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CERTIFICATE

Certified that the thesis entitled " Integrated Photocatalytic and Biological treatment of bio-recalcitrant compounds in textile Industry effluent "being submitted by Mr. Anoop Kumar in the partial fulfillment of the requirements for the award of the degree of Master of Engineering in Environmental Engineering from Thapar Institute of Engineering and Technology (Deemed Univerisity), Patiala, is a record of the student's own work carried out by him under our supervision and guidance. The matter presented in this thesis has not been submitted for the award of degree or diploma in any other Univerisity or Institute.

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CONTENTS

ABSTRACT

The worst impact of rapid development in dyes and textile industries in the recent decades has resulted in the accumulation of large quantities of recalcitrant pollutants into our water cycle. Traditionally physicochemical methods used for wastewater treatment have inherent limitations in their applicability, effectiveness and cost. The biological treatment methods are ineffective because the effluents contain several organic and other recalcitrant compounds that have high aromaticity (aromatic phenols, amines, nitro etc.) and low biodegradability and these are the major environment pollutants.

The combination of photocatalytic process using both homogenous and heterogeneous catalysts like Fenton's process and TiO_2 and its modified forms respectively, with biological treatment for the degradation of organic pollutants can provide a viable alternative for the detoxification and recycling of industrial wastewater.

The project undertaken involves the development of degradation technique that couples solar and biological processes for the treatment of biorecalcitrant, non-biodegradable and toxic organic substances present in the textile effluent. In this study, the optimization of the process using industry effluent (from nearby Textile industry) has been studied by varying catalyst concentration, variation of pH, addition of oxidant, and treatment under solar irradiation as pre and post treatment to the existing biological treatment for maximum degradation. The analysis of the products by measuring COD, BOD, TSS, TS, TDS, pH, Color has been done.

CHAPTER 1

INTRODUCTION

1.0 The problematic of water contamination

One of the characteristics that best defines today's society in what is understood by the developed countries is the production of waste products. There is practically no human activity that does not produce waste products and in addition, there is a direct relationship between the standard of living in a society or country and the amount of waste products produced. Approximately 23% of the world's population lives in developed countries, consume 78% of the resources and produce 82% of the waste products (Blanco and Malato, 1996). In addition, it has to be pointed out that the volume of residual waste increases in an exceptional way with regards to a country's level of industrialization. At present, there are some five million known substances registered, of which approximately 70,000 are widely used worldwide, and it is estimated that 1,000 new chemical substances are added to the list each year. The permitted levels have been vastly exceeded; causing such environmental contamination that our natural resources cannot be used for certain purposes and their characteristics have been altered. The main problem stems from waste coming from industry and agriculture, despite the fact that the population also plays an important role in environmental contamination.

Dyes, phenols, pesticides, fertilizers, detergents, and other chemical products are disposed of directly into the environment, without being treated, controlled or uncontrolled and without an effective treatment strategy.

In this general context, is very clear that the strategy to continue the search for solutions to this problem that every day presents a sensitive growth, mainly in the developing countries, will be guided to two fundamental aspects:

- The development of appropriate methods for contaminated drinking, ground, and surfaces waters.
- The development of appropriate methods for wastewaters containing toxic or non-biodegradable compounds.

Non-biodegradable are persistent materials because in the case of not receiving a specific treatment necessary for their destruction or inertness, they can affect various sectors of the environment. From this, a series of very diverse and irreversible damage can result, ranging from the deterioration or disappearance of a determined environment to changes in the health of those individuals who live in that environment.

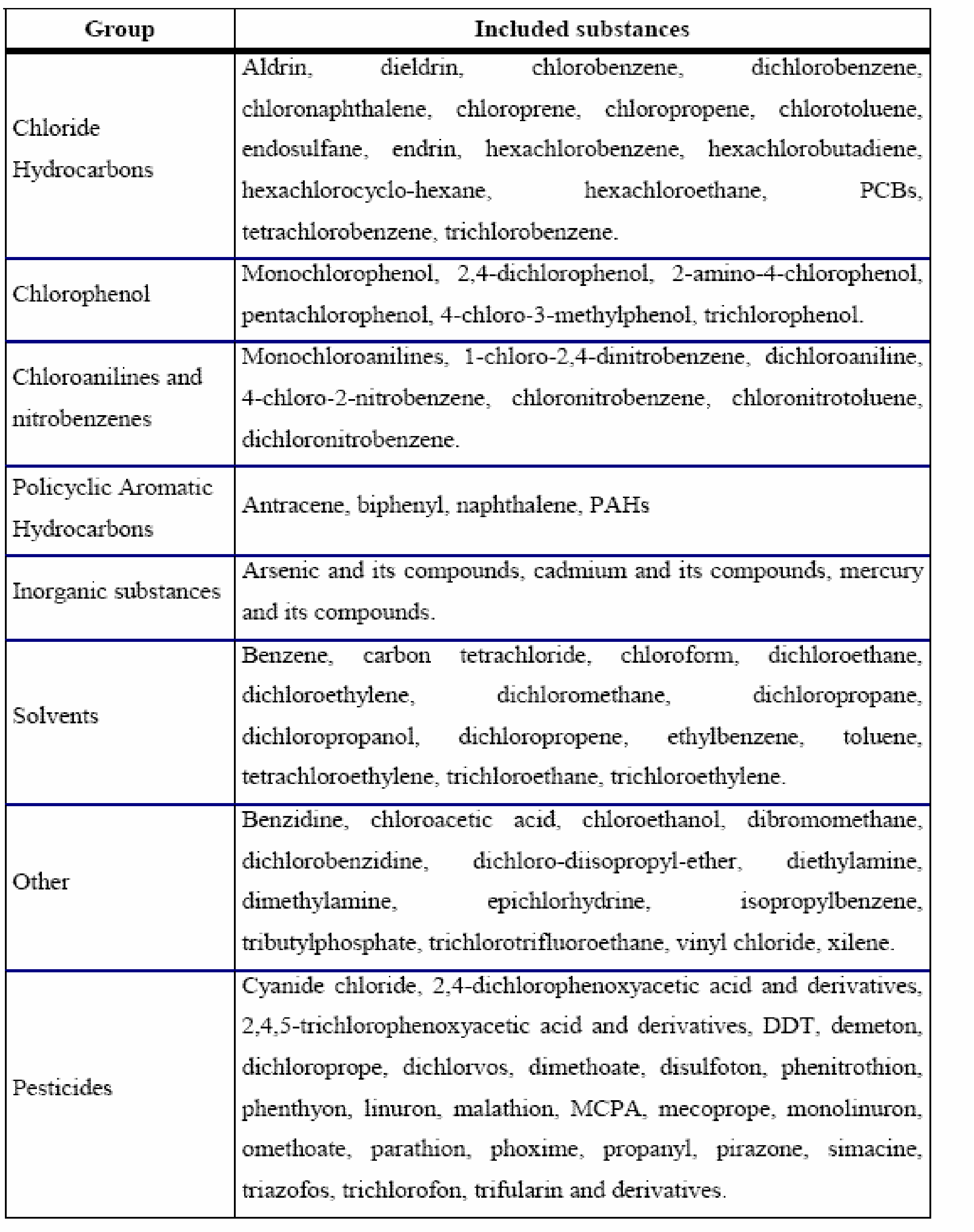
A large part of this type of residual waste is generated in an aqueous solution and, owing to its non-biodegradable nature, the biological treatment procedures (the most commonly used) are not effective, and unless there is an additional specific treatment, they end up being dumped in the environment. The presence of this type of pollutant in an aqueous dissolution is especially problematic as the residual waste cannot be stored indefinitely (as is the case with some solid waste) and it has the peculiarity that a small volume of water is able to contaminate much greater volumes of water.

The situation worsens by the lack, or insufficiency, of adequate water treatment systems capable of diminishing the concentration of toxic substances that represent a chronic chemical risk. It can be said that badly treated wastewaters lead inevitably to a deterioration of water sources quality and consequently, of drinking water. A large part of this type of residual waste is generated in an aqueous solution and, owing to its non-biodegradable nature, the biological treatment procedures (the most commonly used) are not effective, and unless there is an additional specific treatment, they end up being dumped in the environment.

It must also be pointed out that a wide spectrum of compounds can transform themselves into potentially dangerous substances during the drinking water treatment process, particularly by chlorination, as is the case of the precursor compounds of the formation of chlorocarbons (Marhaba and Washington, 1998).

Dangerous and Toxic Waste is defined as "those solid, semi-liquid, and liquid materials, as well as those gaseous materials in recipients, which are the result of a process of production, transformation, use or consumption which are destined to be abandoned and whose composition contains some of the substances or materials that figure in the successive revisions by the EU Committee, in such quantities or concentrations that represent a health risk to humans, natural resources and the environment and that need a treatment process or special elimination”. The European

Union made out a list of dangerous compounds, considered as contaminants, to which constantly new substances are added (“black list” of the E.U., see Fig. 1).



Group	Included substances
Chloride Hydrocarbons	Aldrin, dieldrin, chlorobenzene, dichlorobenzene, chloronaphthalene, chloroprene, chloropropene, chlorotoluene, endosulfane, endrin, hexachlorobenzene, hexachlorobutadiene, hexachlorocyclo-hexane, hexachloroethane, PCBs, tetrachlorobenzene, trichlorobenzene.
Chlorophenol	Monochlorophenol, 2,4-dichlorophenol, 2-amino-4-chlorophenol, pentachlorophenol, 4-chloro-3-methylphenol, trichlorophenol.
Chloroanilines and nitrobenzenes	Monochloroanilines, 1-chloro-2,4-dinitrobenzene, dichloroaniline, 4-chloro-2-nitrobenzene, chloronitrobenzene, chloronitrotoluene, dichloronitrobenzene.
Policyclic Aromatic Hydrocarbons	Antracene, biphenyl, naphthalene, PAHs
Inorganic substances	Arsenic and its compounds, cadmium and its compounds, mercury and its compounds.
Solvents	Benzene, carbon tetrachloride, chloroform, dichloroethane, dichloroethylene, dichloromethane, dichloropropane, dichloropropanol, dichloropropene, ethylbenzene, toluene, tetrachloroethylene, trichloroethane, trichloroethylene.
Other	Benzidine, chloroacetic acid, chloroethanol, dibromomethane, dichlorobenzidine, dichloro-diisopropyl-ether, diethylamine, dimethylamine, epichlorhydrine, isopropylbenzene, tributylphosphate, trichlorotrifluoroethane, vinyl chloride, xilene.
Pesticides	Cyanide chloride, 2,4-dichlorophenoxyacetic acid and derivatives, 2,4,5-trichlorophenoxyacetic acid and derivatives, DDT, demeton, dichloroprope, dichlorvos, dimethoate, disulfoton, phenitrothion, phenthyon, linuron, malathion, MCPA, mecoprope, monolinuron, omethoate, parathion, phoxime, propanyl, pirazone, simacine, triazofos, trichlorofon, trifularin and derivatives.

Fig. 1. Black listed Compounds of the E.U

1.1 Environmental problems caused by textile wastewater

Textile mills are major consumers of water and consequently one of the largest groups of industries causing intense water pollution. The extensive use of chemicals and water results in generation of large quantities of highly polluted wastewater. According to the U.S. EPA, about 1 to 2 million gallons of wastewater per day are generated by average dyeing facility in the US, reactive and direct dyeing generating most of the wastewater. Around 10^9 kg and more than 10,000 different synthetic dyes and pigments are produced annually worldwide and used extensively in dye and printing industries. Textile processing employs a variety of chemicals, depending on the nature of the raw material and products. It is estimate that about 10 % of the chemicals are lost in industrial wastewater (Young and Yu, 1997). The wastewater generated by the different production steps (i.e. sizing of fibers, scouring, desizing, bleaching, washing, mercerization, dyeing and finishing) has high pH and temperature. It also contains high concentration of organic matter, non-biodegradable matter, toxic substances, detergents and soaps, oil and grease, sulfide, sodas, and alkalinity. In addition, the high salt conditions (typically up to 100 g L^{-1} sodium chloride) of the reactive dye baths result in high-salt wastewater, which further exacerbates both their treatment and disposal. The fate of these chemicals varies, ranging from 100% retention on the fabric to 100% discharge with the effluent. As a result, textile industry is confronted with the challenge of both color removal (for aesthetic reasons) and effluent salt content reduction. In addition, reactive dyes are highly water-soluble and non-degradable under the typical aerobic conditions found in conventional biological treatment system (Neppolian *et al.*, 2001; Rodriguez *et al.*, 2002).

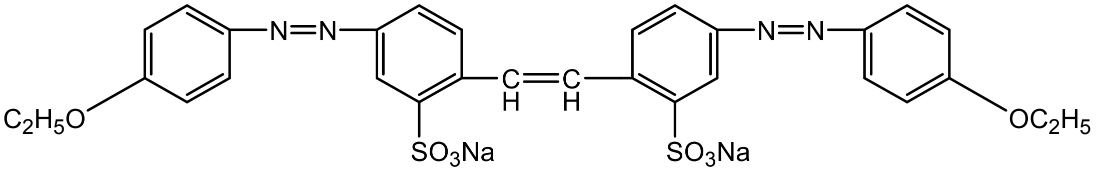
Synthetic dyes are indispensable to the textile and dyeing industries. Fashion would not have so much color and arouse so much interest were it not for the effects of such dyes. Among all synthetic dyes, azo dyes are the most common, being used up to 90 per cent of the time, because they are versatile and easy to synthesize. Yet many azo dyes are toxic and may cause genetic mutations. And because they are synthetic, the natural environment cannot recognize them or degrade their toxicity. Though man has invented sewage treatment plants to deal with different kinds of man-made sewage, technology as it is now is unable to degrade the toxic components of azo dyes. Even a very low concentration of these dyes in industrial effluents is enough to do great damage to the environment.

More worrying is the fact that current legislation only governs the amount of biochemical oxides in, and the level of alkalinity and acidity of industrial effluents, but not the dye concentration. If polluted fluids are discharged directly into the aquatic environment, their toxicity will be absorbed by aquatic creatures and will eventually find its way through the food chain into human beings. The crucial thing right now is to find a way to degrade azo dyes.

Various types of dyes used in textile industry are :

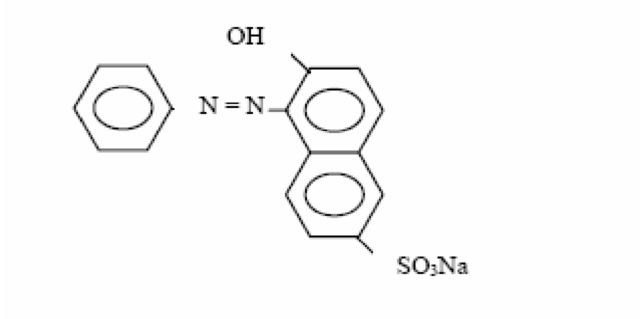
1. Direct dyes
2. Reactive dyes
3. Vat dyes
4. Sulphur dyes
5. Disperse dyes
6. Naphthol dyes

They are organic compounds containing azo groups (-N=N-) mainly bound to substituted benzene or naphthalene rings. The structure of the azo dye is shown in the following scheme:



Chrysophenine G

(a)



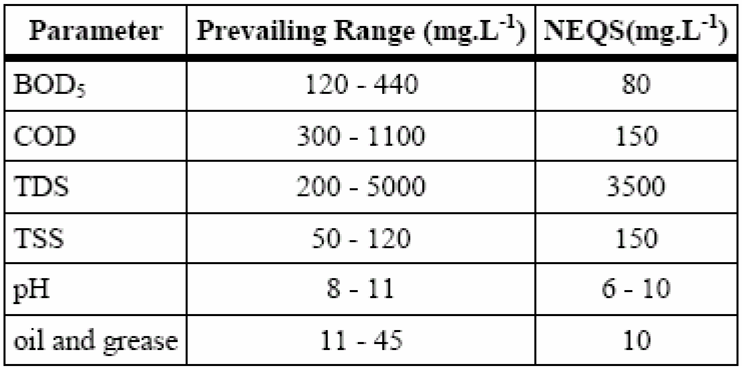
(b)

Fig. 2 Examples of some Textile industry dyes

In general, the current practice in textile mills is to discharge the wastewater into the local environment without any treatment. This wastewater causes serious impacts on natural water bodies and land in the surrounding area. High values of COD and BOD, presence of particulate matter and sediments, and oil and grease in the effluents causes depletion of dissolved oxygen, which has an adverse effect on the marine ecological system. Effluent from mills also contains chemicals; effluents are dark in color, which increases the turbidity of water body. This in turn hampers the photosynthesis process, causing alteration in the habitat. Besides, the improper handling of hazardous chemical content in textile water has some serious impacts on the health and safety of workers. Contact with chemical puts them the high-risk bracket for contracting skin diseases like chemical burns, irritation, ulcers, etc. and even leads to respiratory problems.

The contamination observed in textile wastewater is higher than the limits set by the National Environmental Quality Standards (NEQS) for all important wastewater parameters (see Table 1).

Up until relatively recently, the discharging of waste in the environment was the way of eliminating them, until the auto-purifying capacity of the environment was not sufficient. The permitted levels have been vastly exceeded, causing such environmental contamination that our natural resources cannot be used for certain uses and their characteristics have been altered. The main problem stems from waste coming from industry and agriculture, despite the fact that the population also plays an important role in environmental contamination.



Parameter	Prevailing Range (mg.L^{-1})	NEQS(mg.L^{-1})
BOD_5	120 - 440	80
COD	300 - 1100	150
TDS	200 - 5000	3500
TSS	50 - 120	150
pH	8 - 11	6 - 10
oil and grease	11 - 45	10

Table 1:Parameters for wastewater characteristics

The conventional treatment methods have their own disadvantages like:

(a) The aerobic treatment process is associated with production and disposal of large amounts of biological sludge

(b) Biodegradation, which is a major mechanism in the wastewater treatment, is quite inefficient at low level of substrate concentration. Moreover the organic compounds are oxidized biologically by aerobic and anaerobic treatment method, which does not bring down the pollution parameters to the satisfactory level

(c) 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.

To overcome the shortcomings in the existing treatment techniques research and development in innovative technologies during the last decade have shown that advanced oxidation processes (AOP's) that are combination of powerful oxidizing agents like UV light, UV/TiO_2, O_3/UV, H_2O_2 to mention a few are highly promising for the remediation of complex organic compounds which are present in contaminated water /effluent systems without generating any sludge or solid material of hazardous character. Destruction or mineralization of organic compounds by these processes is based on oxidative degradation by free radical attack, particularly by the hydroxyl radical, which is far more powerful than many other oxidants. Free radicals can be generated by a variety of methods such as:

(i) Photochemical irradiation with ultraviolet light (coupled with a powerful oxidizing agent and /or a semiconductor)
(ii) Fenton and a photo Fenton catalytic processes
(iii) Electron beam irradiation technique and
(iv) Sonolysis.

Heterogeneous and homogeneous photocatalytic detoxification methods (TiO_2/H_2O_2, Fe^{3+}/H_2O_2) have shown recently great promise in the treatment of industrial wastewater, groundwater and contaminated air. Additionally the semi- conductor-mediated photocatalytic process has also shown great potential for disinfections of air and water, thus making a number of applications possible. A general description of heterogeneous photocatalysis under artificial or solar irradiation is presented in several excellent review articles (Malato et al. (2002), Herrmann JM. (1999), Hoffman et al. (1995)). It is well established that by the irradiation of an aqueous TiO_2 suspension with light energy greater than the band gap energy of the semiconductor ($E_g > 3.2$ eV) conduction band electrons (e^-) and valence band holes (h+) are generated. Part of the photo generated carriers recombine in the bulk of the semiconductor, while the rest reach the surface, where the holes, as well as the electrons act as powerful oxidants and reductants, respectively.

The photo generated electrons react with the adsorbed molecular O_2 on the Ti (III)-sites, reducing it to a super oxide radical anion O^-_2; while the photo-generated holes can oxidize either the organic molecules directly, or the OH^- ions and the H_2O molecules adsorbed at the TiO_2 surface to OH^- radicals. These radicals together with other highly oxidant species (e.g. peroxide radicals) are reported to be responsible for the primary oxidizing step in photocatalysis. The OH^- radicals formed on the illuminated semiconductor surface are very strong oxidizing agents, with a standard reduction potential of 2.8 V. These can easily attack the adsorbed organic molecules or those located close to the surface of the catalyst, thus leading finally to their complete mineralization.

Solar heterogeneous photocatalysis is a technology based on the irradiation of a catalyst, usually a semiconductor. The process is heterogeneous because there are two active phases, solid and liquid. (Fig 3)

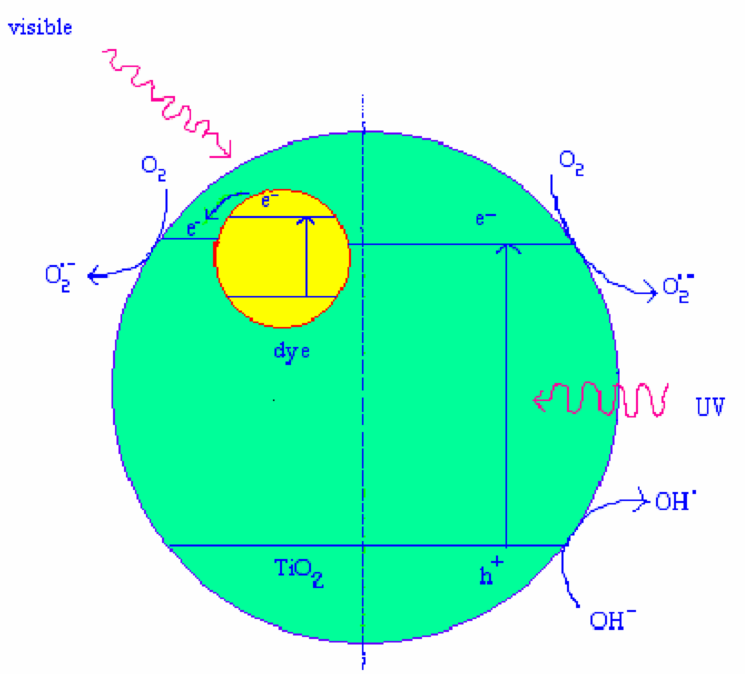


Fig 3. Example of Solar heterogeneous photocatalysis (AOP)

Solar advanced oxidation processes (AOPs) have the advantage over other advanced oxidation technologies of using natural sunlight and having as its main characteristic, that they are environmentally friendly technologies. In principle, the process involves a mild catalyst working with mild oxidants under mild conditions. However, as the concentration and number of contaminants increase, the process becomes more complicated and challenging problems such as slow kinetics, low photo-efficiency and unpredictable mechanisms need to be solved. For these reasons, it is clear that naked TiO_2 needs extra care to undertake practical applications of industrial and environmental interest. The addition of other powerful oxidizing species, such as H_2O_2 or sodium peroxydisulfate ($Na_2S_2O_8$) to TiO_2 suspensions, is a well-known procedure and in many cases leads to an increase in the rate of photo-oxidation (Malato et al., (2000), Wolfrum EJ,and Ollis DF. (1994), Poulios I,and Tsachpinis I. (1999))

CHAPTER 2
LITERATURE REVIEW

The treatment of textile effluents is of interest due to their toxic and esthetic impacts on receiving waters. While much research has been preformed to develop effective treatment technologies for wastewaters containing azo dyes, no single solution has been satisfactory for remediation of the broad diversity of textile wastes. Human and ecological health concerns have prompted the government to ensure that textile effluent discharges have increasingly lower color and nitrogen levels. Despite being aware of the problem, many textile manufactures have failed to adequately remove azo dye compounds from their wastewaters. Until dye and textile manufactures are able to develop efficient technologies, allowing for increased dye- fiber bonding and lower dye house losses (Lewis, 1999), the problem of treating these types of wastes will fall to the wastewater treatment facilities. The focus of the work is mainly in the following three types:

1.Photocatalytic (solar) treatment
2.Biological treatment
3.Coupled Photocatalytic and biological treatment

2.1 Photocatalytic (solar) treatment

The photocatalytic detoxification has been discussed as an alternative method for clean up of polluted water in the scientific literature since 1976(Carey, 1976). Lately, considerable public attention has been focused on this possibility of combining heterogeneous catalysis with solar technologies to achieve the mineralization of toxics present in water. During the last two decades advanced oxidation processes (AOP's) have been applied to the removal of refractory organic pollutants and xenobiotics (Glaze et al., 1987). Destructive oxidation of dyes and textile effluents has recently received considerable attention since colored aromatic compounds have proven to be degraded effectively by a variety of homogenous (Marechal et al., 1997) and heterogeneous AOP's (Akmehet and Aslan, 1998). Among heterogeneous AOP's TiO_2 – mediated photocatalytic oxidation appears to be a promising alternative, since the optical absorption of TiO_2 is in the near UV –A region and is the major advantage of the photocatalytic method over the UV-C driven AOP's that require light of shorter wavelengths and hence cannot make use of solar irradiation.

In an article entitled "Solar photocatalytic detoxification" by Blake et al., (1992), published in "Advances in Solar Energy" they have reviewed in detail the fundamental chemistry of solar photocatalytic detoxification and the preliminaries of engineering system development.

Kositzi et al. (2004) studied photocatalytic organic content reduction of a selected synthetic municipal wastewater by the use of heterogeneous and homogeneous photocatalytic methods under solar irradiation. In the case of heterogeneous photocatalysis the effect of catalysts and oxidants concentration on the decomposition degree of the wastewater was examined. By an accumulation energy of 50 kJL^{-1} the synergetic effect of 0.2 g L^{-1} TiO_2 P-25 with hydrogen peroxide (H_2O_2) and $Na_2S_2O_8$ leads to a 55% and 73% reduction of the initial organic carbon content, respectively. The photo-fenton process appears to be more efficient for this type of wastewater in comparison to the TiO_2/oxidant system. An accumulation energy of 20 kJL^{-1} leads to 80% reduction of the organic content. The presence of oxalate in the Fe^{3+}/H_2O_2 system leads to an additional improvement of the photocatalytic efficiency.

Aaron Wold in 1993 reviewed the photocatalytic activity of $Ti0_2$ toward the degradation of organic compounds in aqueous solutions at low concentrations. The photocatalytic activity of both polycrystalline samples and thin films can be related to the method of preparation of the catalyst. The increase in the catalytic activity of $Ti0_2$ when certain metals such as silver, gold, and palladium are deposited on the surface is also discussed. These catalysts have potential use in removing harmful carcinogens from water as well as possible application in reducing its harmful effects.

Anielak and Anna Maria (1996) reviewed to-date research work on the treatment of textile industry wastewater with application of mechanical, physicochemical, chemical and biological methods. Also, technological systems in operation and suggestions for application in textile industry wastewater treatment have been presented. On the basis of results obtained by various researchers a simple method of post-dyeing wastewater treatment applicable to all dyes and supported with author's own analysis of phenomena occurring in the process of dyes removal has been proposed.

Davis et al., (1994) has examined the photocatalytic decolorization of municipal wastewater contaminated with textile dyes using a batch reactor. Degussa P25 titanium dioxide was used as the photocatalyst and proved to be effective for dye degradation when irradiated with UV light in the presence of air. In addition to removing the color from the wastewater, the photocatalytic reaction simultaneously reduced the COD, which suggests that the dissolved organics had been oxidized. The activation energy for the photocatalytic decolorization reaction was only about 3 to 6 kJ/ mole indicating a weak temperature dependence of the rate. These results suggest that the photocatalytic degradation of textile dyes may be a viable method for decolorizing and oxidizing organics in wastewater.

To implement solar photocatalytic water detoxification in industrial processes, problems have to be identified. The effluents from paper mills contain non-biodegradable substances like polyphenolic polymer lignin. Photocatalysis is a suitable method to degrade this class of substances. Especially in good solar regions, like Brazil, solar radiation should be ideally used for that process. Different photocatalysts and oxidizing agents were tested to shape the degradation process for use in an industrial application. Tests were carried out in lamp reactors as well as in solar reactors to determine the influence of the reactor on the degradation. The kinetic of the degradation was also determined. The test results have shown that the non-biodegradable substances can be very effectively degraded by photocatalytic treatment. Especially in solar reactors like the CPC type reactor, degradation takes place very fast. Total mineralization of the contaminants can be reached. (Sattler et al., (2004)).

Li and Zhang (1996) found that TiO_2/UV treatment of a dyeing wastewater resulted in 95% color removal after 4-6 hours of treatment. Bekbolet and Ozkosemen (1996) observed 40% TOC and 75% color removal during the TiO_2/UV oxidation of humic acid solutions at the optimum catalyst loading of 1 g/L in one hour.

Hachem et al., (2001) studied the photocatalytic degradation of various dyes (Orange II, Orange G, Congo Red, Indigo Carmine, Crystal Violet, Malachite Green, Remazol Blue and Methyl Yellow), using P25 Degussa as catalyst. All dye solutions underwent a decolorization. The kinetics of reaction has been studied and was found to be zero or first order with respect to the dyes. This was compared with the adsorption properties. The effect of the addition of hydrogen peroxide has been studied. An enhancement of the rate has been observed in all cases and the order with respect to the additive was found to be almost zero. It is difficult to give a general picture of the kinetics using these very different dyes but the process was found to be effective for the decolorization of textile wastewater.

Gogate and Aniruddha (2003) reviewed five different oxidation processes operating at ambient conditions viz. cavitation, photocatalytic oxidation, Fenton's chemistry (belonging to the class of advanced oxidation processes) ozonation and use of hydrogen peroxide (belonging to the class of chemical oxidation technologies). The work highlights the basics of these individual processes including the optimum operating parameters and the reactor design aspects with a complete overview of the various applications to wastewater treatment in the recent years.

Neppolian et al., (2002) investigated the photocatalytic degradation of three commercial textile dyes with different structure using TiO_2 (Degussa P25) photocatalyst in aqueous solution under solar irradiation. Experiments were conducted to optimise various parameters viz. amount of catalyst, concentration of dye, pH and solar light intensity. Degradation of all the dyes was examined by using chemical oxygen demand (COD) method. The degradation efficiency of the three dyes is in the increasing order as follows: Reactive Yellow 17(RY17) , Reactive Red 2(RR2), Reactive Blue 4 (RB4). The experimental results indicate that TiO_2 (Degussa P25) is the best catalyst in comparison with other commercial photocatalysts such as, TiO_2 (Merck), ZnO,

ZrO_2, WO_3 and CdS. Though the UV irradiation can efficiently degrade the dyes, naturally abundant solar irradiation is also very effective in the mineralisation of dyes. The comparison between thin-film coating and aqueous slurry method reveals that slurry method is more efficient than coating but the problems of leaching and the requirement of separation can be avoided by using coating technique. These observations indicate that all the three dyes could be degraded completely at different time intervals. Hence, it may be a viable technique for the safe disposal of textile wastewater into the water streams.

The feasibility of photocatalytic decolourisation of real textile dyeing rinse wastewaters (RWWs) collected from the low salt cotton textile dyeing industry was studied by S Kanmani & K Thanasekaran (2003), using two grades of titanium dioxide (TiO_2) under ultraviolet (UV) and solar light sources. The effects of pH in the range of 6 - 10, catalyst concentration in the range of 0.05 – 0.5 g/L for indoor UV studies and 0.25 – 2.0 g/L for outdoor solar studies and catalyst reuse for twenty cycles were studied on photocatalytic decolourisation of four batches of industrial RWWs. Since the RWWs contained more than one dye, their colour measurements were done at multiple wavelengths of 436, 525 and 620 nm. In order to compare the effect of the operating variables on rinse wastewaters, the reaction time at 436 nm was taken into consideration since the reaction time necessary was the maximum at 436 nm. It is concluded that the decolourisation of RWWs could be carried out at the natural pH itself. A catalyst concentration of 1 g/L was found to be necessary in solar studies, whereas only one tenth of 1 g/L was needed for UV studies. The titanium dioxides were found to maintain their photo activity during reuse for 20 cycles.

Noorjahan et al., (2003) focused on the heterogeneous photocatalytic degradation of H-acid, a toxic and non-biodegradable dye intermediate, in TiO_2 suspensions, and TiO_2 thin film fixed bed reactor (TFFBR). The degradation studies in slurry form were investigated using TiO_2 Degussa P25 and different Millennium PC50, PC100 and PC500 photocatalysts under UV illumination. The study includes dark adsorption experiments in different pH conditions, influence of the amount of photocatalyst, effect of H-acid concentration, effect of pH on chemical oxygen demand (COD), biological oxygen demand (BOD) and the sulfate ion formation during the photocatalytic degradation. Photocatalytic treatment significantly reduces COD and increases the biodegradability of

H-acid. The intermediates have been identified by LCMS. The study with slurry is extended to the immobilization of reformed TiO_2 Degussa P25 in thin film using an acrylic emulsion by simple spray technique on inert Cuddapah stone. This method of immobilization does not require the thermal treatment of the catalyst at high temperatures. It may be used for the photocatalytic treatment of effluents at a higher scale.

Freudenhammer et al., (1997) during their research project which deals with the technical application of solar photocatalysis for wastewater detoxification. A non-concentrating thin-film fixed-bed reactor (TFFBR) is used to study applications and areas where a solar-catalytic treatment or recycling of wastewater is possible. This reactor excels by its low cost and an easy-to-build construction using molecular oxygen in air as the oxidizing agent. The design parameters of the reactor as well as the process itself have been determined from the reaction kinetics of a model substance, the hydrodynamics and the mass transfer. The treatment of different real wastewaters was successfully carried out.

2.2 Biological treatment

Conventional biological wastewater treatment plants do not easily degrade the dyes and polyvinyl alcohols (PVOH) in textile effluents. Results are reported on the possible advantages of anaerobic/aerobic co-metabolism in sequenced redox reactors. A six-phase anaerobic/aerobic sequencing laboratory scale batch reactor was developed to treat a synthetic textile effluent. The wastewater included PVOH from desizing and an azo dye (Remazol Black). The reactor removed 66% of the applied total organic carbon (load F: M 0.15) compared to 76% from a control reactor without dye. Color removal was 94% but dye metabolites caused reactor instability. Aromatic amines from the anaerobic breakdown of the azo dyes were not completely mineralized by the aerobic phase. Breakdown of PVOH by the reactor (20-30%) was not as good as previous reports with entirely aerobic cultures. The anaerobic cultures were able to tolerate the oxygen and methane continued to be produced but there was deterioration in settlement as shown by Shaw et. al., (2002).

Textile effluents often contain an array of chemicals with different biodegradation characteristics. Consequently, it is quite difficult to evaluate and interpret the degree of COD removal that can be attained by biological treatment without identifying COD portions that are resistant to biodegradation. This study evaluates the biological treatability of textile wastewaters generated by the knit and woven fabric finishing category with specific emphasis on the assessment of different residual COD components. A new method is proposed to experimentally measure the initial particulates and inert COD. The method is tested to yield a value of 73 mgl^{-1} for this COD component, corresponding to 16% of the particulate COD in the textile sample. A previously developed procedure is used to quantify the initial soluble inert COD and the residual COD generated through microbial metabolism during the treatment process. The ratio of the inert fraction to the soluble COD of the textile effluents is found to vary between 0.076 and 0.22. A similar ratio in the range of 0.04-0.09 is calculated for the residual microbial products. The kinetic and stoichiometric constants associated with the biodegradable COD are also experimentally measured. The residual components, together with the kinetic information about biodegradable fractions, are used to simulate the performance of activated sludge systems by means of a relationship between the total effluent COD and the sludge age. The results indicate that the residual components practically dominate the effluent COD and seriously challenge related effluent standards as shown by Orhon et al., (1992).

Biological treatment of wastewaters discharged by the textile industry could potentially be problematic due to the high toxicity and recalcitrance of the commonly used azo dye compounds. In this paper by Razo et al., (1997) the fate of two azo dyes under methanogenic conditions was studied. Mordant Orange 1 (MO1) and Azodisalicylate (ADS) were completely reduced and decolorized in continuous UASB reactors in the presence of co substrates. In the MO1 reactor, both 5-aminosalicylic acid (5-ASA) and 1,4-phenylenediamine were identified as products of azo cleavage. After long adaptation periods, 5-ASA was detected at trace levels, indicating further mineralization. ADS, a pharmaceutical azo dye constructed from two 5-ASA units, was completely mineralized even in the absence of co substrates indicating that the metabolism of 5-ASA could provide the reducing equivalents needed for the azo reduction. Batch experiments confirmed the ADS mineralization. These results demonstrate that some azo dyes could serve as a carbon, energy, and nitrogen source for anaerobic bacteria.

Beydilli et al., (2000) investigated the decolorization of the azo dye reactive red 2 (RR2) under aerobic, anoxic, and methanogenic conditions. The dye was not decolorized by an aerobic culture kept under aerobic conditions for 7 days. However, incubation of the same culture under anoxic conditions resulted in RR2 decolorization with an initial rate of 40 mg/L center dot d and to an extent of 91.7% after the culture oxidation-reduction potential (ORP) dropped to less than minus 50 mV. A second addition of RR2 to the same culture kept under anoxic conditions resulted in a greater initial RR2 decolorization rate (86 mg/L center dot d) at an ORP value of minus 250 mV. Decolorization of RR2 at an initial dye concentration of 300 mg/L was achieved by an unacclimated methanogenic culture at an initial rate of 83-mg/L center dot d and without any inhibition. However, as a result of acclimation, initial RR2 decolorization rates of 523 and 1050 mg/L center dot d were achieved by the same methanogenic culture after 5 months and 2 years of weekly additions of 300 mg/L RR2, respectively. Dye decolorization followed Michaelis-Menten kinetics. Under methanogenic conditions and at an initial dye concentration of 300 mg/L, the maximum RR2 decolorization rate per unit biomass was 0.12 and 0.70 mg RR2/mg volatile suspended solids center dot d without acclimation and after a 2-year acclimation, respectively. Lack of significant RR2 decolorization was observed in autoclaved methanogenic culture controls. Therefore, the reductive cleavage of the dye azo bond resulting in the decolorization of RR2 and formation of aromatic amines was biologically mediated and is attributed to the reduced conditions created and maintained by the anoxic and anaerobic cultures. Thus, biological decolorization of reactive azo dyes is feasible under anoxic-anaerobic conditions and should be further explored for textile wastewater management.

A method to decolorize wastewater that eliminates the need for inorganic oxidizing agents such as ozone or precipitating agents such as polymeric flocculants is described. This biological approach is unique to the industry and builds on expertise gained from experience with white-rot fungi (e.g., *Phanerochaete chrysosporium*) that have been isolated and characterized. Enzymes such as laccases and manganese peroxides can cleave aromatic rings. These have potential for destroying dyes though individual enzymes, which are capable of breaking down one type of dye molecule with a particular structure, may be blocked from attacking another dye structure. Another drawback of the specific enzyme approach may be the rate of reaction. The approach in this research takes advantage of the environmentally friendly action of enzymes and uses the entire microorganisms to decolorize wastewater, Hardin et al., (2000).

S.M. Ghoreishi and R. Haghighi (2001) investigated the effectiveness of a combined reduction-biological treatment system for the decolorization of non-biodegradable textile dyeing wastewater In this treatment system, a bisulfite-catalyzed sodium borohydride reduction followed by activated sludge technique was used in order to remove the color at ambient temperature and pressure. This experimental study consisted of two major parts: reduction treatment and biological oxidation. Both synthetic and actual wastewater was used in this research. Synthetic wastewater was made by several groups of dyes such as direct, basic and reactive colors. Actual wastewater was collected from two different textile industries in the city of Isfahan, Iran. The characterization of raw and treated wastewater was carried out by infrared and ultraviolet spectrometers. The results of this study demonstrated that the newly developed treatment technique decreased color, BOD, COD and TSS by 74 to 88%, 76 to 83% and 92 to 97%, respectively. The IR and UV analyses showed that non-biodegradable dyes are converted to biodegradable organic compounds such as alkyl and alkenes. Another major advantage of this method with respect to other methods, namely, adsorption and coagulation, was that it removes color without causing any disposal problem. The optimum dosage for treatment of actual wastewater was found to be 50 to 60 mg/l for catalyst bisulfite and 200 to 250 mg/l for sodium borohydride.

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2.3 Coupled Photocatalytic (Solar) and biological treatment

Biological treatment of wastewater has been known for almost hundred years. However, in the case of industrial wastewaters this method is not sufficient because they carry high content of xenobiotics along. The efficiency of biodegradation may significantly be increased by chemical oxidation. Recently, the so-called advanced oxidation processes (AOP's) combined with biological treatment have appeared to be successful in large-scale systems, therefore it is reasonable to present the fundamentals of the application of combined methods in wastewater treatment. The general statements about the integration of biodegradation and chemical oxidation are exemplified by case studies of textile wastewater biodegradation combined with AOP's, which have been the subject of the research from last few years as reported by Ledakowicz and Stanislaw (1998).

Sarria et al., (2003) overviewed recent work in coupling Advanced Oxidation Processes (AOP's) and Biological systems for wastewater treatment and confirms the beneficial effects of such two-step treatment at lab scale. In this paper, an innovative-coupled solar-biological system at field pilot scale was designed and experimental results are presented. The strategy to develop this system implicates the choice of the most appropriate solar collector and the most efficient AOP, the optimization of this AOP, the choice of the biological oxidation system, the monitoring of the chemical and biological characteristics of photo-treated solutions and the evaluation of the performances of the coupled solar-biological flow system. The coupled reactor, operating in semi -continuous mode, has shown to reach a whole mineralization performance between 80 and 90% in the range of initial dissolved organic carbon (DOC) concentration of 300–500 $mgCl^{-1}$. These results indicate that coupling solar-biological processes at pilot scale is a plausible and effective approach for the treatment of real industrial wastewaters.

Ock Koh et al., (2003) studied the leachates from municipal waste deposits which were biologically pre-cleaned, were treated subsequently by photochemical oxidation using three different UV sources. The reactor concept was based on a 'continuous circuit reactor' with back-mixing and thin film. The power was 84 kW/m^3 for the low-pressure mercury lamp, 100 kW/m^3 for the middle pressure mercury lamp, and 30 kW/m^3 for the vacuum mercury lamp. The ratio of chemical oxygen demand (COD) and BOD$_5$ was reduced from ca. 230 to 3–4 (in the case of low pressure and vacuum mercury lamp) and to 6 (middle pressure mercury lamp). After the photochemical oxidation stage, the leachate was treated in an additional step using an activated sludge plant. After this biological stage, the values of COD, BOD, and AOX decreased further below the threshold values defined in the legislative regulation.

Sarria et al., (2002) proposed a general strategy to develop combined photochemical and biological system for biorecalcitrant wastewater treatment. For the development of this strategy, the following points were taken into account: the biodegradability of initial solutions, the operation mode of the coupled reactor, the chemical and biological characteristics of the phototreated solutions, the evaluation of different photoassisted advanced oxidation processes, the optimal conditions of both photochemical and biological processes, and the efficiency of the coupled reactor. The strategy to couple photochemical and biological processes is illustrated by case studies of four different biorecalcitrant pollutants. Three kinds of combined systems were developed using either photo-Fenton, Fe^{3+}/UV, or TiO_2 supported on glass rings for the photocatalytic pretreatment and in all cases immobilized biomass for the biological step. The advantages of the each coupled system are discussed and beneficial effects of such two-step treatments were found. However, this strategy is not a universal solution. Chemical, biological, and kinetic studies must be always carried out to ensure that the photochemical pretreatment increase the biocompatibility of the treated wastewater. Some field experiments using solar reactor indicated that a coupled photochemical–biological treatment system at pilot scale is a possible way to achieve the complete mineralization of the biorecalcitrant pollutants.

Ledakowicz et al.,(2001) studied synthetic wastewater, simulating effluents from the knitting industry. The wastewater contained components that are very often used in Polish textile industry: an anionic detergent Awiwaz_ KG conc., a softening agent Tetrapol CLB and an anthraquinone dyestuff—Acid Blue 40, CI 2125. The toxicity of the detergents and the dye was determined in terms of effective concentration EC_{50} using mixed cultures of activated sludge as well as pure culture of luminescent bacteria *Vibrio fischerii* NRRLB-11177. The dye did not undergo biodegradation without AOP's pretreatment, therefore a degree of its removal (depolarization) by the AOP's has been determined and its bio-sorption properties on the flocks of activated sludge have been studied. They also studied influence of various oxidants like O_3, H_2O_2 and UV light on biodegradation of single components aqueous solution as well as of the whole textile wastewater. The results of kinetic measurements of the biodegradation (by means of acclimated activated sludge) were described by Monod type of kinetic equation. The experimental evidence of the positive effect of chemical oxidation pretreatment on the biodegradation of recalcitrant compounds was quantified by estimation of the kinetic parameters of the Monod equation.

Pulgarin et al., (1999) presented a combined photochemical (Fenton) and biological flow reactor for the degradation of *p*-nitrotolueneortho- sulfonic acid (*p*-NTS). This compound is contained in wastewaters coming from manufactures of dyes, surfactants, and brighteners. The non-biodegradability of *p*-NTS in a fixed bed reactor (FBR) was proved under theoretically favourable conditions such as the presence of cosubstrates and adapted bacteria. From this ascertainment, *p*-NTS can be considered as a non-biodegradable compound. Afterwards, several experiments for sole photo-Fenton treatment were carried out in a laboratory scale photoreactor. By way of Dissolved Organic Carbon (DOC) and HPLC techniques, it was found that mineralization of *p*-NTS via photo-Fenton treatment in continuous or batch mode is not a cost-effective strategy. However, the chemical and biological characteristics studied for the phototreated samples showed that the Fenton system produced within a short time intermediates with very oxidised functional groups that are biodegradable and non-toxic. This thus could permit the integration of photochemical and biological processes. During treatments in continuous mode, it was found that the main inconvenience of this application is related to the difficulty to control the H_2O_2 concentration. With this system, it was hard to avoid the inhibition of bacteria and hence a low biodegradation efficiency. To overcome the inconveniences of the process mentioned above, the semi-continuous mode was applied.

The coupled photochemical-biological reactor was operated at five different treatment times (respectively 50, 70, 95, 110 and 125 min).

Hsieh et al., (2000) used wastewater from manufactured fiber plant for studying the effect of controlling variables on the COD removal efficiency by photocatalyzed degradation of organic pollutants in the presence of titanium dioxide catalyst. By using BOD/COD ratio as index, the treatment of raw wastewater was evaluated for its change of biodegradability as feasibility in the pre-treatment of biological treatment. The experimental results indicated that using Janssen Chemica TiO_2 as catalyst, the optimal addition was 0.25 g/L with increasing COD removal for decreasing pH value. Both with increased light intensity and continuous aeration increased COD removal efficiency, particularly under continuous aeration for significantly raising the ratio of BOD/COD to improve efficiency of subsequent biological treatment.

Augugliaro et al., (2002) carried out the study of heterogeneous photocatalytic oxidation of contaminants present in wastewater produced by a textile industry. The samples were withdrawn from the plant before and after a traditional biological treatment. The effluents were named A and A' (before the biological treatment), B and B' (after the biological treatment). Polycrystalline TiO2 (Degussa P25) was used as the catalyst in a batch photoreactor with immersed lamp. An almost complete decolorization was observed after about 0.5 divided by 1 hour for both kinds of effluents, but the decrease of the total organic carbon (TOC) concentration occurred more slowly. The influence of some chemical oxidants, i.e. ozone, hydrogen peroxide and peroxydisulfate on the photo-oxidation rate was also investigated. After addition of H_2O_2 or $S_2O_8^{2-}$ TOC decreased more quickly only for B and B'. The runs performed by using O_3 as bubbling gas showed a mineralization rate higher than that observed in the presence of O_2.

Lee et al., (2001) have carried out the theoretical and experimental studies and have established that integrated treatment systems (mostly chemical and biological) for various industrial wastewaters can achieve better quality of treatment and can be cost-effective. In this paper the objective is to minimize the use of process water in the textile industry by an economical recycle and reuse scheme. The textile wastewater was first characterized in terms of COD, BOD_5, salinity and color. In order to recycle such wastewater, the contaminants should be mineralized and/or removed according to the reusable textile water quality standards. Typical results show that this is achievable. An economic analysis has been conducted on the proposed integrated system. The economic analysis shows that the integrated system is economically more attractive than any of the single treatment technologies for achieving the same target of treatment. The information presented in this paper provides a feasible option for the reduction of effluent discharges in the textile industry.

M. Pratap Reddy et.al (2003) studied the de-colorization and mineralisation of common industry effluents with TiO_2 Photocatalyst using solar light illumination. The data indicates that the color and COD removal by the photocatalytic treatment is 74% and 62%, respectively (treated under sunlight for 40 hr) whereas the COD removal in biological treatment is only 18% (treated for 120 hr using Up-flow Anaerobic Sludge Blanket(UASB) reactor). The initial value of BOD/COD ratio of common industry effluent is 0.21, whereas the photocatalytic treatment method has improved the BOD/COD ratio to 0.56. Also the samples treated after photocatalytic method are further subjected to biological treatment that resulted an improved levels of COD removal 72%, confirming that the pretreatment of common industry effluent with photocatalytic method is beneficial.

CHAPTER 3

PERSPECTIVES OF SOLAR FIELD TECHNOLOGY

Solar radiation as source of light

Solar radiation and in particular its ultraviolet component**,** is considered of interest being the existence of ultraviolet radiation the key of some heterogeneous and homogeneous photocatalytic processes, such as TiO_2/UV and H_2O_2/Fe^{2+}/UV-vis or H_2O_2/Fe^{3+}/UV-vis system (photo-Fenton). The use of solar light as source of radiation in the TiO_2/UV- vis system has been studied, taking as reference the recent development of solar technology in water detoxification by means of heterogeneous photocalysis (TiO_2/UV) (Bahnemann *et al.*, 1994; Malato, 1999; Blanco and Malato, 2001). In this sense, this section describes the power of sunlight as source of energy, as well as the basic factors related to the photocatalytic technology and its application. In addition, it outlines the basic principles related to the solar spectrum and especially to the solar UV radiation since this part of the solar spectrum is the most important one for driving chemical processes and the main features of the collectors used for wastewater detoxification.

Solar radiation

Solar radiation is all the energy coming from that huge reactor, the sun, from which the earth receives $1.7x10^{14}$ kW, meaning $1.5x10^{18}$ kWh per year, or approximately 28000 times the world energy consumption per year. The wavelength of the radiation beyond the atmosphere ranges between 0.2µm and 50µm. This range is reduced to 0.3 µm and 3.0 µm when reaching the earth surface due to the absorption of part of the radiation by different atmospheric components (e.g., ozone, oxygen, carbon dioxide, aerosols, steam, clouds). Solar ultraviolet radiation is only a very small part of the total solar spectrum, going between 3.5%and 8%, as demonstrated by measurement, although this percentage may vary for a given location on cloudy and clear days. The percentage of global UV radiation (direct + diffuse) generally increases with respect to the total global radiation when atmospheric transmissivity decreases mainly because of clouds, but also because of aerosols and dust. In fact, the average percentage of UV with respect to total radiation on cloudy days is up to two percent points higher than values on clear days.

The solar radiation that reaches the ground level without being absorbed or scattered, is called direct radiation; the radiation, which has been dispersed but reaches the ground level is called diffuse radiation and the addition of both is called global radiation (see Fig 4).

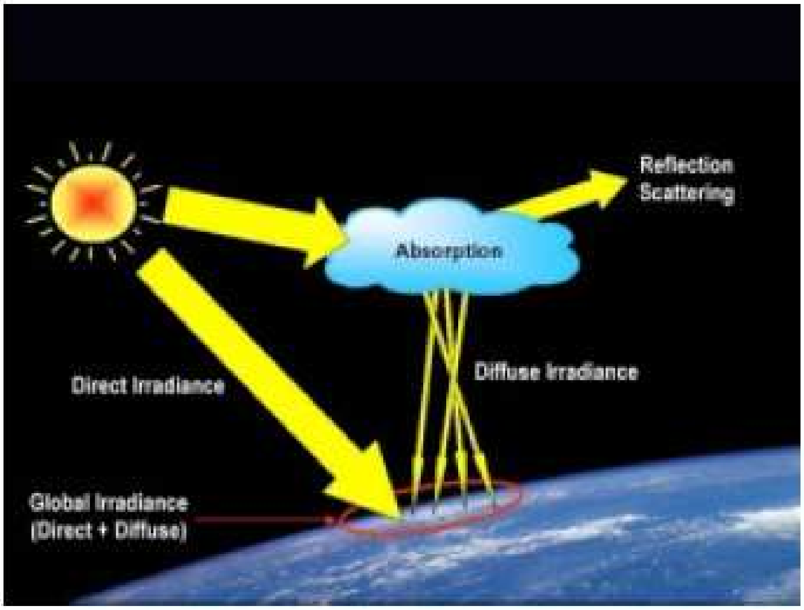


Fig: 4. Direct and diffuse radiation

Solar collectors

Traditionally, the different solar collector systems have been classified depending on the concentration level attained with them (relationship between the collecting surface and the surface where the final result is produced), which is directly related with the system working temperature. According to this criterion, there are three types of collectors:

I. No concentration or low temperature, up to 150º C
II. Medium concentration or medium temperature, from 150º C to 400º C
III. High concentration and high temperature, over 400º C.

Non-concentrating solar collectors (Fig. 5) are static, without any solar tracking device. They are usually a flat plate, in many cases aiming to the sun with a determined tilt, depending on the geographic situation. Their main advantage is the reduced cost and, for many applications, the collected radiation is sufficient.

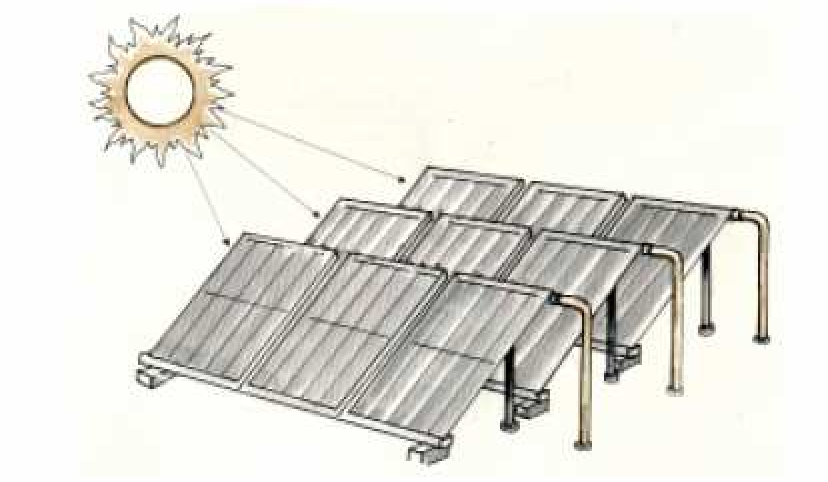


Fig: 5. Non-concentrating solar collectors

Medium concentration solar collectors concentrate the sunlight between 5 and 50 times. Parabolic Trough Collectors (PTC) and collectors with Fresnel lenses are within this group. The first ones have a parabolic reflecting surface (Fig. 6), which concentrates the radiation on a tubular receiver located in the focus of the parabola. They can be of:

- one axis tracking,
- two tracking axis

Fig.6. Medium concentration solar collectors

High concentration collectors have a focal point instead of a linear one and are based on a paraboloid with solar tracking. Parabolic dishes and solar furnaces are among them (Fig. 7). Typical concentration ratios are in the range of 100 to 10000 requiring optimal precision elements.

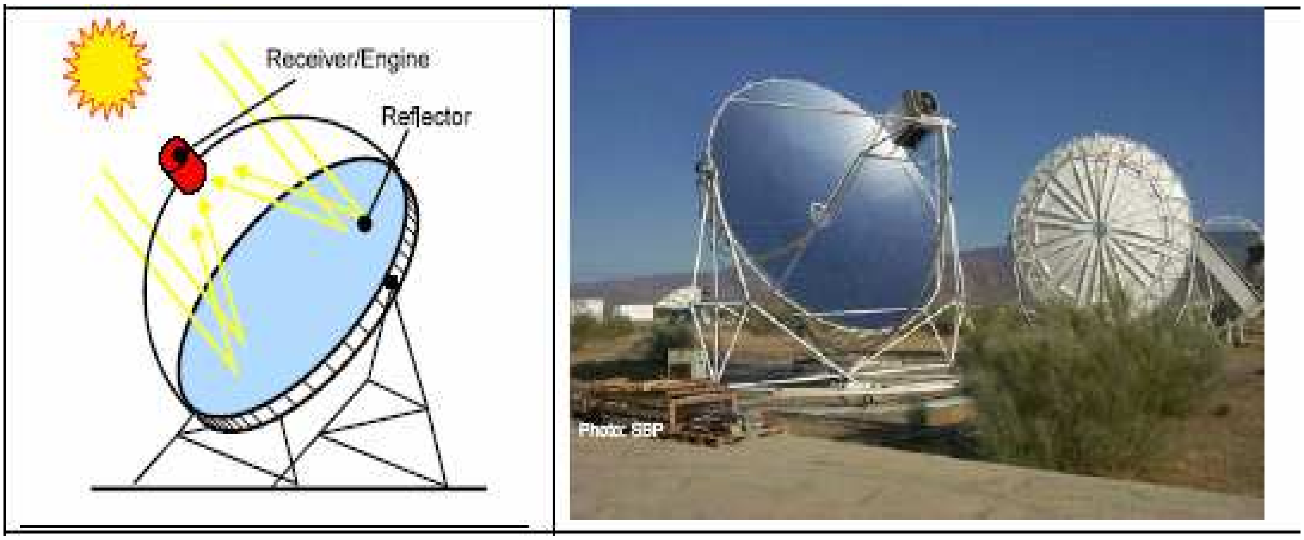


Fig: 7. High concentration collectors

Industrial Applications of Solar Radiation

Solar thermal power is one of the main candidates to provide a major share of renewable clean energy needed in the future because:

- Solar radiation is the largest renewable resource on earth. Approximately 1% of the world's desert area utilized by solar thermal power plants would be sufficient to generate the world's entire electricity demand anticipated for the year 2000.

- Solar radiation is more evenly distributed in the sunbelt of the world than wind or biomass, allowing for more site locations.

- It is among the most cost effective renewable power technologies with power generation costs to be expected in the range of 6 to 15 ct/kWh. And it is the lowest cost solar electricity in the world, promising cost competitiveness with fossil-fuel plants in the future.

- It is a proven and demonstrated technology. Over 100 years of accumulated operating experience, with nine solar thermal power plants of the parabolic trough type feeding over 8 billion kWh of solar-based electricity into the Californian grid, demonstrate the soundness of the concept.

The concentrator captures and concentrates solar radiation, which is then delivered to the receiver. The receiver absorbs the concentrated sunlight, transferring its heat to a working fluid. The transport-storage system passes the fluid from the receiver to the power- conversion system; in some solar-thermal plants a portion of the thermal energy is stored for later use.

One of the most important reactor-design issues is the decision between concentrating or non-concentrating collector systems. Concentrating systems present the advantage of much smaller reactor-tube area, which could mean a shorter circuit in which to confine, control and handle the contaminate water to be treated. If concentrating collector system has to be used, an improving alternative, from both economical and engineering points of view, would be the use of high-quality ultraviolet-light-transmitting reactors.

Nevertheless, concentrating reactors have two important disadvantages compared to non- concentrating ones. The first one is that they cannot concentrate (i.e. use) diffuse solar radiation. This fact is irrelevant for solar thermal applications because diffuse radiation is just a small fraction of the total solar radiation. However, this disadvantage becomes important in solar TiO_2-photocatalytic and photo-Fenton detoxification as it uses only the UV fraction of the solar spectrum from which as much as 50 percent can be diffuse, since it is not absorbed by water vapor (Romero *et al.*, 1999). This percentage can be even higher in very humid location or during cloudy or partly cloudy periods. In this sense, efficiency of non-concentrating solar collectors can be noticeably higher, as they can take advantage of both direct and diffuse UV radiation. The second disadvantage of concentrating collectors is their complexity, cost and maintenance requirements. As a consequence of these disadvantage, the present state-of-the art favors the use of non-concentrating reactors for solar photocatalytic applications.

Parabolic Trough Collectors

The first engineering-scale solar photochemical facility for water detoxification was developed in 1989 by Sandia National Laboratories (USA) using one-axis PTC. The second one was developed by Plataforma Solar de Almería (PSA), Spain in 1992 using two-axis PTC. One-axis tracking PTC has been demonstrated to be the most economically advantageous for solar thermal applications.

Compound Parabolic Collectors (CPCs)

Compound parabolic collectors are a very interesting cross between through concentrators and one-sun system and are one of the best options for solar phototocatalytic applications. These collectors have been found to provide the best optics for low concentrating system.

CPCs are static collectors with a reflective surface describing an involute around a cylindrical reactor tube; it can be designed with a CR=1 (or near one), thus having the advantages of both PTCs and one-sun collectors (Gimenez *et al.*, 1999).

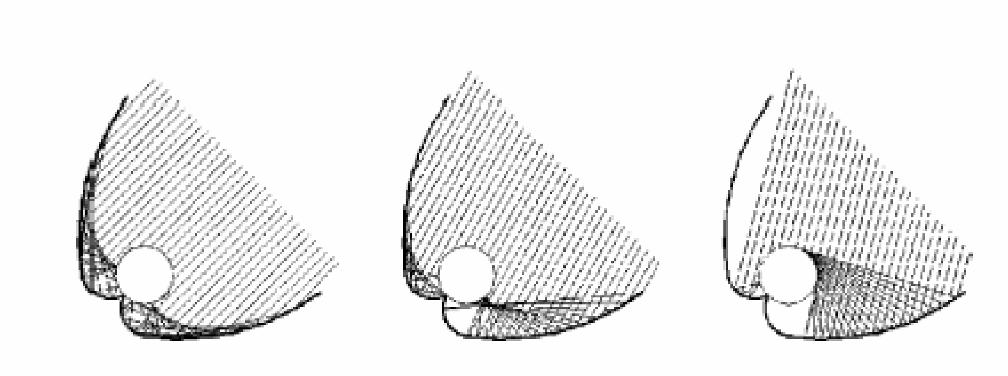


Fig.8. Solar reflection on a CPC collector.

Water Treatment

Often industrial wastewaters are very difficult to clean by conventional treatment technologies. Especially the most common and cost efficient biological treatment fails because many constituents of industrial effluents are non-biodegradable. Research on innovative methods for water treatment has moved from processes involving phase transfer of a contaminant (e.g. from liquid to solid such as activated carbon adsorption, from liquid to gas in the case of air stripping of volatile compounds) towards processes involving chemical destruction of the contaminant.

Solar Photocatalytic mineralisation of organic water pollutants has a strong potential for the efficient treatment of water streams polluted with toxic or non bio-degradable substances. It is using the interaction either between ultraviolet radiation and particulate TiO_2 semi-conductor catalyst or ultraviolet and visible radiation and homogeneously dissolved iron ions (Photo-Fenton catalyst). Pilot-scale water treatment processes have been demonstrated in several cases.

The Solar Photocatalytic Detoxification Process has shown to be very promising for the treatment of contaminated water. It has also shown great potential for water disinfections, making possible a wide number of applications. Nevertheless, the specific solar technology to carry out the process does not presently exist commercially. Trying to solve this problem, an Industrial Consortium has been established throughout a project denominated *"SOLARDETOX"* with the objective of developing and marketing the best available solar detoxification technology to the treatment of recalcitrant water contaminants from industrial or agricultural activities. So, the basic idea of the project is the development, up to commercial level, of a Solar Detoxification System based on the simple, inexpensive and efficient non concentrating solar collector technology which is the best technological solution to Solar Detoxification Systems as static collectors can capture the diffuse UV sunlight as well as the direct beam.

Specifically, the Compound Parabolic Collector technology (CPC), with a concentration ratio = 1, seem the most adequate and feasible to commercial applications. In addition to assessing destruction capabilities, field demonstration identified pre- or post-processing requirements, potential operating problems, and capital and operating costs.

Fig: 9. SOLARDETOX CPC Pilot Plant for Solar Photocatalytic Detoxification of Industrial Waste Waters in Arganda del Rey close to Madrid, Spain

TiO_2 is a photocatalytically active material being resistant to corrosion and to photocorrosion and it can be handled safely. It is activated with solar UV radiation because the energy of UV photons can surpass the band gap energy of the semiconductor (3.2 eV for titanium dioxide in its anatase modification – equivalent to light shorter than 390 nm). This activation leads to the formation of electron/hole pairs in the semiconductor, where e^-_{cb} represents a conduction band (cb) electron and h^+_{vb} a positive hole in the valence band (vb). Recombination of the electrons and holes is an undesired competing reaction within the semiconductor that diminishes the efficiency. On hydrated and hydroxylated TiO_2 surfaces, the holes generate hydroxyl radicals linked to the surface. Hydroxyl radicals ($HO^{*\cdot}$) appear to be the main oxidizing species, which initiate the oxidation of the organic compounds.

CHAPTER 4

MATERIALS AND METHODS

Actual wastewater sample was collected from S.R. Industries (Textile Unit), Dera Bassi. Initial parameters of the sample were checked and further treatment was done. Materials and methods used for this purpose have been presented in this chapter.

REAGENTS AND CHEMICALS

The photocatalyst used in all the experiments was anatase form of titanium dioxide powder, (Degussa P25 TiO_2 procured from Degussa Company, Germany having a BET surface area of 50 ± 15 m^2g^{-1} with average particle size of 30 nm). Hydrogen peroxide (Ranbaxy laboratories) was used as an oxidant. Hydrochloric acid (Merck) was used to adjust the pH. Reagents used for COD determination were potassium dichromate, mercuric sulphate, silver sulphate, conc. sulphuric acid, ferrous ammonium sulphate and ferroin indicator. For BOD determination sodium thiosulphate, manganese sulphate, potassium iodide, sodium azide, starch and sulphuric acid (All chemicals brought from Ranbaxy laboratories). All chemicals were used as received. In all the experiments distilled water was used.

APPARATUS USED

RADIOMETER

Sunlight Intensity (UV) was measured hourly during experimental days with Eppley radiometer.

Fig 10. Eppley (model no. 33013) radiometer was used for measuring the UV intensity.

pH METER

The pH of the solution was varied by adding HCl or NaOH solution as per requirement and measured using ELICO, India LI 120-pH meter.

FILTRATION

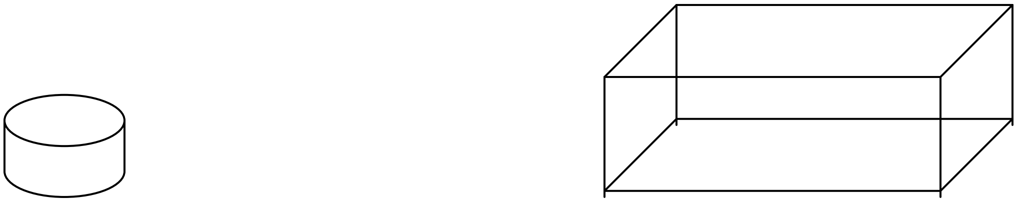
Samples after photocatalytic treatment were filtered through Millipore filter (0.45µm) membrane. Wattman filter papers (No.42) and normal lab filter papers were also used.

AUTOCLAVE

Semi- Automatic autoclave (EQUITRON) was used for the digestion of samples in COD determination.

REACTORS

For the photocatalytic process reactors used were either cylindrical in shape and made of borosil glass, which has a diameter of 5 cm and is 6cm in height with a capacity of approximately 1000ml or rectangular type having dimensions 2’x1’x1.5’m. The experiments were carried out in a shallow pond batch slurry reactor. For the biological teatment the same type of glass reactor was used as shown in figure- 11.



Cylindrical Rectangular shaped

Fig 11. Reactors used for Experimental methods

METHODS

SAMPLE COLLECTION AND STORAGE

Wastewater sample was collected from the effluent treatment plant from the equalization tank. The sampling bottle was cleaned and rinsed carefully with distilled water and then with the effluent. About 2.5 cm air space is left in the bottle to facilitate mixing by shaking. Then samples were stored at 4^{0}C within one to two hours of collection.

WASTEWATER CHARACTERIZATION

Complete analysis of the water was done by measuring COD, BOD, TDS, TSS, TS, Color and pH. The methods used are as follows:

ESTIMATION OF BOD

BOD was determined as per standard method No. 5210 B, page no. 5-4 from STANDARD METHODS for the examination of water and wastewater, 1989, 17th edition. Dilutions for strong industrial effluents are quoted from 0.1% to 1.0%. So accordingly 0.2% and 0.4% dilutions were made. Tests were repeated for getting the reproducibility of results.

ESTIMATION OF COD

COD was calculated as per the standard method No. 5220 C, page no. 5-14 from STANDARD METHODS for the examination of water and wastewater, 1989, 17th edition. For all the samples 1:1 dilution was made so as to get COD within range while using above method. Samples were digested in semi-automatic autoclave.

TOTAL SOLIDS

TS were measured by method No. 2540 B, page no. 2-72 of STANDARD METHODS for the examination of water and wastewater.

TOTAL DISSLOVED SOLIDS

TDS were estimated as per the standard method No. 2540 C, page no. 2-74 of STANDARD METHODS for the examination of water and wastewater.

TOTAL SUSPENDED SOLIDS

TSS was calculated by method No. 2540 D, page no. 2-75 of STANDARD METHODS for the examination of water and wastewater.

BIODEGRADABILITY OF ORGANIC POLLUTANTS

Due to the high cost of photochemical treatments, it must be first confirmed that target pollutants are definitively non-biodegradable since for biodegradable compounds, classical biological treatments are, at present, the cheapest and the most environmentally compatible.

A ratio of BOD&COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD&COD is more than 0.3, the wastewater has a better biodegradability. Whereas the ratio is less than 0.3, the wastewater is difficult to be biodegraded. Table 5 shows that the ratio of BOD /COD in all selected azo dyes solution is less than 0.3. These azo dyes can't be biodegraded by activated sludge.

To investigate the biodegradability of dyes solution after photocatalytically treatment, COD and BOD of the samples at different treatment times were measured.

SOLAR PHOTOCATLYTIC TREATMENT

SAMPLE PREPRATION

Wastewater collected from the textile industry was highly concentrated. So to get the values within range, the sample was diluted in the ratio of 1:1. Distilled water was used for all the dilutions. Initial pH was checked.

PROCEDURE

Sample was treated in natural sunlight, as shown in Figure12. Intensity of UV radiations was measured continuously with the help of radiometer. Samples were withdrawn after every one hour and filtered. COD of the samples were then measured as per the standard methods. Results were then optimized regarding oxidant addition, pH adjustments. Tests were repeated for getting the reproducibility of results.

After photocatalytic treatment (with optimized conditions), water was filtered and checked for COD, BOD, TSS, TS, TDS, pH etc. Then it was sent for biological treatment.

Fig 12: Photocatalytic treatment in sunlight

BIOLOGICAL TREATMENT PROCEDURE

Biological treatment of the sample was done with:

- Raw sewage
- Acclimatized sewage

For photocatalytic treated water

Photocatalytic treated water was filtered and then subjected to biological treatment with raw sewage and acclimatized sewage as a source of microorganisms. After biological treatment again all the parameters were checked.

Direct Biological treatment

Raw effluent was directly subjected to biological treatment with both types of seeds. Before the biological treatment the pH was adjusted within the range of 6-8 suitable for biological treatment.

CHAPTER 5

RESULTS AND DISSCUSSIONS

Results of analysis of the wastewater from the textile industry using heterogeneous AOP's are presented here. Effluent was first subjected to photocatalytic pretreatment and further in conventional biological process.

Wastewater characteristics

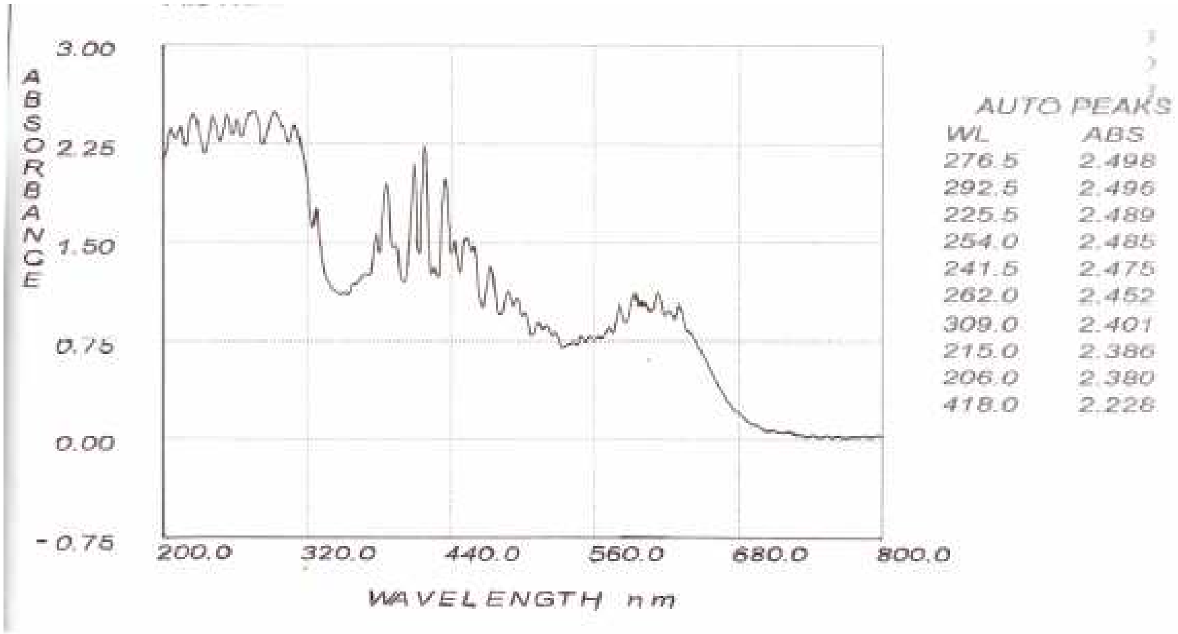
Raw wastewater was collected from S.R. Industries (Textile Unit), Derra Bassi, located 80-90 km from Patiala on Zirkpur- Ambala road. Wastewater was taken from flow equalization tank and analyzed for its various parameters.The results of the various parameters are shown in Table 2.

Table 2: Characteristics of raw textile effluent from S.R.Industries

S.No.	**Parameter**	**Prevailing Range (mg. L^{-1})**
1.	COD	700-800
2.	TDS	8500-9000
3.	TS	9000-9800
4.	TSS	600-800
5.	BOD/COD	0.2-0.25
6.	COLOR	> 5000 Pt CO
7.	pH	10-11
8.	TKN	30
9.	Temperature	40^0C

Thus these parameters show that the wastewater is highly polluted. So some pretreatment is required so as to safely discharge the water.

Abortion spectra for raw effluent



WL	ABS
276.5	2.498
292.5	2.496
225.5	2.489
254.0	2.485
241.5	2.475
262.0	2.452
309.0	2.401
215.0	2.386
206.0	2.380
418.0	2.228

Fig 13. Absorption spectra for the raw effluent

The absorption spectra of the raw sample were taken which showed several peaks in the UV and visible region. This clearly indicates the presence of several organic chromophoric compounds in the wastewater and degradation studies for the complete mineralisation is needed. This confirms the low Biodegradability value (BOD/COD =0.2) for the effluent.

SOLAR PHOTOCATALYTIC PRETREATMENT

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

- ☐ Catalyst concentration
- ☐ Operating pH
- ☐ Oxidant addition
- ☐ Dilution factor

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

Radiation Conditions in Punjab During summers

The Solar Photocatalytic treatment requires the effective exposure of samples to Sunlight so as to collect solar radiations for treatment of the effluents. In Punjab, during summers we can have good intensity of sunlight. The amount of UV radiation, which can be used for TiO_2 photocatalysis on a summer day (April, May, June) with a maximum of about 30-37 W/m^2. Fig 14. shows the variation of solar intensities with time during Experimental days.

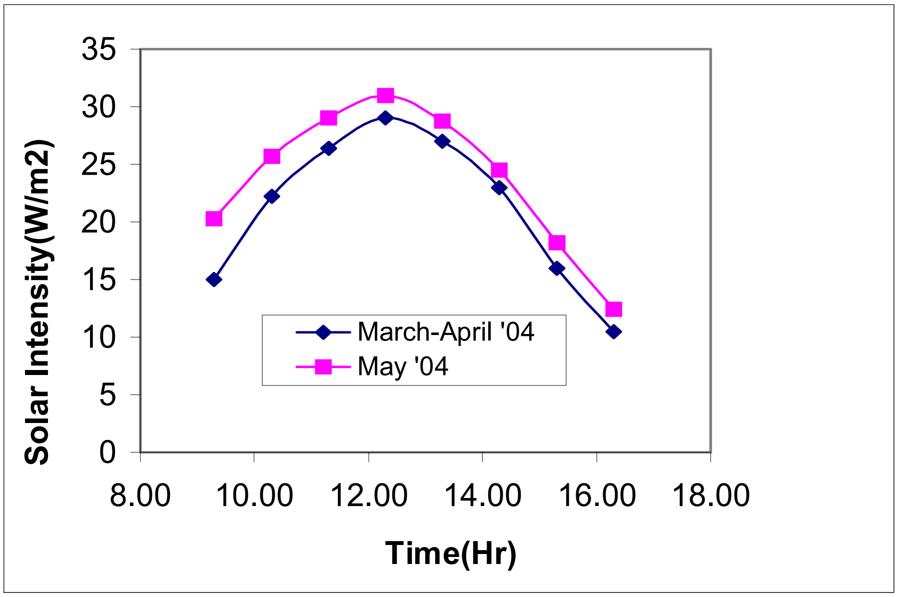


Fig 14. Intensities of solar radiations during experimental days

Catalyst concentration

Catalyst (TiO_2) concentration was varied from 1.0 g/l to 10 g/l (i.e. 0.1% to 1.0%) during reactions in sunlight. It was observed that rate increases with increase in catalyst concentration and becomes constant above a certain level as shown in Figure 15. The reasons for this decrease in degradation rate are:

(i) Aggregation of TiO_2 particles at high concentrations causing a decrease in the number of surface active sites and

(ii) Increase in opacity and light scattering of TiO_2 particles at high concentration leading to decrease in the passage of irradiation through the sample.

As the concentration of catalyst is increased, the number of photons absorbed and the number of pollutant molecules absorbed are increased owing to an increase in the number of TiO_2 particles. The density of particles in the area illumination also increases and so the rate is enhanced. Above a certain level, the substrate molecules available are not sufficient for adsorption by the increased number of TiO_2 particles. Hence the additional catalyst amount is not involved in the catalytic activity and the rate does not increase with an increase in the amount of catalyst beyond a certain limit. Surface active sites also decreases due to aggregations of TiO_2 particles at high concentrations. This observation is in agreement with the observations reported in literature and an amount of 3.0 mg/l has been taken for the subsequent experiments for studying the effect of oxidant addition and pH of the solution.

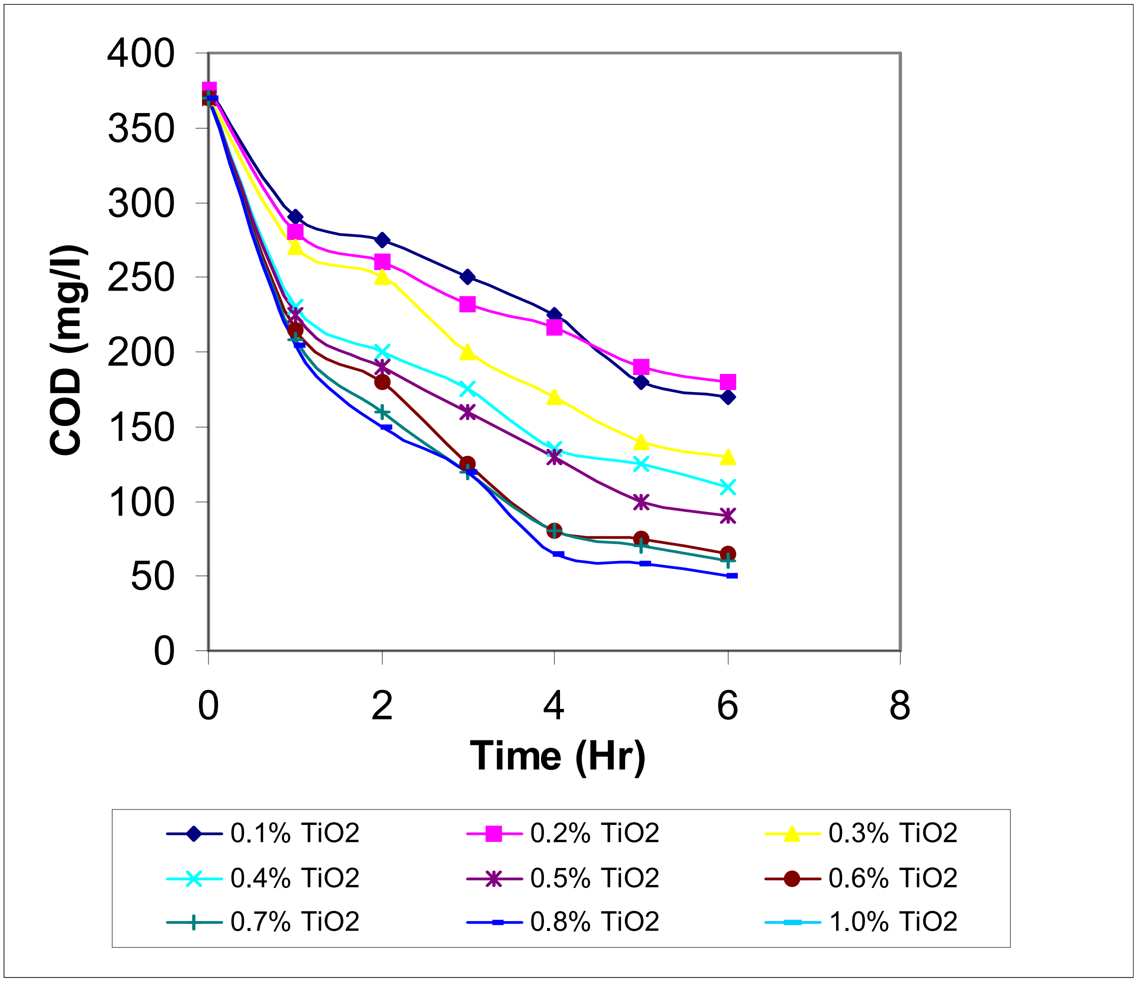


Fig: 15. Effect of catalyst concentration on the COD reduction

In the present study we observe that the COD continuously decreases from 360 to 50 mg/L on increasing the catalyst concentration from 1.0 g/l to 10 g/l. An optimum of catalyst concentration has to be taken when the decrease in COD level are to be within acceptable limits. Use of higher concentration of catalyst will increase the cost of the process and decrease the permeability of sunlight.

Effect of operating pH

The wastewater from textile industries usually has a high pH values (nearly 11). Further, the generation of hydroxyl radicals (AOP's) is also a function of pH. Thus pH plays an important role both in the characteristics of textile wastes and generation of hydroxyl radicals. Hence, attempts have been made to study the influence of pH in the degradation of dye in the range 3 - 11.

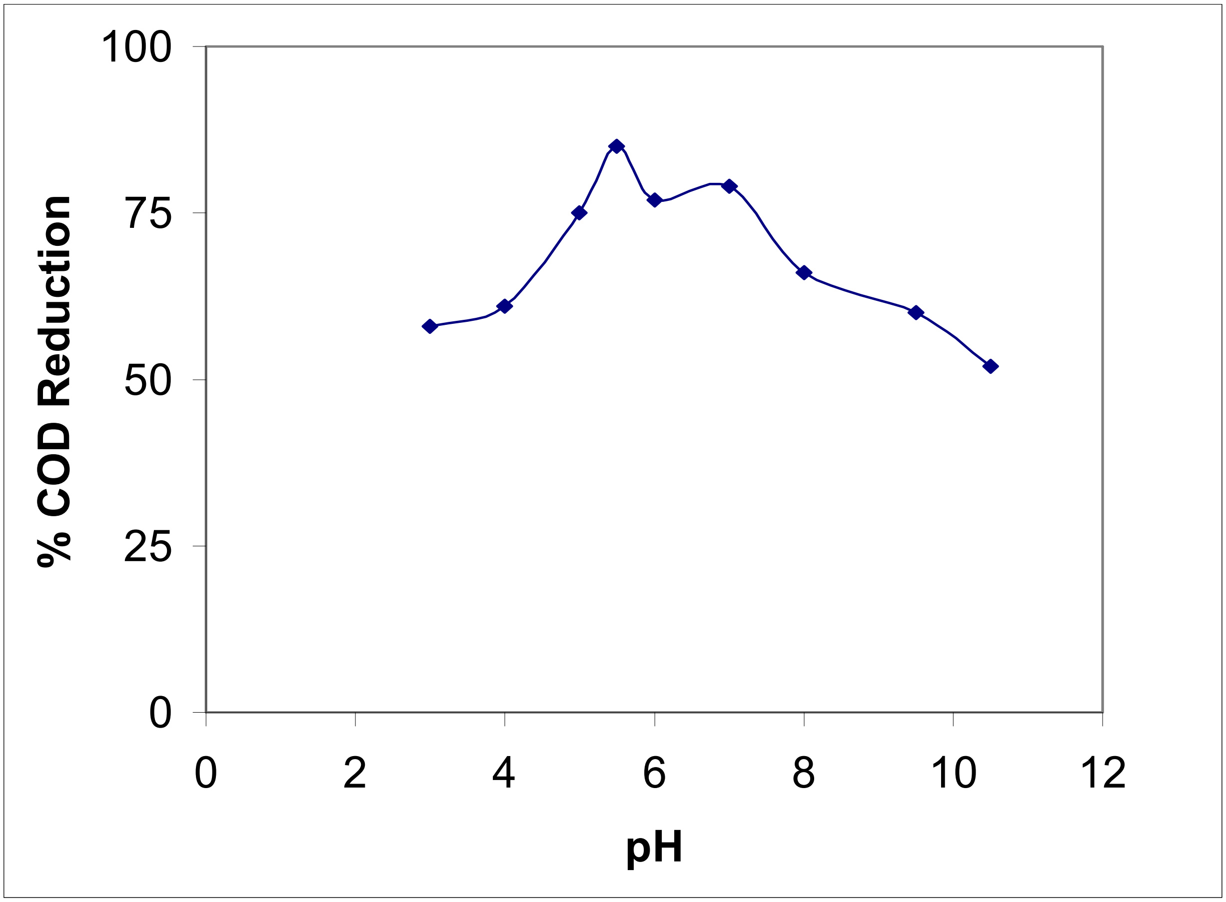


Fig: 16. Effect of pH on the % degradation of the effluent (0.4% catalyst loading)

According to literature reports, the pH of the solution significantly affects TiO_2 activity, including the charge on the particles, the size of the aggregates it forms and the positions of the conductance and valence bands.

In our experiments, maximum degradation was observed at pH near 5.5. Other pH values also responded to good degradation rates but the final pH after photocatalytic treatment which was the deciding factor for determining the optimum pH, which was found to be in the range of 6.8-7.0.This is important because after photocatalytic treatment, the water is to be subjected to biological treatment where the pH should be in the range of 6-8 as shown in Table 3.

So it is clear from above table that optimum pH should be at 5.5 because maximum degradation was achieved at this pH and final pH came out to be 7.0, which was suitable for biological process

pH before Treatment	3.0	4.0	5.0	5.5	6.0	7.0	8.0	9.0	10.0
pH after Treatment	3.2	4.23	5.3	7.0	8.1	8.45	8.5	8.95	9.5

TABLE 3 Showing change in pH values after the photocatalytic treatment

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Effect of Oxidant addition

One possible way to increase the reaction rate would be to increase the concentration of OH radicals because these species are widely considered to be promoters of photocatalytic degradation. The addition of hydrogen peroxide to the heterogeneous system increases the concentration of OH radical, since it inhibits the electron-hole recombination, according to following equation:

$$TiO_2(e^-) + H_2O_2 \rightarrow TiO_2 + OH^- + OH^\bullet \qquad (a)$$

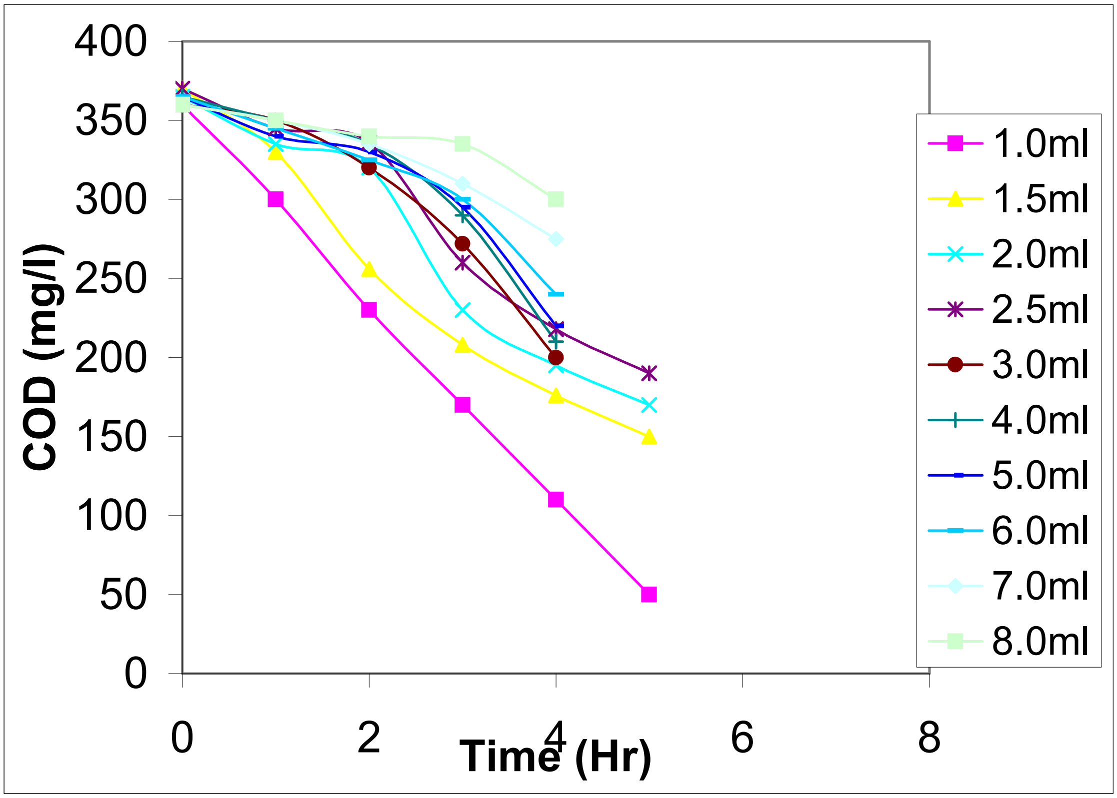


Fig: 17. Effect of oxidant addition (H_2O_2) on the COD reduction at 3.0 g/l of catalyst loading

Hydrogen peroxide is considered to have two functions in the process of photocatalytic degradation. It accepts a photo generated electron from a conduction band and thus promotes the charge separation, and it also forms OH radical, according to Eq. (a).
However at high concentration of H_2O_2, it also acts as a scavenger as shown in the following equations

$$H_2O_2 + OH^\bullet \rightarrow HO_2^\bullet + H_2O$$

$$HO_2^\bullet + OH^\bullet \rightarrow H_2O + O_2$$

From the experiments conducted by varying the hydrogen peroxide concentration from 1.0 to 8.0 ml per 200ml of the effluent. The best results were obtained when oxidant addition came out to be 1 ml/200.ml of effluent and has been taken as the optimum amount required for maximum effective degradation of pollutants as is clear from Figure 17.

Effluent characteristics after Solar Photocatalytic Pretreatment

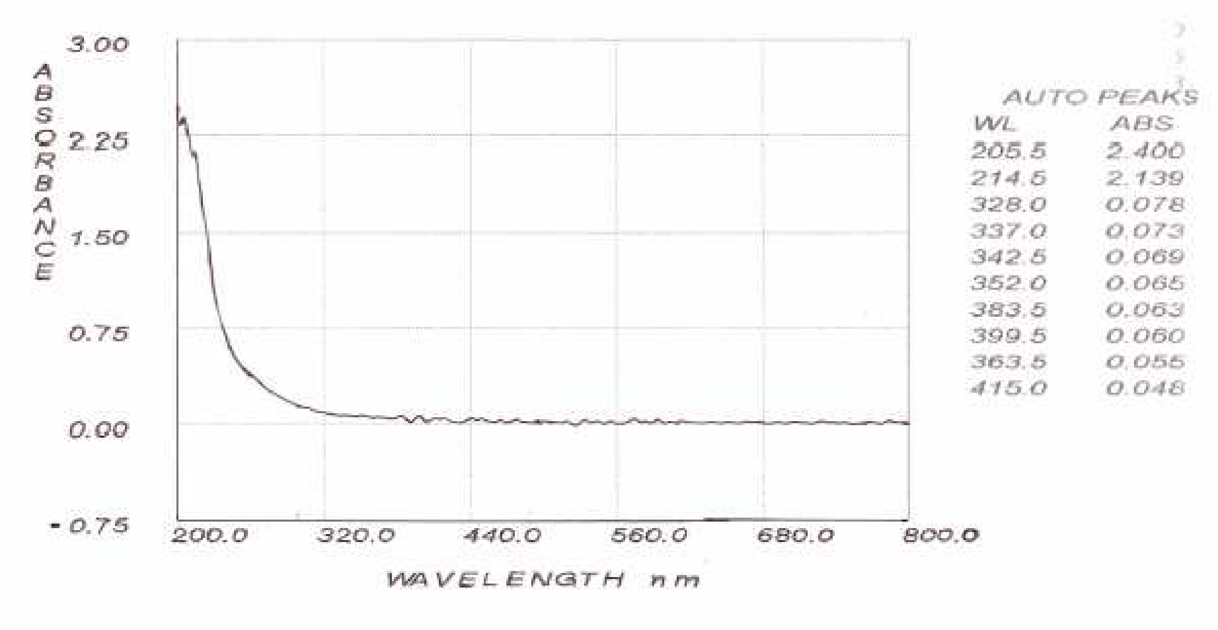
Effluent characteristics were determined after photocatalytic pretreatment under optimized conditions i.e. at TiO_2 concentration of 3.0 g/l, 1 ml of oxidant addition and at 5.5 pH.

Table 4: Characteristics of the wastewater after solar Photocatlytic treatment:

S.No.	Parameter	After Photocatalytic Treatment (mg. L^{-1}) (Optimized Conditions)
1.	COD	50-60 (after4.5 hrs)
2.	BOD/COD	0.7-0.8
3.	TDS	4100
4.	TS	4110-4120
5.	TSS	10
6.	COLOR	50 Pt- Co
7.	pH	7.0
8.	TKN	18.8

During photocatalytic pretreatment, reaction conditions were optimized for getting the economical benefits of the process. Catalyst concentration was optimized at 0.8 gm/l. Then pH of the effluent was optimized at 5.5. Rate of degradation was enhanced by optimizing the oxidant addition.

Abortion spectra for effluent after photocatalytic Treatment



AUTO PEAKS

WL	ABS
205.5	2.400
214.5	2.139
328.0	0.078
337.0	0.073
342.5	0.069
352.0	0.065
383.5	0.063
399.5	0.060
363.5	0.055
415.0	0.048

Fig: 18. Absorption spectra after PKT

Performance of the solar reactor vs. the Artificial UV reactor

Degradation is related to the photons, which are available for the total volume of the reactor, the efficiency of the Solar Reactor (SR) is higher than that of the Artificial UV reactor (AUV). Of course, a higher concentration of radiation can result in a faster degradation but the dependence is not linear. The electric energy, which is needed to produce photons in the lamp, is not used with the highest efficiency. The SR reactor is very efficient in using the available photons and that opens up possibilities for the implementation of the technology in industrial processes

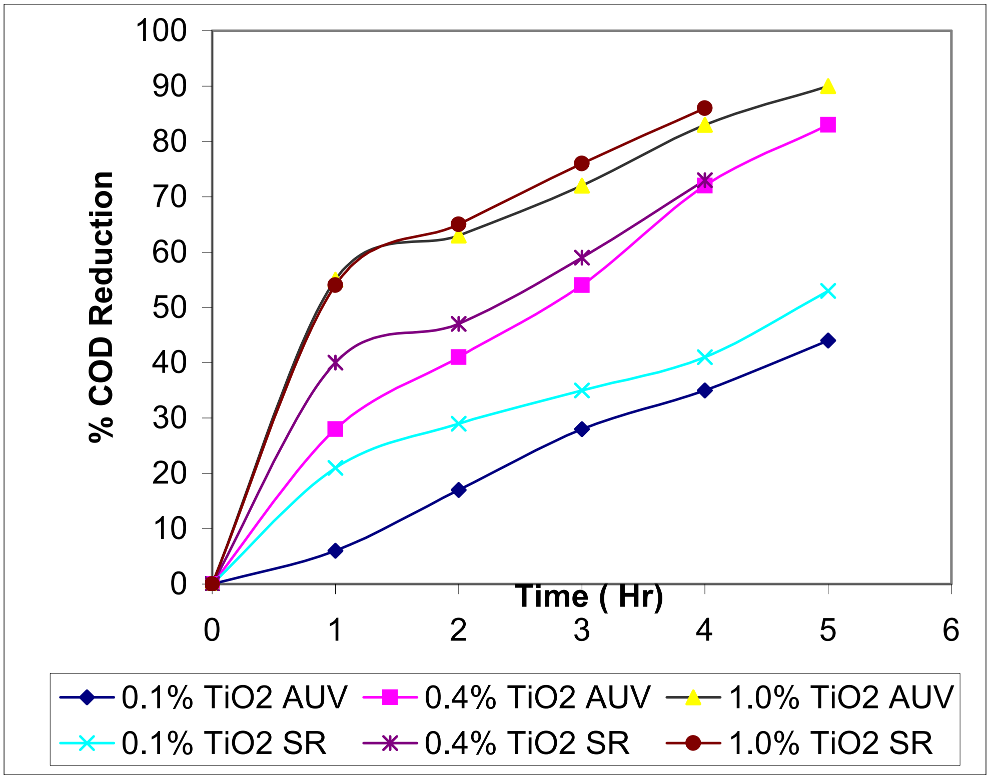


Fig: 19. Comparison between SR and AUV

Color Removal

Color is usually the first contaminant to be recognized in wastewater. Many azo dyes, constituting the largest dye group, may be decomposed into potential carcinogenic amines under anaerobic conditions in the environment. Color removal from wastewater is often more important than the removal of soluble colorless organic substances, a major fraction of which contribute to the COD and BOD besides disturbing the ecological system of the receiving waters.

The traditional techniques used for color removal are activated carbon (charcoal), filtration and coagulation. Each method has few advantages and disadvantages. For example, the use of charcoal is technically easy but has high waste disposal cost. Although filtration potentially provides pure water as the final product, it is possible for low molar mass dyes to pass through the filter system. Coagulation using alums, ferric salts or limes is a low cost process, but all these methods have a major disadvantage of simply transferring the pollutants to another phase rather than destroying them. Biological treatment is a proven technology and cost effective, however it has been reported that the majority of dyes are only adsorbed on the sludge and not degraded

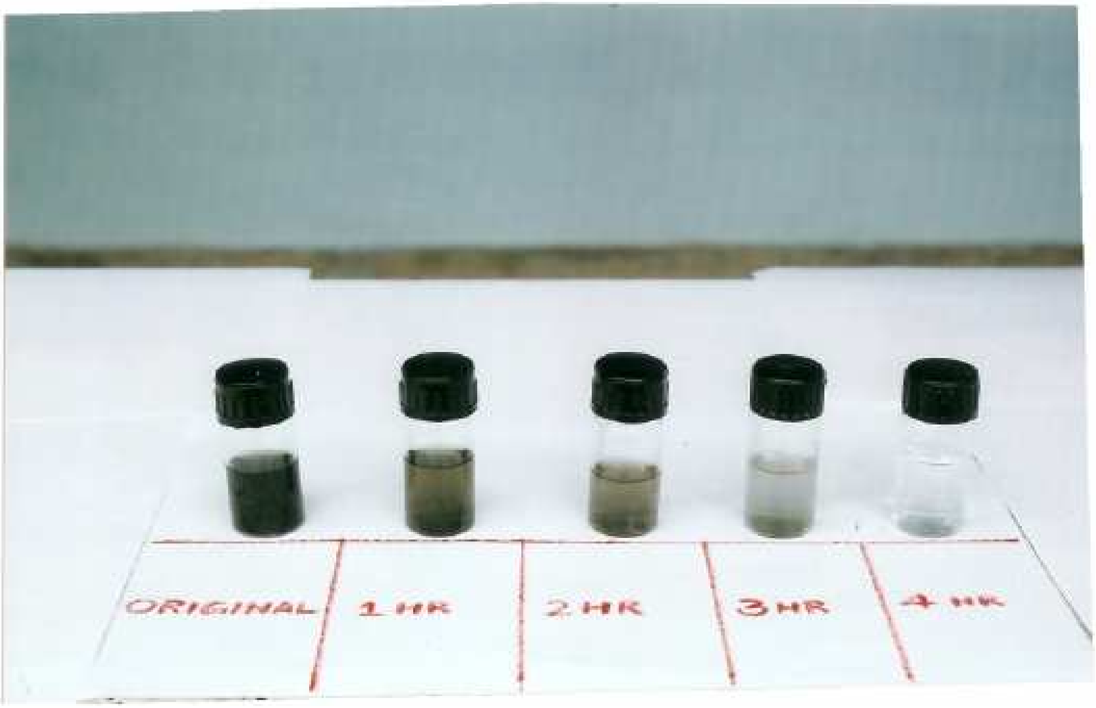


Fig: 20. Color removal after PKT

Reuse of TiO_2

The catalyst's lifetime is an important parameter of the photocatalytic process, due to the fact that its use for longer period of time leads to a significant cost reduction of the treatment. For this reason, the photocatalytic experiment was repeated 4 times with the same amount of TiO_2 P-25 as catalyst. For the series of experiments studying the reuse of the catalyst, the following procedure was adopted:

After the first day of photocatalytic treatment for 4 Hrs at optimized conditions, the catalyst was recovered through filtration. The Catalyst recovered by this method was activated at 100^0C before using. Then process was repeated until reasonable COD reduction was achieved.

The quantity of the catalyst was reduced day by day, but only in a very small percentage (1% of the initial quantity was lost). No more catalyst was added.

Catalyst recycling depends upon the following factors:

1. Fouling of catalyst
2. Nature of pollutants
3. Reaction conditions
4. Activation, etc

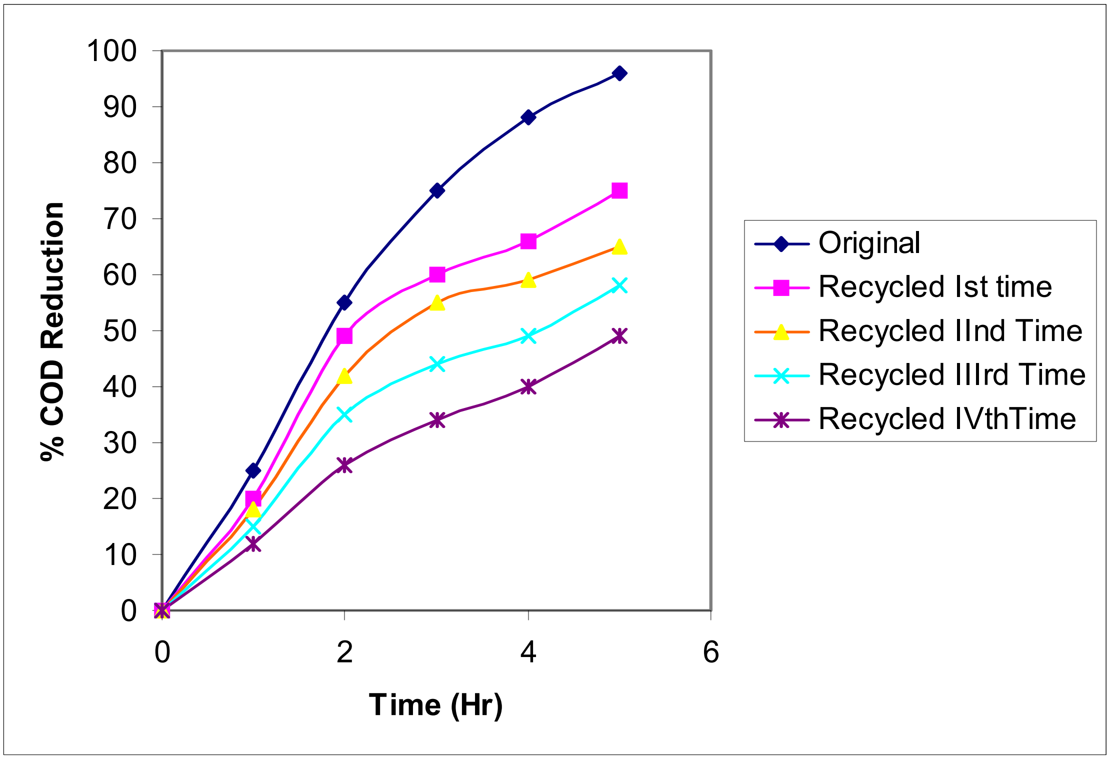


Fig: 21. Recycleability of TiO_2 P-25

Direct Biological Method

The effluent was subjected to direct biological process i.e. raw effluent after making certain dilutions was subjected to aerobic biological treatment. Two kinds of seeds were chosen for this process.

- Direct raw sewage seed
- Acclimatized seed

Acclimatized seed was prepared by continuous aerating the diluted raw effluent sample. Required amount of nutrients were added. The aeration was continued for 3-5 days with each day replacing 25-50ml of solution with fresh raw sample of same dilution. Biological treatment with these two types of seeds was done. Even after 10 days there was no noticeable change in the color and other parameters like BOD, COD etc.

Results are in agreement with literature saying that pollutants are not degraded even after 50 days. (Victor Sarria et.al. (2002)).

These observations are due to:

- High TDS of the raw effluent
- Lack of dissolved organic carbon
- And most important is the biodegradability parameter; in this case the biodegradability of the raw effluent is 0.21, thus non-biodegradable.

From the initial analysis of the untreated water it was observed that the biodegradability of the raw effluent is 0.21, thus is non-biodegradable. Therefore, the third factor is the most impotant and account for the results of direct biological degradation process. From Thus it is clear from the Table 5 that Textile industry effluent is mostly non-biodegradable and requires some sort of pretreatment for safe handling the effluent.

Table 5. shows the biodegradability of some commercial dyes and textile effluent (Hu Chun and Wang Yizhong (1999)).

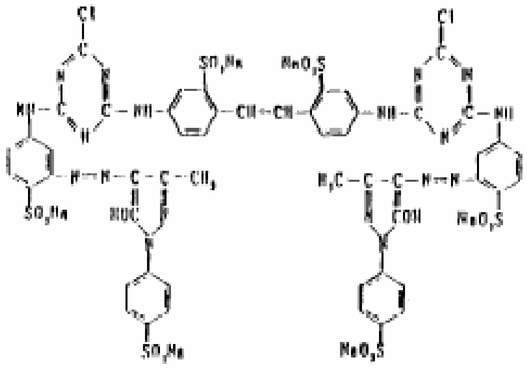
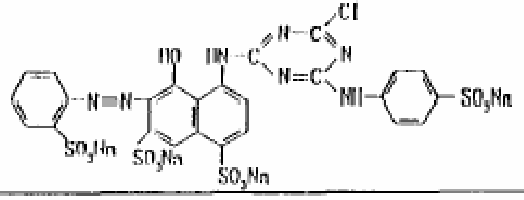
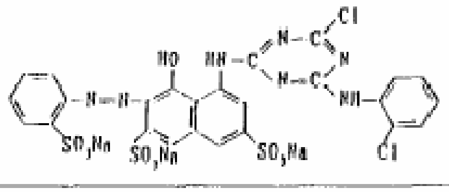
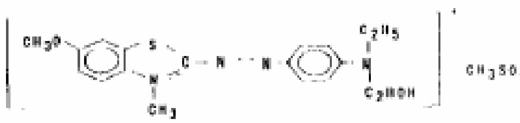
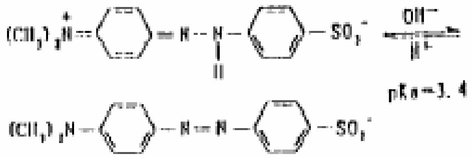
Name	Structure	BOD5 (mg/L)	COD (mg/L)	BOD_5/ COD
Reactive YellowKD-3G		0	60.80	0
Reactive Red 15		0	72.80	0
Reactive Red 24		0	60.80	0
Cationic BlueX-GRL		0	75.31	0
Methyl Orange		25.00	137	0.18
Textile wastewater	-	31.91	121.59	0.2624

Table 5. Biodegradability of some commercial dyes and textile effluent

Photocatalytic coupled biological treatment

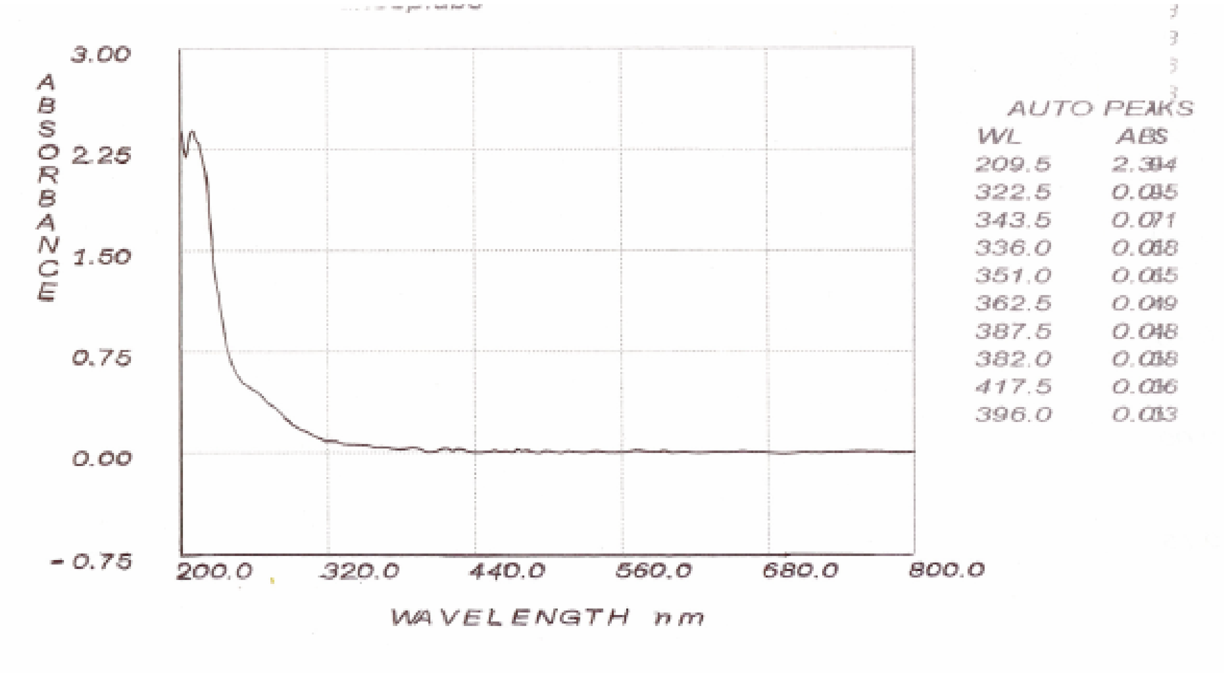
The effluent after photocatalytic treatment subjected to the biological process i.e. coupled photocatalytic and biological treatment. Positive results indicate that effluent being fed to biological reactor is having suitably high value of biodegradability and in this case the effluent which is fed to the biological process is having biodegradability value of 0.70-0.80, thus, clearly highly biodegradable. This effluent is subjected to the aerobic biological treatment.

Small intermediates left during photocataytic treatment are completely degraded in biological process. Thus getting improved values of COD, BOD, and TDS etc. This can be clearer from the absorption spectra obtained after Coupled process in figure 22. Small peaks left in the photocatalytic treatment are further diminished in biological treatment clearly indicating complete mineralisation.

M.P.Reddy et al. (2003) used coupled photocatalytic and biological processes to treat some common industry effluents. GC analysis shows reduced no. of peaks after photocatalytic and coupled treatment.

Table 6. Characteristics of effluent after Coupled treatment

S.No.	**Parameter**	**Range (mg. L^{-1})**
1.	COD	30-40
2.	TDS	3800
3.	TS	3800
4.	TSS	Nil
5.	BOD/COD	> 0.85
6.	COLOR	Nil
7.	pH	Neutral



AUTO PEAKS

WL	ABS
209.5	2.394
322.5	0.085
343.5	0.071
336.0	0.068
351.0	0.065
362.5	0.049
387.5	0.048
382.0	0.038
417.5	0.036
396.0	0.033

Fig: 22. Absorption spectra for coupled system

Perspectives for the coupling of photochemical and biological processes at field pilot scale

Direct solar light is promising and economically attractive source of UV irradiation, which has been applied in combination with oxidants and catalyst for the complete mineralisation of a wide range of organic pollutant in water .We have performed a series of experiments in order to find out whether photo-AOP using solar radiation's could be coupled with a biological system.

Interesting results were obtained using suspended TiO_2-photoassisted process since this catalyst is not sacrificed and can be separated from the treated water. This is very important when an industrial application is contemplated since TiO_2 is recycled and clean treated water could be drained away. Different procedures of filtration or sedimentation have been published for this purpose.

These encouraging results open new possibilities for the coupling of TiO_2-photoassisted and biological processes, at pilot scale, employing TiO_2 and bacteria.

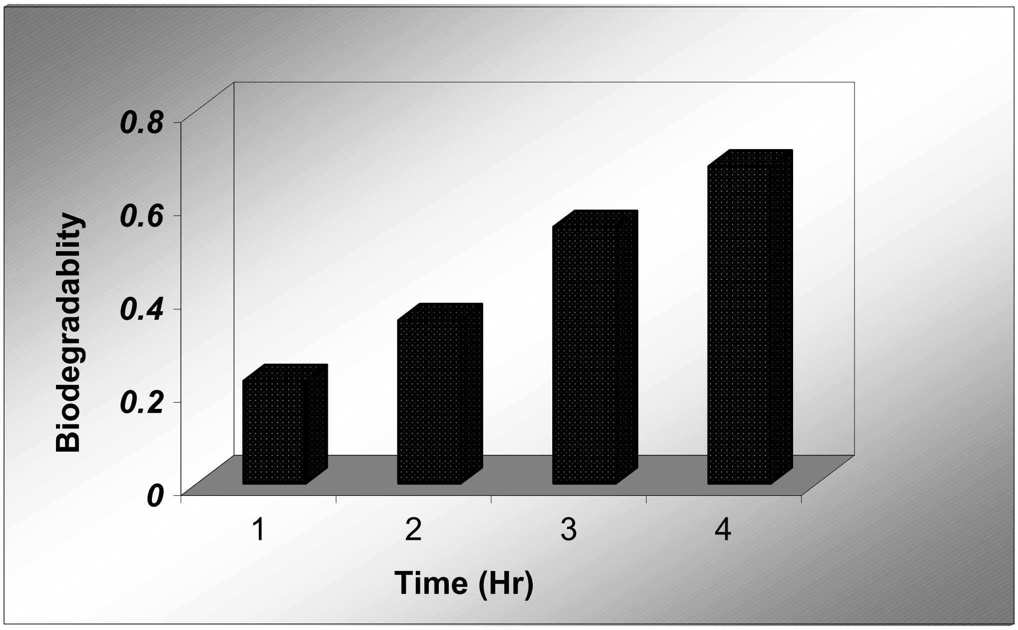


Fig: 23. Biodegradability of the effluent during the treatment

Decolorization and biodegradability of textile wastewater

To verify the relationship between decolorization and biodegradability of Textile wastewater, the wastewater from Textile industry was taken for study purposes. The properties of the wastewater are shown in Table 2. Clearly, it cannot be biodegraded according to the ratio BOD/COD = 0.26. However, the color and COD of the wastewater were removed by TiO_2 photocatalytic treatment

The complete decolorization of wastewater with TiO_2 slurry is achieved for about 130-150 min. irradiation. At the same time, the COD conversion of wastewater was 70-80%. Furthermore, the COD complete removal can be obtained after 240-min.irradiation.

The ratio of BOD / COD of the sample at treatment time 130min. increased from initial 0.26 to 0.44. The result indicates the biodegradability of photo catalytically treated wastewater was enhanced, and the complete decolorization wastewater was biodegradable due to BOD/COD>O.3. Therefore, the more appropriate photocatalytic treatment time was also the period of color disappearing completely for practical wastewater treatment. The interactive relationship between decolorization and biodegradability was demonstrated again.

Initial dyes chemical had inhibition for the biodegradation; however, the ratio of BOD/COD of most dyes solution is more than 0.3 when the color disappeared completely. The byproducts arising from decolorization reaction were biodegraded by biological processes. (Hu Chun and Wang Yizhong (1999)).

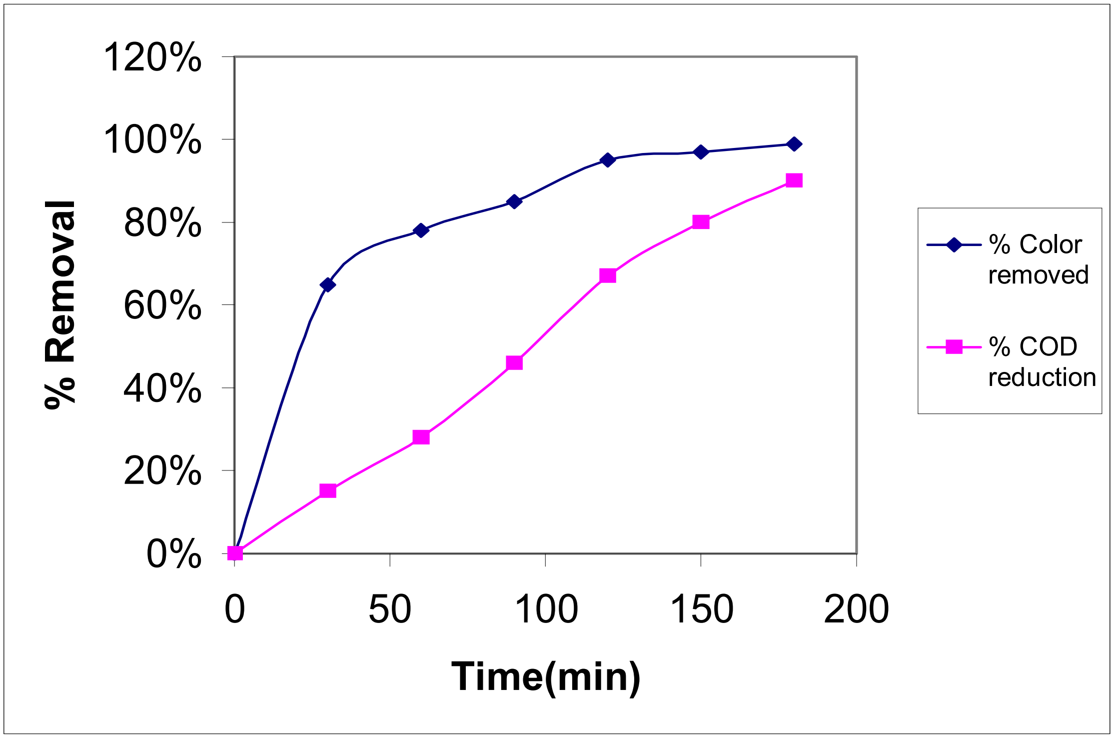


Fig: 24. Graph showing % Color removed and % COD reduction with time of Actual Industry effluent (pH 5.5, H_2O_2= 1ml, TiO_2 = 0.2 gm/200ml, Average sun Intensity = 30W/m^2)

Conclusions

Coupling of Photocatalytic and biological processes is a good alternative to minimize the treatment cost of wastewater containing biorecalcitrant and/or toxic pollutants. The chemical process could be used as pretreatment in order to increase the biodegradability of the wastewater or as a post-treatment to remove the non-biodegradable compounds. First of all, due to the high cost of chemical treatments, biodegradability test should be carried out since for biodegradable compounds classical biological treatments are, at present, the cheapest and most environmentally compatible processes. From the test results three situation could be obtained:

(a) the effluent is biodegradable.
(b) the effluent is partly biodegradable.
(c) the effluent is completely non-biodegradable.

Strategy for each situation is the following:
For case (a) biodegradable non-toxic effluent could be sent directly to centralized biological treatment plant (green line, Fig.25)

When the effluent is partly biodegradable (case b), it may be first treated by means of a conventional biological process and chemical oxidation process could be used in a final step to remove the biorecalcitrant part (blue line, Fig.25).

For toxic or non-biodegradable effluents (case c), the chemical oxidation as pretreatment process would increase the biodegradability and/or remove the toxicity of the wastewater. In this case, the chemical pretreatment is meant to modify the structure of contaminants by transforming them into less toxic and easily biodegradable intermediates, which allows the subsequent biological degradation to be achieved in a shorter time and in a less expensive way (red line, Fig.25).

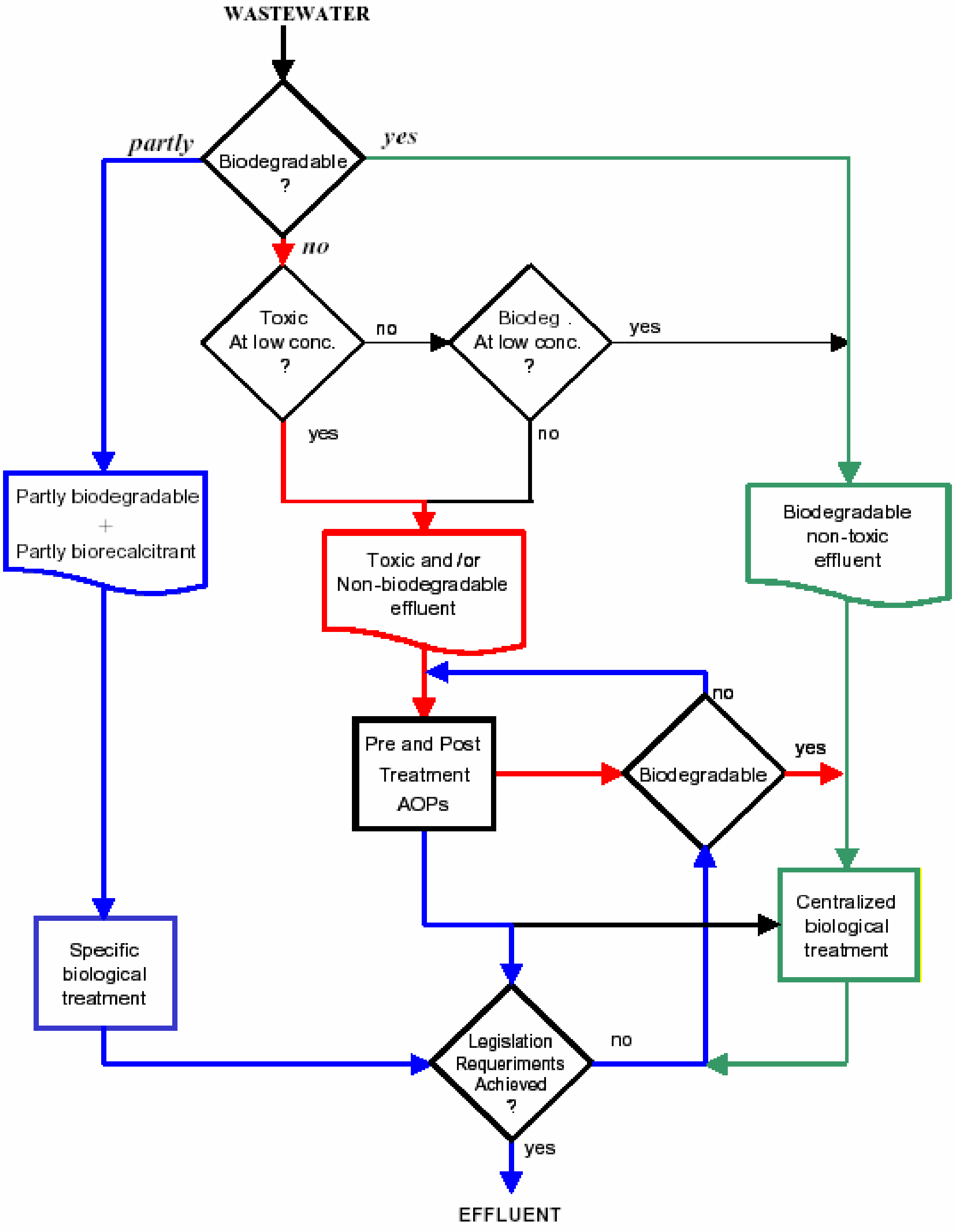


Fig: 25. General strategy of wastewater treatment.

The solution resulting from the photo treatment stage is considered to be biologically compatible after the elimination of:

- the initial biorecalcitrant and/or toxic compounds,
- the inhibitory and/or non-biodegradable intermediates, and
- any chemical reagent (H_2O_2, O_3 ….).

These requirements, together with information concerning the evolution of toxicity and biodegradability of the pretreated solution, allow the determination of optimal operational conditions, which corresponds to the best cost-efficiency compromise. Finally, this strategy could be used as useful guide, as it proposes an easy way to determine the most feasibility method for any industrial wastewater treatment.

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