalyst area in contact with the water has to be maintained high. Thirdly, the mixing and mass transfer limitations in a large scale reactor have to be overcome. Finally, in any design for industrial application high wastewater throughput through the reactor should be attainable. There are mainly two types of configurations as far as the catalyst is concerned - either as a slurry of titania in suspension or immobilized on inert surfaces. Slurry reactors necessitate downstream separation and recycle of the catalyst and are inefficient and difficult to scale up. Therefore, immobilized reactors are preferred.

1.5 Dye:

A dye can generally be described as a colored substance that has an affinity to the substrate to which it is being applied. The dye is generally applied in an aqueous solution, and may require a mordant to improve the fastness of the dye on the fiber.

Textile industries are found in most countries and their numbers have increased, particularly in Asia. These industries have shown a significant increase in the use of synthetic complex organic dyes as the coloring material. The annual world production of textiles is about 30 million tones requiring 700,000 tones of different dyes **Abraham, (1993)** which causes considerable environmental pollution problems. Dyes include a broad spectrum of different chemical structures, primarily based on substituted aromatic and heterocyclic groups such as aromatic amine (C_6H_5–NH_2), which is a suspected carcinogen, phenyl (C_6H_5–CH_2) and naphthyle (NO_2–OH). A large number of dyes are azo compounds (–N–N–), which are linked by an azo bridge. Due to the complex chemical structure of synthetic organic pigments in dyes, they are resistant to breakdown and remain fast for the lifetime of the fabric; they will not break down on exposure to sunlight, water, soap, etc. and are difficult to treat in a wastewater. Color in wastewater is an obvious indicator of water pollution**.** The wastewater characteristics from a dye house are highly variable from day to day, and even hour to hour, depending on the type of dye, the type of fabric and the concentration of the fixing agents added. Treatment of such wastewaters is therefore, essential but difficult.

1.6 Characteristics of waste water having dye:

Scientists raced to formulate gorgeous new colors and before long, dyed fabric was available to all, and natural dyes had become obsolete. This brightly colored, changed new world was not without a down side however. The chemicals used to produce dyes today are often highly toxic, carcinogenic, or even explosive. The chemical Anililine, a popular group of dyes known as Azo dyes (specifically group III A1 and A2) which are considered deadly poisons (giving off carcinogenic amines) and dangerous to work with, also being highly flammable. In addition, other harmful chemicals used in the dying process include:

1) Dioxin – a carcinogen and possible hormone disrupter;

2) Toxic heavy metals such as chrome, copper, and zinc – known carcinogens; and

3) Formaldehyde, a suspected carcinogen.

Table 1.2 Types of Pollutants associated with various Dyes Sheng and Chi (1993)

Effluents from Dye Manufacturing mg/ltr(except for pH) Parameter	**Max Value**
PH	6-9
BOD	30
COD	150
TSS	50
Oil and Grease	10
Phenol	0.5
Copper	0.5
Zinc	2
Aox	1

1.7 Environmental impacts of dye waste water:

"Synthetic dyes are extensively used by industries including dye houses, paper printers, textile dyers, color photography and as additives in petroleum products.

The effluents of these industries are highly colored, and disposal of these wastes into the environment can be extremely deleterious. Their presence in watercourses is aesthetically unacceptable and may be visible at concentration as low as 1 ppm (part per million).

Almost every industrial dye process involves a solution of a dye in water, in which the fabrics are dipped or washed. After dying a batch of fabric, it's cheaper to dump the used water – dye effluent – than to clean and re-use the water in the factory. So dye factories across the world are dumping millions of tons of dye effluent into rivers.**T-1.3** shows the types of pollution associated with dyes.

Table 1.3 Types of Pollution that is associated with various dyes (Arslan et al;2002)

Class	**Fiber**	**Nature of Pollution**
Direct	Cotton	Salt, unfixed Dyes, copper salts, cationic fixing agents
Reactive	Cotton	Salt, unfixed Dyes, Alkali
Vat	Cotton	Alkali, oxidizing agent, reducing agent
Sulphur	Cotton	Alkali, oxidizing agent, reducing agent, unfixed dyes
Acid	Wool	Unfixed dyes, organic dyes
Disperse	Polyester	Carriers, reducing agent, organic acids
1:2 Metal complex dyes	Wool	Metals, organic acids

India is among one of the major producers of dyes and dyes intermediate from Asian region and meets the requirement of the world at large. There are about 900 dyes and dyes intermediate producing industries in India. The wastewater generated from dye and dye intermediate industries mainly have intense color having various shades of red, blue green, brown and black through the production of different color containing dyes and usually have high level of COD, BOD, acidity, chlorides, sulphates, phenoloic compounds and various heavy metals viz. copper, cadmium, chromium, lead, manganese, mercury, nickel, zinc etc. Dyes, as they are intensively colored, cause special problems in effluent discharge and even small amount is noticeable. The effect is aesthetically more displeasing rather than hazardous, and can prevent sunlight penetration decreasing photosynthetic activity in aquatic environment. **Tariq A. et al.,(2008).**

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Dye & Their Intermediates

The textile dyes and dye intermediates with high aromaticity and low biodegradability have emerged as major environmental pollutants **Arslan et al., (2000)** and nearly 10-15% of the dye is lost in the dyeing process and is released in the wastewater which is an important source of environmental contamination.

Considerable amount of water is used for dyeing and finishing of fabrics in the textile industries.

The wastewater from textile mills causes serious impact on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, chemicals which are dark in color leading to turbidity in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. As dyes are designed to be chemically and photolytically stable, they are highly persistent in natural environments. The improper handling of hazardous chemicals in textile water also has some serious impact on the health and safety of workers putting them into the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and respiratory problems.

2.1 Dye classification

All aromatic compounds absorb electromagnetic energy but only those that absorb light with wavelengths in the visible range (~350-700 nm) are colored. Dyes contain chromophores, delocalized electron systems with conjugated double bonds, and auxochromes, electron-withdrawing or electron-donating substituents that cause or intensify the color of the chromophore by altering the overall energy of the electron system. Usual chromophores are -C=C-, -C=N-, -C=O, -N=N-, -NO2 and quinoid rings, while the auxochromes are -NH3, -COOH, -SO3H and –OH groups. Based on chemical structure or chromophore, 20-30 different groups of dyes can be discerned. Each different dye is given a C.I. (Color Index) generic name determined by its application characteristics and its color. The Color Index discerns different application classes which are as follows **Abrahart, (1997).**

2.1.1 Acid dyes

The largest class of dyes in the Color index is Acid dyes. Acid dyes are anionic compounds that find their main application in dyeing nitrogen-containing fabrics like wool, polyamide, silk and modified acryl. They bind to the cationic NH4+ ions of those fibres. Most acid dyes are azo, anthraquinone or triarylmethane, azine, xanthene, nitro and nitroso compounds. Rather than the presence of acid groups (sulphonate, carboxyl) in the molecular structure of these dyes, the term 'acid' refers to the pH of the dyebaths.

2.1.2 Reactive dyes

Reactive dyes are dyes with reactive groups that are capable of forming a covalent bond between a carbon atom of dye molecule and OH-, NH-, or SH- groups in fibres (cotton, wool, silk, nylon). The reactive group is often a heterocyclic aromatic ring substituted with a chloride or fluoride atom, e.g. dichlorotriazine. Another common reactive group is vinyl sulphone. Most (~80%) reactive dyes are azo or metal complex azo compounds but also anthraquinone and phthalocyanine reactive dyes are applied, especially for green and blue color. In the Color Index, the reactive dyes form the second largest dye class. During dyeing with reactive dyes **(Fig. 2.1)**, hydrolysis (i.e. inactivation) of the reactive groups is an undesired side reaction that lowers the degree of fixation. Salt and ureum (up to 60 and 200 g L-1 respectively) is added during the dyeing process to increase the degree of fixation.

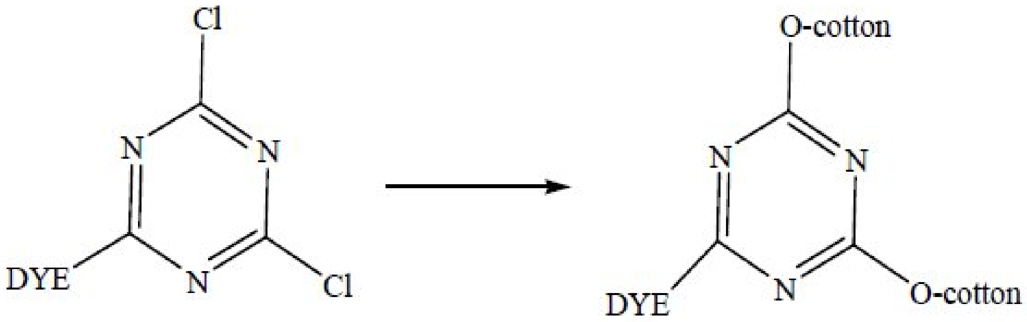


Fig. 2.1 Principle of cotton dyeing with a triazyl reactive dye (Kaur Sumandeep PhD. Thesis,(2008)

The reactive dyes are commercially available important class of textile dyes for which losses through processing operations are significant and the treatment is problematic. It is estimated that 10 to 50% of the dye will not react with the fabric and remain hydrolyzed or unfixed form in the water phase. The problem of colored effluents is therefore mainly due to the use of reactive dyes.

2.1.3 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 i.e. 1:1 and 1:2 metal complex dyes. Metal complex dyes are usually azo compounds.

2.1.4 Direct dyes

Direct dyes are relatively large molecules with high affinity for cellulose fibers. Vander Wall 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. In the Color Index, the direct dyes form the second largest dye class with respect to the amount of different dyes.

2.1.5 Basic dyes

Basic dyes are cationic compounds that are used for dyeing acid-group containing fibers, usually synthetic fibers like modified polyacryl. They bind to the acid groups of the fibers. Most basic dyes are diarylmethane, triarylmethane, anthraquinone or azo compounds.

2.1.6 Mordant dyes

Mordant dyes are fixed to the fabric by the addition of a mordant, a chemical that combines with the dye and the fiber. Though mordant dyeing is probably one of the oldest ways of dyeing, the use of mordant dyes is gradually decreasing. They are used with wool, leather, silk, paper and modified cellulose fibers. Most mordant dyes are azo, oxazine or triarylmethane compounds. The mordants are usually dichromates or chromium complexes.

2.1.7 Disperse dyes

Disperse dyes are scarcely soluble dyes that penetrate synthetic fibers (cellulose acetate, polyester, polyamide, acryl, etc.). This diffusion requires swelling of the fiber, either due to high temperatures (>120 °C) or with the help of chemical softeners. Dyeing takes place in dyebaths with fine disperse solutions of these dyes. Disperse dyes form the third largest group of dyes in the Color Index. They are usually small azo or nitro compounds (yellow to red), anthraquinones (blue and green) or metal complex azo compounds (all colors).

2.1.8 Pigment dyes

Pigment dyes (i.e. organic pigments) represent a small fraction of widely applied group of colorants. 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.

2.1.9 Vat dyes

Vat dyes are water-insoluble dyes 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.

2.1.10 Anionic dyes and ingrain dyes

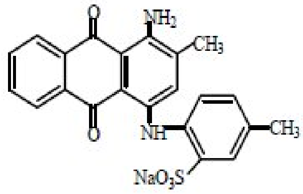
Anionic dyes and Ingrain dyes (naphthol dyes) are the insoluble products of a reaction between a coupling component usually naphthols, phenols or acetoacetylamides and a diazotized aromatic amine. This reaction is carried out on the fibre. All naphthol dyes are azo compounds.

2.1.11 Sulphur dyes

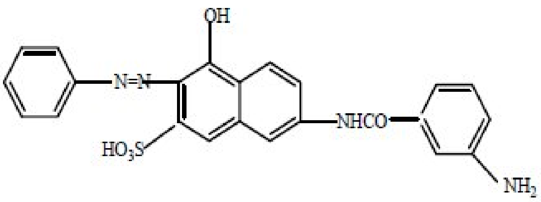
Sulphur dyes are complex polymeric aromatics with heterocyclic S-containing rings. Though representing about 15% of the global dye production, sulphur dyes are not so much used in Western Europe. Dyeing with sulphur dyes involves reduction and oxidation, comparable to vat dyeing. They are mainly used for dyeing cellulose fibers.

2.1.12 Solvent dyes

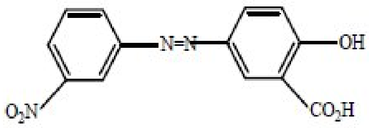
Solvent dyes (lysochromes) are non-ionic dyes that are used for dyeing substrates in which they can dissolve, e.g. plastics, varnish, ink, waxes and fats. They are not often used for textile-processing but their use is increasing. Most solvent dyes are diazo compounds that underwent some molecular rearrangement. Also triarylmethane, anthraquinone and phthalocyanine solvent dyes are applied. **Fig. -2.2** show structures of various dyes.



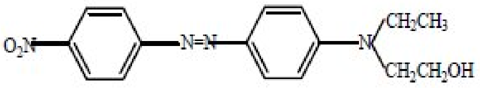
Acid Blue 47



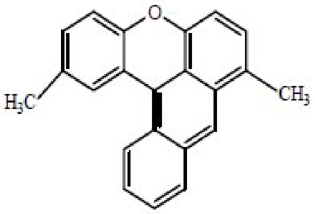
Direct Red 118



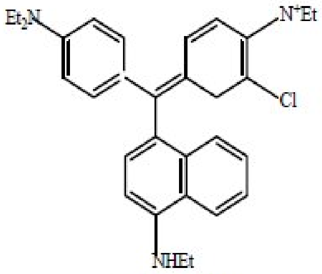
Mordant Yellow 1



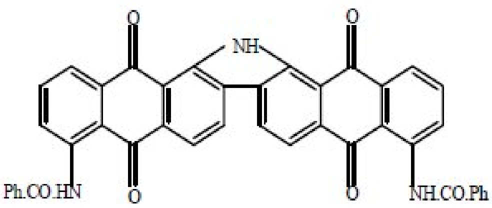
Disperse Red 1



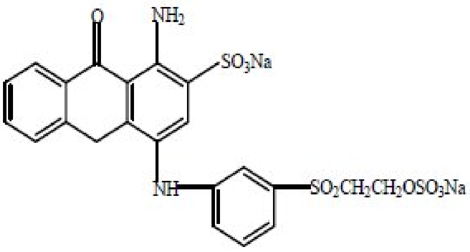
Solvent Green 4



Basic Blue 7



Vat Orange 15



Reactive Blue 19

Fig. 2.2 Molecular Structure of few Organic Dyes (PhD. Thesis of Kaur Sumandeep(2008)

2.2 Methods for removal of dyes and other organic compounds from wastewater:

Various physical, chemical and biological pre-treatment and post-treatment techniques have been developed over the last two decades to remove color from dye contaminated wastewaters in order to cost effectively meet environmental regulatory requirements. Chemical and biological treatments have been conventionally followed till now but these treatment methods have their own disadvantages. The aerobic treatment process is associated with production and disposal of large amounts of biological sludge, while wastewater treated by anaerobic treatment method does not bring down the pollution parameters to the satisfactory level and activated charcoal adsorption and air stripping methods simply transfer the pollutants from one medium to another. They either transfer it to the atmosphere, which causes air pollution, or to a solid which is often disposed off in landfills or must be treated in an energy-intensive regeneration process. Merely transferring toxic materials from one medium to another is not a long term solution to the problem of hazardous waste loading on the environment. The recent developments in water decontamination processes are concerned with the oxidation of these bio-recalcitrant organic compounds. These methods rely on the formation of highly reactive chemical species that degrade more number of recalcitrant molecules into biodegradable compounds and are called advanced oxidation processes (AOP's).

CHAPTER-3

Treatment Technology (Advanced v/s Emerging)

Advanced oxidation processes (AOP's), uniting together ozone and high output ultraviolet technologies, in conjunction with hydrogen peroxide and catalyst are successfully used to decompose many toxic and bio-resistant organic pollutants in aqueous solution to acceptable levels, without producing additional hazardous by-products or sludge which require further handling. Advanced oxidation processes involve the generation of hydroxyl (˙OH) radicals which oxidize the pollutants. After fluorine, the hydroxyl radical is the second strongest known oxidant having an oxidation potential of 2.8 eV. It is able to oxidize and mineralize almost every organic molecule, yielding CO_2 and inorganic ions as shown in Eq.3.1 and 3.2.

$$\bullet OH + RH \rightarrow R\bullet + H_2O \quad \text{(Eq. 3.1)}$$

$$R\bullet + O_2 \rightarrow RO_2\bullet \rightarrow \text{Products and } CO_2 \quad \text{(Eq. 3.2)}$$

Different combinations of homogenous and heterogeneous methods which involve the generation of free radicals are, (i) photochemical irradiation with ultraviolet light (coupled with powerful oxidizing agents like ozone, hydrogen peroxide and /or a semiconductor), (ii) Fenton and Photo-Fenton catalytic processes (iii) Electron Beam Irradiation technique and (iv) Sonolysis.

All these processes use UV range for degradation. The UV spectrum is arbitrarily divided into three bands: UV-A (315 to 400 nm), UV-B (280 to 315nm) and UV-C (100 to 280 nm). Of these bands UV-A and UV-C are generally used in environmental applications. UV-A radiations are referred to as long wavelength radiations or black light and UV-C are referred to as short wave radiations.

Advanced oxidation processes can be broadly classified into the following groups:

1. Homogeneous photocatalysis
2. Heterogeneous photocatalysis

3.1 Homogeneous photocatalysis

The applications of homogeneous photo degradation (single-phase system) to treat contaminated water, involves the use of an oxidant to generate radicals, which attack the organic pollutants to initiate oxidation. The major oxidants used are:

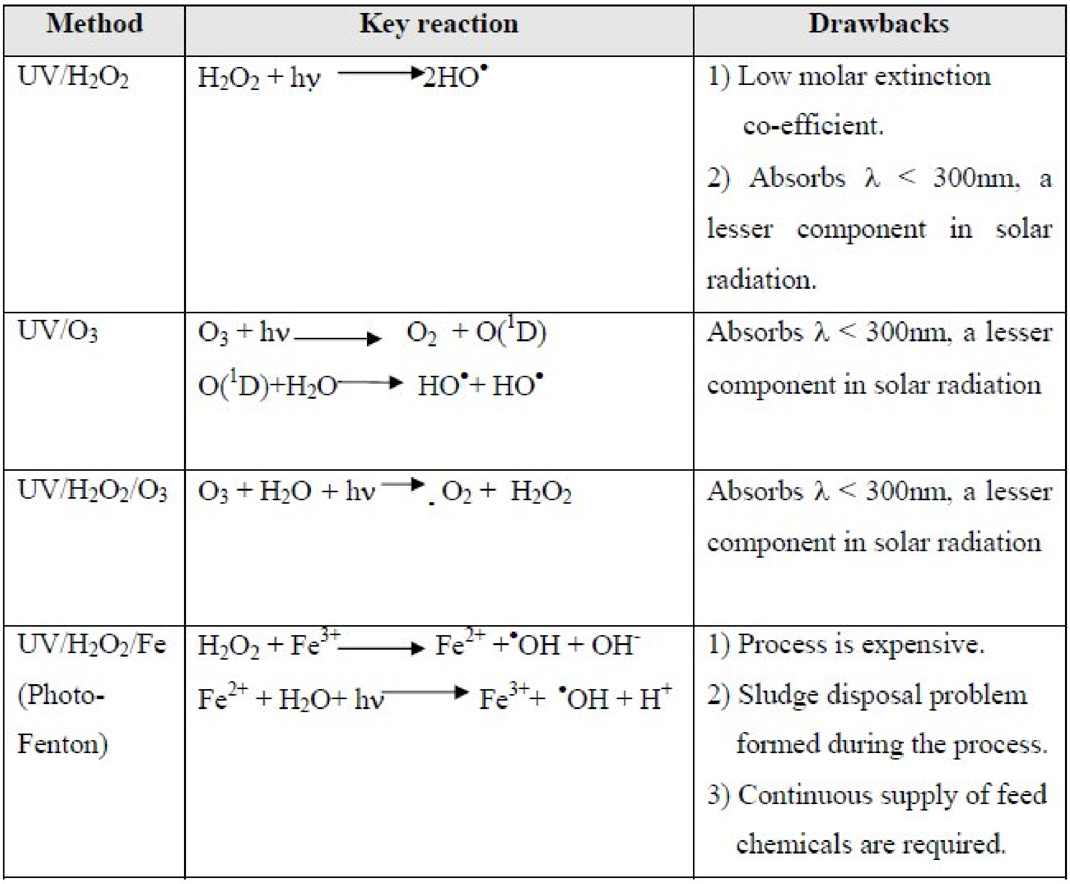
Hydrogen peroxide (UV /H_2O_2)

Ozone (UV /O_3)

Hydrogen peroxide and Ozone (UV /O_3/ H_2O_2)

Photo-Fenton system (Fe^{+3} / H_2O_2)

Table 3.1 Hydroxyl radical generations in different AOP's (Homogeneous)



Method	Key reaction	Drawbacks
UV/H_2O_2	$H_2O_2 + h\nu \longrightarrow 2HO^{\bullet}$	1) Low molar extinction co-efficient. 2) Absorbs λ < 300nm, a lesser component in solar radiation.
UV/O_3	$O_3 + h\nu \longrightarrow O_2 + O(^1D)$ $O(^1D)+H_2O \longrightarrow HO^{\bullet} + HO^{\bullet}$	Absorbs λ < 300nm, a lesser component in solar radiation
UV/H_2O_2/O_3	$O_3 + H_2O + h\nu \longrightarrow O_2 + H_2O_2$	Absorbs λ < 300nm, a lesser component in solar radiation
UV/H_2O_2/Fe (Photo-Fenton)	$H_2O_2 + Fe^{3+} \longrightarrow Fe^{2+} + {}^{\bullet}OH + OH^-$ $Fe^{2+} + H_2O + h\nu \longrightarrow Fe^{3+} + {}^{\bullet}OH + H^+$	1) Process is expensive. 2) Sludge disposal problem formed during the process. 3) Continuous supply of feed chemicals are required.

Many of the AOP's listed in **T-3.1** utilize the chemical, hydrogen peroxide. The oxidizing strength of hydrogen peroxide alone is relatively weak, but the addition of UV light enhances the rate and strength of oxidation through production of increased amounts of hydroxyl radicals. Hydrogen peroxide may also be used to enhance other AOP's if added in low concentrations, as the molecule easily splits into two hydroxyl radicals.

3.2 Heterogeneous photocatalysis

Heterogeneous Photocatalytic process consists of utilizing the near UV radiation to photo-excite a semiconductor catalyst in the presence of oxygen. Under these circumstances oxidizing species, either bound hydroxyl radicals or free holes, are generated as shown in **Fig. 3.1.** Using photocatalysis, organic pollutants can be completely mineralized reacting with the oxidizers to form CO_2, water and dilute concentration of simple mineral acids. The process is heterogeneous because there are two active phases, solid and liquid. This process can also be carried out utilizing the near part of solar spectrum ($\lambda < 380$nm) what transforms it into a good option to be used **Malato et al., (2002)**

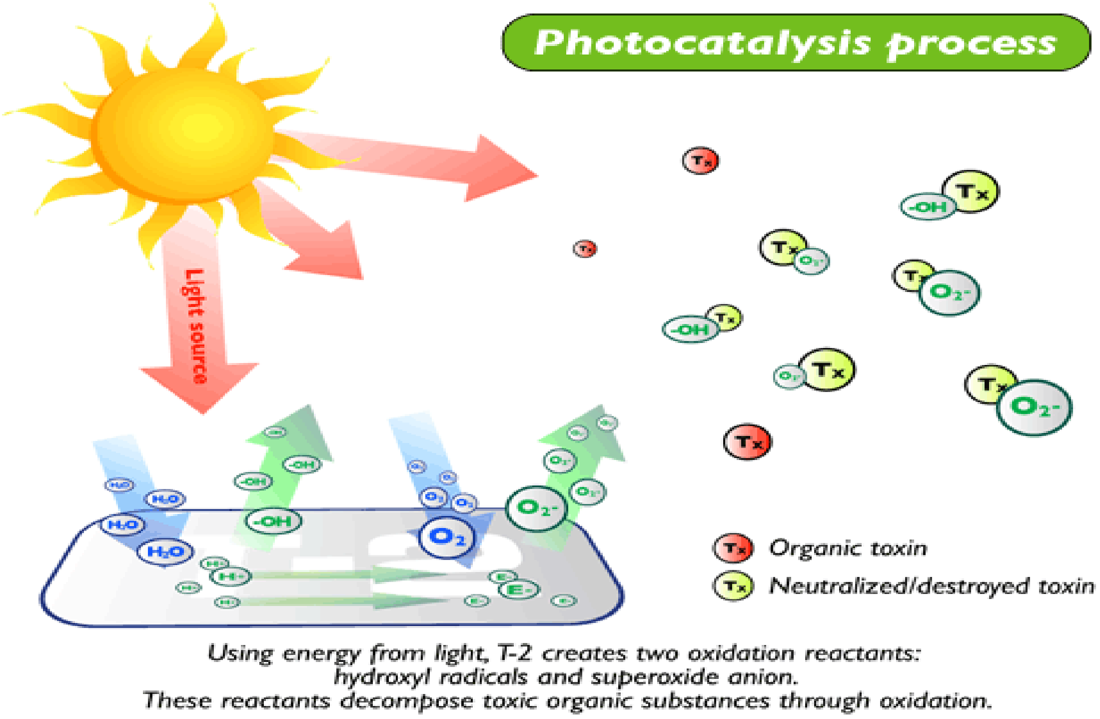


Fig-3.1 Schematic representation of the processes occurring in and on semiconductor particles during the Photocatalytic mineralization of organic molecules by oxygen.

The semiconductor may be in the form of a powder suspended in the water or fixed on a support. The most active Photocatalyst for this application is the anatase form of TiO_2 because of its high stability, good performance and low cost **Andreozzi et al., (1999)**. The primary Photocatalytic mechanism is believed to proceed as follows:

$$
\begin{aligned}
TiO_2 + h\nu &\longrightarrow e^-_{CB} + h^+_{VB} \\
h^+_{VB} + H_2O &\longrightarrow {}^{\bullet}OH + H^+ \\
e^-_{CB} + O_2 &\longrightarrow O_2^{\bullet -} \\
2O_2^{-\bullet} + 2H_2O &\longrightarrow H_2O_2 + 2OH^- + O_2 \\
H_2O_2 + e^-_{CB} &\longrightarrow OH^- + {}^{\bullet}OH
\end{aligned}
$$

In solids, the electrons occupy energy bands as a consequence of the extended bonding network. In a semiconductor, the highest occupied and lowest unoccupied energy bands are separated by a band gap, a region devoid of energy levels. Activation of semiconductor Photocatalyst is achieved through the absorption of a photon of ultraviolet band gap energy which results in promotion of an electron (e^{-1}) from the valence band (VB) into the conduction band (CB) with the generation of hole in the valence band as shown in the **Fig. 3.1.** The resulting hole is an oxidizing agent and the electron is a reducing agent. In the generally accepted mechanism for the Photocatalytic process, the hole can react with water to generate the hydroxyl radical and the electron can reduce molecular oxygen, hydrogen peroxide or some other oxidizing agent in the solution. This creates the reactive radicals responsible for the removal of hazardous components from the water.

TiO_2/ UV process is known to have many advantages:

- A large number of organic compounds dissolved or dispersed in water can be completely mineralized.
- The rate of reaction is relatively high if large surface area of the catalyst can be used.
- TiO_2 is available at a relatively modest price and can be recycled on a technical scale.

- UV lamps emitting in the spectral region required to initiate the Photocatalytic oxidation are well known and are produced in various sizes.
- Absorption cross-section of TiO_2 can be improved by its surface modifications, e.g. by transition metal ion doping.

A common problem of all the AOP's is their high cost, mainly due to high demand of electrical energy for ozonizers and/or UV lamps. Application of solar irradiation to the photochemical process reduces cost but it is possible only for catalyzed homogeneous and heterogeneous reactions using iron ions and titanium dioxide respectively. These catalysts absorb at wavelengths of the solar spectrum while ozone and hydrogen peroxide do not absorb above 300 nm, which is the most important condition for the use of sunlight.

3.3 Ultrasound and Photocatalysis

Furthermore, an integrated approach of ultrasound and photocatalysis of wastewater is found to be advantageous but has not received much attention until recently. When sonication is added to the Photocatalytic system, significant changes are produced. The high energy chemistry generated by ultrasound waves in liquid medium promotes the oxidative destruction of target contaminants. Ultrasonic waves with frequency > 16 KHz are high-energy waves, which are longitudinal and on passing through a liquid medium produce its effects via cavitational bubbles. Formation and behavior of the bubble of cavitations upon the propagation of the acoustic wave in the liquid constitute the essential events that induce the sonochemical effects. The transient cavities in the bubbles, produced using ultrasonic irradiation, exist briefly expanding to at least double their initial size before violently collapsing into smaller bubbles. The collapse of these bubbles can yield local pressures of hundreds of atmospheres and temperatures of thousands of degrees resulting in solute thermolysis and the formation of hydroxyl radical and H_2O_2 by sonolysis of water. Dramatic enhancements in reactivity and rates of chemical processes can arise from the process of cavitational collapse. In this case the transformation of the organic pollutants occurs through reactions with hydroxyl radicals generated from the collapsing bubble. Further, Concentration of the organic material decreases as hydroxylation progresses

$$H_2O \longrightarrow H^{\bullet} + HO^{\bullet}$$
$$O_2 \longrightarrow 2O^{\bullet}$$
$$O^{\bullet} + H_2O \longrightarrow 2OH^{\bullet}$$

Cavitation is the formation, growth and collapse of bubbles in the liquid. **(Ravazzini A. et al, 2002)**. Cavitation occurs whenever a new surface, or cavity, is created within a liquid. A cavity is any bounded volume, whether empty or containing gas or vapor, with at least part of the boundary being liquid. The collapse of the bubbles induces localized supercritical conditions: high temperature, high pressure, electrical discharges, and plasma effects. It has been reported that the gaseous contents of a collapsing cavity reach temperatures of 5500 ^{o}C, and the liquid immediately surrounding the cavity reaches 2100 ^{o}C. The pressure was estimated to be 500 atmospheres, resulting in the formation of transient supercritical water. Thus, cavitation serves as a means of concentrating the diffuse energy of sound into micro reactors. The intensity of cavity implosion, and hence the nature of the reaction, are controlled by such factors as acoustic frequency, acoustic intensity, bulk temperature, static pressure, and the choice of liquid or dissolved gas. The consequences of these extreme conditions are the cleavage of dissolved oxygen molecules and water molecules (into •H atoms and •OH radicals). From the reactions of these entities (•O, •H, •OH) with each other and with H_2O and O_2 during the quick cooling phase, $HO_2{}^{\bullet}$ radicals and H_2O_2 are formed. In this molecular environment, organic compounds are decomposed and inorganic compounds are oxidized or reduced. Ultrasound has been widely known to induce radical reactions. This useful property has found its applications in sonolysis of water, sonolytic degradation of aqueous organic pollutants, and sonochemical synthesis of chemicals. The underlying phenomena include cavitation, microstreaming, and localized supercritical conditions. These phenomena lead to sonolytic splitting of water as well as pyrolysis of a vaporized molecule. **(Yi-Chuan Chen, 2002)**

Figure 3.2 shows that liquids irradiated with ultrasound can produce bubbles.

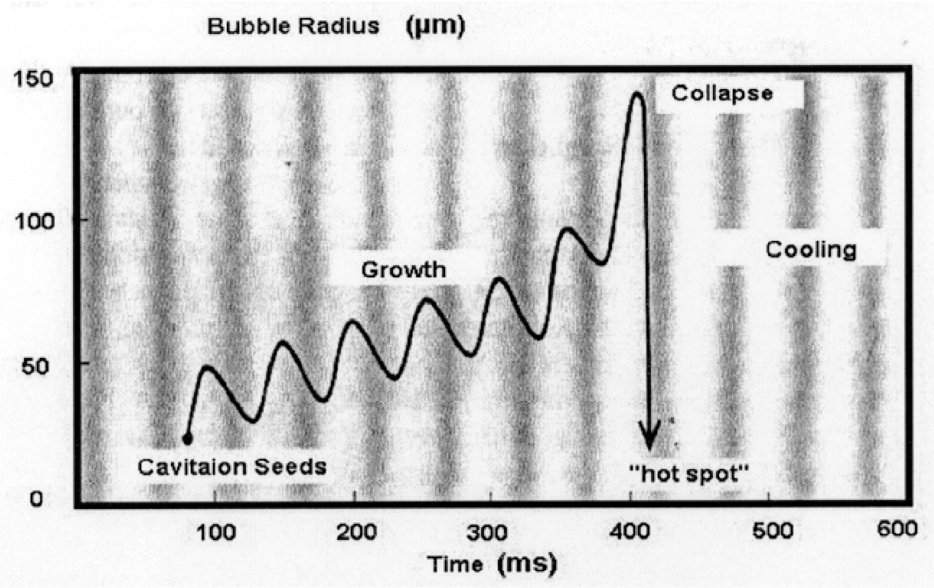


Figure -3.2 Cavitation and Implosion phenomenon (Dehghani M.H. and Changani, F.,(2006)

Thus, one generates a short-lived, localized hot spot in an otherwise cold liquid. It has a temperature of roughly 5000° C (9,000° F), a pressure of about 1000 atmospheres, a lifetime considerably less than a microsecond, and heating and cooling rates above 10 billion° C per second.**(Dehghani M.H. and Changani F., (2006).**

Thus, sonochemical effect augments the photochemical process on simultaneous application to Photocatalytic degradation with dramatic rate enhancement and is effective for degradation of organic pollutants present in the wastewater.

3.4 TiO_2 as a Catalyst

Research over the last three decades has not only confirmed the capability of sunlight for detoxification and disinfection but also accelerated the natural process by the use of catalysts. For oxidation reactions to occur the valence band (VB) must have a higher oxidation potential than the material under consideration. The redox potential of the valence band and the conductance band for different semiconductors varies between +4.0 and -1.5 volts versus normal hydrogen electrode (NHE). Therefore, by careful selection of the semiconductor Photocatalyst, a wide range of species can be treated *via* these AOP processes. Metal oxides and sulphides represent a large class of semiconductor materials suitable for Photocatalytic purposes. **T-3.2** lists some of the selected semiconductor materials, which have been used for Photocatalytic reactions, together with the VB and

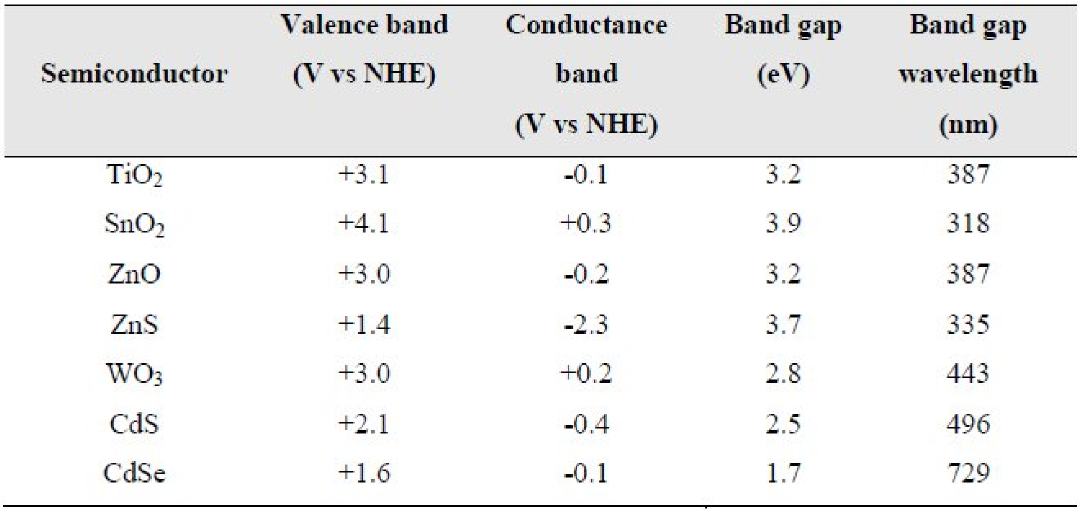
CB potentials, the band gap energy and wavelength required to activate the catalyst that produce this gap, the radiation must be of an □equal or lower wavelength than that calculated by that Planck's equation (Eq.3.4.1).

$$\lambda = hc/ E_{bg} \quad \text{(Eq. 3.4.1)}$$

Where E_{bg} is the semiconductor band-gap energy, *h* is the Planck's constant and *c* is the speed of light.

Among the listed semiconductors, TiO_2 has proven to be the most suitable for widespread environmental applications. ZnO also seems to be a suitable Photocatalyst but it dissolves in acidic solutions and therefore, cannot be used for technical applications. Other semiconductor particles (e.g., CdS) absorb larger fractions of the solar spectrum than TiO_2 and can form chemically activated surface-bond intermediates, but unfortunately, such catalysts are degraded during the repeated catalytic cycles usually involved in heterogeneous photocatalysis.

Table 3.2 Band positions of some common semiconductor photocatalysis in aqueous solution at pH=1



Semiconductor	Valence band (V vs NHE)	Conductance band (V vs NHE)	Band gap (eV)	Band gap wavelength (nm)
TiO_2	+3.1	-0.1	3.2	387
SnO_2	+4.1	+0.3	3.9	318
ZnO	+3.0	-0.2	3.2	387
ZnS	+1.4	-2.3	3.7	335
WO_3	+3.0	+0.2	2.8	443
CdS	+2.1	-0.4	2.5	496
CdSe	+1.6	-0.1	1.7	729

Titanium dioxide is widely used as white paint pigment, sun blocking material, cosmetic, or as builder in vitamin tablets, among many other uses. It is biologically and chemically inert; it is stable to photo and chemical corrosion, and is inexpensive. This semiconductor exists in three crystalline forms: anatase, rutile, and brookite. Anatase and rutile are the most common forms and the former is the most effective in wastewater treatment. The band gap energies are approximately 3.2 eV for anatase and 3.0 eV for rutile but the driving force for oxidative processes are similar. Anatase is thermodynamically less stable than rutile, but its formation is kinetically favored at lower temperature (<600oC), which could explain its higher surface area and its higher surface density of active sites for adsorption and catalysis. Furthermore, TiO_2 is of special interest since it can use natural (solar) UV radiation. This is because TiO_2 has an appropriate energetic separation between its valence and conduction bands, which can be surpassed by the energy of a solar photon as shown by **Fig-3.3**

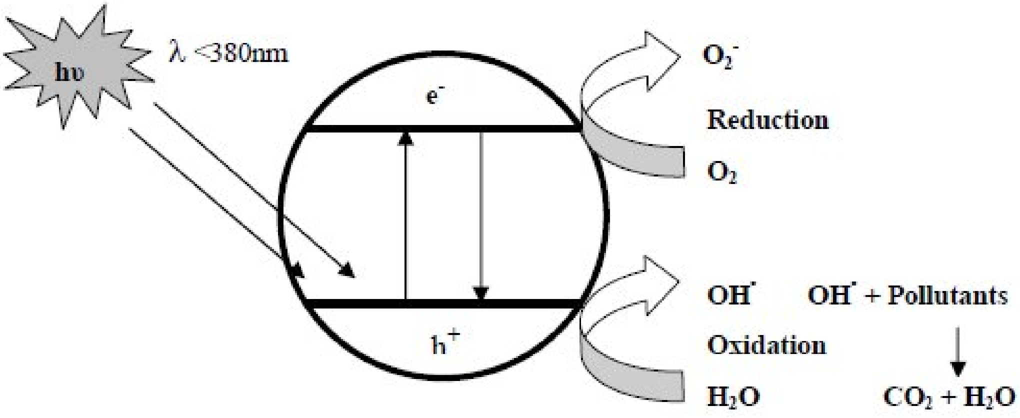


Fig- 3.3 showing the working principle of TiO_2 catalyst.

One of the disadvantages of the particulate excitation of the semiconductors is the high degree of recombination between the photo-generated charge carriers. As a result of this electron-hole recombination, the efficiency of the semiconductors decreases thereby, decreasing the quantum yield of the redox processes.

The other limitation of TiO_2 is that it utilizes only about 4-6% of the solar energy reaching the earth's surface which is in the UV region. This limitation is overcome by its modification. It has been modified by doping of metal ions and photosensitization by various colored organic and inorganic compounds, in order to extend the photo-response of large bandgap semiconductors into the visible region to use them for the degradation of colored organic contaminants and other organic pollutants. The metal ions added into polycrystalline TiO_2 or photo-deposited metals increase the absorption. Therefore, research on catalyst improvement has been done on the following points:

1. Physical and chemical modification of TiO_2 to improve the catalyst performance.

2. Dye sensitization to increase the useful wavelength range of the solar radiation.

3.4.1 TiO_2 as better photo catalyst

TiO2 is unexceptionally most suitable catalyst, having following unique properties:-

1. Inert (chemically and biologically).
2. Stable to corrosion.
3. Better from safety point of view.
4. Having low cost, limits the choice of convenient alternatives.
5. TiO_2 is of special interest as it can use natural UV.
6. An appropriate gap b/w valence and conduction band.
7. Band gap energy = 3.2 eV (VB energy = 3.1 eV & CB energy = -0.1 eV)
8. Absorbs in near UV light (<387 nm) (i.e., natural (solar) energy)

3.5 Solar Collectors For The Photocatalytic Applications

3.5.1Concentrating collectors

Contrary to solar thermal processes, which collect large amounts of photons at any wavelength to reach a specific temperature range, solar photochemical processes use only high-energy short-wavelength photons. The original solar photo reactor designs for photochemical applications were based on line-focusing parabolic-trough concentrators (PTCs). The parabolic-trough collector consists of a structure that supports a reflective concentrating parabolic surface **(Figure 3.4)**. This structure has one or two motors controlled by a solar tracking system on one or two axes respectively that keep the collector aperture plane perpendicular to the solar rays. In this situation, all the solar radiation available on the aperture plane is reflected and concentrated on the absorber tube that is located at the geometric focal line of the parabolic trough.

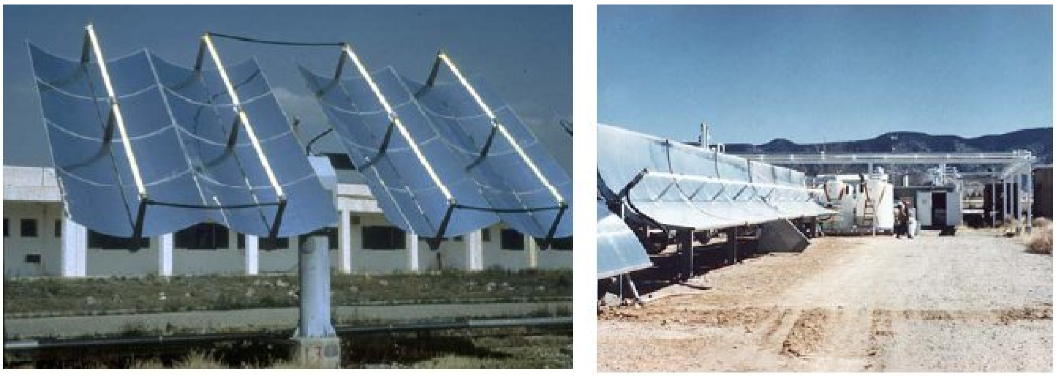


Figure 3.4. Parabolic-troughs with two-axis solar tracking (left) and single-axis solar tracking (right).

The solar radiation that reaches ground level without being absorbed or scattered, is called direct radiation, while radiation which has been dispersed before reaching the ground is called diffuse radiation, and the sum of both is called global radiation.

3.5.2 Non-concentrating collectors

One-sun (non-concentrating) collectors are, in principle, cheaper than PTCs, as they have no moving parts or solar tracking devices . They do not concentrate radiation, so efficiency is not reduced by factors associated with concentration and solar tracking.. Non-concentrating collector support structures are easier and cheaper to install as well, and the surface required for their installation is smaller, because, since they are stationary, there is no shading. They are able to make use of the diffuse as well as the direct solar UV-A **(Fig. 3.5).**

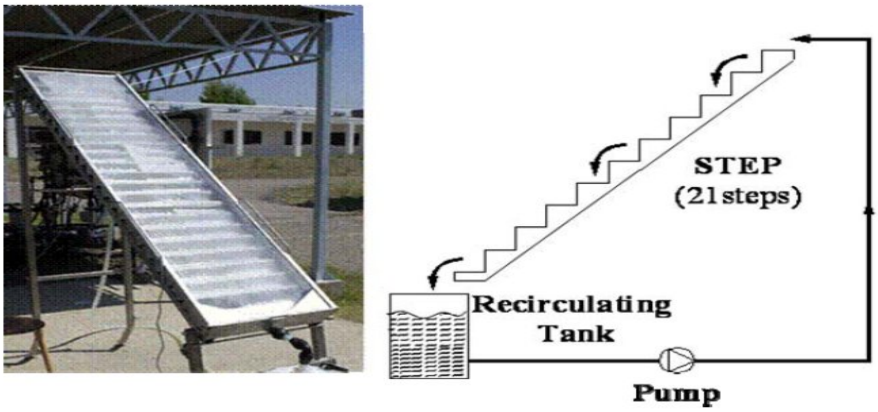


Figure 3.5. Non-concentrating solar collector

3.5.3 Compound parabolic concentrator (CPC)

Compound Parabolic Concentrators (CPCs), a type of low-concentration collector used in thermal applications, is an option of interest. Between parabolic concentrators and flat stationary systems, they combine the characteristics of both. While they concentrate solar radiation, they retain the stationary and diffuse-radiation collection properties of flat plate collectors. They have therefore been chosen as a good option for solar photochemical applications by various research groups.

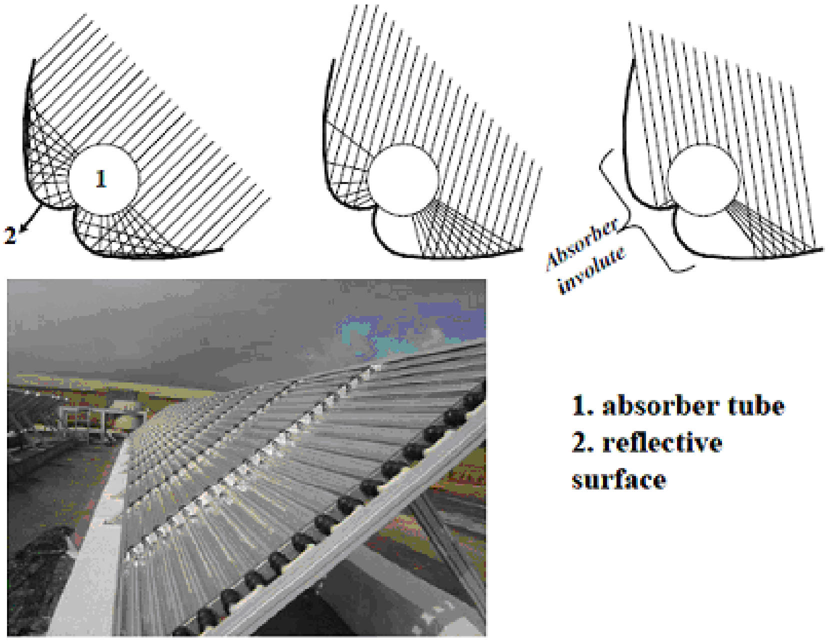


Fig.-3.6schematic drawing and photograph of a compound paraboilic concentrator.

CHAPTER-4

Literature Review

4.1 AOP's- Homogeneous and Heterogeneous

In the last 15 years or so, a rather fast evolution of research activities devoted to environment protection has been recorded as a consequence of the special attention paid to the environment by social, political and legislative international authorities, leading in some cases to the delivery of very severe regulations **Legrini et al., (1993).**

Gogate and Pandit (2004b) in their review aimed at highlighting different processes (belonging to the class of advanced oxidation processes) and the basics of these processes including the optimum parameters and design aspects with a complete overview of the various applications to wastewater treatment in recent years. Destructive oxidation of organic compounds by a variety of homogenous and heterogeneous AOP's has been done effectively thereby increasing the biodegradability of the pollutants **Balchioglu et al., (2003).**

The use of AOP's for wastewater treatment has been studied extensively **Andreozzi et al., (1999)** and it has been concluded that UV radiation by lamps is expensive. Therefore, research is presently focused more and more on the two AOP's i.e. homogeneous catalysis with photo-Fenton and heterogeneous catalysis with UV/TiO_2, with and without addition of oxidants, which can both be powered by solar irradiation i.e. light of wavelength longer than 300 nm**. Goswami, (1997).** The principles and the advantages of several typical homogeneous and heterogeneous AOP's system were summarized by **Wu (1999a).**

Among the homogeneous oxidation processes, in a recent review by **Neyens and Baeyens (2003)** they have emphasized the oxidation processes utilizing activation of H_2O_2 by iron salts, classically referred to as Fenton's reagent, known to be very effective in the destruction of many hazardous organic pollutants in water. Few researchers **Modirshahla et al.,(2007); Liu et al., (2007)** have studied the degradation and decolorization of few organic dyes by Fenton and photo-Fenton processes by varying the various parameters like catalyst loading, initial substrate concentration and pH. The photo-Fenton process proved to be the most efficient and occurs at a much higher oxidation rate than Fenton process. Studies have been done on treatment of wastewater using UV/H_2O_2, UV/O_3 and photo assisted Fenton degradation techniques **Shu, (2006)** investigated the decolorization of Malachite Oxalate Green (MG) dye using UV radiation in the presence of H_2O_2 in a batch photo reactor at different light intensities. The semi-logarithmic graphs of the concentration of MG versus time were linear, suggesting pseudo-first order reaction. **Shu and Chang (2005)** studied the decolorization of six azo dyes by means of O_3, UV/O_3 and UV/H_2O_2 processes. He reported that dyes with di-azo links were more difficult to decolorize than mono-azo dyes and the results showed that UV/H_2O_2 used maximum energy which was 5-11 times that of UV/O3 process, and 265-520 times more than that of the ozonation process. **Lafi and Al-Qodah (2006)** successfully combined advanced oxidation processes (O_3/UV) with biological treatment processes to remove both dyes and the COD load from aqueous solutions.

Photocatalysis is a rapidly expanding technology for wastewater treatment. The Photocatalytic detoxification has been discussed as an alternative method for cleaning up of polluted water in the scientific literature since 1976 **Carey et al., (1976).** In his review **Bhatkhande et al., (2002)** has discussed the applications of Photocatalytic degradation and chemical effects of various variables on the rate of degradation of different pollutants. A growing interest in the purification of water by semiconductor photocatalysis especially in the removal of toxic organic pollutants is evident by the ever-increasing number of studies in this area **Inel and Okte,(1996); Mathews, (1988).**

Among heterogeneous AOP's TiO_2 – mediated Photocatalytic oxidation appears to be a promising alternative. Various investigators **Muruganandham and Swaminathan, (2004b)** have demonstrated that solar radiation is a useful UV source for driving Photocatalytic processes. There are number of general reviews which cover aspects of the TiO2 Photocatalytic destruction of organic compounds in water **Fox and Dulay, (1993); .** In their review, **Fujishima et al., (2000)** have discussed progress in the area of TiO_2 photocatalysis mainly for Photocatalytic air purification, sterilization and cancer therapy, together with some fundamental aspects and have presented a novel photo-induced super hydrophilic phenomenon involving TiO2 and its applications. **Herrmann (1999)** has described the basic fundamental principles as well as the influence of the main parameters like mass of the catalyst, wavelength, initial concentration, temperature and radiant flux governing the kinetics of heterogeneous photocatalysis in wastewater treatment.

Mills and Lee (2002b) reviewed the major commercial applications of semiconductor photochemistry. The basic principles behind the different applications are discussed, including the use of semiconductor photochemistry to photo-mineralize organics, photo-sterilize and photo-demist. The range of companies, and their products, which utilize semiconductor photochemistry are examined and typical examples are listed. They have done an analysis of the geographical distribution of current commercial activity in this area. **Blake (2001)** published a bibliography listing 1200 publications and patents on Photocatalytic processes. He compiled a list of organic and inorganic compounds with references which shows over 300 compounds including about 100 on the US EPA priority list that can be treated by the Photocatalytic process. **Blake (1994)** also listed 42 review articles that cover various aspects of Photocatalytic chemistry and technology. In an article entitled “Solar Photocatalytic detoxification” published in Advances in Solar Energy; **Blake et al., (1992)** have reviewed in detail the fundamental chemistry of solar Photocatalytic detoxification and the preliminaries of engineering system development. The degradation of many different model compounds has been studied and it has been clearly shown that most of the organochlorine compounds as well as many pesticides, herbicides, surfactants and colorings present in water can be completely oxidized into non-toxic products like carbon dioxide, hydrochloric acid and water **Mohamed,(2002); Morsi et al., (2000).**

In 1998, the US EPA (Environmental Protecting Agency) made an inventory of more than 800 molecules that can be degraded by this process as shown in **T- 4.1 Robert and Malato,(2002).**

Table 4.1 Main ranges of pollutants

Source	Products
Chlorinated solvents	Chloroform, carbon tetrachloride, Trichloroethylene, chlorobenzene
Non-chlorinated solvents	Acetone, acetonitrile, benzene, cyclohexane, formaldehyde, phenol, methylbenzene
Insecticides	Aldrin, dichlorvos, lindane, parathion, Monocrotophos
Pesticides	Atrazine, monuron
Dyes	Acid Orange 7, Green Malachite, Naphthol Blue Black, Reactive Blue 19
Detergent	Octoxynol (triton X-100)

4.2 Degradation of Dyes and Dye Intermediates

4.2.1 Review

Dyes and dye intermediates with high degree of aromaticity and low biodegradability are introduced into the aquatic system resulting in increase of environmental risk. Dye pollutants from the textile industry are an important source of environmental contamination. Several studies of Photocatalytic degradation of dyes have been reported **(Chatterjee and Mahata, 2002)**. Factors influencing the degradation rate of aqueous systems have been studied such as effect of pH, dissolved oxygen contents and the amount of Photocatalyst added **(Schrank et al., 2002)**. There are very few studies related to the use of semiconductors in the photo degradation of photo-stable dyes**.** With the aim of elucidating the potential application of advantageous Photocatalytic processes, the kinetic and mechanistic aspects of dye degradation have been investigated and reported in literature **(Galindo et al., 2002)**. TiO_2-mediated Photocatalytic degradation of various dyes was investigated in aqueous suspensions of titanium dioxide under a variety of conditions by monitoring the change in substrate concentration employing UV spectroscopic analysis and decrease in total organic carbon content as a function of irradiation time **(Saquib and Muneer, 2003). Qaradawi and Salman (2002)** used titanium dioxide (TiO_2) as a Photocatalyst for the detoxification of water containing Methyl Orange (MO), which was used as a model compound using solar radiation as an irradiation source. **Khalil et al., (1999)** investigated photo degradation processes of two azo dyes at TiO_2/H_2O interface under visible and ultraviolet light irradiation with different experimental techniques (absorption and fluorescence spectroscopy as well as total organic carbon analysis).

4.3 Ultrasound and Photocatalysis

Use of ultrasound as a catalyst for water and wastewater treatment and solar detoxification for environmental applications in materials chemistry is reported in literature **(Suslick, 1999). Vajnhandl and Marechal, (2005)** in his paper reviewed some fundamentals of ultrasound, its broad applications and gathered some new research regarding its applications in textile wet processes, with the emphasis on textile dyeing and the discoloration/mineralization of textile wastewaters. **Gogate and Pandit (2005)** in a review reflected the current status of the hydrodynamic cavitation reactors discussing the bubble dynamics analysis and optimum design considerations illustrating the utility of these reactors.

Fly ash samples modified by NaOH solution and sonochemical treatment were tested for the adsorption in aqueous solution of a basic dye, Methylene Blue by **Wang and Zhu (2005a)**. He concluded that sonochemical treatment of fly ash could significantly increase the adsorption capacity depending on the concentration of NaOH and treatment time.

Some studied the sonochemical degradation of dichlorvos in a batch reactor and found that acoustic power and sparge gas are the two factors which greatly affect sonochemical degradation efficiency. **Dukkanci and Gunduz (2006)** studied the effect of ultrasound power, H_2O_2, NaCl, external gases on the degradation of oxalic acid. He observed that H_2O_2 had negative contribution on the degradation of oxalic acid and there was an optimum concentration of NaCl for enhancing the degradation degree of oxalic acid. Further, Shemer and Narkis (2005) concentrated on the kinetics of degradation of trihalomethanes ($CHCl_3$, $CHBrCl_2$, $CHBr_2Cl$, $CHBr_3$ and CHI_3) under ultrasonic frequency of 20 kHz. He found that vapor pressure was the most important parameter affecting the sonodegradation kinetics and efficiency. **Inoue et al., (2006)** studied the degradation of Rhodamine B and Orange II dyestuff solutions using ultrasonic irradiation under different ultrasonic frequencies. He found that decolorization rate increases with the increase in frequency of the ultrasound. **Okitsu et al., (2005)** studied the sonochemical decolorization and decomposition of azo dyes, such as Reactive Red 22 and methyl orange. He concluded that azo dye molecules were mainly decomposed by OH radicals formed from the water sonolysis. **Mahamuni and Pandit (2006)** studied a hybrid technique of ozonation coupled with cavitation for the degradation of phenol. He concluded that this hybrid technology leads to the formation of intermediates that can further be subjected to bio-degradation. **Zhang et al., (2006)** studied the combination of ultrasound and ozone for the decolorization of methyl orange dye .The results showed that the synergistic effect was achieved by combining ozone with ultrasonic irradiation for the decolorization of methyl orange. Further, it was observed that the decolorization rate increased with the increase of ultrasonic power, ozone gas flow rate and gaseous ozone. **Zeng and James (2006)** studied the degradation of pentachlorophenol (PCP) in aqueous solution by audible-frequency sonolytic ozonation. The first-order rate constant of PCP degradation by ozonation with sonication was found to be 15 times faster than that with bubbling ozone alone, while the rate constant with mechanical stirring was only four times faster**. Martins et al., (2006)** in his study aimed at investigating the chemical oxidation of Pararosaniline dye by ozonation and sonolytic processes. Experimental results indicated that ozonation of pararosaniline solution is more efficient than ultrasonic irradiation alone or in combination with O_3.

Gultekin and Ince (2006) reported the laboratory scale degradation of Acid Orange 8 with ultrasound, ozone and both. He concluded that the combined operation of ultrasound and ozone improved the rate of bleaching and UV absorption decay and remarkably enhanced the mineralization of the dye.

Guo et al., (2005) studied the influences of ultrasonic output intensity, solution pH, H2O2 concentration and addition of Fenton reagent on the degradation of 2, 4-Dinitrophenol (DNP) under ultrasonic irradiation. He observed that sono-oxidation treatment in combination with $FeSO_4/H_2O_2$ showed a synergistic effect for DNP degradation. The hybrid effect of the irradiation by light and ultrasonic waves in conjunction with H_2O_2 was first confirmed to achieve the complete mineralization of propyzamide by **Yano et al., (2005)**.

Further combination of ultrasound and photochemistry has been used to degrade an aqueous solution of phenol by **Wu et al., (2001). Harada et al., (2001)** investigated the role of a Photocatalyst in the sonophotocatalytic reaction of water splitting using TiO_2 Photocatalyst. **Naffrechoux et al., (2000)** combined the sonochemical and photochemical action in a 'sonuv' reactor and concluded that there was enhancement in the degradation rate of phenol. **Selli et al., (2005)** studied the kinetics of degradation of methyl tert butyl ether in water employing either sonolysis at 20 kHz or photocatalysis on TiO_2 or simultaneous sonolysis and photocatalysis as degradation techniques and found that rate enhancement under sonophotocatalytic conditions was stirring dependent. **Chen et al., (2002b)** observed the synergistic effect from the ultrasound on the photocatalytic degradation of phenol and chlorophenols in the presence of Hombikat TiO_2 suspensions in a sonophotocatlytic reactor. **Hirano et al., (2005)** subjected the chlorinated organic compounds to pre-sonication followed by photocatalytic treatment. The pre-sonication effect results in the formation of some intermediate products, which are rapidly oxidized to carbon dioxide on further photocatalysis. Decolorization and COD removal from synthetic wastewater containing Reactive Brilliant Orange K-R dye using sonophotocatalytic technology was investigated by **An et al., (2003)**. He concluded that this hybrid technology could efficiently remove the color and reduce COD from the synthetic dye containing wastewater, and that both processes followed pseudo first-order kinetics. **Selli (2002)** in another paper reported that photocatalysis and sonolysis exhibit the synergistic effects in the degradation of Acid Orange 8 in aqueous suspensions, when low ultrasound frequency is used. **Chen et al., (2003)** and studied the mechanistic aspects of the role of 20 kHz ultrasonication in photocatalytic oxidation of dimethyl methylphosphate in a batch reactor. He concluded, the increase or the rate of DMMP photocatalytic mineralization in the presence of ultrasound was not due to deagglomeration of TiO_2, but was associated with enhanced mass transport of reagents.

CHAPTER-5

Material and Methods

This chapter deals with the materials and methods used during this research , including the chemicals, glass ware , instruments like UV photo reactor, pH meter and analysis by UV- Vis Spectrometer , COD digester, and procedures used to treat the dye with UV/ TiO_2 catalysis ,UV/TiO_2/H_2O_2 and Sonophotolytic degradation. By optimization of different-2 parameters, Alizarin Red is treated.

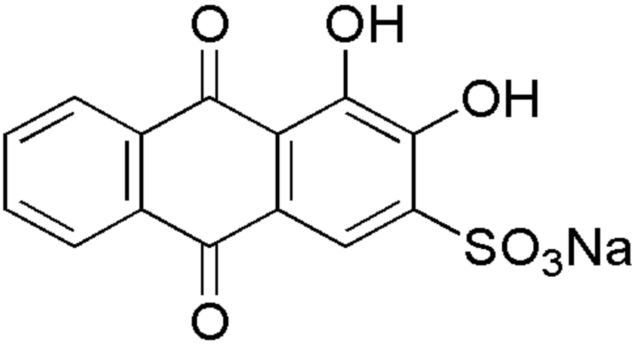
5.1 Materials:

5.1.1 Dye

Alizarin is an organic compound that is historically important as a prominent dye. It is an anthraquinone originally derived from the root of the madder plant. In 1869, it became the first natural pigment to be duplicated synthetically.Alizarin is also the name for a variety of related dyes, such as "Alizarine Cyanine Green G" and "Alizarine Brilliant Blue R."

Alizarin red is used in a biochemical assay to determine, quantitatively by colorimetry, the presence of calcific deposition by cells of an osteogenic lineage. As such it is an early stage marker (days 10-16 of in vitro culture) of matrix mineralisation, a crucial step towards the formation of calcified extracellular matrix associated with true bone.**Fig-5.1** shows the structure of Alizarin Red.

5.1 Structure of dye:



Fgure:.5.1.Structure of Alizarin Red Dye

Full scan of dye was taken with the help of UV- Vis spectrophotometer and max absorbance was observed at 427 nm .

5.1.3 Reagents and Chemicals Used

The Photocatalyst TiO_2 (P25) was procured from Degussa Company. Hydrogen peroxide was used as an oxidant. COD of industrial effluent and treated sample was determined by using potassium dichromate solution (Containing Mercuric sulphate and Concentration Sulphuric acid), COD reagent (containing Silver sulphate and Conc. Sulphuric acid), ferrous ammonium sulphate solution (0.05 N) and Ferroin indicator. For all the experiments single distilled water were used. Different normality of (0.1, HCl and .1 N, NaOH were used for adjustment of pH of dye solution and textile wastewater.

5.2 Instrument Used

5.2.1 pH meter

pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of .1 N, NaOH and .1 M HCl. Instrument was calibrated with freshly prepared buffer solutions (of pH 4 and 9) from time to time throughout the study.

Fig-5.2 showing pH meter

5.2.4 Magnetic Stirrer

Magnetic stirrer was used during experimentation to solve the problem of mixing and titanium dioxide remains in suspension.

5.2.5 Air sparger

Air is continuously supplied during experiments in UV reactor as well as solar experiments in order to oxidize the organic matter.

5.2.6 Photo reactor

Photo catalytic treatment of dye was performed in batch experiments. For Photocatalytic UV reactor was used which was rectangular having dimensions of 4.5 feet length, 3 feet width and 3.5 feet height and made up of iron. Roof of the reactor was made up of wooden; seven UV tubes (36 Watt each) were attached with the roof. Temperature inside the reactor was maintained by an exhaust fan. Four magnetic stirrers were fitted in the reactor to carry out the photo catalytic reaction in slurry mode.

Fig-5.3 Photo reactor at lab scale during Photocatalytic treatment

5.2.7 Filtration

After photo catalytic treatment by photo reactor dye and effluent sample were filtered through syringe filters having milipore filters of 0.45 um pore size.

5.2.8 COD Digester

COD digester (Hatch) was used for the digestion of samples in the process of COD determination.

5.2.9 Sonicator

For sonication Sonicator also called ultrasonic bath model no. EN 60 US, tank size: 12” x 6” x 6” (H), tank capacity 6.5 litre was used. **Fig-5.4** shows Sonicator

Fig-5.4 showing Sonicator

5.2.10 Sonophotocatalytic reactor

Above mention Sonicator bath is placed in UV chamber, so this makes the sonophotocatalytic reactor

5.2.11 Reaction vessel

Glass bowls were used for the photo catalytic reactions having a capacity of 1 L.

5.2.12 Spectrophotometer

The spectrum was taken with UV-vis. Spectrophotometer (Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer).**Fig.- 5.5**

Fig. 5.5 showing spectrophotometer

5.3 Methods

5.3.1 Preparation of solution

a) **Dye solutions:** The dye solutions were prepared by adding a known amount of dye into a small amount of deionized water in a 1-liter volumetric flask and filling it to the mark with single distilled water. The flasks were covered with aluminum foil to avoid degradation by the laboratory fluorescent lights. Before the oxidation experiments could be performed, it was necessary to choose the appropriate concentration of dye solutions. For most of the experiments, dye solutions of 100 ppm concentration were prepared by dissolving 100 mg in single distilled water and make the solution quantity to1 L. (If 1 g is present in 1 L then solution is said to be 1000 ppm and 0.1 g in 1000 ml then it becomes 100 ppm.)

b) **Hydrogen Peroxide:** Hydrogen peroxide (30% w/v) was obtained from S.D. fine-chem. Limited having M.W. of 34.01. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg. If this solution is diluted ten times then 1 ml contains 30 mg of H_2O_2. Hence for adding 300 mg/l of H_2O_2 in dye or effluent, add 10 ml in 1 L of dye or 1 ml of diluted peroxide solution in 100 ml of dye solution.

The value of color is pH dependent so color in this test is reported at 4.8 pH. The maximum absorbance of textile wastewater was found at 427 nm wavelength during full scan. So the initial and final absorbance was measured at this wavelength using spectrophotometer (M.Tech Thesis).

5.3.2 Estimation of COD

COD was estimated as per the standard method No. 5220C, page No.5-14 from Standard methods for the examination of water and wastewater, 1989(17thedition).

5.3.3 Estimation of BOD

BOD was estimated as per standards method No. 5210 B, page No.5-4 from Standard methods for the examination water and wastewater, 1989(17th edition).BOD was estimated by BOD bottle method.

5.3.4 Analysis for decolorization/degradation

The decolorization/degradation studies were conducted by measuring absorbance in UV/VIS spectrophotometer, having a wavelength range from 190-700nm using a 1 cm quartz cell. Spectrophotometer is having both Tungsten and Deuterium lamp at operating temperature of 0-40^{o}C.Full scan was taken after treatment for the Alizarin Red dye.

5.3.5 Analysis of Sulphates

The sulphates were estimated by standard method 4550-D ,4-206.

5.4 Photocatalytic Treatment

Photocatalytic treatment was done for Alizarin Red dye. The dye was treated and the various parameters like pH, catalyst dose, concentration of oxidant, initial concentration of dye were varied and optimized.

5.5 Degradation of dye

Photocatalysis: Alizarin Red dye solution 100 ppm was prepared by the single distilled water. 200 ml of sample taken in reaction vessel (1000ml capacity), .1 gm of TiO_2 and 3 ml of H_2O_2 was added and reaction vessel was covered with transparent thin foil; air is also supplied by the aerator during experimentation. Sample was taken in intervals of half hours for 3 hrs. The concentration of these samples was detected by Spectrophotometer.

Sonophotocatalysis: 200 ml of 100ppm Alizarin Red dye solution was taken in reaction vessel, 0.1 gm of TiO_2 and 3 ml of H_2O_2 was added and reaction vessel was covered with transparent thin foil; air is also supplied by the aerator. Then reaction vessel was placed in the Sonicator which is inside the photo reactor or UV chamber. Samples were taken after every half an hour. The concentration of these samples was checked by using UV-vis Spectrophotometer.

CHAPTER-6

Results and discussions

6.1 Dye Characteristics: The Dye sample of technical grade was taken and analyzed for its various parameters. The values of the various parameters are shown in **(T 6.1)** before treatment and their degradation studies were done using different parameters like different catalyst concentration, different pH, different H_2O_2 concentration and then process was optimized for the different parameters. The degradation of the Dye was studied in UV visible spectrophotometer at different time intervals.

Parameters	Value
pH of Dye	5.8(acidic)
COD of Dye	280(mg/l)
Absorb.(max.)	426(nm)
Sulphate	350mg/l
BOD(mg/l)	125mg/l

Table 6.1 showing characteristics of dye Alizarin Red.

6.2 Absorption spectra of Dye Alizarin Red

The Photocatalytic experiments were conducted under both UV as well as solar light. The decolorization and degradation was recorded in term of change in intensity of characteristics peaks. Alizarin Red dye (100ppm) shows the absorption peaks at 427 nm.

Fig. 6.1 shows the UV-Vis. Spectra of 100 ppm of Alizarin Red dye solution. The rate of degradation was recorded with respect to change in intensity of absorption of peaks at 427 nm.

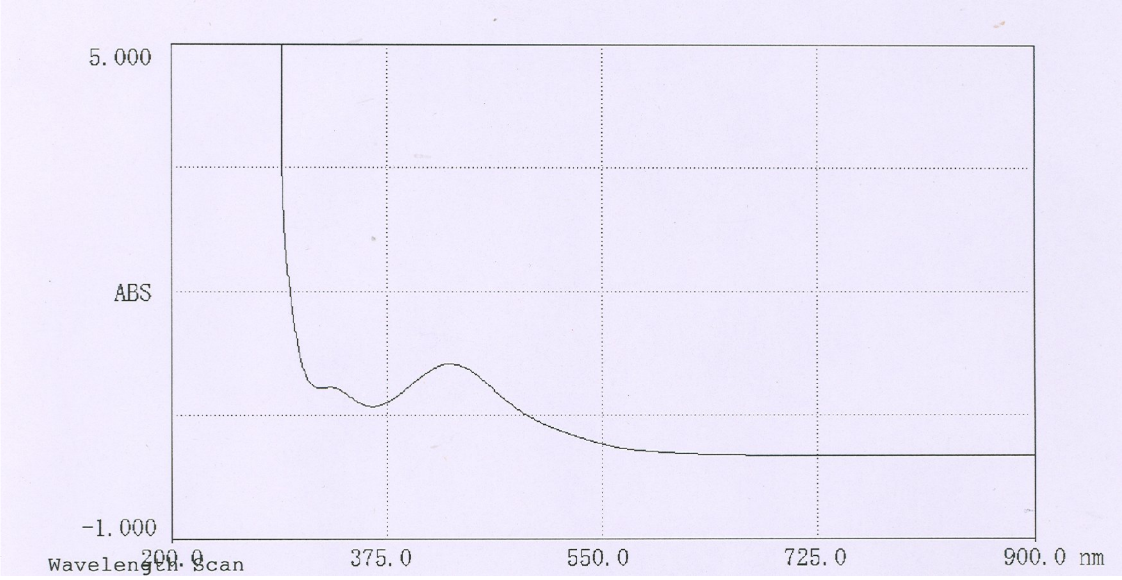


Fig.6.1 showing absorption spectra of dye Alizarin Red before treatment

6.3 Dark adsorption studies

Dark adsorption studies were carried out with the dye under study to correlate the results for adsorption and degradation under UV light. The addition of the catalyst concentration in the dark showed a very little decrease in concentration. The rate became constant after some time as confirmed by the constant conc. values because of the monolayer formation on the catalyst surface. As soon as the catalyst was added, dye from solution adsorbed on the surface, thus lead to decrease in conc. values in the solution. But after the formation of monolayer on the catalyst surface, reduction in conc. values became constant. Thus results observed from adsorption experiment confirmed that decrease in conc. was due to adsorption i.e. no degradation of the dye was confirmed. So for the complete degradation of the dye some alternative method should be used.

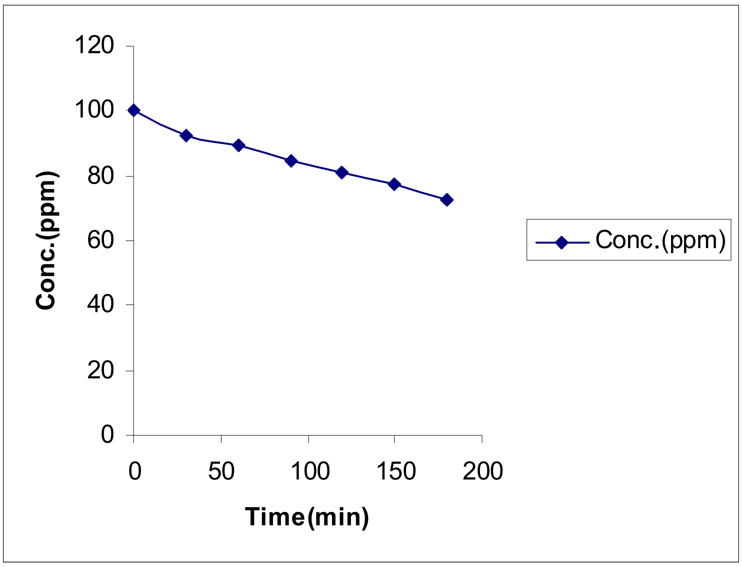


Fig 6.2 Showing degradation of Alizarin Red dye in dark reaction

In this study, the Aizarin Red dye sample of 200ml was placed for many hours with the addition of the catalyst; neither pH nor addition was done in this process after 3-4hrs period the sample was tested for the conc. reduction process.

6.4 Photolytic Studies

Alizarin Red dye solution was irradiated under ultraviolet (UV) light alone in the absence of catalyst. It was observed that after 180 minute of UV treatment the degradation of dye is not significant as compared to Solar/TiO_2 and UV/TiO_2. **W.S.Kuo and P.H.Ho, 2006** have reported the similar behavior during the photolysis of dye under ultraviolet irradiation. As the Photocatalytic mechanism suggests, both TiO_2 and a light source are necessary for the photo-oxidation reaction to occur. A control experiment was conducted on the irradiation of Alizarin Red under only UV light, in the presence of TiO_2, with and without UV irradiation over a period of 180 min. No degradation was observed in the presence of UV light only. In the presence of TiO_2, but without irradiation, slight loss was observed due to the adsorption of the dye on to the surface of TiO_2. However on irradiating the dye with TiO_2 in aqueous dispersion about 89% of the dye was degraded within 180 min of irradiation as shown in **Fig . 6.3**

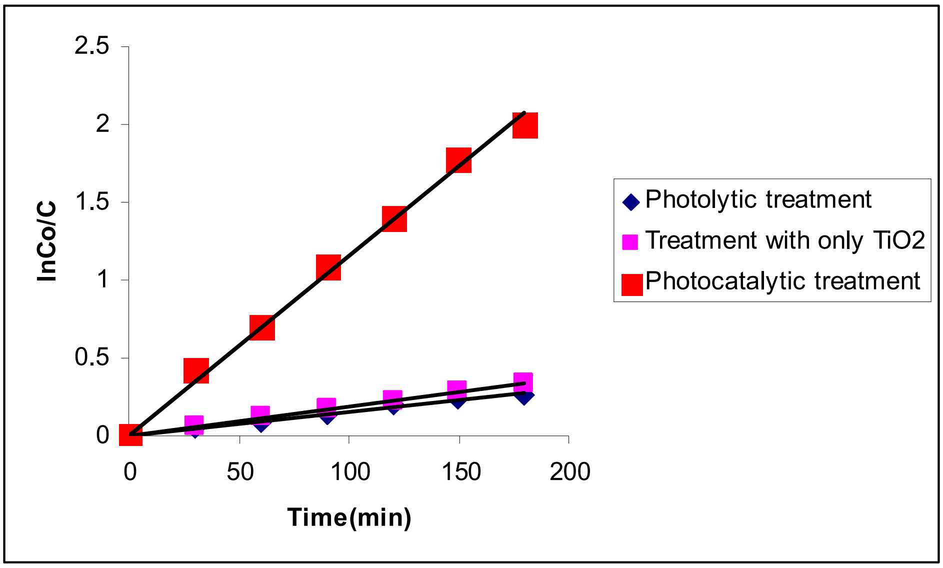


Fig - 6.3 Kinetics of Photolytic and Photocatalytic degradation of dye

6.5 Standard curve of Alizarin Red Dye

Figure 6.4 shows the standard curve for Alizarine Red S that is prepared by plotting the absorbance of Alizarine Red S dye solution of varying known concentration from 10 ppm to50 ppm at 427 nm against concentrations. For any solution of unknown concentration can be determined from the absorbance curve with slope of 0.0099 and value of R^2 is 0.993.

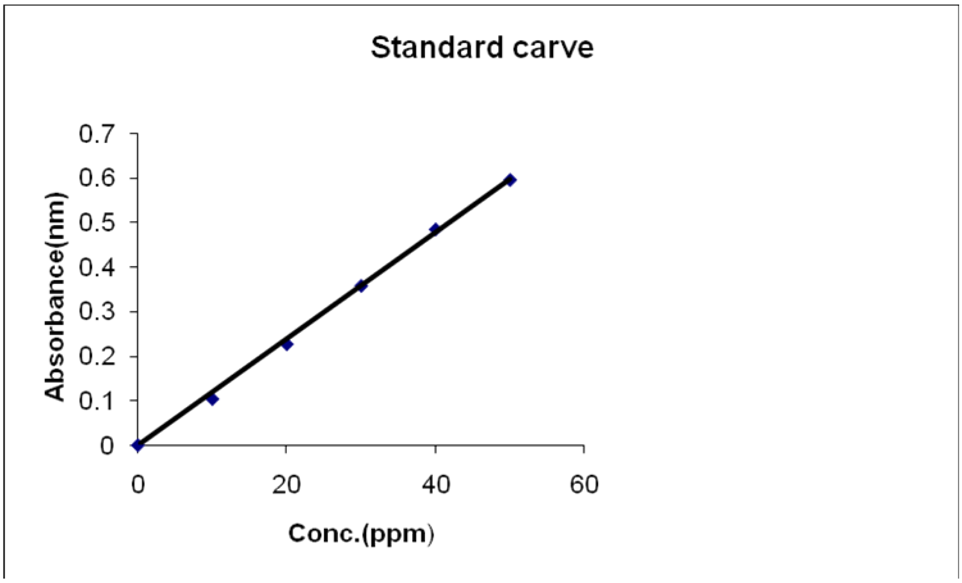


Fig- 6.4 showing standard curve of Alizarin Red Dye

6.6 Photocatalytic treatment

After characterization of the waste sample, its Photocatalytic treatment was done. Photocatalytic treatment depends upon the following factors:

1. Catalyst concentration
2. Operating pH
3. Oxidant addition
4. Initial concentration

So depending upon these above listed factors, optimized reaction conditions were calculated and used throughout the process.

6.6.1 Effect of Catalyst Dose

The catalyst dose is important parameter which has strong influence on the degradation kinetics of dye solution. Degussa P-25 TiO_2 catalyst was used in slurry mode. In order to determine the optimal amount of catalyst concentration, a series of experiments were carried out using different concentrations of TiO_2 catalyst varying from 0.1 to 0.6 gms, with 100 ppm dye solution and results are presented in **Fig-6.5.** Litrature shows that the initial rate increases with the increase in catalyst concentration, becomes maximum and then concentration decreases continuously with increasing TiO_2 concentration. In our study we keep the optimum catalyst concentration for the degradation of Alizarin Red dye is 0.2 g/200 ml (i.e. 0.1%) so as to economize the process. Although after some increase in catalyst concentration the rate of degradation was not so faster due to agglomeration and sedimentation of TiO_2.

The increased degradation rate that follows the increase in the catalyst loading can be attributed to the fact that a larger amount of photons are adsorbed, thus accelerating the process. When all the dye molecules are adsorbed on TiO_2 no improvement is achieved by adding more catalyst. The decrease in efficiency, which is observed in the figure 6.5, may be due to an increasing opacity of the suspension and to an enhancement of the light reflectance, because of the excess of TiO_2 particles. Additionally, in the case of high catalyst loads we observed agglomeration and sedimentation of TiO_2 which makes a significant fraction of catalyst to be inaccessible to either absorbing the dye or absorbing the radiation, with consequent decrease in active sites available to the catalytic reaction.

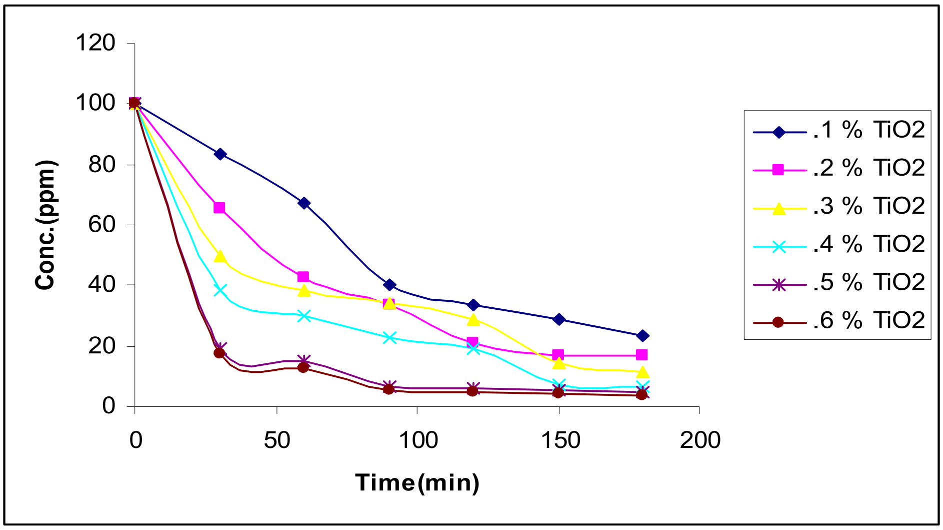


Fig. 6.5 Showing the effect of catalyst concentration on dye conc.

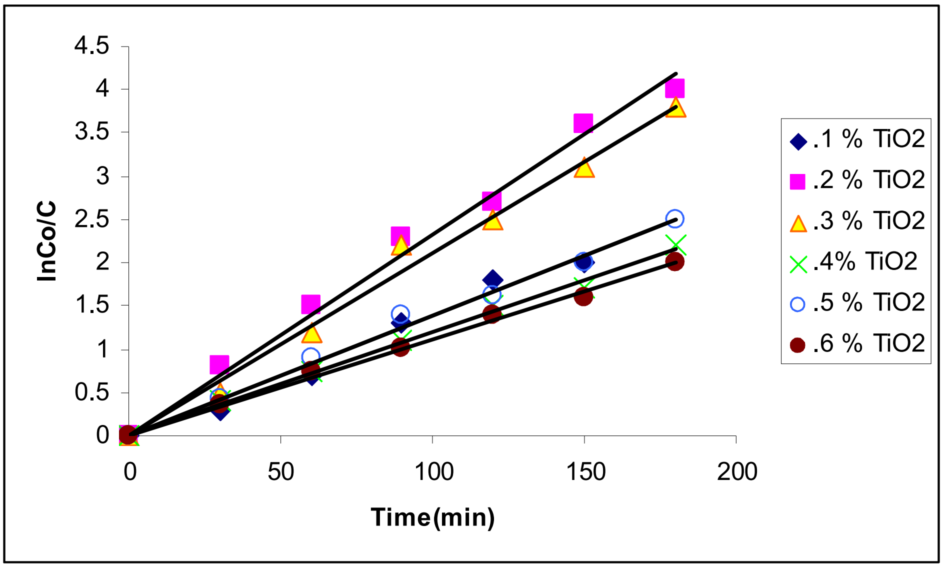


Fig.6.6 Linear transform of the kinetic curves of Alizarin Red Dye degradation at various concentrations of TiO_2

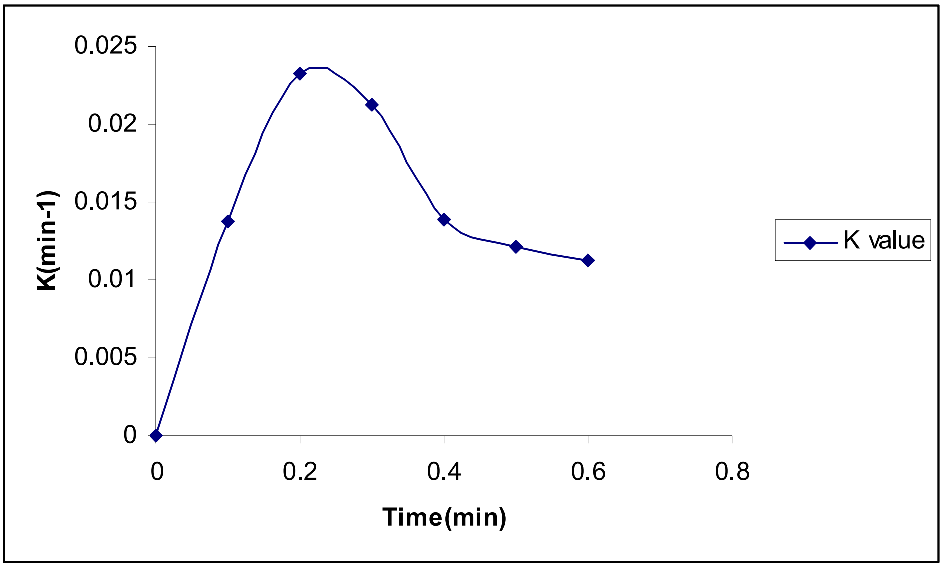


Fig. 6.7 showing the effect of TiO_2 dose on rate constant K.

C. G. Silva et. al., (2006) has reported that degree of decolorization increases with the increasing amount of catalyst concentration up to a certain limit and beyond after that further increase in catalyst dose decolorization has been decreased.

6.6.2 Influence of Initial pH

The Dye sample pH varies with time and the generation of hydroxyl radicals is also a function of pH. Thus, pH plays an important role both in the characteristics of the wastewater and generation of hydroxyl radicals. Hence, employing Degussa P25 as Photocatalyst the degradation of Alizarin Red in the aqueous suspensions of 0.1 g/200 ml TiO_2 was studied in the pH range between 2.8 and 10.8 as shown in Fig. 6.8, the natural pH of dye being 5.8.

The effect of the solution pH on the degradation rate can be explained mainly by adsorption of dye on TiO_2 surface. In acidic suspensions, the adsorption of dyes on the TiO_2 particles was significantly increased comparing to the extent of adsorption in alkaline suspensions. This is attributed to the fact that TiO_2 shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge (pzc) of the used TiO_2 (Degussa P-25) is widely reported at pH≈6.5. The TiO_2 surface is positively charged in acidic solution and negatively charged in basic solution. Because the dye is negatively charged, the acidic solution favors adsorption of dye onto photo catalyst surface.

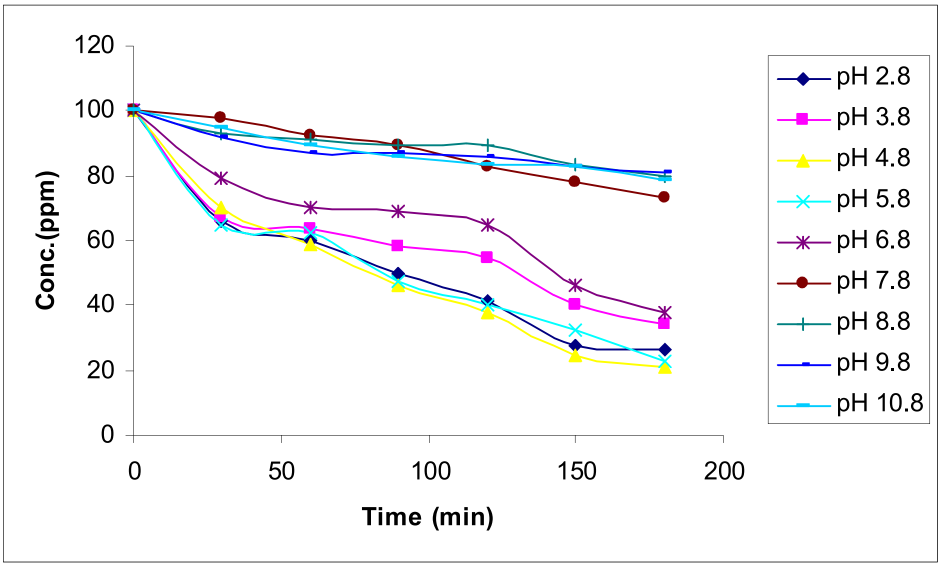


Fig 6.8 Showing the effect of different pH range on conc. of dye with time.

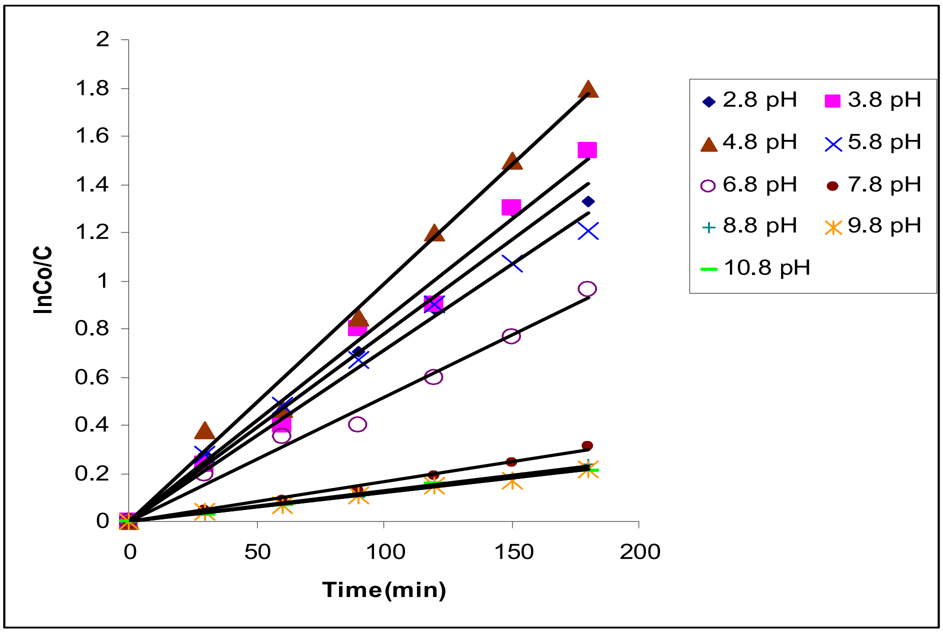


Fig. 6.9 Linear transform of the kinetic curves of Alizarin Red Dye degradation at various pH

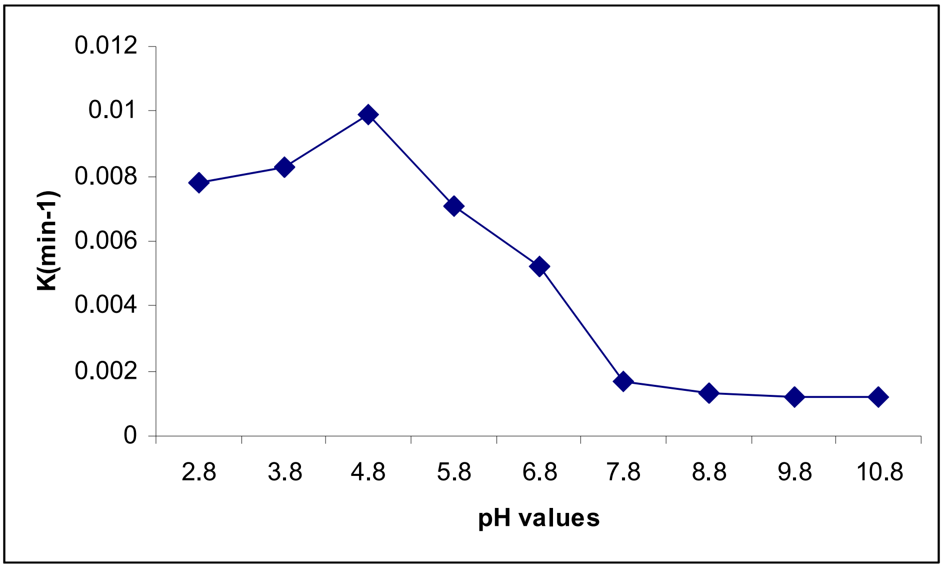


Fig. 6.10 Effect of initial pH on rate constant

6.6.3 Effect of Oxidant Dose

Limitation to the rate of Photocatalytic degradation had been attributed to the recombination of photo generated hole-electron pairs. Since the addition of H_2O_2 may play an important role in accelerating the degradation rate of azo dyes, experiments were conducted to examine its effect on degradation of the dye. The degradation rate increases initially by the addition of H_2O_2 and beyond a certain concentration of H_2O_2, rate of degradation decreases. The optimum H_2O_2 concentration for degradation of dye with an initial concentration of 100 mg L-1 at pH of 4.8 is 3 ml / 200 ml as shown in **Fig.6.11**

This dual effect of H_2O_2 can be explained by radical reaction mechanisms. The added H_2O_2 could accelerate the reaction by producing hydroxyl radicals from scavenging the electrons and absorption of UV-light. By addition of excess H_2O_2, it acts as hydroxyl radical or hole scavenger to form the per hydroxyl radicals (HO_2•) which is a much weaker oxidant than hydroxyl radicals.

S. S. Reddy et. al., (2005) have studied the initial concentration of H_2O_2 for the reactive dye bath in the term of rate of decolorization. At 1500 mg/l concentration color removal efficiency was 99 % and further increase in dosages of H_2O_2 did not increase the color removal efficiency.

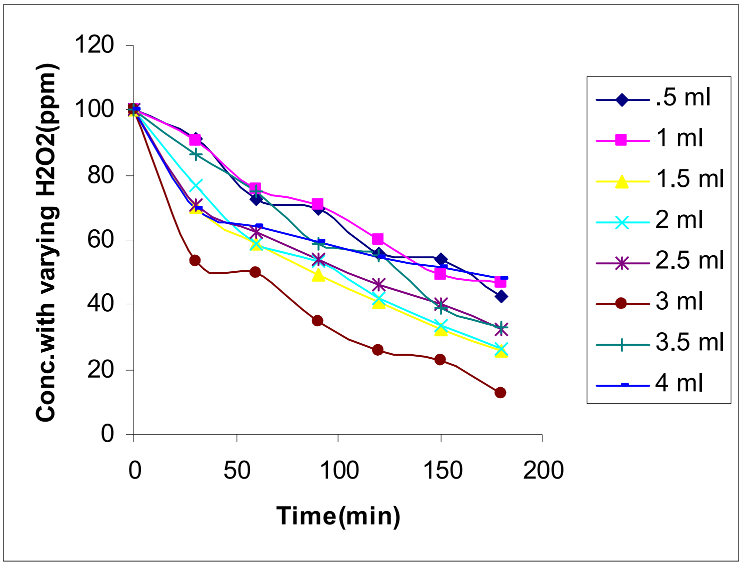


Fig 6.11 Showing the effect of different H_2O_2 range on conc. of dye with time.

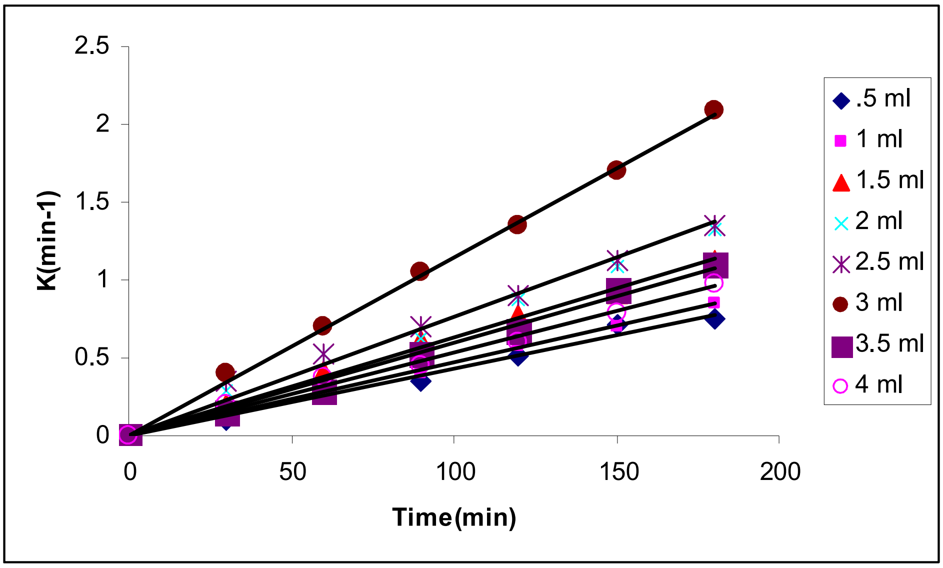


Fig. 6.12 Linear transform of the kinetic curves of Alizarin Red Dye degradation at various concentrations of H_2O_2

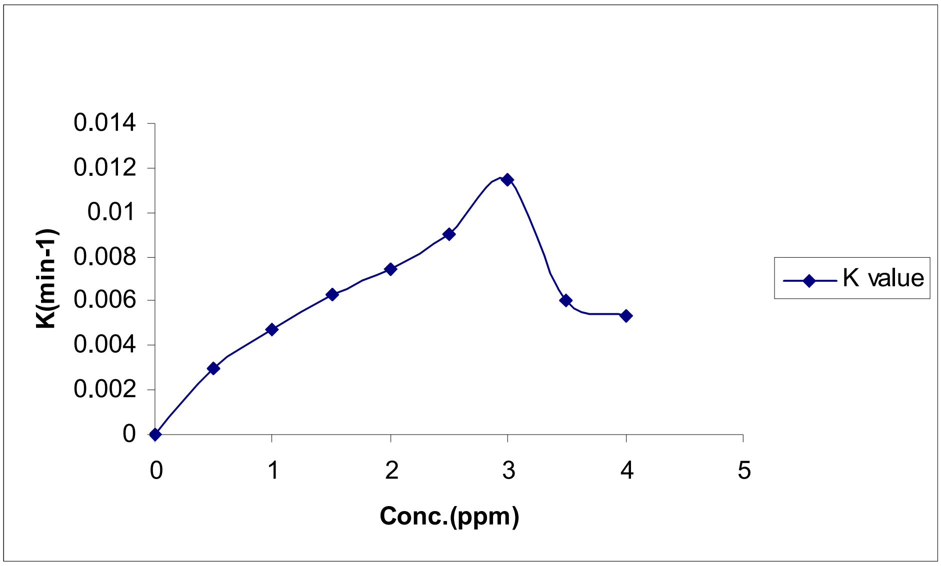


Fig.6.13 Effect of hydrogen peroxide concentration on reaction rate of Alizarin Red (100 ppm) at 4.8 pH & [TiO_2] = 100 mg/200ml.

6.6.4 Effect of the Initial Dye Concentration

The pollutant concentration is very important parameter in wastewater treatment. The influence of initial concentration of the dye solution has been investigated on the Photocatalytic degradation of dye after the optimization of pH and catalyst dose and

H_2O_2. As initial concentration is an important parameter to be studied, the effect of initial concentration of dye solution on the degradation rate of Alizarin Red dye has been investigated by varying the dye concentrations from 50 mg L^{-1} to 150 mg L^{-1} in the presence of 0.1 g/200 ml TiO_2, pH 4.8 and 3 ml H_2O_2 under UV light as shown in **Fig 6.14**. This shows that the photo-oxidation process is more suitable for low concentration of the pollutants. The reason behind this behavior may be due to the increase in the extent of adsorption on the catalytic surface at necessary dye concentration which reduces the catalytic activity of TiO_2. The increases in the dye concentration also decrease the path length of photon entering into the dye solution. At high dye concentration a significant amount of UV-light may be absorbed by the dye molecule rather than the catalyst and this may also reduce the catalytic efficiency.

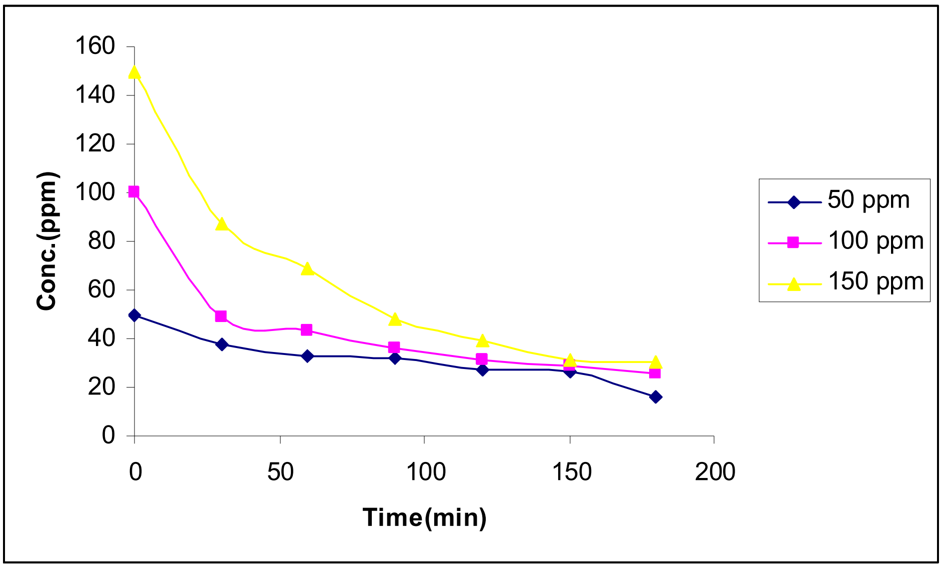


Fig- 6.14 Effluence of initial dye concentrations on the rate degradation of Alizarin Red Dye

Similar results have been reported for the photocatalytic oxidation of different dye by different author **(Chin-Chaun Liu et. al., 2006.)**

6.7 Comparison of Solar/UV Light

The effect of UV light on the degradation of Alizarin Red dye by Photocatalytic process has been investigated. The comparative study has been carried out for the degradation of dye solution in Solar/UV as well as normal room light. The aqueous suspensions of TiO_2

(100 mg/200ml) containing Alizarin Red dyes (100 ppm dye) was exposed to Solar, UV conditions at pH 4.8. **Fig- 6.15** shows the degradation rate as a function of irradiation time on illumination of an aqueous suspension of dye under sunlight, visible and UV light source, respectively. The rate of degradation was found to be slightly more in the solar light in comparison to UV light. It is evident from the graph that percentage degradation of solar light is very close to UV light degradation so solar light can be efficiently used for the Photocatalytic degradation of wastewater.

This is due to their ability to absorb part of the visible light, another mechanism of degradation connected with visible light could occur as well. According to this mechanistic approach, the adsorbed dye molecule onto the TiO_2 surface form appropriate excited states due to visible illumination and then these excited states mainly transfer electrons to the conduction band of TiO_2 particles.

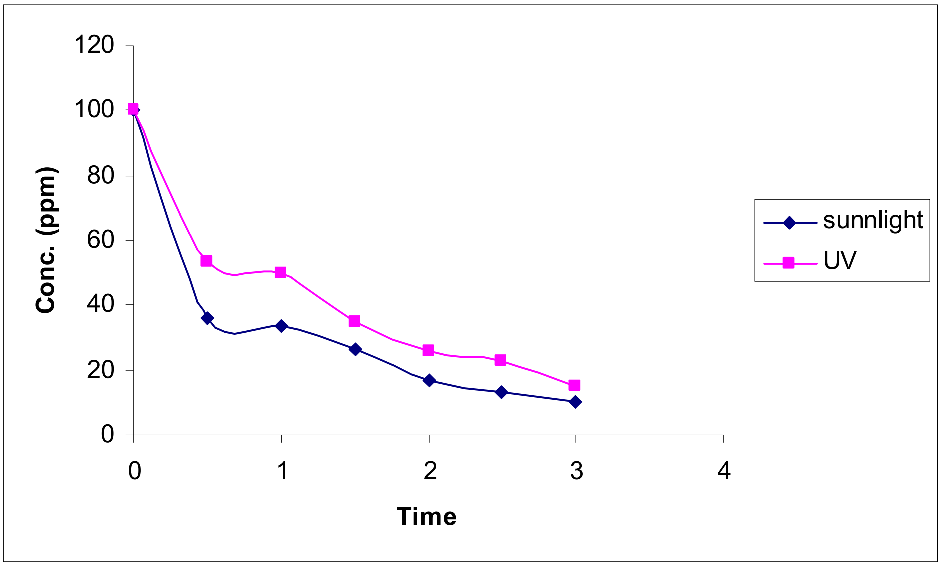


Fig.6.15 Effect of UV/Solar light on photo catalytic degradation of Alizarin Red

Muruganandham M. et. al., (2006) studied the Solar/TiO_2 process for photo catalytic decolorization of Reactive Yellow 14 dye which was completely decolorized in 80 min.

6.8 Absorption spectra after Photocatalytic treatment

The spectra shown in **Fig.-6.16** below is of the Alizarin Red, from this spectra it reveals that after treating the sample with optimized conditions in the UV-reactor for more than 3 hours time period, the toxic and harmful compounds breakdown to the harmless ones. As in this spectra no peak was observed in the visible region i.e. the peak observed in the raw sample was completely disappeared after treating the sample with optimized conditions in the UV-reactor.

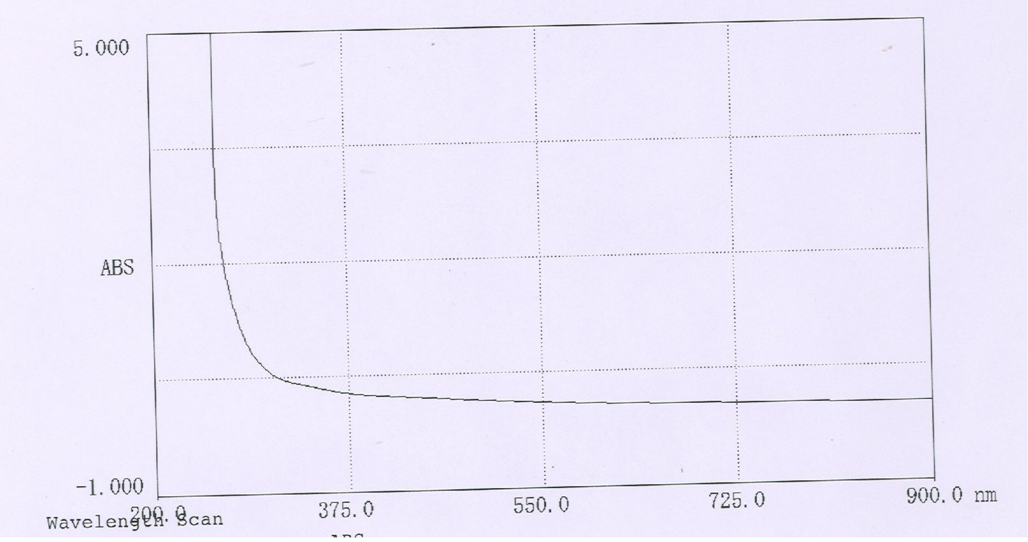


Fig- 6.16 Absorption Spectra of Alizarin Red after Photocatalytic treatment of 3 hrs

6.9 Absorption Spectra showing the degradation with time

The time dependent electronic absorption spectrum of Alizarin Red dye is presented in **Fig 6.17** during photo irradiation. As the spectrum of the dye is in the visible region and exhibits a main band with a maximum at 427 nm. Gradually after 1.5 h of irradiation time under UV light in a TiO_2 aqueous suspension the dye disappears totally which reveals that it is completely eliminated and decolourisation of solution is observed. In parallel, the same experiments were carried out in dark and in the presence of TiO_2 and in the absence of TiO_2 by UV illumination revealing in both cases no observable loss of dye molecules. Besides no new bands appear in the UV-Vis region due to the reaction intermediates formed during the degradation process.

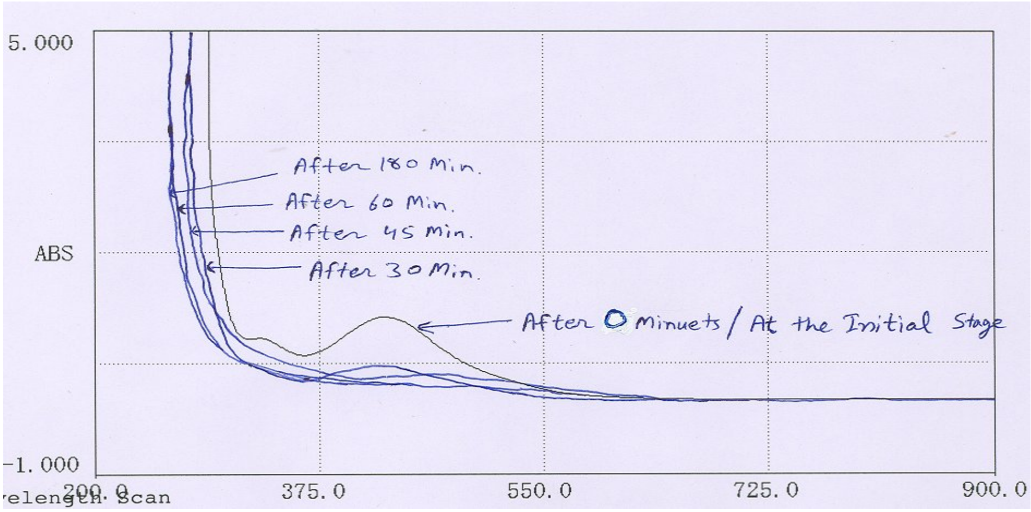


Fig-6.17 Absorption Spectra of Photocatalytic degradation of Alizarin Red dye at different time intervals

6.10 Sonolytic and Sonocatalytic Treatment

In sonication, the reaction is exited by the so called cavitation phenomenon. Cavitation is the formation, growth and collapse of bubbles in the liquid. Cavitation occurs whenever a new surface, or cavity, is created with in a liquid. A cavity is any bounded volume, whether empty or containing gas or vapor, with at least part of the boundary being liquid. The collapse of the bubbles induces localized supercritical condition: high temperature, high pressure. Thus cavitation serves as a means of concentrating the diffuse energy of sound into micro reactors. The consequences of these extreme conditions are result in formation of hydroxyl radical and these hydroxyl radicals are mean ingredients for the oxidation of pollutants.

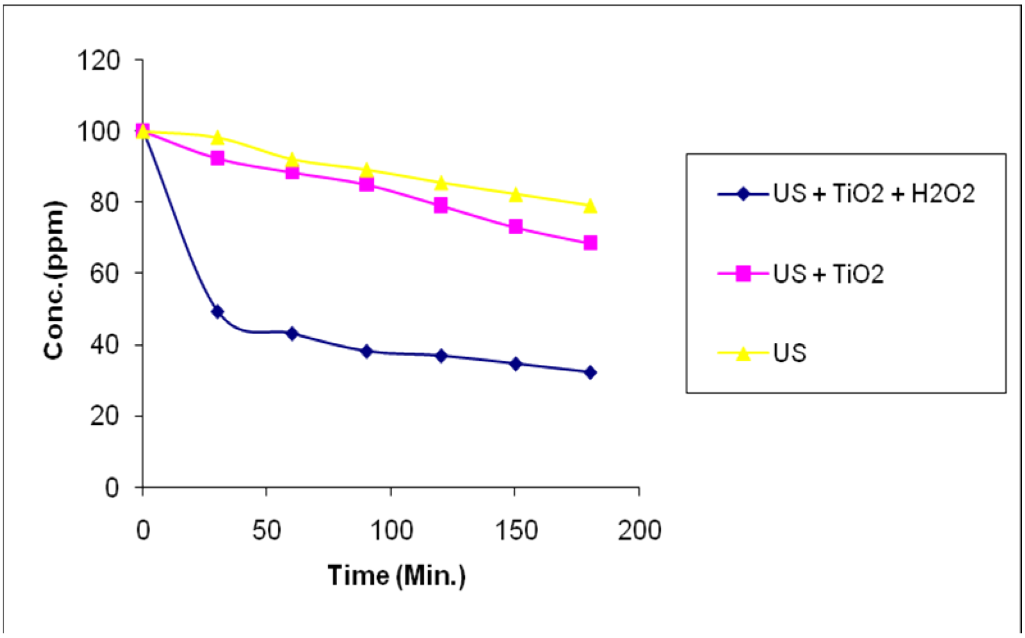


Fig.- 6.18 Degradation of Alizarin Red under sonolysis and sonocatalytic conditions.

As the graph 6.18 shows the sonocatalytic degradation shows better results then sonolytic degradation because ultrasound play a profound role due to substantial increase in the no. of active sites and also the surface area available due to defregmentation of the catalyst agglomerates under the action of turbulence by acoustic streaming along with an increase in the diffusional rates of contaminants.

6.11 Comparison of degradation efficiency under Photocatalytic and sonophotocatalytic conditions

The results were compared for the degradation of Alizarin Red at an initial concentration of 100 mg /1L using Photocatalytic conditions and sonophotocatalytic conditions to study the effect of ultrasound on the degradation rate as per the procedure given in section 6.18. As is observed from **Fig 6.19** that the degradation is more decreased in case of sonophotocatalytic degradation.

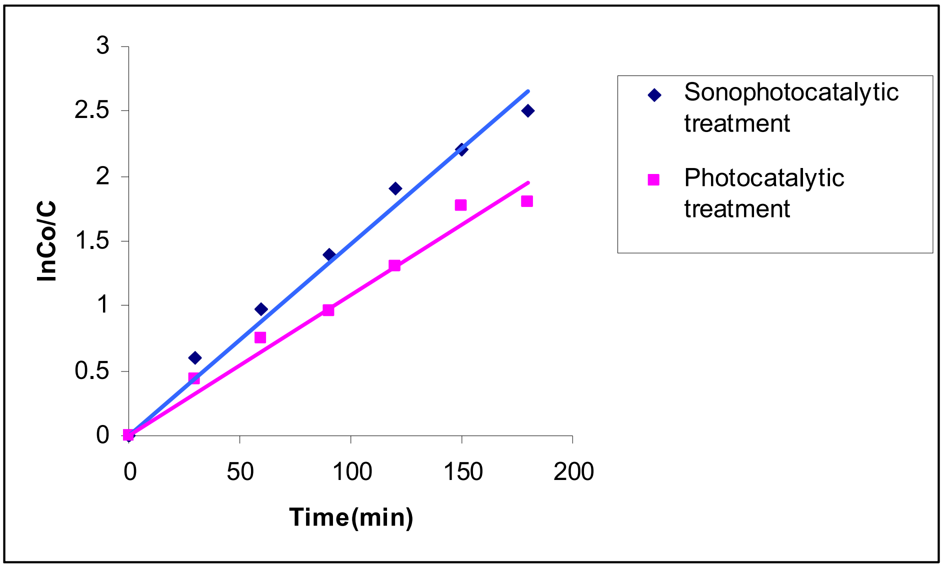


Fig.6.19 Kinetics of the Sonophotocatalytic and Photocatalytic degradation of dye

The reason for this is that the basic mechanism for both ultrasound and photocatalytic oxidation is generation of free radicals. If these mode of irradiations are operated in combination, more no. of radicals will be available for the reaction there by increasing the rate of reaction.

6.12 Comparision of sonocated catalyst with powdered catalyst

In this study, results were compared by sonicating the TiO_2 slurry. The same amount of catalyst which was used for photocatalysis, sonicated for half and hour in an ultrasonic bath. The purpose of doing sonication of TiO_2 was to get the uniformly dispersed catalyst. The results showed the increase in the degradation rate as clear from **Fig.6.20** using sonocated catalyst. A Very few literature survey have coated this type of effect.

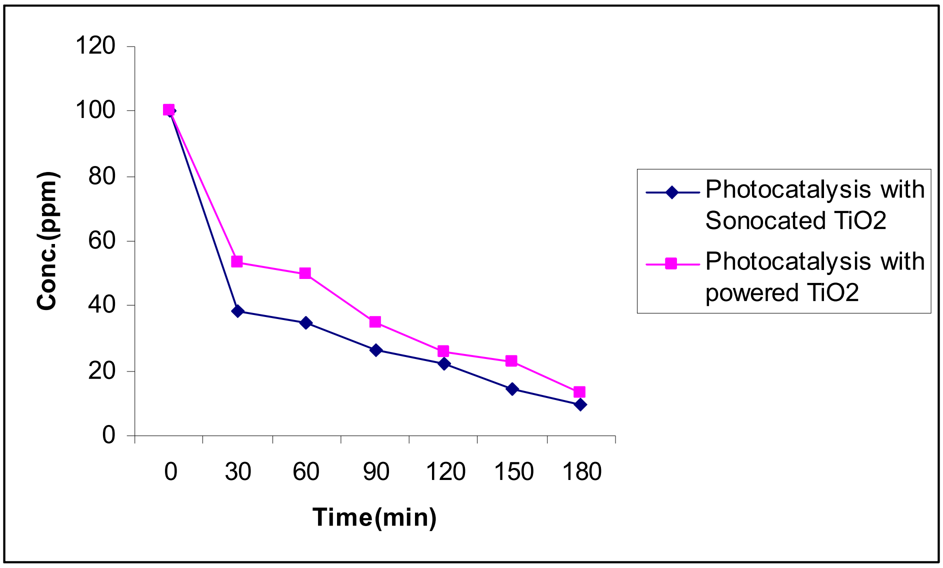


Fig-6.20 Photocatalytic degradation of Alizarin Red Dye under sonocated TiO_2 and powdered TiO_2.

CHAPTER-7

Conclusion

Since the beginning of industrialization, the variety and quantity of pollutants emitted into the environment has steadily increased. While the rates of development and waste production are not likely to diminish, efforts to control and dispose of wastes appropriately are rising. One of the key concerns in waste control is the protection and remediation of the world's finite potable water supply. Although there are various methods for water purification, they are typically dated and inadequate for the removal of the toxins known to be in today's water sources. .

Heterogeneous photocatalysis process is eco-friendly way to reduce the pollution load of wastewater. This process has proved its superiority to other conventional methods of wastewater treatments, in the presence of biorecalcitrant compounds. It leads to complete destruction of hazardous contaminants and avoid transfer of pollutants from one phase to another. Photocatalytic process is expensive due to application of UV light and catalyst. India being a tropical country, there is plenty availability of sunlight so solar photocatalysis is an attractive and cost effective option for the application of this technology at industrial scale.

Alizarin Red dye has been successfully degraded in the presence of TiO_2 Photocatalyst. In case of dye solution of 100ppm concentration, degradation was found to be 85% and 89.90 % in UV and solar light respectively at the optimized reaction conditions like pH of 4.8, catalyst dose of 100 mg/200ml and oxidant concentration of 3ml/200ml. Hence, it is deduced that solar light can be effectively used for the degradation and decolorization of dye solution. The diminishing of peaks in the UV and visible region of Alizarin Dye dye during solar/UV Photocatalytic treatment shows the complete degradation of dye into simpler end products which results in the complete mineralization of resulting solutions.

Sonophotocatalytic treatment has synergy effect on the degradation of pollutants as confirmed by the percentage degradation in this case reaches up to 94% in 180 minutes.

The mineralization studies were done in terms of COD reduction also the degradation of 83.3% shows that organic compounds are converted into simpler ones. Sulphates had been reduced 64 %. BOD also reduced 80%.

Results from the study indicate, Advanced Oxidation Process may become most widely used technologies for organic pollutants not treatable by conventional techniques due to their high chemical stability and/or low biodegradability in the near future. Combination of AOP_S as preliminary treatment method with inexpensive biological process seem very promising from an economical point of view. Heterogeneous catalysis using sunlight provides an alternative and effective method for degrading the various organic chemicals. Addition of ultrasound treatment with AOP's can has synergetic effect on the degradation of most priority pollutants.

Hence, it can be concluded from the observations that sonophotocatalysis can be suitably and effectively employed for the degradation of Dyes.

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