Decolourization of Dye & Textile Effluent using Advanced Oxidation Processes

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By:
Somdutt Yadav
(Regn. No.-60601010)

Under the Supervision of

Mr. Amit Dhir
Lecturer
Deptt. of Biotech. & Environmental Sciences

DEPARTMENT OF
BIOTECHNOLOGY & ENVIRONMENTAL SCIENCES
THAPAR UNIVERSITY
PATIALA-147004 (PUNJAB)

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DEPARTMENT OF BIOTECHONOLOGY AND
ENVIRONMENTAL SCIENCES,
THAPAR UNIVERSITY, PATIALA-147004 [PUNJAB]

Date: _____

DECLARATION

I hereby declare that the work embodied in dissertation entitled **"Decolourization of Dye & Textile Effluent using Advanced Oxidation Processes"** is original piece of work and was conducted in the Department of Biotechnology and Environmental Sciences, Thapar University, Patiala. The matter presented in this thesis has not been submitted in part or full, to this or any other University/Institute for any degree or diploma.

SOMDUTT YADAV
(REGN. NO. 60601010)

DEPARTMENT OF BIOTECHONOLOGY AND
ENVIRONMENTAL SCIENCES,
THAPAR UNIVERSITY, PATIALA-147004 [PUNJAB]

Date: _____

CERTIFICATE

This is to certify that the dissertation entitled, **"Decolourization of Dye & Textile Effluent using Advanced Oxidation Processes"**, is an authentic work carried out by Mr. Somdutt Yadav student of M.Tech. (Env. Sc. & Tech.) Thapar University, Patiala, during the year 2007-2008, in partial fulfillments for the award of the Degree of Master of Technology and that the dissertation has not formed the basis for the award previously of any degree, associate ship, fellowship or any other similar title to any other university or institute.

Amit Dhir
Lecturer, (Department of Biotech. & Env. Sc.)
Thapar University, Patiala

Head
(Department of Biotech. & Env. Sc.)
Thapar University, Patiala

Dean
(Academic Affairs)
Thapar University, Patiala

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ABSTRACT

Industrialization is vital to nation's economy because it serve as a vehicle for development. The world's ever increasing population and its progressive adoption of an industrial based lifestyle has inevitably led to an increased anthropogenic impact on the biosphere. Increasing urbanization and industrialization have thus resulted in a dramatic increase in the volume of wastewater. Global water pollution scenario suggests that nearly 1.5 billion people lack safe drinking water and at least 5 million deaths are attributed to waterborne diseases such as cholera, hepatitis every year. The major industries contributing to water pollution are – textile mills, electroplating industry, metal processing industry, pulp and paper mill and tannery industry.

The effluent generated from such industries generally contains alkanes, haloalkanes, polymers, surfactants, aromatic dyes etc. These compounds are toxic and persistent in nature Therefore it becomes imperative to completely degrade these organic compounds. Major pollution in textile effluent is due to high suspended solids, chemical oxygen demand, heat, color, acidity and other non biodegradable substances. In order to tackle this menace of pollution problem, it is desirable to degrade the dye into non toxic form before its discharge into the main stream.

The traditional treatment techniques applied in textile wastewaters, such as coagulation/flocculation, membrane separation (ultrafiltratation, reverse osmosis) or elimination by activated carbon adsorption, only do a phase transfer of the pollutant, and biological treatment is also not a complete solution to the problem. So Advanced Oxidation Processes (AOP´s), like Fenton and Photo-Fenton processes, could be a good option to treat and eliminate textile dyes. Advanced Oxidation Processes are the one that offers a highly reactive, non-specific oxidant namely hydroxyl radicals ($HO^{\bullet}$), capable of destroying wide range of organic pollutants in water and wastewater. Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton's reagent is its simplicity in usage. In an acidic environment if hydrogen peroxide is added to an aqueous system

containing an organic substrate and ferrous ions, a complex redox reaction will occur.

The work done has been presented in five chapters. After introducing the problem and its content in the first chapter, the study begins with the background history of AOP's in second chapter. Then literature review on Fenton and Photo Fenton decolourization of various dyes and textile effluents has been given in the third chapter. The fourth chapter discusses experimental materials and methods that have been employed. Results and their discussion for decolourization of model dye compound and real effluent has been presented in fifth chapter.

In the present study, industrial effluents were collected from textile mill and its characterization was done by measuring pH, EC, total solids, TSS, TDS, COD, and Color etc. Decolourization studies of Malachite Green dye was carried out with Photo Fenton process in specially designed reaction vessel in the photo reactor equipped with UV tubes. Experiments were performed in both UV and solar light at optimized condition. The decolourization of dye and textile effluent has been investigated in terms of change in color by measuring absorbance and reduction in COD. Various process parameters like pH, concentration of oxidant, Fenton ratio, and initial pollutant concentration were varied and their effects have been analyzed.

The objective was to determine the best treatment for reducing color and COD of these colored solutions. In the case of MG dye (25 ppm), Fenton ratio 3:1 and oxidant dose was optimized at 300:100 mg/l at 2.0 pH. At optimized conditions 82% reduction in color is obtained. In case of textile wastewater pH optimized was 2.0, Fenton ratio of 3: colour, 61% reduction in TDS and 76% removal of COD in 4hrs. of exposure. In some technological cycles of dye industry, it is necessary only to remove the color completely, and sometimes it is necessary to purify water slightly to enable its re-use as cooling or technological water so these Fenton and Photo-Fenton processes can be used efficiently and cost effectively for color elimination and biodegradability improvement of dyes effluents in order to close water circulation in factories, which results not only in economic but above all ecological advantages.

TABLE OF CONTENTS

CONTENTS **PAGE No.**

LIST OF TABLES

LIST OF FIGURES

CHAPTER-1

Introduction

1.1 WATER POLLUTION

Earth is the only planet having an abundance of liquid water on its surface. Water is an important agent for changing the appearance of the earth. It determines the climate and weather. The life originated in water and is also sustained by water; hence, water is mother of all living word. We could not last, neither this world, if there is no water. Water is master solvent and all metabolic reaction of living depends mainly on its presence. It is the one of the most abundant gifted to man by the nature. It has a unique status of covering almost three quarters of the earth surface. The amount of water on earth is immense .The amount of water on earth is immense. An estimated 1.3 billion cubic kilometer (360 million cubic miles) of this total, the vast bulk (97%) is part of world oceans, which is unfit for human consumption and other process because of its high salt content. Of the remaining 3%, 2.01% is locked up in polar icecaps, and a meager part is available as fresh water in surface lakes, river, and water trapped with in the rocks and swamps, and water contained in the ocean basins, constitute the hydrosphere. Water keeps on exchanging in various components of environment atmosphere, land, sea, living plants and animals through hydrological cycle drive by thermal energy of Sun and gravitation.

Table 1.1.1: Relative Proportion of Water in Different Sources

Source	**Relative proportion (%)**
Water in oceans	97.39
Water in the river and lakes	0.02
Water present in the atmosphere as vapors	0.001
Water in glaciers and polar ice caps etc.	2.01
Underground water r and soil moisture	0.58
Total hydrosphere fresh water	2.6

(Source: Dash and Mishra, 2001)

In most industries water is used as input and mass & heat transfer media. In these industries a very small fraction of water is actually consumed and lost. Presently, industry accounts for 22 percent of the global fresh water consumption. It is expected that the figure will double over the next two decades. Most of this increase in industrial water use likely to happen in fast growing developing countries and this trend is likely to continue since there has been significant migration of manufacturing industries from developed countries to developing ones. According to CPCB data, the water consumption in Indian industry in 40 billion cubic meters that is 8 per cent of the total fresh water use in the country and the annual wastewater discharge is about 30.7 billion cubic meters.

Water consumption depends on the type of industry e.g. thermal power, textiles, pulp and paper and iron and steel are highly water intensive sector, where as cholro-alkali, cement, copper and zinc and plastics require little water as shown in Table 1.1.2

Wastewater handling, disposal & treatment are serious worldwide problem. Many industrial and agricultural activities use water in an excessive way. However, it is now well known that the fresh water resources are limited and fragile, so they must be protected. The availability of clean water for various human needs in the next decades seems to become a challenge to take up.

Table 1.1.2: Water Consumption & Wastewater Discharge from Different Industries

Industrial Sector	Annual wastewater water discharge (million cubic meters) (%)	Annual consumption (million cubic meters)	Proportion of water consumed in industry
Thermal power plants	27000.9	35157.4	87.87
Engineering	1551.3	2019.9	5.05
Pulp and paper	695.7	905.8	2.26
Textiles	637.3	829.8	2.07
Steel	396.8	516.6	1.29
Sugar	149.7	194.9	0.49
Fertilizer	56.4	73.5	0.18
Others	241.3	314.2	0.78
Total	30729.2	40012.0	100.0

(Source: Estimated by CSE based on the wastewater discharged data published by CPCB in "Water quality in India (Status and trends) 1990 - 2001".)

1.1 TEXTILE WASTEWATER

The textile industry in India guzzles double the accepted amount for consumption. A major factor is obsolete technology that permits minimum recycling and reuse of process water. For instance most textile mills in India do not use counter-washing systems instead they use clean water at every stage of the wash cycle. Similarly the reuse

of final rinse water from dyeing for dye bath make-up or reuse of soaper wastewater is absent in most mills.

Discharges of highly colored dye effluents in natural water constitute one of the most important problems of the surface water. The chemical reagents used are very diverse in chemical composition, ranging from inorganic compound to polymers and organic compound *(Venceslau M.C ea al., 1994).* The color is an evident indicator of water pollution by the dyes. Industrial dye effluents are visible even at concentrations lower than 1 mg/l. Synthetic organic dyes are generally recalcitrant in nature. Moreover, some dyes and their degradation products are carcinogenic *(Dae-Hee A et al., 1999).*

Composite textile wastewater is characterized mainly by measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dissolved solids (DS). Typical characteristics of textile industry wastewater are presented in Table 1.1.3, which show a large extent of variation from plant-to-plant and sample-to sample. As presented in Table 1.1.3, COD values of composite wastewater are extremely high as compared to other parameter. In most cases BOD/COD ratio of the composite textile wastewater is around 0.25 that implies that the wastewater contains large amount of non-biodegradable organic matter *(Pagga U et al., 1999).*

Table 1.1.3: Composite Textile Industry Wastewater Characteristics

Parameters	Values
pH	7.0 ─ 9.0
Biological Oxygen Demand (mg/L)	80 ─ 6000
Chemical Oxygen Demand (mg/L)	150 ─12000
Total Suspended Solids (mg/L)	15─ 8000
Total dissolved solids (mg/L)	2900 ─3100
Chloride (mg/L)	1000 ─1600
Total Kjeldahl Nitrogen (mg/L)	70─ 80
Color	50─2500

(Source: Adel Al-Kdasi et al, 2005)

Development of the appropriate techniques for treatment of dye wastewater is important for the protection of natural waters. To eliminate dyes from aqueous colored effluents and reduce their ecological consequences, several biological and chemical techniques have been proposed: anaerobic/aerobic degradation *(Marco S et al., 2006)* coagulation/flocculation *(M.A. Behnajady et al., 2004)* and also oxidative/reductive chemical and photochemical processes *(Adel Al-Kdasi et al., 2005).* Other techniques including radiation and depolarization with ozone in combination with H_2O_2 are also employed *(Marco S et al., 2006).*

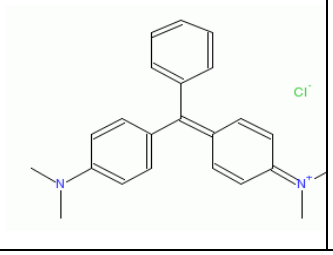
1.3 DYES

There are many kinds of dyes available in the market. Based on the chemical structure or chromophore, 20─30 different groups of dyes can be discerned. Anthraquinone, phthalocyanine, triarylmethane and azo dyes are quantitatively the most important groups. The azo dyes, characterized by having an azo group consisting of two nitrogen atoms (─N≡N─), are the largest class of dyes used in textile industry *(Jain Hui et al., 2007)*. Inside the azo dyes there are wide types of dyes, namely acid, reactive, disperse, vat, metal complex, mordant, direct, basic and sulphur dyes. Additionally, these dyes are the most problematic pollutants of textile wastewaters. This fact occurs because after the basic dyeing process is finished, more than 15% of the textile dyes is lost in wastewater stream during dyeing operation *(Muruganandhan et al., 2004)*. In the present study Malachite Green, one of the most widely used basic dyes has been chosen as a model dye compound.

Malachite Green

Malachite green, also called analine green, basic green 4, diamond green B or Victoria green B having IUPAC name 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline is a toxic chemical primarily used as a dye. It is a green crystal powder with a metallic luster, very soluble in water, extremely soluble in ethanol, solutions are blue-green; malachite Green dye become yellow in high concentration sulphuric acid, becomes dark orange when diluted; if becomes orange in high concentration nitric acid, becomes brownish orange when diluted.Table 1.1.4 shows the dye molecule, which is basically consist of an azo (-N =N-) linkage three benzene ring indeed the chromophore compounds shows absorption in the visible region, while the benzene ring absorb in the UV region. Indeed, the disappearance of the absorbance signal at 425 nm reflects, unequivocally, an almost complete decolourization and the breakdown in the chromophore group. Physical and chemical properties of Malachite green are shown in Table 1.1.5

Table 1.1.4: IUPAC Name, Molecular Structure, and Molecular Mass

Name	IUPAC Name	Molecular Structure	Molecular Mass
Malachite green	4-[(4 dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline		364.911 g/mol (chloride)

(Source: basic-green.com)

Table 1.1.5: Physical & Chemical Properties of Malachite Green

Physical State	Green Crystalline powder
Melting point	164º C
Solubility in water	Soluble
Stability	Stable under ordinary condition
Odour	less
Molecular weight	927.03
Polymerization	Will not occur
Toxic effect on human	Causes skin & severe Eye irritation
Charge	Positive electrical charge

(Source: Material safety data sheet, Science lab.com)

1.4 TEXTILE WASTEWATER TREATMENT

The treatment of textile wastewater is very complex, because the raw materials processed and the intermediate products manufactured vary greatly in their nature and composition. The composition of waste varies even in same industry as a result of transition from one raw material to another and continual changing of process lines and also due to type of fabric manufactured. Before treatment, a separation of different types of wastewater into following group takes place:

- Concentrated liquids (e.g., dyeing, finishing, printing)
- Medium polluted wastes (e.g., washing, rinsing)
- Low to zero polluted wastes (e.g., cooling water).

The various methods of treatment of textile wastewater are as follows:

- Physical treatment
- Physico-chemical treatment
- Biological treatment
- Advanced oxidation processes

1.4.1 Physical Treatment

Physical processes such as sedimentation *(Fiola R et al., 1998)*, equalization, segregation, filtration (e.g., sand filter) are capable of removing the suspended solids, however the removal of organic load is found to be negligible. Physical processes followed by physico-chemical or biological process show good results.

1.4.2 Physico-chemical Treatment

Physico-chemical processes such as chemical coagulation/ flocculation ($Fe^{2+/3+}$, Al^{3+}, polyelectrolyte) *(Papic et al., 2000)*, ion exchange, adsorption (e.g., activated carbon) *(Schulze-Rettmer, 1998 & Netpradit et al., 2003)*, chemical oxidation using ozone, chemical oxidation using hydrogen peroxide at elevated temperatures and

different membrane processes depending on desired application (nanofiltration, microfiltration, ultrafiltration and reverse osmosis operating at different pressure) *(Wehlmann, 1997 & Majewska-Nowak et al., 1989)* have proven to be highly efficient in removing solids, BOD and COD from textile effluents.

1.4.3 Biological Treatment

Biological treatment of textile wastes is considered necessary when they are to be discharged into rivers and lakes (IS: 9508-1980). Biological treatment is the first stage in a combination with additional physico- chemical processes. They are very effective methods to reduce biodegradable organics as BOD_5 and a main part of COD. It is also an effective method to oxidize ammonium to nitrate by means of denitrification to gaseous nitrogen.

Types of Biological Treatment Employed in Textile Wastewater

Aerobic Treatment

An aerobic system includes lagoons, activated sludge processes, bio towers, sequencing batch reactors, trickling filters, land applications and artificial wetlands *(Perkins, 2006).* In aerobic process, the influent is aerated and microorganisms feed on the waste and oxidize organic materials. Metal ions in the wastewater form a complex with organic matter as well as dye molecules are adsorbed on organic matter in the treatment system and are partially removed with the sludge. After biological treatment, the wastewater enters the clarifier where most of the water is separated from the sludge. Part of the sludge rich in microorganisms is recycled back to aeration tank. Polymeric flocculants may be added to help in solid/liquid separation and color removal in clarifier. An average of 10% and a maximum of 30% of reactive dyes are adsorbed onto aerobic biomass *(Pierce, 1994, Waters, 1995),* the remainder passing through activated sludge plants. Hence, aerobic system is not effective in color removal from textile wastes containing azo dyes *(Neill et al, 1999).* Aerobic system shows good capability to treat for low to medium BOD_5 wastewater, long extensive operating history, low generation of greenhouse gases and effective removal of nitrogen. The limitation of this treatment is high-energy requirement for aeration and mixing, sensitivity to load fluctuations and

excess sludge production and is difficult to handle.

Anaerobic Treatment

Anaerobic processes present a more attractive alternative since they can be developed a clean and renewable energy sources. The anaerobic treatment is suitable for high BOD_5 wastewater, for handling load fluctuations, low energy requirement because no oxygen has to be supplied and potential for energy (gas) production but they have a narrow temperature range, required for the growth of anaerobes *(Perkins, 2006)*. Technical anaerobic processes need adequate temperature of 35ºC to 55ºC. As the effluent quality is not as good as obtained with aerobic treatment, anaerobic treatment is commonly used as a pretreatment step prior to discharge to a municipal collection system or is followed by an aerobic process *(Metcalf and Eddy, 2003)*. During anaerobic treatment, a complex microbial community *(Grotenhuis, 1992)* consisting of many interacting microbial species degrades natural polymers such as polysaccharides, proteins, nucleic acids and lipids in the absence of oxygen into methane and carbon dioxide. Anaerobic degradation of textile waste, in general, takes place in following steps:

- **Hydrolysis**: It is a process whereby particulate or high molecular weight soluble substrates are broken down to smaller molecules by the incorporation of water molecules. In fermentation hydrolytic enzymes excreted by bacteria catalyze hydrolysis.

- **Fermentation or Acidogenesis:** In this step, carbohydrates, amino acids and fatty acids are degraded further by enzymes, bacteria, yeasts, or molds in the absence of oxygen and they are converted into simple compounds, (volatile fatty-acids, alcohols, lactic acid, CO_2, H_2, NH_3, H_2S) and new cell-matter. Various acids such as acetic acid, propionic acid, and butyric acid are formed here.

- **Acetogenesis:** This process is also called anaerobic oxidation of short-chain fatty acids and the acids are fermented further to produce final products of fermentation

and they thus are precursors of methane formation. The final products are acetate, hydrogen and carbon dioxide. The free energy change associated with the conversion of propionate and butyrate to acetate and hydrogen requires that hydrogen be at low concentrations in the system ($H_2 < 10^{-4}$ atm) or the reaction will not proceed *(Metcalf and Eddy, 2003)*.

- **Methanogenesis:** In this last step of anaerobic digestion, methane formers or methanogens produces methane either by splitting acetate into methane and carbon dioxide or by using hydrogen as the electron donor and carbon dioxide as an electron acceptor. The former are called aceticlastic methanogens and latter are termed as hydrogen utilizing methanogens. Acetate is the prime precursor for methane production, contributing about 70% of the total methane produced. It has been seen that methanogens are sensitive to pH so, for efficient digestion the acid formers and methane fermentors must remain in a state of dynamic equilibrium. A pH value of 6.5-8.0 is the best for fermentation and normal gas production. If organic acids are formed at the faster rate than the limited population of methane formers can assimilate, then the accumulated acids will reduce the pH to levels unfavorable to methane formers, thereby decreasing the efficiency of the process.

1.5 THE POWER OF LIGHT

Light is one of the various electromagnetic waves present in space. The electromagnetic spectrum covers an extremely broad range, from radio wavelength of a meter or more, down to x-rays with wavelengths of less than one billionth of a meter. The UV-visible portion occupies an intermediate position, having both wave and particles in varying degrees (Figure 1.1.1).

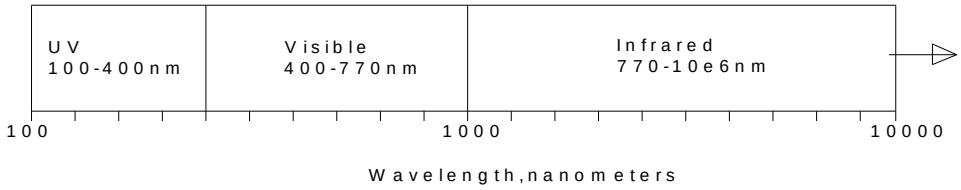


Fig 1.1.1 The Optical Portion of Electromagnetic Spectrum

1.5.1 Ultraviolet (UV) Light

Ultraviolet radiation (UV) is radiation whose wavelength is shorter than the violet end of the visible spectrum. Being very energetic, UV can break chemical bonds, making molecules unusually reactive or ionizing them, in general changing their mutual behavior. Short wavelength UV light exhibits more quantum properties than its visible or infrared counterparts. UV light is arbitrarily broken down into three bands. UV-A (315-400 nm),which is the least harmful type of UV light, as it has the least energy, is often called black light, and is used for its relative harmlessness and its ability to cause fluorescent materials to emit visible light-thus appearing to glow in the dark. UB-B (280-315nm) typically the most destructive form of UV light because it has enough energy to damage biological tissues and UV-C (100=280nm) is almost completely absorbed in the air within a few hundred meters. The Sun emits a large amount of UV radiation, which could quickly turn Earth into a barren desert; however, most of it is absorbed by the atmosphere's ozone layer before reaching the surface. The electromagnetic spectrum of ultraviolet light can be subdivided in a number of ways. The draft ISO standard on determining solar irradiances (ISO-DIS-21348) describes the following ranges shows the subtypes of ultraviolet light in Table 1.1.6.

1.5.2 Visible Light

Visible light is concerned with the radiation perceived by the human eye having wavelength (λ) range of 400-750 nm. The lumen (lm) is the photometric equivalent of the watt, weighted to match the eye response of the “standard observer”. Yellowish-green light receives the greatest weight because it stimulates the eye more than the blue or red

light of equal radiometric power (1W at 555 nm=683.0 lumen).

Table 1.1.6 Various subtypes of ultraviolet light

Name	Abbreviation	Wavelength range in nanometers	Energy per photon
Ultraviolet A, long wave, or black light	UVA	400 nm - 315 nm	3.10 - 3.94 eV
Near	NUV	400 nm - 300 nm	3.10 - 4.13 eV
Ultraviolet B or medium wave	UVB	315 nm - 280 nm	3.94 - 4.43 eV
Middle	MUV	300 nm - 200 nm	4.13 - 6.20 eV
Ultraviolet C, short wave, or germicidal	UVC	280 nm - 100 nm	4.43 - 12.4 eV
Far	FUV	200 nm - 122 nm	6.20 - 10.2 eV
Vacuum	VUV	200 nm - 10 nm	6.20 - 124 eV
Extreme	EUV	121 nm - 10 nm	10.2 - 124 eV

1.5.3 The Solar Spectrum

Of all the energy coming from that huge reactor, the sun, the earth receives $1.7x10^{14}$ kW, meaning $1.5x10^{18}$ kWh per year. Fig 1.1.2 shows the standards solar radiation spectra at ground level on a clear day *(Hulstrom et al., 1985).* The dotted line corresponds to the extraterrestrial radiation in the same wavelength interval.

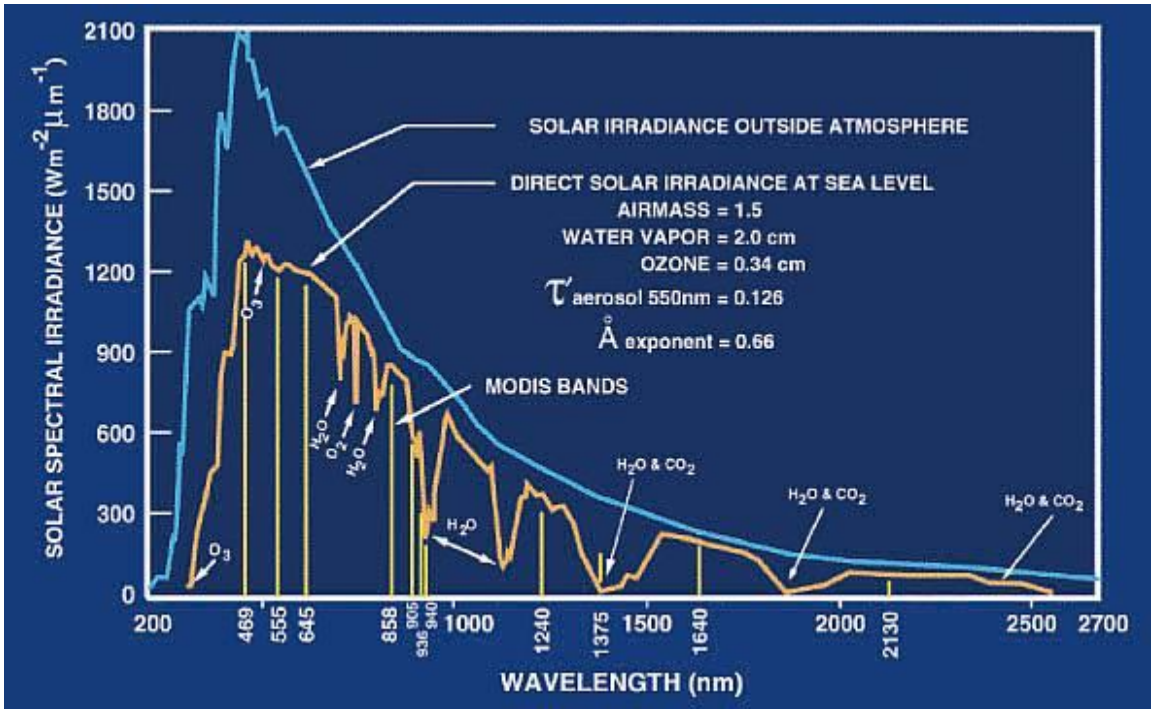


Fig: 1.1.2 Solar radiations measured above the atmosphere and at the surface.

Solar ultraviolet radiation, as explained above is, only a very small part of the solar spectrum (3.5% to 8%). However this ratio may be different for a given location on cloudy and clear days. The percentage of global UV radiation (direct + diffuse) generally increase with regard to total global when atmospheric transmissivity decrease mainly because of clouds, aerosols and dust etc. in fact, the average percentage ratio between UV and total radiation on cloudy days is up to two percentage points more than values on clear days.

1.6 Objectives of Present Study

In an attempt to increase the efficiency of decomposition of the impurities present in the wastewater and to improve the economics of the process, I have carried out the research on the decolourization of Malachite Green dye and effluents containing dyes using advanced oxidation processes. A single dyeing operation can use a number of dyes from different chemical classes resulting in a very mixed wastewater. The description of textile effluent color in terms of absorbance is more useful than is dye concentration, as different dyes give rise to different intensities and colors. The wastewater used in this study was treated effluent from the Textile dyeing industry near Ludhiana. The plant treats approximately 4 million gallons per day and discharges into the local River. During this project, color levels in samples of the WWTP final clarifier effluent delivered to the environmental laboratories where this study was conducted were consistently greater than the permissible color levels. The objectives of this research project were:

- Study the decolourization efficiency of textile wastewater and model dye compound using Fenton and Photo Fenton Processes.
- Study the effect of variables on Fenton and Photo Fenton process efficiency & their optimization.

CHAPTER-2

Background of AOP’s

2.1 History of AOP

Since the 1970s attempts have been made at improving the oxidation processes to make them faster, more efficient and safer for the natural environment, that is in such a way which would not cause secondary pollution.

Garrison was the first to apply advanced oxidation methods to oxidize wastewater from photographic studios, in the form of joint application of O_3 and UV radiation at the wavelength of λ=254 nm. Prengle used the same system for solutions containing pesticides and hydrocarbochlorides. Nakayane used the O_3+H_2O_2 system for the first time to oxidise wastewater, which contained organic compounds (acetic acid, alcohols, ketones, amines, ethylene glycol and others).

The first installation in which AOP was used was built in North Hollywood (USA) in 1992. A combined O_3/H_2O_2 method was applied to remove trichloroethylene (TCE) and tetrachloroethylene (PCE) from ground water. A year later (in 1993), in South Gate near Los Angeles, an installation was built to treat water for consumption purposes where a triple system O_3/H_2O_2/UV (λ=254 nm) was used. IBM built the first water treatment installation for industrial purposes.

The next systems built in the USA mainly included installations in which ozone and hydrogen peroxide were used jointly. It was only in 1994, in a military plant in Milan (USA), that a triple O_3/H_2O_2/ UV system was used to oxidise explosives, which had infiltrated the sewage.

2.2 Advanced oxidation processes

At present, advanced oxidation processes are used in many countries for treatment of drinking water. In the case of industrial wastewater, pilot plant installations are operating in several countries:

- the tanning industry (Germany)
- the paper industry, wastewater from bleaching (USA, Germany, France)
- the textile industry (USA, Germany, Canada)
- the chemical industry (Spain, USA, Germany)
- the petroleum industry (Estonia)
- the synthetic fuel industry (Republic of South Africa)

Since 1999, over 100 installations using the advanced oxidation method for treating leachate, toxic wastewater in electronic industry and for industrial water recirculation have been operating. Traditional processes for treatment of these effluents prove to be insufficient to clean up the important quantity of wastewaters after different operations of textile dyeing and washing. On the other hand, these techniques do not eliminate definitively the dyes but only separate and concentrate them. The destruction of the concentrated pollutants requires an additional operation as incineration. However, the advanced oxidation processes (AOPs) that use hydroxyl radicals, a very strong oxidant to destroy compound that cannot be oxidized by conventional oxidant. *(Amal Lahkimi et al., 2007)* Table 2.1.1 shows the relative oxidation potential of several chemical oxidizers. An advanced oxidation method is a result of their high potential. The chain mechanism of oxidation, which involves hydroxyl and hydroperoxide radicals guarantees efficiency and quick rate of the process. The high reactivity and low selectivity of the reaction enable the method to be applied to a large number of organic compounds present in the wastewater. Further advantages include a lack of by-products, which can produce secondary pollution of the environment and thus risk over dosage of the oxidizing agents.

Table 2.1.1: Oxidizing Potential for Conventional Oxidizing Agents

Oxidizing agent	Electrochemical oxidation potential (EOP),V	EOP relative to chorine
Fluorine	3.06	2.25
Hydroxyl radical	2.80	2.05
Oxygen (Atomic)	2.42	1.78
Ozone	2.08	1.52
Hydrogen peroxide	1.78	1.30
Hypochlorite	1.49	1.10
Chlorine	1.36	1.00
Chlorine dioxide	1.27	0.93
Oxygen (molecular)	1.23	0.90

(Source: Carry, 1992, Techcommentry, 1996; Zhou and smith 2002: Metcalf and Eddy; 2003)

Advanced oxidation processes are environmentally friendly methods capable of destroying the organics without the production of harmful by product and disposal problems. They can be broadly divided classified as:

- Homogeneous processes: Those involving homogeneous oxidation reaction, utilizing hydrogen peroxide, Fenton and Photo - Fenton reagents.

- ❖ Heterogeneous processes: Those employ heterogeneous reaction, such ozonation and semiconductor-mediated photo catalysis.

2.2.1 UV Photolysis

UV photolysis is the destruction process by which chemical bonds of the contaminants are broken under the influence of UV light. Oxidation of target contaminants is caused by direct reaction with the oxidizers, UV photolysis, and through the synergistic action of UV light, in combination with ozone (O_3) and/or hydrogen peroxide (H_2O_2). Products of photo-degradation vary according to the matrix in which the process occurs, but the complete conversion of an organic contaminant to CO_2, H_2O, etc. is not probable. The duration of operation and maintenance of UV oxidation depends on influent water turbidity, contaminant, existence of free radical scavengers, and the required maintenance intervals on UV reactors and quartz sleeves *(Zappi, 1990)*. The main advantage of UV oxidation is that it is a destruction process, as opposed to air stripping or carbon adsorption, for which contaminants are extracted and concentrated in a separate phase. UV oxidation processes can be configured in batch or continuous flow modes, depending on the throughput under consideration *(EPA, 1990)*.

Applicability: Practically any organic contaminant that is reactive with the hydroxyl radical can potentially be treated. A wide variety of organic and explosive contaminants are susceptible to destruction by UV/oxidation, including petroleum hydrocarbons; chlorinated hydrocarbons used as industrial solvents and cleaners; and ordnance compounds such as TNT, RDX, and HMX. In many cases, chlorinated hydrocarbons that are resistant to biodegradation may be effectively treated by UV/oxidation. Typically, easily oxidized organic compounds, such as those with double bonds (e.g., TCE, PCE, and vinyl chloride), as well as simple aromatic compounds (e.g., toluene, benzene, xylene, and phenol), are rapidly destroyed in UV/oxidation processes *(Christman, 1990)*.

The UV/oxidation is an innovative ground water treatment technology that has been used in full-scale ground water treatment application for more than 10 years. Currently, UV/oxidation processes are in operation in more than 15 full-scale remedial applications. A majority of these applications are for ground water contaminated with petroleum products or with a variety of industrial solvent-related organics such as TCE, DCE, TCA, and vinyl chloride *(EPA, 1993).*

Limitations:

- The aqueous stream being treated must provide for good transmission of UV light (high turbidity causes interference). This factor can be more critical for UV/H_2O_2 than UV/O_3.
- Free radical scavengers can inhibit contaminant destruction efficiency. Excessive dosages of chemical oxidizers may act as a scavenger.
- The aqueous stream to be treated by UV/oxidation should be relatively free of heavy metal ions (less than 10 mg/L) and insoluble oil or grease to minimize the potential for fouling of the quartz sleeves.
- When UV/O_3 is used on volatile organics such as TCA, the contaminants may be volatilized (e.g., "stripped") rather than destroyed. They would then have to be removed from the off-gas by activated carbon adsorption or catalytic oxidation.
- Costs may be higher than competing technologies because of energy requirements.
- Pretreatment of the aqueous stream may be required to minimize ongoing cleaning and maintenance of UV reactor and quartz sleeves.
- Handling and storage of oxidizers require special safety precautions.

Factors that influence the cost to implementing UV/oxidation include:

- Types and concentration of contaminants (as they affect oxidizer selection, oxidizer dosage, UV light intensity, and treatment time).
- Degree of contaminant destruction required.
- Desired water flow rates.

- Requirements for pretreatment and/or post-treatment.

2.2.2 Photo catalysis

Photo catalysis is a process in which the initial absorption of photons by a semiconductor, lead to the formation of electrons and holes. The band structure of the electronic energy levels of the semiconductor consists of the highest occupying band, called the valence band and the lowest unoccupied band called the conduction band separated by band gap energy .The band gap energy falls in the UV-Visible region of the electromagnetic spectrum. Hence, activation of the semiconductor surface with UV or visible radiation result in the promotion of the valence band electron to the conduction band, generating electron (e-)/hole (h+) pair. In aerated aqueous suspensions of the semiconductor in contact with organic substances, the photo generated e- /h+ pairs initiate a series of redox reaction via a number of mechanisms *(B.Sivasankar, 2001).* Which include:

- Oxidation of absorbed water molecules and hydroxyle ions by the photogenrated holes to give hydroxyle radicals.
- Reduction of dissolved oxygen by the photo generated electron to produce super oxide anion radicals, which in turn, can lead to the generation of H_2O_2 through a series of redox reaction.
- The photo-generated hydrogen peroxide undergoes further decomposition to yield hydroxyle radicals.
- Direct participation of the holes and electrons in oxidation/reduction reaction.
- Formation of singlet oxygen, which can participate in oxidation reaction.

2.2.3 Fenton and Photo Fenton processes

Fenton's reagent oxidation is a homogeneous catalytic oxidation process using a mixture of hydrogen peroxide and ferrous ions. The main advantage of the Fenton's reagent is its simplicity. The chemicals are readily available at moderate cost and there is no need for special equipment. In an acidic environment if hydrogen peroxide is added to

a system containing an organic substrate and ferrous ions, a complex redox reaction will occur *(Marco S et al., 2006)*. The overall reaction is:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + HO^- + HO^{\bullet} \quad (1)$$

The ferrous ion initiates and catalyses the decomposition of H_2O_2, resulting in the generation of hydroxyl radicals, $HO^{\bullet}$. Hydroxyl radicals are powerful oxidation agents that have an oxidation potential only lower than fluorine and higher than ozone and H_2O_2: 3.0 V for fluorine, 2.8 V for $HO^{\bullet}$, 2.07 V for ozone and 1.78 V for H_2O_2. Then, hydroxyl radicals are capable of rapidly attacking organic substrates (RH) and cause chemical decomposition of these compounds by H- abstraction and addition to C─C unsaturated bonds

$$RH + HO^{\bullet} \rightarrow R^{\bullet} + H_2O \quad (2)$$

$$R^{\bullet} + Fe^{3+} \rightarrow R^{+} + Fe^{2+} \quad (3)$$

$$R^{+} + H_2O \rightarrow ROH + H^{+} \quad (4)$$

Numerous competing reactions which involve Fe^{2+}, Fe^{3+}, H_2O_2, hydroxyl radicals, hydroperoxyl radicals and radicals derived from the substrate, may also be involved. Hydroxyl radicals may be scavenged by reacting with Fe^{2+} or hydrogen peroxide:

$$HO^{\bullet} + Fe^{2+} \rightarrow HO^{-} + Fe^{3+} \quad (5)$$

$$HO^{\bullet} + H_2O_2 \rightarrow H_2O + HO_2^{\bullet} \quad (6)$$

Fe^{3+} formed through reactions (1) and (5) can react with H_2O_2 following a radical mechanism that involves hydroxyl and hydroperoxyl radicals, with regeneration of Fe^{2+}

$$Fe^{3+} + H_2O_2 \leftrightarrow Fe-OOH^{2+} + H^{+} \quad (7)$$

$$Fe-OOH^{2+} \rightarrow HO_2^{\bullet} + Fe^{2+} \quad (8)$$

$$Fe^{2+} + HO_2^{\bullet} \rightarrow Fe^{3+} + HO_2^{-} \quad (9)$$

$$Fe^{3+} + HO_2^{\bullet} \rightarrow Fe^{2+} + H^{+} + O_2 \quad (10)$$

In photo-Fenton process in addition to the above reactions the formation of hydroxyl radical also occurs by the following reactions *(Arnold S M et al., 1995).* The addition of UV to Fenton's process could be an interesting option in dye decolourization due to its capacity to influence the direct formation of $^{\bullet}OH$ radicals *(P.K.Malik et al., 2003, J Henery et al., 2005).*

$$H_2O_2 + UV \rightarrow HO^{\bullet} + HO^{\bullet} \quad (11)$$

$$Fe^{3+} + H_2O + UV \rightarrow HO^{\bullet} + Fe^{2+} + H^{+} \quad (12)$$

2.2.4 Ozonation

Ozone is a strong oxidant and effective in many applications like elimination of color, disinfection, elimination of magnesium and organic compound *(Sevener M ea al., 1990). (Staehelin ea al., 1982)* reported that ozone has an average life of few minutes. There fore it has to be introduced in greater quality in reaction medium that what is actually required. Ozonation can also consist as an AOP as it gives hydroxyl radicals on decomposition .The pH of the wastewater is in direct reaction to the rate of decomposition of ozone.

The disadvantages of ozone as an oxidizer are the need of onsite production and installation within the ozone production system, increasing its cost. .It is used as tertiary treatment in drinking water plants and for the oxidation of organic pollutants of industrial or agriculture effluent. Ozonation has been found very efficient in decolonization of textile wastewaters *(Balcioglu et al., 2001).* The ozone treatment may be enhanced by the addition of hydrogen peroxide.

CHAPTER-3

Literature Review

3.1 Introduction

Extensive air and water pollution has plagued the planet for a long time. As a response to the looming threat, the humankind has been expediting its efforts in pollution abatement. Several approaches are used: to utilize environmentally benign processes, to provide in-situ destruction of pollutants during the process, and to decontaminate the air or water stream emanating from the high throughput production facility.

The treatment of industrial wastewater before discharge to prevent the quality of natural water body from deterioration and to meet regulatory requirements continues to be a significant challenge of environmental protection. In the field of wastewater treatment, many kinds of technologies in the areas of chemistry, physics, and even biochemistry have been applied under the considerations of economics and practicability. Recently, considerable interest has been shown by researchers all over the world in the application of Advanced Oxidation Processes (AOP's) for the destruction of organic and inorganic contaminants in aqueous streams. Many literatures have reported that a lot of toxic or hazardous industrial chemicals could be destroyed by this novel technique. However, even faster decomposition is needed to carry out the oxidation at the commercial level, and in some cases, more toxic intermediates are produced during the degradation of parent chemicals.

The treatment of spent dye wastewater effluent is a growing concern for the textile industry because of aesthetic conditions, as well as eco toxicological issues regarding colored rinsing and process wastewater and the impact of that wastewater on the receiving streams. As regulations become more stringent, the effectiveness and cost of treatment processes becomes more significant. Conventional biological treatment can be ineffective for color removal, but chemical oxidative processes seem to provide an opportunity for future use in industrial wastewater. The concept behind an AOP is that exposure of a strong oxidizing agent exposed to UV light generates hydroxyl free radicals which are even stronger oxidants *(Ince G et al., 1997).* Color reduction in textile wastewater is measured in terms of absorbance by UV-VIS Spectrophotometer. Two

other analyses commonly used for the analysis of wastewaters are total organic carbon (TOC) and chemical oxygen demand (COD), neither of which is specific for determining color reduction. A reduction in color level following the addition of an oxidant can occur either by degradation or alteration of the conjugated system of the dyes with the potential to create even more toxic chemicals in the effluent *(Yang et al., 1998)*. The toxicity associated with color degradation will prove to be an important factor in the choice between oxidative treatments. Previous research into the decolourization of dyes and spent textile dye effluent by chemical oxidation appeared to focus on specific dye decomposition (rates and kinetic models), initial dye concentrations, hydrogen peroxide concentrations, and UV intensity with different contact times as important factors affecting color reduction.

3.2 Textile Wastewater - A Global Scenario

Textile industries are large industrial consumers of water as well as producers of wastewater *(Asia et al., 2006)*. The U.S. Department of Commerce has predicted a 3.5 fold increase in textile manufacturing between 1975 and 2020 *(Ganesh, 1992., Walsh et al., 1980)*. Increasingly strict environmental legislation, has led to textile finishing industries being labeled high priority industries with respect to pollution *(Licis et al., 1991)*. In Europe, environmental legislation has necessitated increasingly green textile processing. This has, and is being achieved, through recycling of chemicals and water, production and use of biodegradable textile chemicals and dyes, as well as efficient effluent treatment *(Mohr, 1992)*.

Textile industries consume water on a large scale, so constituting a major group to cause intense water pollution. According to U.S E.P.A, an average dying facility generates 1 to 2 million gallons of wastewater per day. About 10,000 different dyes and pigments are produced annually worldwide. The industry uses various chemicals depending upon the nature of raw material and product. Estimation says that about 10%

dyes are lost in the wastewater *(Young and Yu., 1999).* Different processes involved in production like sizing, desizing, scouring, bleaching, washing, mercerization, dying and finishing gives wastewater having a high pH ,temperature, organic matter, non biodegradable matter, toxic substances, detergents & soaps, oil & grease, sulphide, sodas and high alkanity which exacerbates their treatment and disposal .The fate of these chemicals varies depending up on retention on fabric or discharge in effluent. Moreover, reactive dyes are highly water soluble and non biodegradable under aerobic condition *(Neppolian et al., 2001, Rodriguez et al., 2002)*

3.3 Textile Wastewater - An Indian Scenario

In India, an average mill producing 60 x 10^4 m of fabric per day is likely to discharge approximately 1.5 million per day of effluent (CPCB, 2000). The textile wastes are extremely diverse, and perhaps, one of the most potential polluters of our aquatic environment. Aquatic life is highly susceptible to change in pH of water body and effluents from textile industry are usually basic in nature which can drastically alter the habitat of organisms. The high temperature effluents which when discharged into the receiving water body reduce the solubility of oxygen in the water and induce unfavorable conditions for survival of aquatic ecosystem *(Karthikeyan et al., 2006).* The organic matter like starch, dextrin, inorganic chemicals like sulphides, nitrites will exert an immediate oxygen demand, thus reducing the dissolved oxygen in water. The solids present in the effluent will increase the turbidity of water thereby retarding the photosynthetic activity. The essential metals in effluent increase the fertility of water column and sediment and consequently lead to eutrophication *(Asamudo et al., 2005).*

The pollution load in textile wastewater is higher than the limits prescribed by different agencies. Generally the textile mills discharge the wastewater in-to the environment without treatment. This cause serious problem for natural water bodies and land in surrounding area. High BOD, COD, particulate matter and sediments and oil & grease in the effluent result in dissolved oxygen tension affecting adversely on marine ecosystem. Presence of chromium, chemicals and color in the effluent increase turbidity

of the water body, affecting photosynthesis and causing alteration of the habitat that leads to disappearance of organisms. *(ETPI, 2003).*

The high alkalinity may be harmful to crops and high salinity of the wastes will impair their growth and sodium hardens the texture of the soil, prevents penetration of the roots. The suspended and colloidal matter may clog the pores of the soil by forming an impervious mat. As a cumulative effect, the soil will lose its productivity (IS: 9508-1980). Treatment of textile wastewater for reuse using an electrochemical oxidation step combines with a membrane filtration step is reported by *(Chen et al., 2005).* Electrochemical oxidation has a high COD removal efficiency (89.8%) of the textile wastewater while membrane filtration can almost totally remove TSS (nearly 100% reduction) and turbidity (98.3% elimination) in it. The treated can be reused in many productional areas of the textile dye house factory. This offers a promising way for recycling textile wastewater.

3.4 Textile Dye Characteristics

According to *Shore (1990),* most of the dyes and pigments in the color Index are placed in one of the 25 structural classes according to their chemical type. Azo dyes, the largest class, are subdivided into four sections. Classification of the four sections depends on the number of azo groups within the dye molecule. The depth of color is related to the molecular structure of the dyes, which is related to the chromophores (-N=N- or >C=O) involved within the structure. In addition, visible and the UV irradiation electron transfer effects at varying wavelengths on the dye structures have been observed, supporting tautometic capabilities of the dye molecules. An oscillation between the double and single bonds occurs along the conjugated molecular chain; therefore, as the chain becomes longer, the vibration rate becomes slower resulting in a slower kinetic degradation rate *(Shore, 1990).*

Dye fixation onto fibers depends on the dye property known as fastness, which describes its ability to bond to the material. Reactive dyes are very soluble in water and,

therefore, are poorly adsorbed *(Churchley et al., 1997).* Any additional chemicals that are added during the dye application, such as salts or detergents, will affect the wastewater and subsequently the treatment process.

3.5 Textile Wastewater Characteristics

Composite textile wastewater is characterized mainly by measurements of biochemical oxygen demand (BOD), chemical oxygen demand (COD), suspended solids (SS) and dissolved solids (DS). Typical characteristics of textile industry wastewater are presented in Table 1.3.3 in appendix. Results in Table show a large extent of variation from plant-to-plant and sample-to sample & COD values of composite wastewater are extremely high as compared to other parameter. In most cases BOD/COD ratio of the composite textile wastewater is around 0.25 that implies the wastewater contains large amount of non-biodegradable organic matter *(Al-Kdasi et al., 2004).*

Shyh et al., (1999) investigated the removal of colour and COD from a dye manufacturing plant wastewater using the Fenton and photo-Fenton process. The results showed that removal of Colour and COD is 90% with photo-Fenton whereas colour and COD reduction reduces to about 80% in Fenton process within 2 hrs of reaction time. UV irradiation favours colour removal more than the COD removal in terms of rate or rate per unit power.

Adel Al-Kdasi et al., (2005) carried out a study on treatment of textile wastewater by advanced oxidation processes. Conventional treatment such as biological treatment discharges will no longer be tolerated as 53% of 87 colors are identified as non-biodegradable. Advanced Oxidation Process represents a powerful treatment for refractory and toxic pollutants in textile wastewater.

3.6 Ultraviolet Lamp and Reactor Characteristics

Ultraviolet light is an electromagnetic radiation spread between the wavelengths 100 nm and 400 nm. Most UV lamps used in wastewater treatments perform at a wavelength of 254 nm. A mercury vapor lamp is the most common UV light source *(Hanzon and Vigilia., 1999)*. The UV dosage applied to a wastewater is determined by the intensity of the UV radiation and the contact time involved and is commonly expressed in mile watt-seconds per square centimeter (mW-sec/cm^2). Ultraviolet lamps are classified as low, medium or high-pressure units. The intensity is a function of the lamp array's geometry as well as the UV transmittance of the wastewater. The literature investigated for this study dealt with low, medium and high-pressure lamps. The UV chambers vary in size and were configured by either vertical or horizontal lamp placement. Other factors that limit the effectiveness of the system are the wattage and output. The UV lamps described in the literature varied from 14 watts to 35 watts for a low-pressure lamp *(Shu et al., 1994; Namboodri and Walsh, 1996; Liao et al., 2000)* and 200 and 300 watts for medium pressure lamps *(Glaze 1993; Yang et al., 1998)*.

3.7 Decolourization of Dyes Using Fenton & Photo Fenton

Advanced electrochemical oxidation process (AEOP's) under potential controlled electrolysis conditions was used by (*Elodie et.al)* to degrade the azo dyes azobenzene, pmethyl red and methyl orange in aqueous solution at room temperature. A comparative study of natural Red discoloration by photo-Fenton and photocataylitic process was carried out by *(Maitha M. et. al, 2006),* they found the order of efficiency as photo Fenton processes, followed by Fenton process, then photolytic, and then with photocatalytic processes. *(A.Riga et.al, 2006)* carried out the comparison of H_2O_2/UV, Fenton, UV/Fenton, TiO_2/UV and TiO_2/UV/H_2O_2 processes with system parameters and of inorganic salts on the depolarization and degradation of Procion H-exl dyes. It was found that decolarization of the Procion H-exl solutions considered was found to strongly depend on the system parameters in all five AOPs. *(Amal Lahkimi et Al.,)* applied electro-Fenton process, to the synthetic dismissal composed of three dyes, yellow drimaren,

congo red and methylene blue, frequently used in textile and dye houses. Here, they show that those dyes and their mixture were quickly degraded under current controlled electrolysis conditions; the results show the efficiency of electro- Fenton process to quickly degrade aqueous effluents polluted by synthetic organic dyes.

Zollinger (1987) reported availability of about 10,000 dyes and annual production of about 7×10^5 tones of dyestuff. *(Vaidya and Datye, 1982)* worked out that 5 to 10% dye bath solution is lost in effluent during the process. *(Shore, 1995)* reported about 50% loss of reactive dyes in dye bath effluent.

Marmagne et al., 1996 reported that reactive dyes are having more non-biodegradability factor than other dyes. Residual color is imparted by insoluble dyes having low biodegradability. BOD_5/COD ratio is a count of biodegradability as explained by the *(Marmagne et al., 1996).* More the biodegradability factor more is the suitability of biological process to treat the industrial effluent and vice versa. Main pollution problem caused by the dyes are color/COD, toxicity. Dyes generally have high COD values *(Marmagne et al., 1996).* Moreover as they are having very low biodegradability factor (BOD/COD ratio) they are difficult to be treat with the help of biological treatment processes. Toxicity is the main problem enounced by bacteria engaged for the degradation of dyes, which makes it very difficult to treat it in biological processes. Anaerobic processes however have been reported to be little effective, but they have limited applications. Physico-chemical treatments are either pollutant specific or they have low degradation rates in general.

3.8 Degradation of Dyes Using Fenton & Photo Fenton Processes

Mioara Supateanu et al. (2004) carried out investigations for the decolorization of Acid Red G azo dye by photo oxidation with hydrogen peroxide. The influences of pH, oxidant concentration, and the presence of Fe^{+2} or other metal ions ($C0^{+2}$, Cu^{2+}, Ni^{2+}, Mn^{2+}) as potential catalysts, were investigated**.** Similarly acid red 114 was photo degraded by *(Jong-Min lee et al.,)***.** They use photo Fenton process with TiO_2 and carried

out that a dye acid red 114 (C.I. 23635) was photo chemically removed by adding ferric ion (Fe^{3+}), TiO_2 particles, and H_2O_2 in the presence of the UV radiation.

Fenton and photo Fenton processes were used by *(Lluis Nunez et al., 2006)* for the decolourization and mineralization of two reactive azo dyes, Procion Red H-E7B (CI Reactive Red 141) and Cibacron Red FN-R (CI Reactive Red 238). The experimental results showed that the Fenton's process run under solar light was the most effective.Similar work was done by *(Marco S et al., 2005)* to decolorize the Reactive Black 5 (RB5) in aqueous solution by using Fenton (H_2O_2/Fe^{2+}) and photo-Fenton (H_2O_2/Fe^{2+}/UV) processes. This investigation reveals that both methods can remove the color of RB5. Mineralization of 2, 4-dichlorophenoxyacetic acid (2, 4-D) in the presence of zero-valent iron and hydrogen peroxide (the advanced Fenton process - AFP) whilst being subjected to acoustic or hydrodynamic cavitation by *(David et al., 2007)*

J. Herney Ramirez et. al., (2005) optimizes the degradation condition for the synthetic dye orange II using Fenton's reagent. They found that both H_2O_2 concentration and temperature have an important effect in the organic matter degradation efficiency. *(Jian-Hui Sun et al., 2007)* carried out the degradation of azo dye Acid black I using low concentration iron of Fenton process facilitated by ultrasonic irradiation. They found that the Fenton can be an effective technology for the treatment of organic dyes in water. Similarly effect of ultrasonic irradiation with Fenton-like oxidation on oxidative degradation of para-chlorobenzoic acid was studied by *(B. Neppolian et.al., 2004).*

To understand the photodegradation of azo dyes in natural aquatic environment, a novel photo-Fenton-like system, and the heterogeneous iron oxide–oxalate complex system was set up. Five iron oxides were prepared and their adsorption capacity was investigated in the dark. The results showed that the photodegradation of orange I under UVA irradiation could be enhanced greatly in the presence of oxalate. *(Jing Lie et al., 2006).* The degradation and decolorization of direct dye (Everdirect supra turquoise blue FBL), acidic dye (Isolan orange S-RL) and vat dye (Indanthrene red FBB) have been investigated by Fenton and UV/Fenton processes. A comparative study for Fenton and

UV/Fenton reactions by photo reactor has also been carried out by *(Robert Liu.et al., 2005)* Fenton process is highly efficient for color removal for three dyes tested and for TOC removal of FBB and FBL. UV/Fenton showed slighter increase in treatment efficiency than that of Fenton process for both FBB and FBL dye solutions.

3.9 Fenton & Photo Fenton Processes in the Treatment of Textile Effluent

Conventional oxidation treatments have found difficulty to oxidize dyestuffs and complex structure of organic compounds at low concentration or if they are especially refractory to the oxidants. To ease the stated problems advanced oxidation processes (AOP's) have been developed to generate hydroxyl free radicals by different techniques. AOP's processes are combination of ozone (O_3), hydrogen peroxide (H_2O_2) and UV irradiation, which showed the greatest promise to treat textile wastewater. These oxidants effectively decolorized dyes, however did not remove COD completely.

Advanced Oxidation Processes (AOP's), based on the in-situ generation of highly reactive hydroxyl radicals as a primary oxidant species ($HO\cdot$, E = 2.8 V *vs* NHE), are a powerful alternative to conventional treatment methods for wastewater decontamination. Among the considered AOPs, the Fenton ($HO^{\bullet}$ generated by interaction of H_2O_2 with ferrous salts) and photo-Fenton type reactions are very promising since they achieve high reaction yields with a low treatment cost. In addition, since photo-Fenton reaction requires radiations up-to 410 nm, the process offers the possibility of sunlight exploitation. *(Julio et.al). & [Jan Perkowski et.al]* investigate the decomposition of an anthraquinone dye (polan blue E2R) in an aqueous solution by means of advanced oxidation with ozone, hydrogen peroxide and UV radiation. The decolouration efficiency in combined systems was compared. The best results were obtained using ozone, hydrogen peroxide and UV radiation simultaneously.

Rein Munter et. al provides an overview of theoretical basis, efficiency, economics, laboratory and pilot plant testing, design and modeling of different advanced oxidation processes (combination of ozone and hydrogen peroxide with UV radiation and

catalysts) Colour of Remazol Turquoise Blue G-133 was removed by Fenton process (involving oxidation and coagulation), ferric coagulation and H_2O_2/pyridine/Cu (II) system *(Ulusoy Bali et al., 2006).*

Jan Perkowski et.al conclude that in industrial processes, when it is sufficient to decolourize a solution before reuse of water in a technological cycle, advanced oxidation processes can be applied successfully.

CHAPTER-4

Materials & Methods

4.1 MATERIALS

Described in this chapter are the materials and methods used during this research, including the chemicals, glassware, the UV photo reactor, pH adjustment and analysis by UV-Vis Spectrophotometer, COD reduction, conductivity measurement, and procedures used to dose the dye and effluent solutions with $H_2O_2/Fe^{2+}{}_+$ and NaOCl. The compilation of the varying Fenton reagent and Sodium Hypochlorite dosages and the varying UV contact times for the Methyl Orange dyes with varying concentrations and effluents make up the experimental matrix.

4.1.1 Dye

Malachite Green dye is a basic dye that was purchased from Merck and used without further purification. Molecular structure of Malachite green has been illustrated in Table 1.4. Malachite green, also called analine green,basic green 4,diamond green B, or victoria green B having IUPAC name 4-[(4-dimethylaminophenyl)-phenyl-methyl]-N,N-dimethyl-aniline is a toxic chemical primarily used as a dye. It is a green crystal powder with a metallic luster, very soluble in water, extremely soluble in ethanol, solutions are blue-green; basic green dyes become yellow in high concentration sulphuric acid, becomes dark orange when diluted; it becomes orange in high concentration nitric acid, becomes brownish orange when diluted. Dye solutions were prepared by dissolving requisite quantity of dye in double distilled water from a double distilled purification system with a concentration varying from 10-100 ppm.

4.1.2 Wastewater

Wastewater collected from the homogenous tank of effluent treatment plant (ETP,s) of textile industry near Ludhiana. Wastewater sample was highly polluted as the wastewater characteristics showing in table 5.2.1. So to get the value within range sample

was diluted 1:1. Single distilled water was used for the all dilutions.

4.1.3 Chemical and reagents

Hydrogen Peroxide (H_2O_2) solution was purchased from S.D. fine-chem limited having 30% W/V AR and was freshly prepared. Hydrated ferrous sulphate ($FeSO_4.7H_2O$) was procured from SISCO Research laboratories, Mumbai, (extra pure AR) and was used as such without purification. pH of the solutions was adjusted with 1M HCl or 1M NaOH

4.1.4 Instrumentation

Photo reactor/UV chamber

UV reactor used was rectangular in shape having dimensions of 4.5 feet length, 3.0 feet width, & 3.5 feet height. It was made up of cast iron. Reactor was mounted with wooden roof. It is equipped with seven 36 W UV tubes (Philips) attached to the roof having wavelength of 365 nm. An exhaust fan maintained temperature inside the reactor. Two different views of photo reactor are shown in Fig 4.1.1 and 4.1.2.

Fig: 4.1.1 Outer view of photo reactor

Fig: 4.1.2 Photo reactor at lab level during photo Fenton treatment

pH meter

pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of 0.1M NaOH and 0.1M HCl.

EC meter

EC of the samples was determined by using a deluxe conduvtivity meter model 601 E (Microsil, India)

COD Digester

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

Reaction Vessels

Photochemical decolourization was carried out in specially designed double walled reaction vessels in the UV chamber/reactor. The experiments were conducted in

batch mode. Constant stirring of the solution was ensured using magnetic stirrers. Reaction vessel with magnetic stirrer is shown in Fig 4.1.3

Fig: 4.1.3 Reaction vessel with magnetic stirrer during Fenton treatment.

Spectrophotometer

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

Turbidometer

Turbidity of the samples was measured by Radio Turbidometer, Hatch

Radiometer

Intensity of UV and solar light was measured with Eppley radiometer.

4.2 METHODS

4.2.1 Collection and storage of wastewater and dye sample

Sample was collected from homogenous tank of effluent treatment plant of textile industry near Ludhiana. Sampling vessel was cleaned and rinsed carefully with distilled water and then washed with sample during sample collection. Then effluent was stored in cold store ata temp.of 4°C within 2 to 3 hrs of collection.

Parameter studied includes pH, EC, TDS, BOD_5, COD and turbidity. Parameters were analyzed by method given in APHA (1996) standard methods. Reagents used for the present investigation were of AR Grade and double distilled water was used throughout the study.

4.2.2 Preparation of solution

a) **Dye Solutions:** The dye solutions were prepared by adding a known amount of dye into a small amount of deionized water in a 1-liter Erlenmeyer flask and filling it to the mark with double distilled water. The flasks were covered with aluminum foil to avoid degradation by the laboratory fluorescent lights. Before the oxidation experiments could be performed, it was necessary to choose the appropriate concentration of dye solutions. For most of the experiments, dye solutions of 25 ppm concentration were prepared by dissolving 0.025g in deionized water and make the solution quantity to1 L. (If 1 g is present in 1 L then solution is said to be 1000 ppm and 0.1 g in 100 ml then it becomes 100 ppm.)

b) **Handling and Storage of Dye**

Precautions:

Keep locked up. Keep away from heat. Keep away from sources of ignition. Empty containers pose a fire risk, evaporate the residue under a fume hood. Ground all equipment containing material. Do not ingest. Do not breathe dust. Wear suitable protective clothing. In case of insufficient ventilation, wear suitable respiratory equipment. If ingested, seek medical advice immediately and show the container or the label. Avoid contact with skin and eyes. Keep away

from incompatibles such as oxidizing agents.

Storage: Keep container tightly closed. Keep container in a cool, well-ventilated area. Do not store above 25°C (77°F).

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

d) Ferrous Sulphate: Ferrous sulphate hydrated ($FeSO_4.7H_2O$) was prepared as 10% w/v, which implies that the 10g of salt were dissolved in 100 ml of double distilled water. In order to dissolve ferrous sulphate completely in distilled water, few drops of concentrated sulphuric acid were added to shift the equilibrium of reaction backward. Hence 1 ml of prepared solution contains 100 mg of salt. If the solution is diluted ten times, then 1 ml contains 10 mg. For adding 150 mg/l, add 15 ml in 1L of dye or 1.5 ml of diluted ferrous sulphate solution in 100 ml of dye solution or effluent sample.

e) Calcium Hypochlorite: Sodium Hypochlorite (4 % w/v) was procured from Merck, which implies 4 g of NaClO is present in 100 ml of solution or 40 mg in 1ml. For adding 40 mg/l of NaClO in dye, add 1ml in 1 L or 0.1 ml in 100 ml.

4.3 ANALYSIS

4.3.1 pH Estimation

The pH is a logarithmic scale generally used to express the acidic, alkaline or neutral nature of a solution. In fact, it presents the hydrogen ion concentration or, more precisely, the H^+ ion activity in a given solution. The pH value is the best indication of the presence of acid or alkali in the water sample. Due to hydrolysis of dissolved salts, the pH value can decrease or increase beyond neutral value, i.e. 7.0, showing the presence of salts of strong base and weak acid, e.g. Na_2CO_3 increases pH value; salts of weak base and strong acid, e.g. $CaCl_2$ decrease pH level. Thus, a fundamental relationship exists among pH, acidity and alkalinity.

Significance

The pH is an essential factor to be estimated factor to be estimated in each and every phase of water and wastewater treatment. In water the processes involved in the treatment of potable water, such as chemical coagulation, disinfection, softening and corrosion control are pH dependent. In case of wastewater the biological treatment involves decomposition of organic matter available in wastewater by different species of aerobic bacteria. The growth and activity of these depend on the pH level in wastewater. Generation and emission of malodorous gases are also controlled by pH variations. In chemical treatment of wastewater, the coagulation of wastewater, dewatering of sludge and oxidation of certain substances such as cyanide are also pH dependent processes.

Hence, accurate measurement and monitoring of this factor in optimum range is of great significance in water and wastewater management and treatment.

Apparatus

- pH meter: pH of the solution was monitored by using a digital desktop, pH Meter (CP 901) from Century Instrument Company and pH was adjusted with the help of NaOH and HCl
- Beakers

Reagents

- **Buffer solution of 4.0 pH (Thallate buffer):** 10.2 grams of potassium hydrogen thallate was dissolved in one litter double distilled water.
- **Bufer solution of 7.0 pH (Phosphate buffer):** 3.4 gram of borax was dissolved in one liter double distilled water.
- **Buffer solution of 9.2 pH (Borax Buffer):** 3.81 gram of borax was dissolved in one liter of double distilled water.

Procedure

1. After calibration with buffer solution, rinse the electrode with DDW and wipe gently.
2. Take the sample in a beaker. Bring the temperature of the sample to room temperature.
3. Deep the electrode in the beaker in such a way that bulb of the electrode deep in to sample. Bring the temperature to homogeneity by stirring.
4. Record the reading from display, which will give the pH value of the sample.

Calculation

The read out of the pH meter will gives direct pH value of the sample.

4.3.2 Electrical conductivity (EC)

EC is an important parameter to assess the wastewater quality. It is a measure of ionic concentration. It is an indicator of salinity also and measured in mS/cm.

Apparatus

The EC of dye sample and textile effluent was estimated using conductivity meter.

Reagents

Standard KCL solution: The EC meter was calibrated with standard KCL solution (0.1N). The standard KCL solution of 0.1N was prepared by dissolving 0.747

gm of KCL (AR grade) in 100 ml double distilled water. The EC of standard solution was set at 12.88 mmho cm^{-1}. After calibration of instrument, EC of sample was recorded.

4.3.3 TOTAL DISSOLVED SOLIDS (TDS)

Principle

A filtered sample containing the dissolved solids is evaporated to dryness at 180°C. The residue is known as TDS.

Apparatus

- Filtration unit comprising filtration flask of 1 litre capacity, a funnel, a filter holder and a vacuum pump.
- Filter paper: Whatman GF/C or equivalent 4.25 cm disc size.
- Oven set at 103°C.
- Desiccating cabinet.
- Forceps: Flat bladed without serrated tips.
- Analytical balance

Procedure

The estimation is carried out with the filtrate collected after the filtration of the sample containing suspended solids.

1. Take an evaporating dish cleaned with chromic acid and rinsed well with tap water, then with DDW. Dry it overnight in an oven set at 180°C.
2. Cool the dish in a desiccating cabinet to room temperature. Weigh until a constant weight is achieved.
3. In a pre-weighed evaporating dish, place 100ml filtrate collected in the estimation of TSS.
4. Place it in a oven set at 180°C until all the filtrate evaporates, leaving behind the dissolved solids.

Cool in a desicating cabinet and weigh the dish. Repeat the steps of cooling and weighing until a constant weight is achieved. Record the final weight

Calculation

$$\text{mg TDS / l} = \frac{(A - B) \times 1000}{\text{Volume of sample, ml}}$$

Where A = Weight of dish and filtrate, g

B = Weight of dish, g

4.3.4 CHEMICAL OXYGEN DEMAND (COD)

The COD is considered mainly the representation of pollution level of domestic and industrial wastewater or contamination level of surface, ground and potable water. This is determined in terms of total oxygen required to oxidize the organic matter to CO_2 and water. The COD values include the oxygen demand created by biodegradable as well as non-biodegradable substances because it involves oxidation of organic matter with strong oxidizing chemicals. As a result, COD values are greater than BOD and may be much greater when significant amounts of biologically resistant organic matter is present.

Apparatus

- Close refluxing unit.
- Titration assembly

Reagents

- **Mercuric Sulphate, $HgSO_4$**
- **Ferroin Indicator**: Weigh 1.485g of 1, 10-phenanthroline monohydrate and 0.695g $FeSO_4.7H_2O$. Transfer both the chemicals to a 100 ml volumetric flask.

Dissolve in DDW. Dilute up to the mark with DDW.

- **Potassium dichromate solution, $K_2Cr_2O_7$, 0.25N:** Dry an adequate quantity of analar $K_2Cr_2O_7$ in an oven set at 103 C for 2 hours. Cool to room temperature. Accurately weigh 12.259g dry and cool $K_2Cr_2O_7$ and transfer to a 1 litre volumetric flask. Dissolve in DDW. Add 0.12g of sulfamic acid to the concentrated dichromate solution. Dilute up to the mark.
- **Concentrated sulphuric acid, H_2SO_4**
- **Sulphuric acid concentrated with silver sulphate, $H_2SO_4 – Ag_2SO_4$ catalyst:** Weigh 22g of silver sulphate (Ag_2SO_4) and add to a 2.5 litre concentrated H_2SO_4 bottle. Keep this solution on magnetic stirrer. Stir for 1-2 days for complete dissolution of Ag_2SO_4.
- **Ferrous ammonium sulphate (FAS) solution, $Fe(NH_4)_2(SO_4)_2.6H_2O$, approx. 0.25N:** Weigh 98g FAS and transfer to a 1 litre volumetric flask. Dissolve in about 500 ml DDW. Add 20 ml conc. H_2SO_4. Dilute to 1 litre with DDW and cool it.
- **FAS titrant, 0.10 N:** Measure 400 ml of the 0.25 N FAS solution in a 1 L volumetric flask. Dilute to 1 L with DDW. Standardize this solution daily before estimation.

Standardization

FAS titrant, 0.10 N

1. Fill the burette with 0.10 N FAS titrant.
2. Accurately measure 10 ml of 0.25 N $K_2Cr_2O_7$ solutions into a clean Erlenmeyer flask and add 90 ml DDW into the flask.
3. Dispense 30 ml concentrated H_2SO_4 with constant stirring and cool the solution.
4. Add 0.5 ml ferroin indicator.
5. Titrate with FAS titrant till the endpoint is achieved. First the solution turns bluish green and then attains a reddish brown color at endpoint.

Calculation

$$\text{Normality of FAS} = \frac{A \times N}{V} = \frac{10 \times 0.25}{V} = 0.10\ N$$

Where, A = volume of $K_2Cr_2O_7$ taken, ml = 10

N = normality of $K_2Cr_2O_7$ = 0.25

V = ml of FAS used

4.3.5 BIOCHEMICAL OXYGEN DEMAND (BOD)

Principle

BOD is measure of biodegradable organic material present in wastewater and can be defined as the amount of oxygen required by the microorganisms in stabilizing the biologically degradable organic matter under aerobic conditions. The principle of the method involves, measuring the difference of the dissolved oxygen concentration of the sample and after incubation it for 5 days at 20^0 C.

Apparatus and reagents

- BOD bottles
- BOD incubator

Preparation of nutrients

- **Phosphate buffer:** 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4 g $Na_2H.\ PO_4.7H_20$ and 1.7 g NH_4Cl was dissolved in 500 ml distilled water and diluted to 1 liter.
- **Magnesium sulphate solution:** 82.2 g $MgSO_4.\ 7H_2O$ was dissolved in distilled water and diluted to 1 litre
- **Calcium chloride solution:** 27.5 g of anhydrous $CaCl_2$ was dissolved in distilled water and dilute to 1 litre
- **Ferric chloride solution:** 0.25 g $FeCl_3.\ 6H_2O$ was dissolved in distilled water and

diluted to 1 liter.

Preparation of dilution water (Aerated water)

About 2ml/ 5 litre seed was added to a required volume of dilution water (distillation water) and aerated about on night to have the sufficient dissolved oxygen in it. After aeration 1 ml each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solution each was added per liter of water.

Procedure

Two bottles for sample and two bottles for blank were filled up by the dilution water to get the required dilution factor. One set of dilution sample and blank was kept in BOD incubator at 25^0C for 5 days, and DO contend in another set was estimated on the same day. After 5 days DO was also estimated from the second set of the sample and blank from the incubator.

Reagents

- **Manganese suplhate solution:** 100 mg of $MnSO_4$. H_2O was dissolved in boiled distilled water,filter and diluted to 1 liter.
- **Alkali-iodide-azide reagent:** Dissolve 500 g of NaOH and 135 g NaCl in distilled water and dilute to 1 liter. Add 10 g NaN_3 dissolved in 40 ml of distilled water.
- **Starch Solution:** 1 g of starch was added in 100 ml of warm (80^0C-90^0C) distilled water and a few drop of formaldehyde solution were added.
- **Sulphuric acid:** H_2SO_4, concentration (sp gr. 1.84)
- **Standard Sodium Thiosulfate solution (0.025N):** 24.82 g of NaS_2O_3. $5H_2O$ was dissolved in boiled distilled water and made volume to 1 liter and 0.4 g of NaOH pallet added as stabilizer. Then the solution was diluted to 4 times with boiled distilled water to prepare 0.025 N solutions

Procedure

2 ml manganese sulfate solution followed by 2 ml alkali-iodide-azide reagent

were added to the sample collected in 300 ml BOD bottle and mixed by inverting the bottle for complete fixation of DO as brown colour manganese hydroxide precipitation. Then 2 ml conc. H_2SO_4 was added and dissolved the precipitation by gentle inversion. This solution was titrated with 0.025 N sodium thiosulphate solution using starch indicator and end point was blue to colorless.

Calculation

$$\text{DO (mg/l)} = \frac{V \times N \times 8000}{\text{Volume of Sample (m/l)}}$$

Where: V = Volume of sodium thiosulphate thiosulphate used in ml.

N= Normality of Sodium Thiosulphate

BOD (mg/l) = $(S_1-S_5) – (B_1-B_5) \times$ dilution factor

Where S_1 = DO of sample of 1st day

B_1 = DO of blank on 1^{st} day

S_5 = DO of blank on 5^{th} day

B_5 = DO of sample on 5^{th} day.

4.3.6 Analysis for decolouration

The decolourisation/degradation studies were conducted by measuring absorbance in UV/VIS spectrophotometer, having a wavelength range from 190-1100nm using a 1 cm quartz cell. All the experiments reported were carried out in a 4 ml quartz cuvette. The scan speed is 200 nm/min with a step of 1.0 nm. Wavelength resolution is 0.1 nm. Spectrophotometer is having both Tungsten and Deuterium lamp at operating temperature of 0-40^oC. Scans were collected from 190-600 nm.

CHAPTER-5

Results & Discussions

The effectiveness of the various oxidative treatments for reducing color in dye solutions and wastewater was evaluated in batch photo reactors at 298K. A matrix of experimental variables was developed in which the UV exposure time, H_2O_2 concentration, $FeSO_4.7H_2O$ concentration were varied and applied to dye solution and the textile industry effluent. The goal was to evaluate the best effective treatment i.e. Fenton Reagent and its combination with UV/Solar for reducing color of Malachite Green (MG) azo dye solutions used in textile-dyeing operations and in the treated effluents from the Textile Dyeing Wastewater Treatment Plant (WWTP).

5.1 TREATMENT OF MALACHITE GREEN DYE WITH FENTON & PHOTOFENTON PROCESS

5.1.1 UV-VIS Spectra of Malachite Green Dye

The Fenton and Photo Fenton oxidation experiments were conducted for decolorization. Photo Fenton experiments were conducted under both UV as well as solar light. The decolorization of dye was recorded in term of change in intensity of characteristics peaks. Fig. 5.1.1 shows the UV-Vis. spectra of 25 ppm of MG dye solution. As evident from the spectra, Malachite Green was characterized by two peaks at 430 and 620 nm.

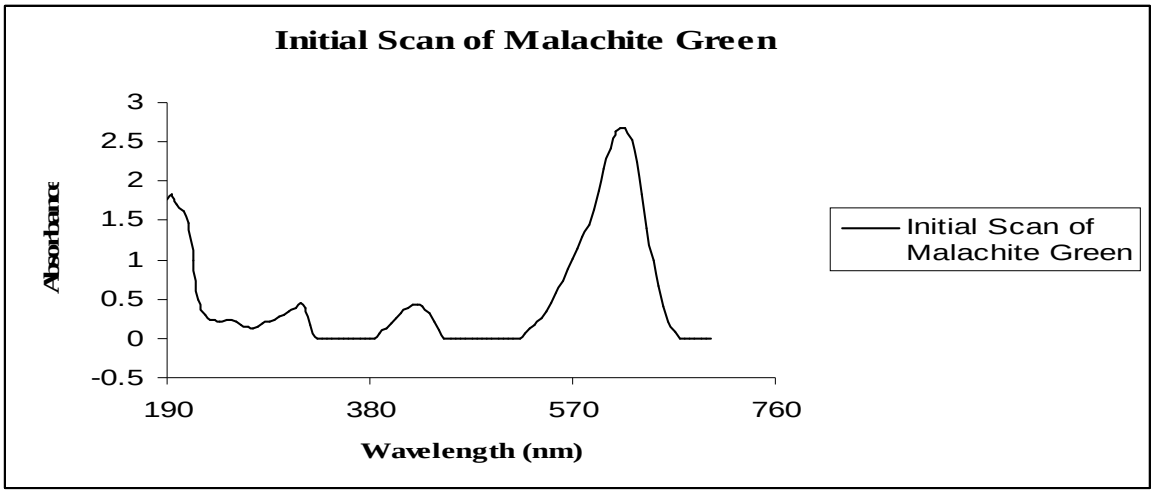


Fig 5.1.1: The full scan spectrum of Malachite Green (25 ppm)

5.1.2 Effect of pH on Decolorization without Addition of Fenton Dose

The pH of the solution is an important parameter for Fenton oxidation process, which controls the production rate of hydroxyl radical and the concentration of Fe^{+2}. It is also an important operational variable in actual wastewater treatment initially. A series of experiments were conducted at different pH value of 2.0, 4.0, 6.0, 8.0, 10, and 12 without addition of Fenton dose. Without addition of Fenton dose highest decolorization was observed at pH 12 (80%) and lowest decolorization was observed at pH 4 as shown in Fig. 5.1.2.

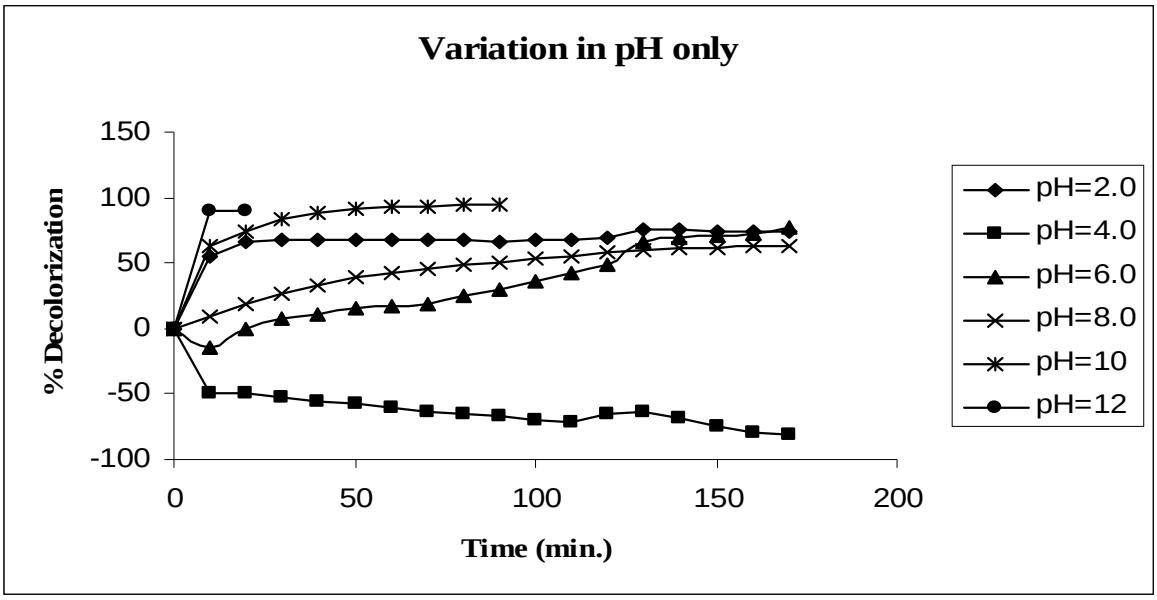


Fig 5.1.2: Effect of pH on the decolorization of Malachite Green dye (25 ppm) with out addition of fenton reagent.

5.1.3 Effect of pH on Fenton Process

In order to find the optimal pH for the decolorization of Malachite Green in Fenton oxidation, a series of experiments were conducted at different pH 2.0 to 12. The results with addition of Fenton dose are illustrated in Fig 5.1.3. The results indicated that the decolorization of Malachite Green was significantly influenced by the pH of the solution. The 96 % decolorization is achieved at pH 2 for 90 min. reaction time. In alkaline pH the decolorization is not sufficient. In this case decolorization decreases as pH increases. Above pH 4 the decolorization decline because of the decreasing of the free iron species in the solution, probably due to the formation of Fe^{2+} complex high impeded further reaction of Fe^{2+} and H_2O_2 .Moreover it is because of the precipitation of ferric oxyhydroxides.

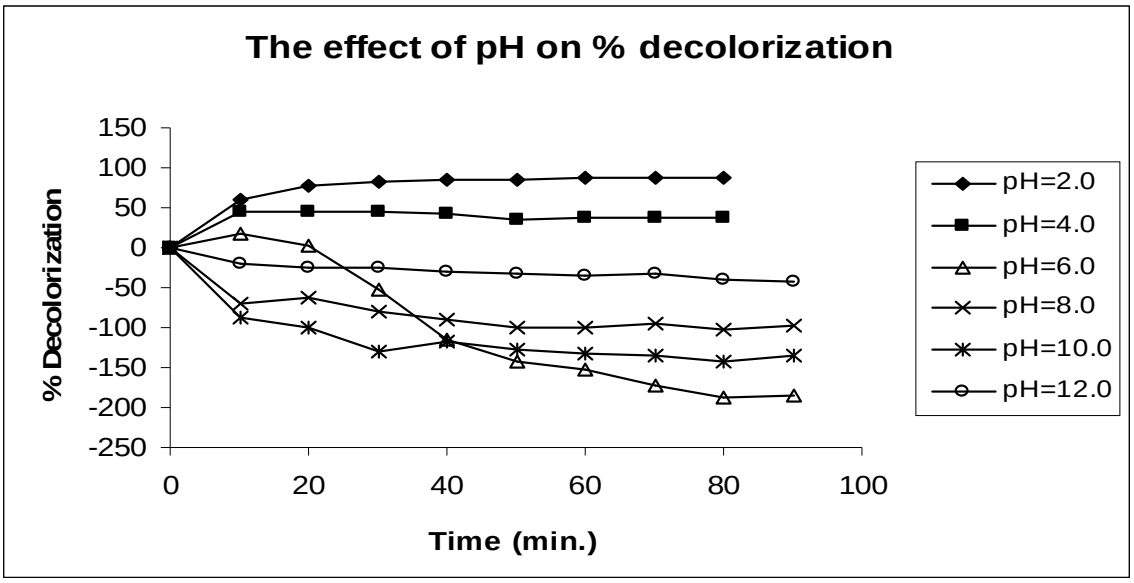


Fig 5.1.3: Effect of pH on the decolorization of Malachite Green dye (25 ppm) Fenton process. [H_2O_2:$FeSo_4$] =300:100mg/L

Jian-Hui et al., 2006 studied the degradation of azo dye Amido black 10B in aqueous solution by Fenton oxidation process. They found that the degradation of Amido black 10B was significantly influenced by the pH of the solution. The optimum solution pH was observed in acidic range that is about 3.50. *(Mioara S et al., 2004)* studied the decolorization of Acid Red G azo dye by advanced oxidation processes they found satisfactory degradation on all acidic (89.16), basic (82.48) and neutral pH (81.03) but in acidic medium results were favorable.

5.1.4 Effect of H_2O_2 dose alone

Hydrogen peroxide plays the important role as an oxidizing agent. The selection of an optimal hydrogen peroxide concentration is important aspect from a practical point of view due to its high cost. Fig. 5.1.4 shows the relationship between the decolorization of dye and the concentration of H_2O_2 in the Fenton process. The objective was to select the best operational dosage of H_2O_2 in Fenton process. Dose of hydrogen peroxide was raised from 300 to 900 mg/l. The result indicates that decolorization efficiency increases from 5 % to 72 % with increase in H_2O_2 dose from 300 mg/l to 900 mg/l after 200 min.

of reaction time.

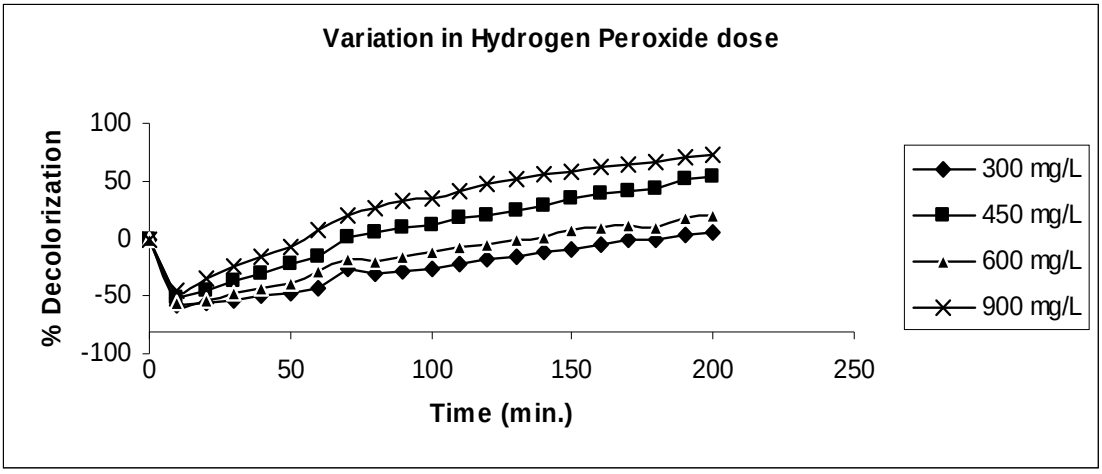


Fig 5.1.4: Effect of H_2O_2 dose on the decolorization of dye (25 ppm) at 2 pH.

Mioara et al., 2004 observed that hydrogen peroxide alone can not achieve decolorization of the dye within reasonable time periods; it is used in association with Fe^{2+} ions. By using hydrogen peroxide, UV radiation and ferrous ions at the same time, the dye decolorization can be archived. *(Tunlawit et al)* found that H_2O_2 dose increased the color removal efficiency of Remazol carbon, Remazolred, Remazal Yellow gradually. Generally, the concentration of $HO^{\bullet}$ is expected to increase with increasing of H_2O_2 dose, leading to increase decolorization efficiency.

5.1.5 Effect of Ferrous Dose Alone

The amount of ferrous ion is one of the main parameter influencing the Fenton processes. The effect of the addition of Fe^{2+} ion on the decolorization of Malachite green has been studied. Different dose of ferrous from 100 to 400 mg/l were tested and as shown in Fig 5.1.5, there is no significant decrease in absorbance with the increase in Fe^{2+} concentration. Hence the alteration of ferrous dosage has no significant effect on the decolorization efficiencies.

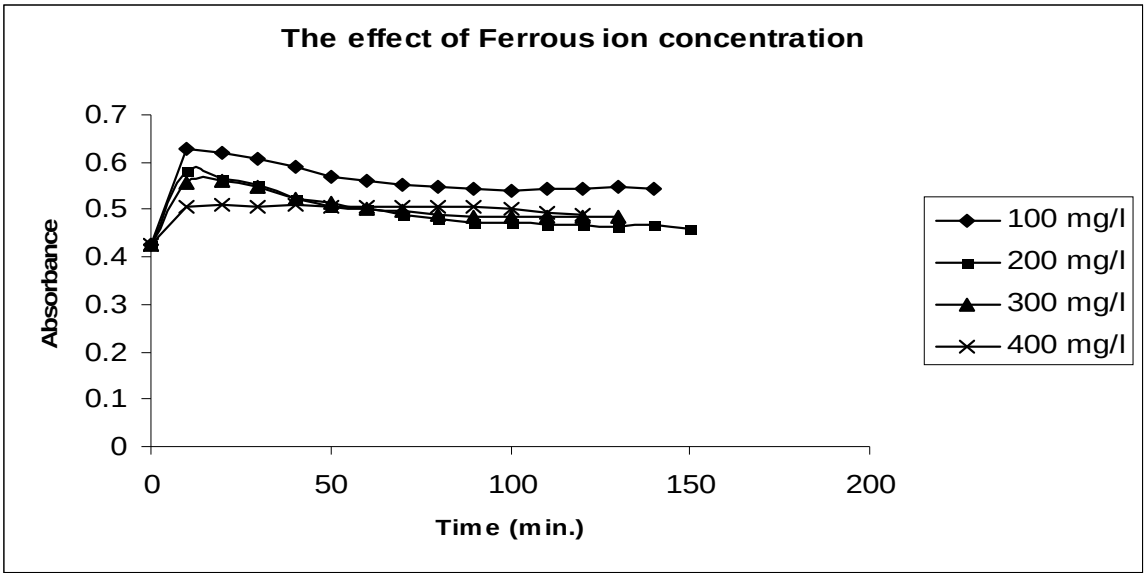


Fig 5.1.5: Effect of Fe^{2+} concentration on absorbance of MG dye (25 ppm) at 2 pH.

5.1.6 Effect of the Fenton Dose (H_2O_2+$FeSO_4$)

Hydrogen peroxide and Ferrous sulphate plays an important role in an oxidizing agent in Fenton oxidation process. The selection of an optimal Fenton dose (hydrogen peroxide and ferrous sulphate concentration) for the degradation of Malachite Green by Fenton oxidation is important from a practical point of view due to the cost of hydrogen peroxide. Fig. 5.1.6 shows the effect of Fenton dose on the decolorization of Malachite Green during Fenton treatment. To optimize the Fenton dose different dose i.e. 240:80, 300:100, 450:150, 600:200 were tested. After 80 min. reaction time 83% decolorization was achieved. On all other doses the decolorization became constant after a reaction time of 60 min.

According to the graph shown below, the optimal Fenton dose is 300:100 mg/L for the most effective decolorization of Malachite Green at 25 ppm dye concentration at optimized pH 2.

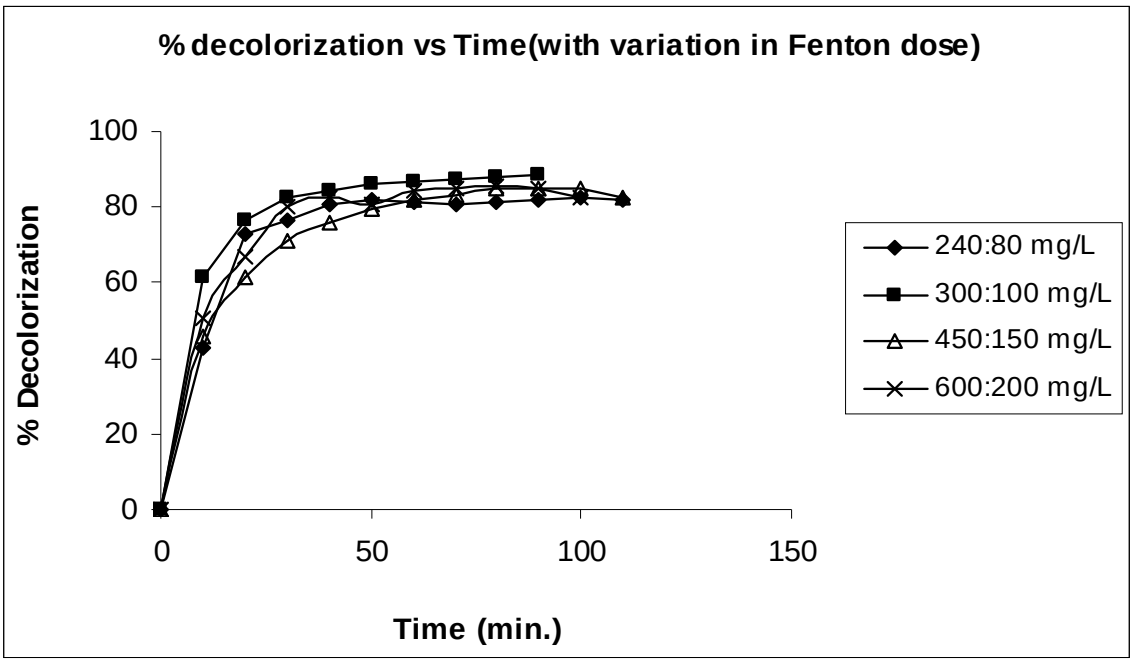


Fig 5.1.6: Effect of Fenton dose (3:1) on the decolorization of dye at 2 pH.

5.1.7 Effect of Fenton Ratio (H_2O_2:$FeSO_4$)

Ratio of H_2O_2 and $FeSO_4$ play an important role in decolorization of Malachite Green. To optimize the ratio a number of experiments were carried out with different ratio of H_2O_2 and $FeSO_4$ varying from 3:1 to 1:1. Results depicts that after 90 min., 82% decolorization occurred corresponding to Fenton ratio 3:1 (300:100 mg/L), 80.47% corresponding to Fenton ratio 2:1 (200:100 mg/L), and 82.11% decolourization corresponding to ratio 1:1 (300:300 mg/L). It is quiet evident from the results that 3:1 ratio is the optimum ratio as maximum decolourization occurs at this ratio as shown in Fig 5.1.7 Marco et.al observed degradation of RB5 dye at different ratio of H_2O_2 and $FeSO_4$ and found that 3:1 ratio is the best for the decolorization of dye.

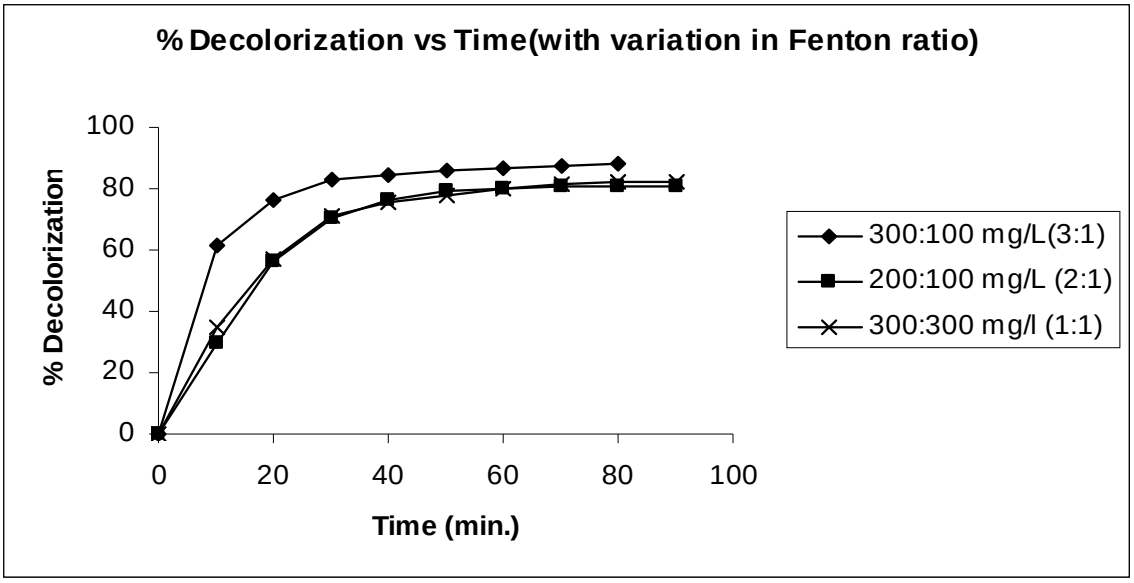


Fig 5.1.7: Effect of Fenton ratio (H_2O_2:$FeSO_4$) on the decolorization of dye (25 ppm)

5.1.8 Effect of the Initial Dye Concentration

Pollutant concentration is an important parameter in wastewater treatment so, to study the effect of initial Malachite Green concentration (dye) on its decolorization, the concentration range 10 - 100 mg/l of Malachite Green dye was investigated. Fig. 5.1.8 shows the changes of Malachite Green concentration with the reaction time. It was observed that lower the dye concentration (<50 mg/L), shorter is the reaction period needed to decolorize dye completely. At a higher dye concentration of 75 mg/l and 100 mg/l, more time is required.

The decolorization efficiencies were 96.24% (10pp), 85.88% (25ppm), 81.77% (50 ppm), 63.20% (75 ppm), 58.79% (100 ppm) after the 50 min reaction time. This is due to the fact that with constant H_2O_2 and Fe^{+2} more hydrogen peroxide was consumed in the initial time of reaction because of a higher dye concentration. After 30-40 min, the amount of hydrogen peroxide became smaller and the degradation of Malachite Green slowed down significantly.

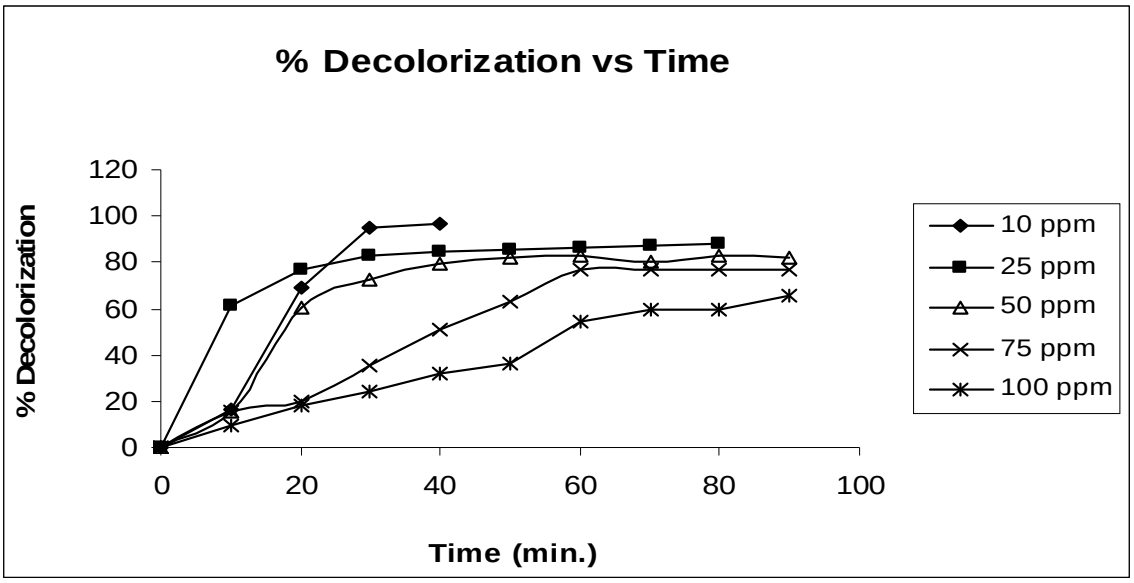


Fig 5.1.8: Effect of initial dye concentration on the decolorization of dye [pH] = 2.0, [H_2O_2: $FeSO_4$] = 300:100 mg/L

The extents of degradation decrease with the increase of initial dye concentration. The increase of RB5 concentration from 0.5×10^{-4} mol/l to 1.5×10^{-4} mol/l decrease the decolorization from 99% to 83% for Fenton process in 20 min. *(Marco et al., 2006).* Jian-Hui et.al studied the effect of initial Amino black 10B concentration on its decolarization, they selected the dye concentration from 10 to 100 mg/l. The decolorization efficiencies were 69.25% and 52.41% after the 10 min reaction time for 75 and 100 mg/l dye respectively.

5.1.9 Comparison of Solar and UV radiations

After optimizing pH and Fenton dose, presence of irradiation source i.e. UV/Solar light was tested, it was observed that disappearance of color was too fast in presence of light. This improvement in the reaction yields may be due to the production of extra hydroxyl radicals and the recovery of Fe (II) needed in Fenton's reaction. At optimized condition and 90 min. exposure time the results obtained for decolorization of malachite green dye under UV & solar photo-Fenton's processes are shown in Fig. 5.1.9.

The best results were obtained under UV light conditions, because UV light has the largest fraction of photons with the energy needed to drive photochemical reactions involved in the present reactive system. In Malachite Green dye 93% color removal occurred in case of UV radiation and more than 85% color removal was obtained in case of sun light after 90 min of exposure in same time Fenton process results 82% color removal.

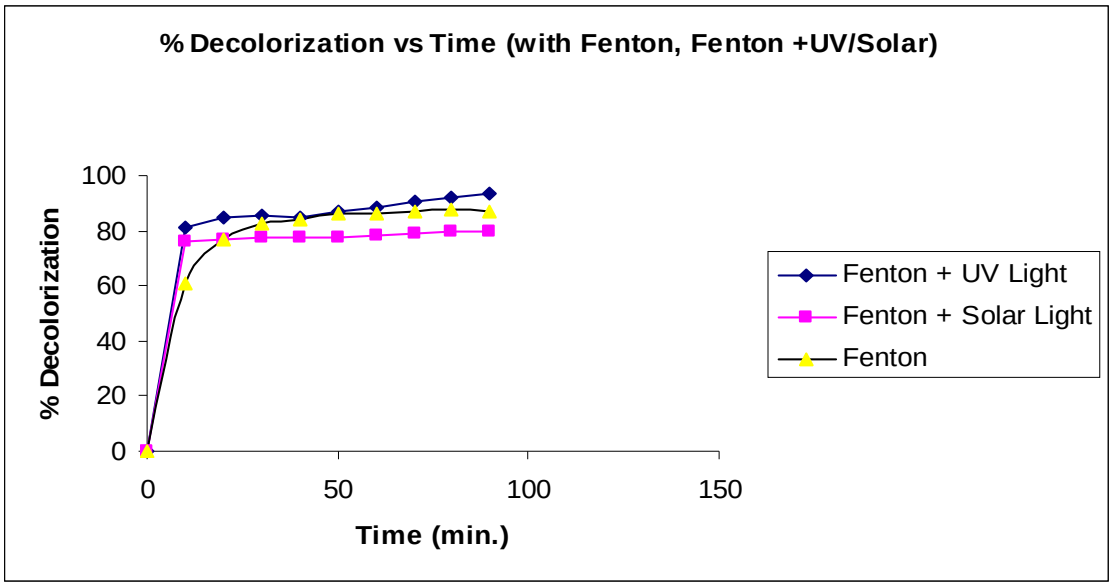


Fig 5.1.9: Comparison of UV and solar radiation by decolorization of dye (25 ppm)

[pH] =2.0, [Fenton ratio] =3:1, [Fenton dose] = 300:100

Lluis et.al used UV radiation and solar light for decolorization and mineralization of reactive dye. They found that after 90 min of treatment, solar light condition was best for Procion Red and Cibcron Red.

5.1.10 Decolourization of Dye During the Course of Reaction

The graph (Fig 5.1.10) depicts that as the reaction time increases, both peaks (430 & 620 nm) disappear gradually and degradation was complete after 120 min. the full spectrum became change after 120 min. It indicates that the main chromophores in the original dye solution are destroyed with the Fenton reaction and proves that Malachite

Green was fully decomposed in the system.

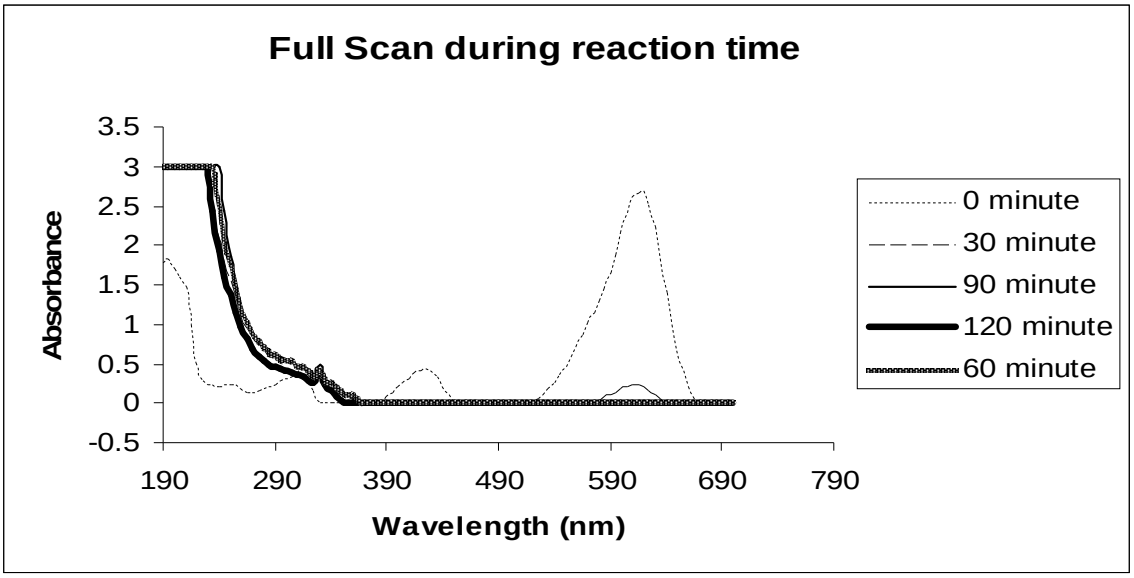


Fig 5.1.10 The full scanning spectrum of MG (25 ppm) at different time intervals. [Fenton dose] = 300:100 mg/l, [pH] =2.0.

5.2 Treatment of Textile Wastewater with Fenton/Photo Fenton

Textile wastewater includes a large variety of dyes and chemicals additions that make the environmental challenge for textile industry not only as liquid waste but also in its chemical composition. Main pollution in textile wastewater came from dyeing and finishing processes. These processes require the input of a wide range of chemicals and dyestuffs, which generally are organic compounds of complex structure. Because all of them are not contained in the final product, became waste and caused disposal problems. Major pollutants in textile wastewaters are high-suspended solids, chemical oxygen demand, heat, color, acidity, and other soluble *(Venceslau et al., 1994, A. A. Kdasl et. al., 2004)*.

5.2.1 Characteristics of Wastewater

Raw wastewater sample was collected from homogeneous tank of textile industry. Firstly sample was analyzed for some initial parameters. Textile wastewater was highly concentrated so sample was diluted before Fenton and photo Fenton treatment with single distilled water. The values of various wastewater parameters before treatment are shown in table 5.2.1

These wastewater parameters shows in above table are that it is highly polluted. So treatment of wastewater is required to facilitate the biological treatment processes and disposal of water in surface water body within in the specified disposable limits. The permissible limits for the discharge of textile effluent are given in table 5.2.2. The wastewater was diluted to 1:1 with distilled water and then it was treated with Fenton reagent and the parameters like pH, Fenton dose, Fenton ratio well optimized to have maximum decolourization efficiency.

Table 5.2.1 Characteristics of raw wastewater from textile industry

S. No.	Parameter	Value (mg/L)
1.	pH	6.5
2.	EC	2.18 mS/cm
3	Temperature	36 ˚C
4.	Turbidity	152.8 NTU
5.	TSS	440
6.	TDS	5850
7.	COD	600
8.	Color	1534.09

Table 5.2.2 National Environmental Quality Standards (mg/l)

Parameters	**Values**
Temperature or Temperature increase	+<30ºC
Color (Pt-Co))	7
pH value	6-10
BOD at 20ºC	80
COD	150
Total Suspended Solids (TSS)	150
Total Dissolved Solids (TDS)	3500

Oil and Grease	10
Ammonia (NH_3)	0.2
Nitrate	20
Phospate	5
Chromium (total)	1.0
Sulphide	0.2
Calcium	200
Magnesium	200

Note: All values are in parts per million except pH

(Source: CPCB)

The industrial effluent has high color value and it has show also peaks through absorption spectra. Peak obtained in UV as well as visible region and shows that shows the presence of different organic and chromophoric compounds shown in Fig. 5.2.1

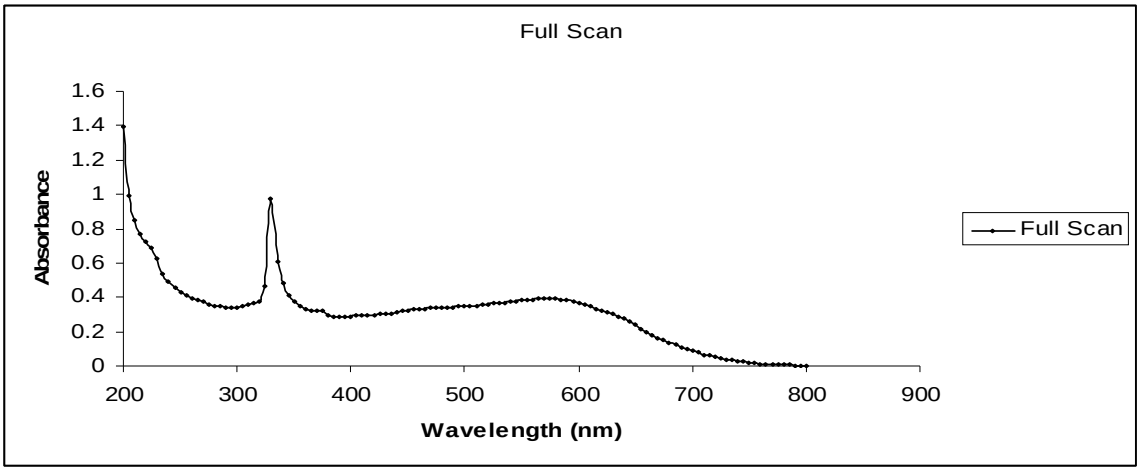


Fig 5.2.1 Absorption spectra of textile effluent.

5.2.2 Effect of pH

The pH play an important role in generation of hydroxyl radical so, attempts have been made to study the effect of pH in the Fenton and Photo Fenton treatment of wastewater in the range of 2 to 10. Fig. 5.2.2 shows the effect of pH on decolorization of effluent. The removal of color occurred rapidly in first 10 min. then the removal rate become slow at pH 4 and 10 but at pH 2 removal efficiency increases with the passage of time. After 240 min. of reaction, 70.5% color removal occurred at pH 2 and 46.6% color removal occurred at pH 10 so pH 2 was considered as the best pH for decolorization.

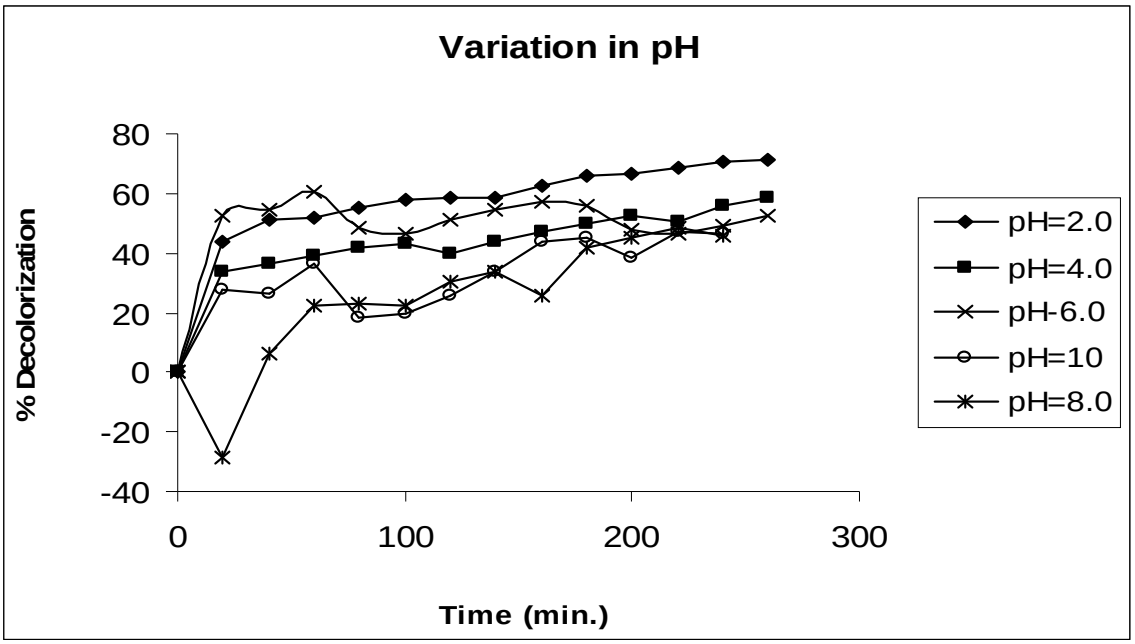


Fig 5.2.2 Effect of pH on decolorization of effluent by Fenton oxidation.

Idil et al carried out work on acid dye bath effluent and found that pH has a significant effect on performance of Fenton's reactions and reported highest color removal and COD degradation at pH 3. *(Chantanapha et al)* treated the textile dying wastewater and observed that removal of color occurred rapidly and reached the maximum point, around 78-83%, at the initial pH 3 to 5 with in 5 min. *(Tunlawit et al)*

optimized the pH for treatment of waste water from bleaching process of textile industry. They found that color removal efficiencies of RC, RR and RY were 98%, 93% and 80% respectively at optimized pH 3. *(Swaminathan et al)* reported that when the pH was increased, the color of the solution intensified and the absorbance also increased which may be due to a hyperchromic shift in the molecule.

5.2.3 Effect of Fenton Ratio

Color removal efficiency of effluent was tested with three different ratios of peroxide to ferrous sulphate at pH 2. Three different ratios 1:1 (1200:1200), 2:1 (1200:600) and 3:1 (1200:400) were tested. After a treatment time of 240 min. 84% decolorization was achieved corresponding to ratio 3:1 while in case of 1:1 and 2:1 ration only 77% decolorization was achieved. Hence 3:1 ratio appears as an optimized ratio. As shown in fig 5.2.3

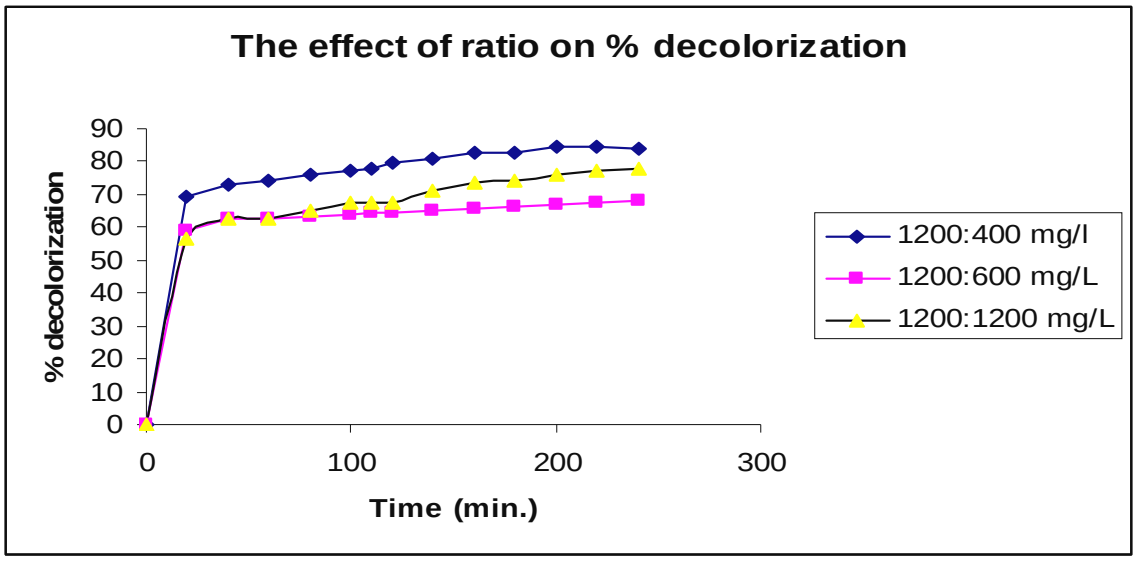


Fig 5.2.3: Effect of ratio of Fe^{2+} and H_2O_2 on decolorization of effluent at 2 pH.

Tunlawit et. al study the removal efficiency of RC, RR and RY with 1:5 and 1:10 ferrous to peroxide ratio. Lower efficiency was noted on 1:15 ratio and 1:5 was the optimized ratio. It can be explained due to the scavenging effect of over dose of $FeSO_4$ on $HO^{\bullet}$ *(Idil et al)* carried out work on acid dye bath effluent. They found that 1:3 is the most suitable ratio in terms of both COD degradation and color removals at pH 3. *Eisenhauer* obtained exactly the same molar ratio for phenol oxidation. Similarly, *Sedlak and Andren* found a ratio of 1:4 for the degradation of chlorinated biphenyls.

5.2.4 Effect of Fenton Dose

The effect of Fenton dose on treatment efficiency was investigated by trying different concentration of H_2O_2 and $FeSO_4$. Different concentration were 900:300, 1200:400, 1500:500, 1800:600, 2100:700. The results are displayed in Fig 5.2.4 in terms of percent decolorization after 260 min.

It can be seen from Fig.5.2.4 that decolorization efficiency initially increases with all the concentration. Then above the optimized concentration decolorization rate decrease as Fenton dose increases; the decrease in removal efficiency is due to occurrence of scavenging of OH radicals, which can be expressed by the equation.

$$HO_2^{\bullet} + HO^{\bullet} \rightarrow H_2O + O_2$$

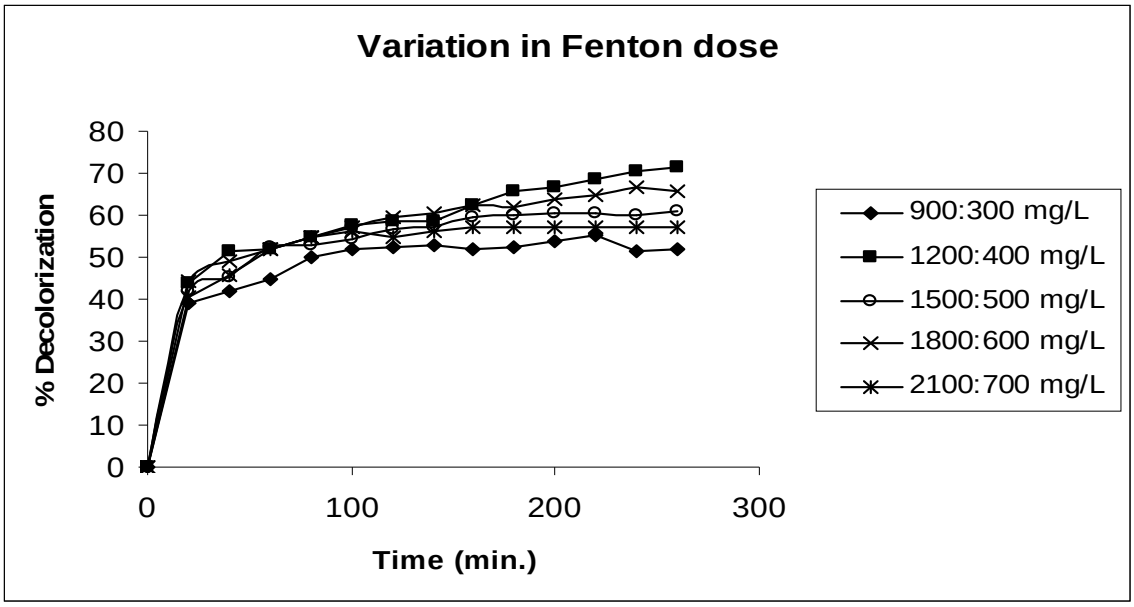


Fig 5.2.4: Effect of Fenton dose on decolorization of effluent at 2 pH.

5.2.5 Effluent Characteristics after Fenton and Photo Fenton Treatment

Industrial effluent was treated under optimized conditions i.e. at pH 2, Fenton ratio 3:1 and Fenton dose 1200:400 and the characterization of the treated effluent was done. Table 5.2.3 shows the parameters analyzed after the Fenton treatment of textile effluent which shows a major reduction in pollution load.

Table 5.2.3 Effluent characteristics after Fenton treatment

Sr. No.	**Parameter**	**Value**	**% Reduction**
1	pH	1.45	_
2	E.C (mS/cm)	2.86	_

3	Turbidity (NTU)	53.72	64
4	TSS (mg/L)	148	66
5	TDS (mg/L)	2760	53
6	COD (mg/L)	210	65
7	% decolorization	_	78

Table 5.2.4 Effluent characteristics after Fenton and UV treatment

Sr. No.	**Parameter**	**Value**	**% Reduction**
1	pH	1.58	_
2	E.C (mS/cm)	2.18	_
3	Turbidity (NTU)	23.1	85
4	TSS (mg/L)	123	72
5	TDS (mg/L)	2260	61
6	COD (mg/L)	140	76
7	% decolorization	_	85

Table 5.2.5 Effluent characteristics after Fenton and solar treatment

Sr. No.	Parameter	Value	% Reduction
1	pH	1.95	_
2	E.C (mS/cm)	3.97	_
3	Turbidity (NTU)	21.7	85
4	TSS (mg/L)	132	70
5	TDS (mg/L)	2370	59
6	COD (mg/L)	150	75
7	% decolorization	_	81

After Fenton treatment, parameters of textile effluent like COD, TDS and EC was examined and it was found that there is 65% reduction in COD and 78% color reduction. In Photo Fenton treatment, UV light results in 76% COD reduction, 61% TDS and 85% color removal after 4 hrs of reaction time as shown in table 5.2.4. While under solar light it was found that there is significant reduction in COD (75%), TDS (59%) and color (81%) after 4 hrs of treatment time as shown in table 5.2.5. Electrical conductivity has been observed to increase from 2.18 to 3.97 mS/cm. Highest Color, COD, TDS reduction occurs in case of UV Fenton process but solar Fenton also shows significant reduction in pollution load

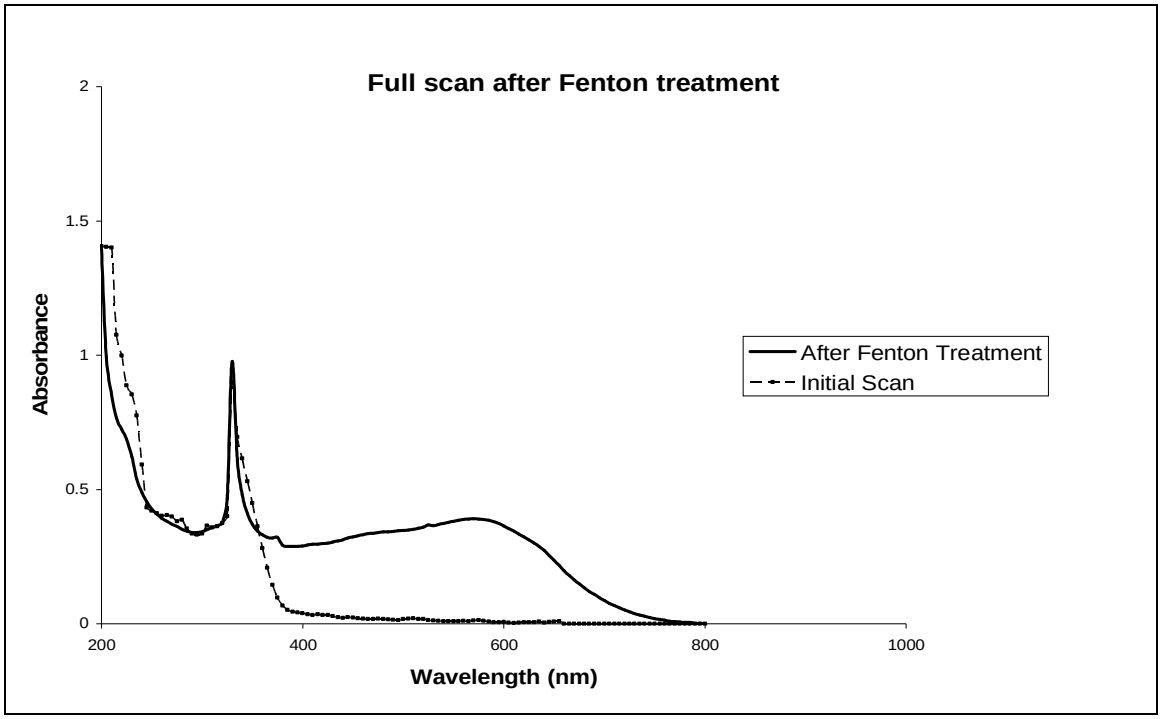


Fig 5.2.5 Absorption spectra of textile effluent after treatment

As Fig 5.2.5 shows the absorption spectra of the textile effluent after Fenton treatment which depicts depression of the peaks, indicating the mineralization of several chromophoric compounds previously present in effluent. This ensures that decolorization of effluent is complete. Thus, Fenton processes can be efficiently & cost effectively be used for the treatment of textile effluents.

CHAPTER-6

Conclusion

CONCLUSION

If water is colored its uses can be limited and the aesthetics of the situation can lead to many complaints and possible breaches of discharge limits. The disturbance of biological processes in surface water induced by changes in color and intensity is a serious problem. This leads to changes in the quantity of light penetrating deeper water layers and the related changes in biological life. Therefore, there has been much research into colour removal from textile effluents, both using complex real effluents and synthetic dye compounds, which are also useful for obtaining information on how individual dyes react to different types of treatment. As evidenced in this study, reactive azo dye (Malachite Green) and spent textile dye treated wastewater (WWTP) can be decolourized by chemical oxidation. The dye was generally more easily decolourized than the effluent. The results of this investigation performed on the effluent indicated that colour reduction to the permissible limits could be achieved by each of the treatments ($H_2O_2/Fe^{2+}$and $UV/H_2O_2/Fe^{2+}$) once the optimum operating conditions are established.

In case of dye solution (25ppm), decolourization rate was found to be 82% in Fenton treatment in 90 min of treatment time while 85% in solar light and 93% in UV light at the optimized parameters like pH (2.0), Fenton dose (300:100 mg/l) and Fenton ratio of 3:1. In case of textile wastewater, 75% and 61% decolourization was achieved with Photo Fenton in the presence of UV and solar light respectively after 4 hours of treatment at 2.0 pH and Fenton dose of 300:100 mg/l. It is further reported that the Fenton treatment yields 65% reduction in COD, 53% TDS reduction after 4 hours of reaction time. In presence of UV radiations there is appreciable decrease in COD (76%) and TDS (61%), while in presence of solar light 75% of COD and 85% of TDS reduction was observed after 4 hrs of treatment. Hence, solar treatment is well competing with the UV operation.

After photo Fenton treatment of textile effluent, it is quite evident that outlet

parameters satisfies all the discharge standards prescribed by Central pollution control board e.g. COD, TDS, TSS become 140, 2260, 123 mg/l respectively while discharge standard for all these parameters are 150, 3500, 150 mg/l respectively. Fenton process has proved its superiority to other conventional methods of wastewater treatments, because of lack of toxicity of the reagents and due to simplicity of process. This technology leads to completely destruction of hazardous contaminants and avoid transfer of pollutants from one phase to another. In terms of commercial application, the main setback is the cost of reagents such as ozone, titania and hydrogen peroxide or energy light sources. A potential viable solution proposed is the combination of these processes with biological processing. In these combined processes, the chemical process would be utilized as pre-treatment step to enhance the biodegradability and eliminate the toxicity of the effluents, while the total mineralization would be completed in the conventional biological process. So it can be concluded that photo-oxidation system employing Fenton and solar light has potential to decolourize the textile dyes and is recommended as pretreatment step before conventional biological treatments for consideration at the WWTP.

The future scope of this technology can be the replacement of H_2O_2 by any other suitable but less expensive oxidant. The by-products produced during treatments by UV, UV/H_2O_2/Fe^{2+}, and H_2O_2/Fe^{2+} are unknown so more research is necessary to analyze the by-products in the effluent and their potential toxicity to stream organisms.

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