DEGRADATION AND DECOLOURIZATION OF REACTIVE BLACK 5 DYE USING SONO PHOTO FENTON

Thesis submitted in partial fulfillment of the requirements for the award of degree of
Master of Technology
In
Environment Sciences and Technology

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Date: ______________

DECLARATION

I hereby declare that the work embodied in dissertation entitled **"Studies on the decolourization and degradation of reactive black 5 using sono photo fenton process"** 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.

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CERTIFICATE

This is to certify that the thesis entitled **"Degradation and decolourization of Reactive Black 5 dye using sono photo fenton"**, is an authentic record of my own work carried out as requirements for the award of degree of Master of Technology in Environmental Science & Technology from Thapar University, Patiala, under the guidance of Mr. Anoop Verma (Assistant Professor, DBTES) during January to June 2012.

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ABSTRACT

Wastewaters from textile and dye industries are highly coloured with significant amount of auxiliary chemicals. The discharge of these wastewater introduced intensive colour and toxicity to aquatic environment causing serious environmental problem. Reactive dyes are widely used in the textile industries because of its simple dyeing procedure and good stability during washing process. Reactive black 5 (RB5) gives bright, high intensity color to water which is one of the most important sources of environmental pollution and because of their visibility and bearing toxic chemicals, it is very important to be treated before released into the environment. Due to the complex aromatic structure and stability of these dyes, conventional biological treatment methods are ineffective for degradation. Hence, the concentration remains constant in the environment or these techniques transfer the toxic dyes from one medium to the other without converting it to harmless non-toxic substances. A number of physical and chemical techniques had been reported for the treatment of dye effluents.

In this direction, Advanced Oxidation Processes (AOPs), based on the generation of highly reactive hydroxyl radicals (HO*) as primary oxidant, appear as the emerging alternatives for the organic pollutants abatement. These, the advanced oxidation processes are more efficient as they are capable of mineralizing a wide range of organic pollutants ranging from chlorophenols, chlorobenzene, nitrophenols and dye pollutants.

Among various AOP's, Fenton's and photo- Fenton's type reactions are very promising since they achieve high reaction yields with a low treatment cost. These AOPs have been successfully applied to treat reactive dyes as well as textile effluents.

In the present work, we investigated that oxidative degradation and decolourization of the RB5 occurs by dark fenton, photo fenton, sono fenton and sono photo fenton. Batch runs were carried out to investigate the process's optimal operational conditions: pH, H_2O_2 dosage, Fe^{+2} dosage and RB5 concentration, to obtain the best results at low cost, render AOP competitive with other processes and to ensure the rapid and complete transformation of the toxic organic compounds to benign chemicals.

Degradation observed was 55% under Dark Fenton, 61% under Sono Fenton and 92% under Photo Fenton with optimized conditions i.e. 4 pH, catalyst ($FeSO_4.7H_2O$) concentration of 0.15 mM and oxidant dose (H_2O_2) of 4.4 mM after 20 mins. Sono Photo Fenton treatment enhances the degradation up to 98% with optimized parameters.

The results of Sono Photo Fenton degradation of dye showed that it could be used as efficient and environmental friendly technique for the complete degradation of recalcitrant organic pollutants which will increase the chances for the reuse of wastewater.

Key words: Dye, Dark Fenton, Photo Fenton, Sono Fenton and Sono Photo Fenton.

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CHAPTER – 1

INTRODUCTION

1.1 WATER:

Water is widely distributed on **Earth** as freshwater and salt water in the oceans. The Earth is often referred to as the "blue planet" because when viewed from space it appears blue.

Over 70% of the Earth’s surface is covered in water, yet most of this is made up of seawater in oceans. Just a small amount is fresh-water as shown in Fig 1.1

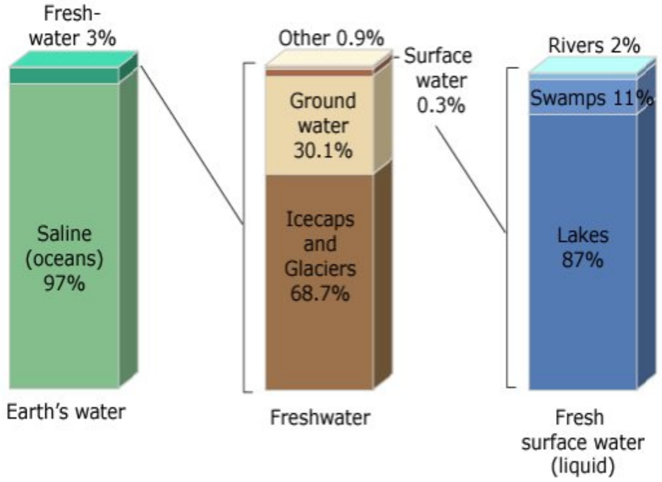

Fig 1.1: Earth’s water distribution (USGS – Earth’s water distribution, 1996)

1.2 WATER CYCLE:

The water cycle describes the existence and movement of water on, in, and above the Earth. Earth's water is always in movement as shown in Fig 1.2 and is always changing states, from liquid to vapor to ice and back again.

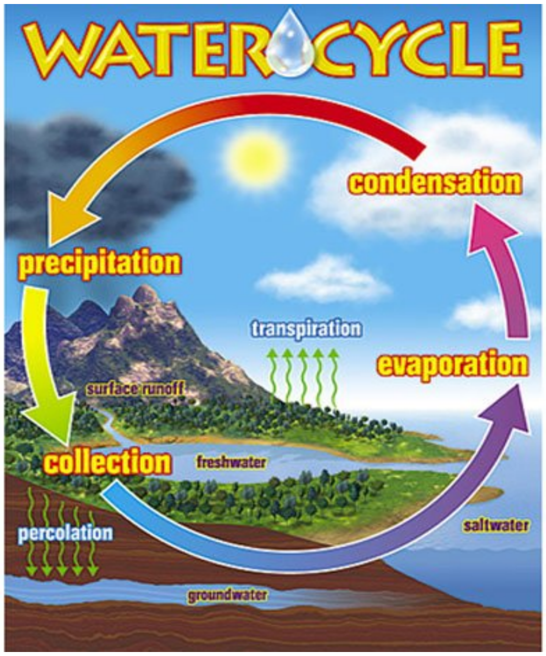

Figure: 1.2 Summary of the water cycle (Ohio State University - Nitrogen and the Hydrologic cycle, 24 October 2006)

1.3 WASTE WATER CYCLE:

Water is naturally cleaned and reused as part of the hydrologic cycle in the outside world. In the human world, water is also cleaned and reused. Our wastewater is channeled to a wastewater treatment plant where it is cleaned and released for irrigation purpose, municipal use, industrial use etc. This water from irrigation re-enters to the hydrologic cycle and will eventually be pumped back up by another water treatment plant to be purified and released to consumers as shown in Fig 1.3.

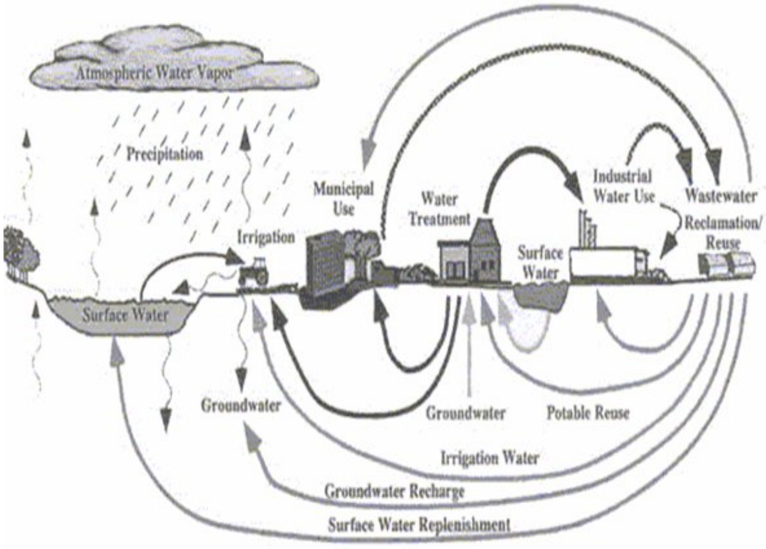

Figure: 1.3 Diagrammatically representation of waste water cycle (UNEP/Grid Arendal - The central role of wastewater management in sustainable development, 2010)

1.4 HEALTH IMPACTS:

It is a well-known fact that clean water is absolutely essential for healthy living. Adequate supply of fresh and clean drinking water is a basic need for all human beings on the earth, yet it has been observed that millions of people worldwide are deprived of this.

Freshwater resources all over the world are threatened not only by over exploitation and poor management but also by ecological degradation. The main source of freshwater pollution can be attributed to discharge of untreated waste, dumping of industrial effluent, and run-off from agricultural fields. It is a generally accepted fact that the developed countries suffer from problems of chemical discharge into the water sources as shown in Fig 1.4, while developing countries face problems of agricultural run-off in water sources.

Fig 1.4: Contaminated drinking water

Ground water can be contaminated through various sources such as *pesticides*, *sewage, nutrients*, *synthetic organics, acidification* etc.

Chemicals in water (*fluoride,* a*rsenic,* l*ead,* p*etrochemicals, dyes* and *other heavy metals. chlorinated solvents)* can be either naturally occurring or introduced by human interference and can have serious health effects.

Table 1.1: Water-borne diseases by various infections

Cause	Water borne diseases
Bacterial infections	Typhoid Cholera Paratyphoid fever Bacillary dysentery
Viral infections	Infectious Hepatitis (jaundice) Poliomyelitis
Protozoal infections	Amoebic dysentery

Out of all the industries, one important industry i.e. Textile industry, which is generating large amount of industrial effluents in each year causes the main source of environment pollution. Usually, dye effluents from textile industries are the major source of water pollution. Waste water from textile industries is not only harmful for aquatic life but also mutagenic to human **(Chung K.T. et al., 1992)**.

In the entire world, production of dyes is approximately 800,000 tons per year. Approximately 10-15% of synthetic dyes lost during different processes of textile industry. Synthetic dyes are useful in many industries such as textile, paper printing, food, pharmaceutical, leather and cosmetics and classified into acid, reactive, direct, basic, vat, disperse, metal complex, mordant and sulphur dyes. There are more than 10,000 dyes used in textile industry, out of them 70% are azo dyes which is complex in structure and synthetic in nature. A dye known to be azo dye because of azo bond between nitrogen (-N=N-) and their basic structure is Ar-N=N-Ar, where Ar is aromatic compound. The nature of the aromatic substituents on both sides of the azo group controls the colours of the azo compounds as well as the water-solubility of the dyes and how well they bind to a particular fabric. The colour of azo dyes is due to geometrical isomerism of azo group and associated with chromophores **(Muruganandham M. et al., 2004)**. Azo dyes are highly stable, highly soluble, higly toxic and less expensive in nature. Due to this conventional method alone is not enough for the effective removal of azo dyes, so finding an effective method for the degradation of azo dyes is necessary. Traditionally, different techniques i.e. coagulation/flocculation, adsorption, biological treatment etc were used for the treatment of textile waste water, which are not compatible for complete degradation of azo dyes due to the presence of some biological resistance compound in waste water (**Marco L.S. et al., 2006**) and the second disadvantages associated with above techniques are the production of sludge so that organic compounds transfer from one form to another and not degraded from the environment. So over the last decades, Advanced Oxidation Process (AOP's) represents a new generation of environment technology that provides effective decolourization and degradation of azo dyes simultaneously.

AOP's provides non specific oxidant **(Chan-Li H. et al., 2007)** i.e. Hydroxyl radicals (OH*) which is highly reactive and having high electrochemical oxidation potential i.e. 2.8. AOP's are capable for the complete degradation of azo dyes and do not transfer it from one form to another.

CHAPTER –2

2.1 WASTE WATER FROM TEXTILE INDUSTRY

Textile is one of the important sectors in India and the leading sector which produces excessive waste. Thus wastewater amount, pollutant types and concentrations show different data. In textile industry wastewater are changeable in terms of amount and composition. The first reason of pollutants in the wastewater is the natural impurity in fibers. The second is the chemical materials that are used in processes. A huge amount of dye, carriers, chrome and its derivations and sulphur are found in wastewater **(Bharat P. N. et al., 2010)**. Apart from that, considering technological differences in production process and the other different variations that can come out, there are alterations in factories which use the same fibers. Even if the amount can differ, the characteristics of wastewater are usually similar in the factories that use the same fiber. The common characteristics of textile wastewater are high chemical oxygen demand (COD), high biological oxygen demand (BOD), total suspended solids, high pH, total dissolved solids materials, chloride, total kjedahl nitrogen and the colours caused by different dyes as shown in Table 2.1.

Table 2.1: Composite textile industry waste water characteristics (Al-kdasi A. et al., 2004)

S. No.	Parameters	Values
1.	pH	7.0 – 9.0
2.	BOD (mg/l)	80 – 6000
3.	COD (mg/l)	150 – 12000
4.	TSS (mg/l)	15 – 8000
5.	TDS (mg/l)	2900 – 3100
6.	Chloride (mg/l)	1000 – 1600
7.	TKN (mg/l)	70 – 80
8.	Colour (Pt-Co)	50 – 2500

Important pollutants in textile wastewater are especially the organics and then colour, toxic materials, inhibitor compounds, active substances, chlorine compounds, pH, salt and dying substances.

In textile industry most of the wastewater that carries great importance with respect to the formation amount and the pollutants which it comprise, are caused by dying processes. Large number of dyes uses in textile industry as shown in Table 2.2

Table2.2: Characteristics of Textile Dyes (Price, Cohen, & Johnson, 2005)

Dye Class	Description	Fibers Typically Applied to	Typical Fixation (%)	Typical Pollutants Associated with Various Dyes
Acid	Water-soluble anionic compounds	Wool, nylon	80-93	Colour; organic acids; unfixed dyes
Basic	Water-soluble, applied in weakly acidic dyebaths; very bright dyes	Acrylic, some polyesters	97-98	N/A
Direct	Water-soluble, anionic compounds;can be applied directly to cellulosics without mordants (or metals like chromium and copper)	Cotton, rayon, other cellulosics	70-95	Colour; salt; unfixed dye; cationic fixing agents; surfactant; defoamer; leveling and retarding agents; finish; diluents
Disperse	Not water-soluble	Polyester, acetate, other synthetics	80-92	Colour; organic acids; carriers; leveling agents; phosphates; defoamers; lubricants; dispersants; delustrants; diluents
Reactive	Water-soluble, anionic compounds; largest dye class	Cotton, other cellulosics, wool	60-90	Colour; salt; alkali; unfixed dye; surfactants; defoamer; diluents; finish
Sulfur	Organic compounds containing sulfur or sodium sulfide	Cotton, other cellulosics	60-70	Colour; alkali; oxidizing agent; reducing agent; unfixed dye
Vat	Oldest dyes; more chemically complex; water-insoluble	Cotton, other cellulosics	80-95	Colour; alkali; oxidizing agents; reducing agents

2.2 OCCURANCE OF TEXTILE WASTE WATER

Textile industry is considered as a water intensive sector. As most of this water is used either for washing purposes or as carrier for transporting chemicals to fabric, the processes generate wastewater in almost same proportion (**Nese T. et al., 2007)**

A typical textile unit is expected to generate various types of wastewater, differing in magnitude and in quality of environmental parameters. This is due to the variety of processes involved in textile value added manufacturing processes.

Apart from wastewater from processing activities, domestic wastewater is also generated from office building, canteen, workshop, mosques, etc (**The textile sector "Environment Report-1998" Environment technology program for industry**). A brief description of some important sources of waste water is given below:

- **Bleaching / scouring**

Generation of wastewater is either continuous or periodic in its pattern. Wastewater from bleaching process may contain sodium hydroxide, hydrogen peroxide, different kinds of an-ionic stabilizers and anionic detergents.

- **Mercerizing**

The process is usually considered as optional in textile unit and generate small amount of waste water. Effluent may contain spent sodium hydroxide as well as some intermediate reaction-products of wetting agents and detergents.

- **Dyeing**

Dyeing process is mostly carried out in jet, winch or jigger machines. Wastewater generated from dyeing process may contain residuals of dyes, leveling agents, salts, caustic soda, etc.

- **Printing**

Generation of wastewater is continuous and they may contain residuals of pigments or reactive dyes and chemicals used as fixers, binders, thickeners, etc.

- **Boiler**

This source generates a significant amount of wastewater as blow down which is high in total dissolved solids, sludge and chemical residuals used for water conditioning for the boiler system.

Out of them two important processes that generate colour containing wastewater are printing and dyeing. Now a days synthetic dyes are used to colour the fabrics that has been available pre-packaged in almost every colour while in the past, dyes used that were produced individually by harvesting natural fruits, vegetables **(Joseph, 1977)** and other items having significant effect on society but this was a long and tedious process.

The most important dye used in textile industries are azo dyes; dye containing Ar-N=N-Ar group is called azo dye and the common characteristics of azo dye is given below:

1. These dyes use AZO-groups as coloring agent.
2. These chemical groups release amines upon cleavage, which are harmful.
3. They are used mostly for cotton dyeing.
4. Cheapest alternative to "reactive dyes".
5. Good color fastness, dyeing process short and easy.
6. Pollute waste-water with heavy metals.

Different type of azo dyes are there, which are hazardous to health as shown in Fig 2.1 and 2.2

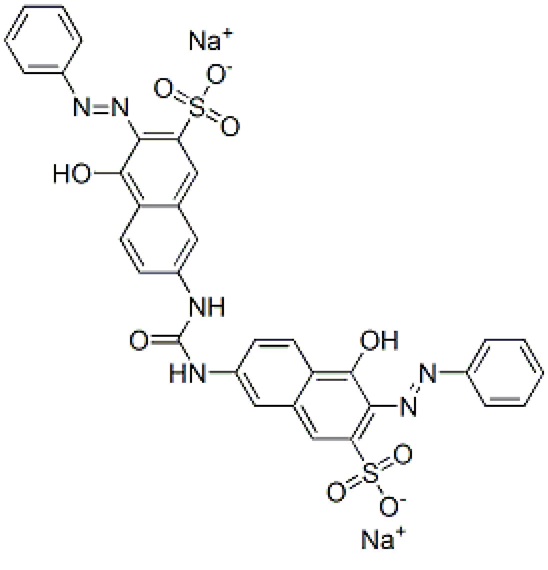

Figure 2.1: Structure of Direct Orange

Direct Orange is toxic and may cause genetic mutations. It is absorbed through skin and the respiratory and intestinal tract. It is toxic and carcinogenic. (Goyal R.N. et al., 1998)

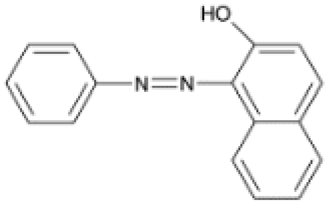

Figure 2.2: Structure of 2-Napthol

2-Naphthol is harmful if swallowed or inhaled. May be harmful in contact with the skin. Eye, skin and respiratory irritant **(Fujita S. et al., 1982)**

2.3 HEALTH EFFECTS OF DYES AND CHEMICALS

There is no evidence to suggest that the majority of the dyestuffs currently used in textile dyeing and finishing are harmful to human health at the levels of exposure that workers generally face in the factories. However, with long-term or accidental over exposure, there can be potential health hazards and all dyes and chemicals must therefore be treated with care. The most common hazard of reactive dyes is respiratory problems due to the inhalation of dye particles. Sometimes they can affect a person’s immune system and in extreme cases this can mean that when the person next inhales the dye their body can react dramatically. This is called respiratory sensitization and symptoms include itching, watery eyes, sneezing and symptoms of asthma such as coughing and wheezing.

Perhaps the most prevalent health problems associated with dyeing and finishing processes arise from exposure to chemicals acting as irritants. These may cause skin irritation, itchy or blocked noses, sneezing and sore eyes. They include formaldehyde-based resins, ammonia, acetic acid, some shrink-resist chemicals, some optical whiteners, soda ash, caustic soda and bleach. Certain reactive, vat and disperse dyes are also recognized as skin sensitive (HSE, 1996).

Fire is a common hazard that may arise from the use of flammable liquids that are easily ignited or oxidising agents that may make an existing fire more intense by fuelling it with oxygen. The presence of large quantities of dry fabric or paper can increase the risk and spread of fires. Faulty electrical wiring can also cause fires.

Another source of risk is corrosive chemicals, which can cause serious burns and may react dangerously with other chemicals. Violent reactions may be caused by substances which are dangerous when wet such as sodium hydrosulphite (Hydros). Hot liquids can lead to scalding accidents.

To become safe from the effects of dye and chemical hazards, step wise management of them is important as shown in Table 2.3

Table 2.3: Assessing and managing the risks of dyes and chemicals to health

Step 1	Collected information	Collect appropriate H&S data and literature such as MSDS.
Step 2	Assess the risks	Assess the risks to health from hazardous substances used in or created by your workplace activities.
Step 3	Decide what precautions are needed	You must not carry out work that could expose your employees to hazardous substances without first considering the risks and the necessary precautions
Step 4	Prevent or adequately control exposure	You must prevent employees from being exposed to hazardous substances. Where preventing exposure is not reasonably practicable, then you must adequately control it.
Step 5	Ensure that control measures are used and maintained	Ensure that control measures are used and maintained properly and that safety procedures are followed.
Step 6	Monitor the exposure	Monitor the exposure of employees to hazardous substances, if necessary.
Step 7	Carry out appropriate health and surveilliance	Carry out appropriate health surveillance where your assessment has shown this is necessary.
Step 8	Prepare plans and procedure to deal with accidents, incidents and emergencies	Prepare plans and procedures to deal with accidents, incidents and emergencies involving hazardous substances, where necessary.
Step 9	Ensure employees are properly informed, trained and supervised.	Provide employees with suitable and sufficient information, instruction and training, on a regular basis.

OBJECTIVES OF PRESENT STUDY

Main objective of study is to treat the recalcitrant dye present in textile wastewater which is not treated by conventional treatment processes. On the basis of literature reactive black 5 was selected, the work was carried out on the degradation of RB5 using homogeneous sono photo fenton treatment. To increase the efficiency of degradation US combine with UV.

Combining of these two modes of irradiations i.e. US and UV eliminate the drawbacks of individual process and generate more number of hydroxyl radicals. This treatment does not transfer pollutants from one phase to another and leads to complete mineralization of organic non biodegradable compounds into simpler end products. The study was undertaken with the following objectives:

- To study the degradation of model dye using photo fenton process used in textile industry.
- To study the effect of various parameters such as concentration of Fe^{+2}, pH, H_2O_2 on degradation rate of these compounds and their kinetic studies.
- To study the degradation of model dye using sono photo fenton process.
- To study the degradation of model dye using sequential US and UV process and vice versa.

CHAPTER – 3

TREATMENT TECHNOLOGY

3.1 CONVENTIONAL TECHNOLOGY

Unit operations and treatment of waste water

(a) Physical Unit Operations

Treatment methods in which the application of physical forces predominates are known as physical unit operations. It is a primary method to treat the waste water. Screening, mixing, flocculation, sedimentation, floatation, filtration, and gas transfer are examples of physical unit operations.

(b) Chemical Unit Processes

Treatment methods in which the removal or conversion of contaminants is brought about by the addition of chemicals or by other chemical reactions are known as chemical unit processes. It is a tertiary treatment to treat waste water. Precipitation and adsorption are the most common examples used in wastewater treatment.

(c) Biological Unit Processes

Treatment methods in which the removal of contaminants is brought about by biological activity are known as biological unit processes. It is a secondary method to treat waste water. Biological treatment is used primarily to remove the biodegradable organic substances (colloidal or dissolved) in wastewater. Basically, these substances are converted into gases that can escape to the atmosphere and into biological cell tissue that can be removed by settling. Biological treatment is also used to remove nutrients (nitrogen and phosphorus) in wastewater.

The use of conventional water and wastewater treatment processes **(Zhou. H. and Smith D.W., 2001)** becomes increasingly challenged with the identification of more and more contaminants, rapid growth of population and industrial activities, and diminishing availability of water resources.

The actual state performance of conventional methods is clearly not suitable to treat toxic, non-biodegradable organic pollutants and new improved treatments have to be developed and tested. To overcome the inconveniences of conventional treatment methods, Advanced

Oxidation Techniques (AOP's) have emerged in the last decades, in particular for the treatment of industrial wastewaters.

3.2 EMERGING TECHNOLOGY

Emerging technologies **(US-EPA)** typically follow a development process that leads from laboratory and bench-scale investigations to pilot studies and to initiate use or "full-scale demonstrations" before the technology is considered established. Not all technologies survive the entire development process. Some fail in the laboratory or at pilot stages; others see limited application in the field, but poor performance, complications, or unexpected costs may cause them to lose favor. In short, technologies are subject to the same evolutionary forces present in nature; those that cannot meet the demands of their environment fail, while those that adapt to changing technological, economic and regulatory climates can achieve long-standing success and survival in the market.

The emerging wastewater treatments methods like advanced oxidation processes are increasingly gaining popularity since they have shown the potential of converting harmful organic pollutants into innocuous compounds such as carbon dioxide and water. The emerging treatment technologies have been already demonstrated to successfully remove various potentially harmful compounds that could not be effectively removed by conventional treatment processes. **(Paradowska M.A., 2004).**

The major advantage of this technology is that it can completely or partially destroy organics at ambient temperature by converting them into various harmless intermediates and end products, such as carboxylic acids, carbon dioxide and halide ions. The major oxidants of AOP are hydroxyl radicals and ozone which can react with organic compounds at very high reaction rates. In particular, hydroxyl radicals can attack most organics non-selectively through hydrogen atom abstraction or by addition of the hydroxyl radical. Advanced oxidation processes (AOP) combine (O_3), ultraviolet, hydrogen peroxide (H_2O_2) and/or catalyst to offer a powerful water treatment solution for the reduction (removal) of residual organic compounds as measured by COD, BOD or TOC. All AOP are designed to produce hydroxyl radicals. It is the hydroxyl radicals that act with high efficiency to destroy organic compounds.

The technique of ultrasound when combined with other AOPs, the combination would lead to faster degradation rates as compared to other processes. The use of ultrasound has been recognized, for many years, in a wide variety of processes such as cleaning, floatation, drying, degassing, plastic welding filtration, emulsification, biological cell disruption, extraction and crystallization and stimulus for chemical reactions. By using ultrasound the complicated reactions are performed with inexpensive equipment and often in fewer steps than the conventional methods. So, the process of Sonication (i.e. the act of applying sound usually ultrasound energy to agitate particles in a sample, for various purposes) can also be an attractive treatment option.

There is always scope for improvement, so we can use the application of ultrasound in conjugation with photocatalysis or fenton process because many literatures have shown that the highest degradation and mineralization rate was attained with the combined use of these techniques. If the two modes of irradiations (UV and ultrasound) are operated in combination, more number of free radicals will be available for the reaction thereby increasing the rates of reaction. **(Gogate P.R., 2008)**.

3.3 AOP v/s EMERGING TECHNOLOGY

Advanced oxidation processes involve the production of highly reactive radicals such as hydroxyl radicals which have the ability to oxidize almost all complex organic molecules into smaller molecules. Complete mineralization of the compounds into CO_2, water and inorganic structures such as $SO_4^{2-,}$ NO_3^- and N_2 is possible. These treatment processes are considered as very promising methods for the remediation of contaminated ground, surface, and wastewaters containing non-biodegradable organic pollutants. Hydroxyl radicals are extraordinarily reactive and non-selective and for this reason it reacts with all surrounding chemicals, organic pollutants and inhibitors as well. That attacks most of the organic molecules. AOPs involve the two stages of oxidation: 1) The formation of strong oxidants (e.g., hydroxyl radicals) and 2) The reaction of these oxidants with organic contaminants in water. However, the term AOP refer specifically to processes in which oxidation of organic contaminants occurs primarily through reactions with hydroxyl radicals. Hydroxyl radicals are known to be the second strongest oxidants after fluorine. Table: 3.1 summarized the oxidation potential of most powerful oxidants.

Table 3.1: The oxidation potential of the most powerful oxidants

Oxidizing Agent	**Electrochemical oxidation potential, eV**
Fluorine	3.06
Hydroxyl radical	2.80
Oxygen (atomic)	2.42
Ozone	2.08
Hydrogen Peroxide	1.78
Hypochlorite	1.49
Chlorine	1.36
Chlorine dioxide	1.27
Oxygen (molecular)	1.23

Hydroxyl radicals are characterized by a little selectivity of attack, attractive feature for an oxidant to be used in wastewater treatment. Several and different organic compounds are susceptible to be removed or degraded by means of hydroxyl radicals, as it is shown in Table 3.2.

Table 3.2: Oxidizable compounds by hydroxyl radicals (Ozencilh.H., 2007).

Acids	Formic, gluconic, lactic, malic, propionic, tartaric
Alcohols	Benzyl, ethanol, ethylene glycol, glycerol, isopropanol, methanol, propenediol
Aldehydes	Acetaldehyde, benzaldehyde, formaldehyde, glyoxal, isobutyraldehyde, trichloroacetaldehyde
Aromatics	Benzene, chlorobenzene, chlorophenol, dichlorophenol, hydroquinone, phenol, toluene, trichlorophenol, xylene, trinitrotoluene
Amines	Aniline, cyclic amines, diethylamine, dimethylformamide, EDTA, propanediamine

Dyes	Anthraquinone, diazo, momoazo
Ethers	Tetrahydrofuran
Ketones	Dihydroxyacetone, methyl ethyl ketone

Advanced oxidation processes differ from the other treatments processes because wastewater compounds are degraded rather than concentrated or transferred into a different phase. Because secondary waste materials are not generated, there is no need to dispose of or regenerate materials. **(Metcalf and Eddy, 2003)** There are many oxidation processes or combination of processes which can produce hydroxyl radicals. Advanced treatment technology classified into two parts as shown in Fig 3.1.

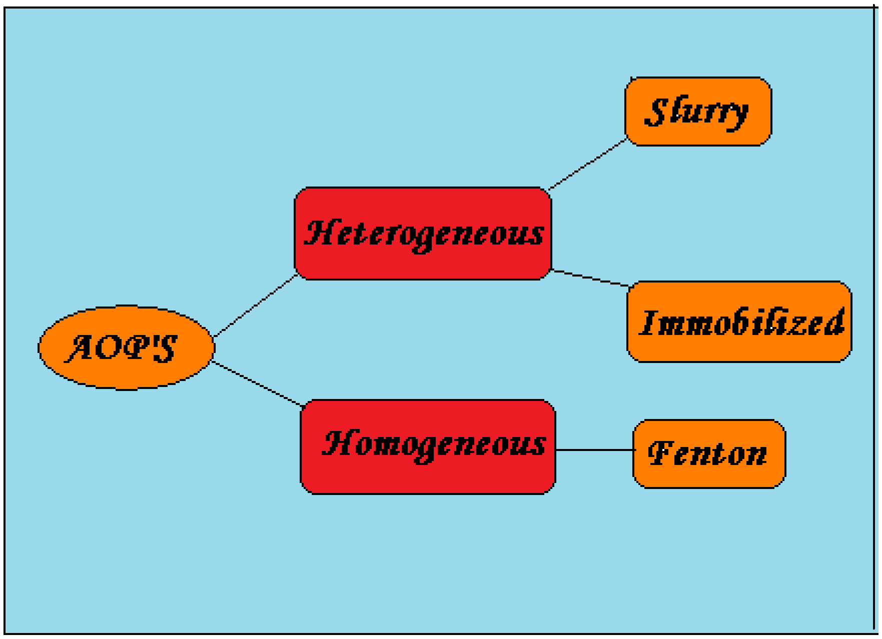

Fig 3.1: Classification of AOP's

(a) Homogenous photocatalysis The Homogeneous Fenton reaction is a process that does not involve any light irradiation as compared with the heterogeneous TiO_2 photocatalysis reaction, whereas the photo-Fenton does react up to a light wavelength of 600 nm. It was first recognised in the 1960s and remains one of the most applied AOPs for its ability to degrade high loading of organic compounds in highly saline conditions. In the absence of a light source, hydrogen peroxide (H_2O_2) will decompose by Fe^{2+} ions that present in the aqueous phase, resulting in the formation of hydroxyl radicals **(Jose P.P., 2007)**.

(b) Heterogeneous photocatalysis

The process is heterogeneous because they have two phases: solid and liquid

The word photocatalysis is composed of two parts:

1. The prefix *photo*, defined as "light",
2. *Catalysis* is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy.

Heterogeneous photocatalysis employing semiconductor catalysts (TiO_2, ZnO, Fe_2O_3, and ZnS) has demonstrated its efficiency in degrading a wide range of ambiguous refractory organics into readily biodegradable compounds, and eventually mineralized them to innocuous carbon dioxide and water. Among the semiconductor catalysts, titanium dioxide (TiO_2) has received the greatest interest in R&D of photocatalysis technology **(Balcioglun I.A. et al., 2011)**.

A number of important features for the heterogeneous photocatalysis have extended their feasible applications in water treatment, such as;

(1) Ambient operating temperature and pressure,

(2) Complete mineralization of parents and their intermediate compounds without secondary pollution and

(3) Low operating costs.

3.4 FENTON REACTION

Fenton's reagent (Bromme H.J. et al., 2002) is a solution of hydrogen peroxide and an iron catalyst that is used to oxidize contaminants or waste waters. Fenton's reagent can be used to destroy different organic compounds such as trichloroethylene **(Eakalak Khan et al., 2009)**, tetrachloroethylene **(Yoshida M. et al., 2000)**, different dyes (reactive black 5, amaranth etc) and so on.

It was developed in the 1890s by Henry John Horstman Fenton **(Fenton H.J.H., 1894)** as an analytical reagent.

Ferrous Iron(II) is oxidized by hydrogen peroxide to ferric iron(III), a hydroxyl radical and a hydroxyl anion. Iron(III) is then reduced back to iron(II), a peroxide radical and a proton by the same hydrogen peroxide (disproportionation).

$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{*} + OH^{-}$ .... (1)

$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OOH^{*} + H^{+}$ .... (2)

Reaction (1) was suggested by Haber and Weiss in the 1930s. In the net reaction the presence of iron is truly catalytic and two molecules of hydrogen peroxide are converted into two hydroxyl radicals and water. The generated radicals then engage in secondary reactions. Iron(II) sulfate is a typical iron compound in Fenton's reagent. The exact mechanisms are debated and, therefore, it may be appropriate to broadly discuss 'Fenton chemistry' rather than a 'Fenton reaction'.

In the Electro-Fenton process, hydrogen peroxide is produced in the required amount from the electrochemical reduction of oxygen.

Fenton's reagent is also used in organic synthesis for the hydroxylation of arenes in a radical substitution reaction such as the classical conversion of benzene into phenol.

$C_6H_6 + FeSO_4 + H_2O_2 \rightarrow C_6H_5OH$……………….. (3)

A recent hydroxylation example involves the oxidation of barbituric acid to alloxane. Another application of the reagent in organic synthesis is in coupling reactions of alkanes. As an example *tert*-butanol is dimerized with Fenton's reagent and sulfuric acid to 2,5-dimethyl-2,5-hexanediol.

3.5 FENTON AND PHOTO-FENTON REACTION

The Fenton reaction was discovered by Fenton H.J. in 1890’s (Fenton, 1894). Forty years later the Haber-Weiss (1934) mechanism was postulated, which revealed that the effective oxidative agent in the Fenton reaction was the hydroxyl radical. Since then, some groups have tried to explain the whole mechanism **(Gomathi D.L. et al., 2010)**. The Fenton reaction can be outlined as follows:

$$Mn^{2+} + H_2O_2 \rightarrow M^{(n+1)} + OH^* + OH^-$$

Where, M is a transition metal as Fe or Cu.

In the absence of light and complexing ligands other than water, the most accepted mechanism of H_2O_2 decomposition in acid homogeneous aqueous solution, involves the formation of hydroxyperoxyl (HO_2*) and hydroxyl radicals HO*.

The metal regeneration can follow different paths. For Fe^{2+}, the most accepted scheme is described in the following equations.

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^* + OH^- \text{.........................} (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + OH^* + OH^- \text{.........................} (2)$$

$$Fe^{2+} + HO^* \rightarrow Fe^{2+} + OH^* \text{...................................} (3)$$

$$OH^* + H_2O_2 \rightarrow HO_2^* + H_2O \text{...................................} (4)$$

$$Fe^{3+} + HO_2^* \rightarrow Fe^{2+} + O_2 + OH^+ \text{.............................} (5)$$

$$Fe^{3+} + O_2^* \rightarrow Fe^{3+} + O_2 \text{.......................................} (6)$$

$$Fe^{2+} + HO^* \rightarrow Fe^{3+} + O_2H^- \text{....................................} (7)$$

Fenton reaction rates are strongly increased by irradiation with UV/visible light **(Arslan I. and Balcioglu I.A., 2011)**. During the reaction, Fe^{3+} ions are accumulated in the system and after Fe^{2+} ions are consumed, the reaction practically stops. Photochemical regeneration of ferrous ions (Fe^{2+}) by photoreduction of ferric ions (Fe^{3+}) is the proposed mechanism. The new generated ferrous ion reacts with H_2O_2 generating a second HO* radical and ferric ion, and the cycle continues.

In the presence of light

$$Fe^{3+} + H_2O \rightarrow Fe^{2+} + OH^*$$

Fenton and photo-Fenton reaction depend not only on H_2O_2 concentration and iron added, but also on the operating pH value. The stoichiometric coefficient for the Fenton reaction was approximately 0.5 mol of organic compound. The process was found to eliminate the toxic substances and increased the biodegradability of the treated water. Some works about textile waters treatment by means of Fenton and photo-Fenton process have been published. Most of them showed their effectiveness for color removal and COD reduction. An improvement of photo assisted Fenton processes is the UV vis/

ferrioxalate/ H_2O_2 system, which has been recently demonstrated to be more efficient than photo-Fenton for the abatement of organic pollutants.

Recently, two new electrochemical procedures for the detoxification of acidic waste waters, the so-called electro-Fenton and photoelectro-Fenton processes, where H_2O_2 is electrogenerated, have been developed and have shown their good efficiencies for the mineralization of aniline **(Marco L.S. et al., 2006)** 4-chlorophenol and 2,4-Dichloropehnol.

3.6 SONICATION and SONO-FENTON

Ultrasound is the term used to describe sound energy at frequencies above the range that is normally audible to human beings (i.e.>16 kHz). At its upper limit ultrasound is not well defined but is generally considered as 5MHz in gases and 500MHz in liquids and solids which are subdivided to reflect applications. The range 20 to 100 kHz (though in certain cases up to 1 MHz) is designates as the power ultrasound reason, while the frequencies up to 1 MHz are known as high frequencies or diagnostics frequencies. **(Amarnath R.K., 1998)** Sound is composed from longitudinal waves comprising rarefactions (negative pressures) and Compressions (positive pressures). It is these alternating cycles of compression and rarefaction that, in high power ultrasonic applications, can produce a phenomenon known as “cavitation”.

Fig 3.2 shows that liquids irradiated with ultrasound can produce bubbles. These bubbles oscillate, growing a little more during the expansion phase of the sound wave than they shrink during the compression phase. Under the proper conditions these bubbles can undergo a violent collapse, which generates very high pressures and temperatures. This process is called cavitation. The compression of cavities when they implode in irradiated liquids is so rapid that little heat can escape from the cavity during collapse. The surrounding liquid, however, is still cold and will quickly quench the heated cavity.

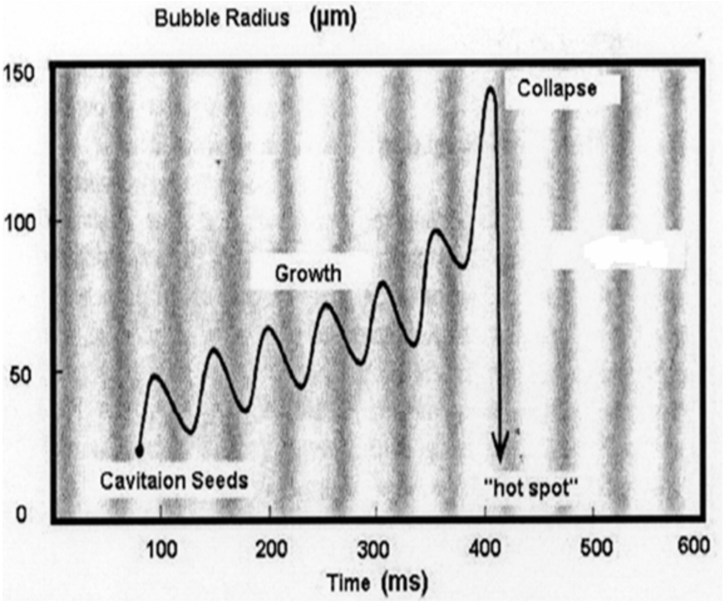

Figure 3.2: Cavitation and Implosion phenomen (Dehghani M.H. and Changani F., 2006)

Ultrasound has been widely known to induce radical reactions. This useful property has found its applications in sonolysis of water, sonolytic degradation of aqueous organic pollutants, and sonochemical synthesis of chemicals. The underlying phenomena include cavitation, microstreaming, and localized supercritical conditions. These phenomena lead to sonolytic splitting of water as well as pyrolysis of a vaporized molecule. **(Anju S.G., 2012)**

Advantage of Sonication:

1. Able to treat very toxic wastes at mild conditions.
2. Environmentally friendly technology using only electricity as a reactant.
3. The energy consumption depends on the chemical oxygen demand (COD).
4. The sono- treatment can be simply stopped by switching the power off.
5. Cost effective and safe.
6. Fully-controlled by a computer.
7. Even effluents with low conductivity can be treated.

In case of sono fenton experimental condition is identical to the Fenton process but the reactor is immersed into the ultrasonic bath, where the ultrasonic wave frequency is between 20 to 34 kHz. Ultrasonic treatment generates OH radicals through the cavitation:

$$H_2O \rightarrow H^* + HO^*$$

3.7 SONO PHOTO-FENTON

Catalytic runs with ultrasonic and UV–visible irradiation alone, as well as experiments coupling ultrasonic and UV–light irradiation simultaneously or sequentially, can be performed in order to determine benefits and synergistic effects of combined techniques in the oxidation process. Sono-Fenton reactions occur with an ultrasonic Sonicator while Photo-Fenton reactions occur with a pressure mercury lamp. The lamp is surrounded by a quartz jacket in which an aqueous copper sulphate solution is circulated to prevent overheating of the suspension and block radiation at wavelengths shorter than 313 nm. In a typical experiment, a cylindrical glass vessel is filled with aqueous solution and hydrogen peroxide. Temperature should be controlled at 22 ± 2˚C for the ultrasound irradiation to avoid significant (Fig 3.3 a and c) overheating of the solution. In the sequential step and UV alone (Fig 3.3 b) the temperature during the UV radiation is not controlled. The catalyst is suspended into the aqueous solution ($FeSO_4$) and the pH is initially adjusted. Fig 3.3 depicts a simplified scheme of the experimental set-ups used for the study of single and combined ultrasound and UV–visible irradiation systems **(Segura Y. et al., 2008).**

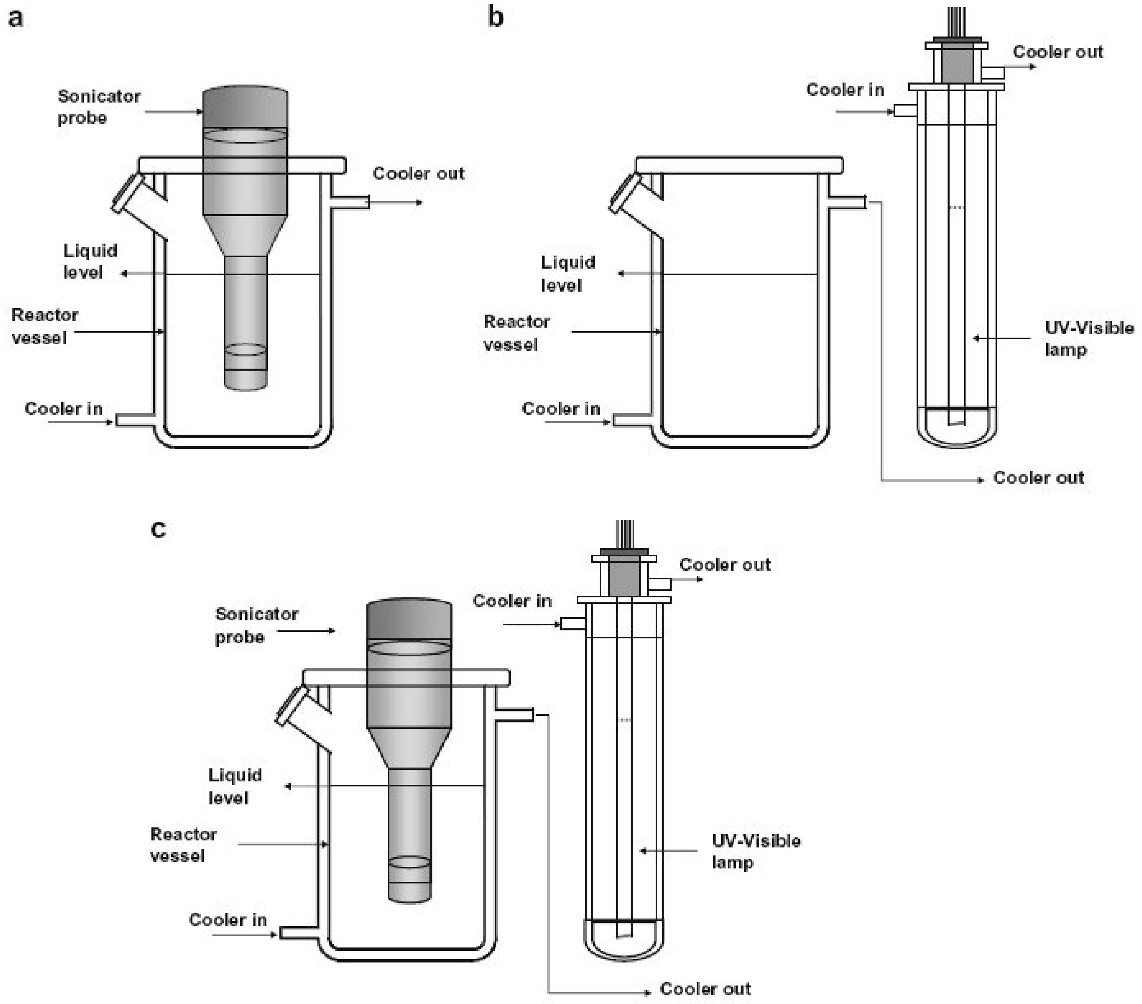

Fig 3.3: Schematic representation of (a) sono-Fenton, (b) photo-Fenton and (c) coupled sono–photo-Fenton experimental set-ups.

In the case of the experiments assisted by the UV–visible irradiation, the glass reactor and the lamp located outside the reactor were wrapped in aluminum foil, in order to reduce the loss of light irradiation. In all the cases aeration system should be used for the Fe^{+2} dispersion of the catalyst within the reaction medium.

In case of RB5, the total reaction time (tr) is different for all the experiments. In case of simultaneous US + UV reaction tr was 20 minutes and in case of sequential combination reactions, each system is applied for 10 minutes. These reaction times were selected in order to supply the same energy for coupling systems, 20 minutes for the simultaneous US + UV reaction and 10 minutes each for the sequential US → UV and UV → US processes. Note also that for alone sono fenton runs or photo fenton runs, the real reaction times (tr) were 30 minutes. The different systems applied in this work are coded in Table 3.3.

Table 3.3: Codification and identification of Fenton-like catalytic experiments.

Catalytic Run	**Codification (tr)**	**Type of reaction system**
Ultrasonic	30 min	‘a’
UV-light irradiation	30 min	‘b’
Sequential combination: Ultrasonic followed by UV- light irradiation	US (10 min) → UV (10 min)	‘a’ followed by ‘b’
Sequential combination: UV-light irradiation followed by Ultrasonic	UV (10 min) → US(10 min)	‘b’ followed by ‘a’
Simultaneous combination: UV-light irradiation and Ultrasonic	US + UV (20 min)	‘c’

CHAPTER - 4

LITERATURE REVIEW

Colour containing wastewater generated from textile industries discussed in previous chapter is posing a great threat not only to mankind but also to the landmass fertility as well as natural flora and fauna. In order to meet the stringent international standards, treatment of dyes is mandatory. Fenton and photo fenton is a process of great potential for pollutant abatement and waste treatment. In order to improve the overall performance of the process, fenton and photo fenton reaction is being combined with sonolysis, which affect the overall efficiency. This review addresses the various possibilities to couple fenton, photo fenton and sono fenton reaction to degrade dye pollutants dissolved in actual or synthetic aqueous effluents. A literature survey was carried out to know the latest advancements in the field of homogeneous photo fenton as well as ultrasonic treatment of waste water. This review basically aims at degradation of dyes generated as textile effluent.

4.1 Photo fenton and fenton in dark

The photodegradation of Malachite Green (MG) under visible light irradiation in the presence of Fe^{+3}/ H_2O_2 or Fe^{+2}/H_2O_2 is compared with the dark reaction, and this study was achieved by **Kaiqun W. et al., (1998).** It was found that visible light irradiation can accelerate significantly the rate of MG degradation, comparing to that in the dark. This provides possibly another approach to the treatment of dye-polluted waters using visible light or sunlight. Evidence for enhancement of OH* radical generation by visible light irradiation was obtained using spin-trapping EPR spectroscopy.

Liu X. et al., (2011) were investigated Fenton and Fenton-like reactions to oxidize the commercial azo dye of Reactive Black 5. Different parameters affecting the decolorization efficiency of Reactive Black 5 such as initial concentration of Fe^{2+}, Fe^{3+},H_2O_2 and initial pH of dye solution. The results evaluated that decolorization efficiency of Reactive Black 5 in Fenton oxidation was much faster than that of Fenton-like oxidation in the initial stages and efficiency was similar for both systems after 45 min. For the two oxidation systems, decolorization efficiency of Reactive Black 5 depends on Dye, Fe^{2+} or Fe^{3+}, H_2O_2 and pH.

The study of degradation of two azo reactive dyes, Reactive Yellow 84 (RY84) and Reactive Red 120 (RR120) by photo-Fenton and Fenton-like oxidation were reported by **Mariana N. et al., (2003)**. The effects of different reaction parameters such as initial pH, contact time, effect of light and hydrogen peroxide concentrations on the oxidation of the dye aqueous solutions have been assessed. The color removal efficiency at the optimum conditions during different Fenton-like processes was also evaluated. The results show that the color removal of RY84 after 15 min reaction time follows the decreasing order: solar/ Fe^{2+}/ H_2O_2 > UV/Fe^{2+}/H_2O_2 > UV/Cu^{2+}/Fe^{3+}/H_2O_2 > UV/Fe^{3+}oxalate/H_2O_2 > UV/ Fe^{3+}/ H_2O_2 > dark/ Fe^{2+}/ H_2O_2 > solar/Fe^{3+}oxalate/H_2O_2 > UV/ H_2O_2 > UV/ Fe^{2+} = UV. During the same reaction period the relative order for RR120 removal rate was slightly different: solar/ Fe^{2+}/ H_2O_2 > UV/Fe^{2+}/H_2O_2 > UV/Fe^{3+}/H_2O_2 = UV/Cu^{2+}/Fe^{3+}/H_2O_2 > UV/Fe^{3+}oxalate/H_2O_2 = UV/ H_2O_2 > UV.

Garcia-Montano J. et al., (2007) were evaluated that solar photo-Fenton reactions as a stand-alone process and as a pre-treatment of an aerobic biological treatment for Procion Red H-E7B and Cibacron Red FN-R reactive dyes degradation have been carried out at pilot plant scale. Photo-Fenton oxidation was conducted using a Compound Parabolic Collector (CPC) solar photo-reactor and the biological treatment was carried out with an Immobilised Biomass Reactor. Artificial light photo-Fenton experiments carried out at laboratory scale have been taken as starting point. When applying photo-Fenton reaction as a single process, 10 mg/L Fe^{+2} and 250 mg/L H_2O_2 for 250 mg/L Procion Red H-E7B treatment, and 20 mg/L Fe^{+2} and 500 mg/ L H_2O_2 for 250 mg/L Cibacron Red FN-R treatment closely reproduced the laboratory mineralization results, with 82% and 86% Dissolved Organic Carbon (DOC) removal, respectively. Nevertheless, the use of sunlight with the CPC photo-reactor increased the degradation rates allowing the reduction of Fe^{+2} concentration from 10 to 2mg/L (Procion Red H-E7B) and from 20 to 5 mg/L (Cibacron Red FN-R) without yield loses. Carboxylic acids, SO_4^{2-}, NH_4^+ and NO_3^-

generation were monitored along with dye mineralization. Finally, in the combined photo-Fenton/biological system, reagents doses of 5 mg/L Fe^{+2} and 225 mg/L H_2O_2 for Cibacron Red FN-R and 2mg/L Fe^{+2} and 65 mg/L H_2O_2 for Procion Red H-E7B were enough to generate biodegradable solutions that could be fed to the IBR, even improving bench-scale results.

Jonstrup M. et al., (2011) were compared anaerobic pre-treatment and aerobic post-treatment coupled to photo-Fenton oxidation for degradation of azo dyes. The processes were compared with regards to decolorization, chemical oxygen demand (COD) reduction and chemical consumption. When applying photo-Fenton alone for treatment of Remazol Red RR (100 mg/l), optimal conditions were 3.0 mM H_2O_2 and 0.25 mM Fe^{2+}. These conditions resulted in complete decolorization and a residual COD of 2.9 mg/l. When reducing the H_2O_2 dose to 1 mM, residual COD was 22 mg/l. In the combined photo-Fenton/aerobic treatment complete decolorization and COD removal was achieved at 3 mM H_2O_2 and 0.25 mM Fe^{2+}, while 9 mg/l of residual COD remained at the H_2O_2 concentration 1 mM. When applying photo-Fenton as post-treatment after the anaerobic step, the residual COD was 14 mg/l independent of the H_2O_2 concentration being set to 1 or 3 mM, however the Fe^{2+} concentration needed to be increased to 2 mM, due to complex formation with the phosphate added as a macronutrient. Their results thereby show that incorporation of a biological step leads to improved mineralization and reduced residual toxicity at lower H_2O_2 doses.

The oxidative decolorization of Reactive Black 5 (RB5) in aqueous solution has been studied by **Marco L.S., Jose P.A., (2005)** using Fenton and photo-Fenton processes. This investigation reveals that both methods can remove the color of RB5. The decolorization experiments indicate that RB5 can be effectively decolorized using Fenton and photo-Fenton processes with a little difference between the two processes, 97.5% and 98.1%, respectively. This small difference in dye decolorization is not similar to TOC removal: with photo-Fenton process there is a significant increment (46.4% TOC removal) relatively to Fenton process (only 21.6% TOC removal). This fact indicates that although

UV low-pressure mercury lamp has little effect on dye decolorization it is particularly important in dye mineralization.

Rahmani R. et al., (2010) have discussed removal of two azo dyes, Acid Orange 7 and Reactive Black 5 by Fenton like reaction. In this process, OH* radicals will be generated by using Fe^{2+} and UV light, so it can occur without the addition of hydrogen peroxide. It was observed that high removal of dyes for UV system was obtained at pH=11, while in the Fe^{2+} and Fe^{2+} /UV system, high removal occurred at pH=3. Removal of dye was increased by increasing the iron mass and contact time. By increasing the initial dye concentration of Acid Orange 7 has increased dye removal in the Fe^{2+} /UV and Fe^{2+} system, while it was decreased in the UV system. For RB5 removal, it was decreased in the Fe^{2+} /UV and Fe^{2+} system by increasing the initial dye concentration, while it increased in UV system.

Dias, Fernando F.S. et al., (2009) were degraded reactive black 5 in a photo Fenton reactor, the removal of the dye color is completed in a short time of about 3 min reaction. TOC removal is strongly dependent on hydrogen peroxide concentration and ferrous ion catalyst concentration. Based on dye concentration of 55 mg/L, the maximum TOC removal was 90% after 90 minutes reaction with optimal condition on peroxide concentration of 280 mg/L and ferrous ion concentration of 78 mg/L.

Nilesh T.P. and Chaudhari S., (2007) were discussed a two stage sequential Fenton's oxidation followed by aerobic biological treatment, to achieve decolorization and to enhance mineralization of azo dyes, viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13), and Acid Orange 7 (AO7). Results reveal that pH 3 was optimum pH for achieving decolorization and dearomatization of dyes by Fenton's process. Degradation of dye was assessed by COD reduction and reduction in aromatic amines (naphthalene chromophores). More than 95% of color was removed with Fenton's oxidation process in all dyes. In overall treatment 81.95%, 85.57%, and 77.83% of COD reduction was achieved in RB5, RB13, and AO7 dyes, respectively. In the Fenton's oxidation process 56%, 24.5%, and 80% reduction in naphthalene group was observed in RB5, RB13, and

AO7, respectively, which further increased to 81.34%, 68.73%, and 92% after aerobic treatment. Fenton's oxidation process followed by aerobic SBRs treatment sequence seems to be viable method for achieving significant degradation of azo dye.

4.2 Sono fenton, fenton and photo fenton

Zhihui A. et al., (2009) have developed a novel ultrasound-assisted electrocatalytic oxidation (US–EO) process to decolorize azo dyes in aqueous solution. Rhodamine B was decolorized completely within several minutes in this developed US–EO system. Oxidation parameters such as applied potentials, power of the ultrasound, initial pH of the solution, and initial concentration of RhB were systematically studied and optimized. An obvious synergistic effect was found in decolorization of RhB by the US–EO process when comparing with either ultrasound (US) process or electrocatalytic oxidation (EO) one. Additionally, the decolorization of other azo dyes, such as methylene blue, reactive brilliant red X-3B, and methyl orange, were also effective in the US–EO system. The results indicated that US–EO system was effective for the decolorization of azo dyes, suggesting its great potential in dyeing wastewater treatment.

In the review of **Segura Y. et al., (2008),** the efficacy of the different systems has been assessed using Fenton-like processes and phenol as model pollutant. Sono- and photo-Fenton processes separately applied as well as combined systems were studied in order to evaluate of possible beneficial effects on the use of coupled systems. The sequential system evidences an enhancement in terms of phenol and TOC conversions compared to the ultrasound or UV–light irradiation processes. A total phenol degradation and 90% TOC reduction are achieved by sequentially ultrasound followed by UV–visible light irradiation.

Comparison between dye removal by fenton, photo fenton and sono fenton process were reported by **Sundararaman T.R. et al., (2009)**. This study was performed to investigate the removal of COD and color for Reactive yellow 16 using Fenton oxidation. Removal of COD and color of 80% & 90%, 90% & 98%, and 82% & 95% can be achieved by

Fenton, Photo Fenton and Sono Fenton process. The results showed that H_2O_2/ Fe^{2+}/UV process was more effective in COD and color removal.

Papadopoulos A.E. et al., (2007) were examined the effectiveness of chemical oxidation using Fenton's reagent for the reduction of the organic content of wastewater generated from a textile industry. The experimental results indicate that the oxidation process leads to a reduction in the chemical oxygen demand (COD) concentration up to 45%. Moreover, the reduction is reasonably fast at the first stages of the process, since the COD concentration is decreased up to 45% within four hours and further treatment time does not add up to the overall decrease in the COD concentration (48% reduction within six hours). The maximum color removal achieved was 71.5%.

The study of Sono-Fenton process for the degradation of 2,4-dichlorophenol (DCP) were observed by **Praveena J.D. et al., (2007)**. The influential parameters such as H_2O_2, Fe^{2+} sand pH for the Sono-Fenton process were investigated. Sono-Fenton method was found to be the best one for degradation efficiency of DCP when compared with that of the Fenton process. The optimum concentrations for the degradation of DCP using conventional Fenton's method were found to be 20 mg/ L of Fe^{2+} and 580 mg/L of H_2O_2 at pH 2.5. In the case of Sono-Fenton, the optimal concentrations were found to be 10 mg/L of Fe^{2+} and 400 mg/L of H2O2 at pH 2.5. Sono-Fenton method resulted in the reduction of required Fe^{2+} concentration (50%) and H_2O_2 concentration (31%). In addition, this method could be applicable even at pH 5.0 and a degradation efficiency of DCP was 77.6%.

Ozdemir C. et al., (2010) were removed colour from synthetic textile waste water. The optimum condition have been found as $Fe^{2+} = 20$ mg/L, $H_2O_2 = 20$ mg/L, pH 3 for Fenton process and $Fe^{2+}= 20$ mg/L, $H_2O_2 = 15$ mg/L, pH 3 for sono-Fenton process. The color and COD removal efficiencies have been obtained as 91% and 47% by Fenton process, and 95 and 51% by sono-Fenton processes, respectively. Hence the result proved that sono fenton process is more effective than fenton process.

CHAPTER - 5

MATERIALS AND METHODS:

5.1 MATERIALS

5.1.1 Chemicals: Chemicals were used in experiments are $FeSO_4.7H_2O$, $Na_2S_2O_3$, H_2O_2, H_2SO_4, NaOH. The dye used was azo dye i.e. RB5, Molecular weight is 991.82. The structure of RB5 is shown below in fig 5.1. Distilled water was used throughout the investigations. Dye solution was prepared by dissolving requisite amount of dye in distilled water. $FeSO_4.7H_2O$ and H_2O_2 (30% w/v, Ranbaxy laboratories) were used as received without further purification. For adjusting the pH, H_2SO_4 and NaOH were used and initial pH monitored by basic pH meter from Century instrument company.

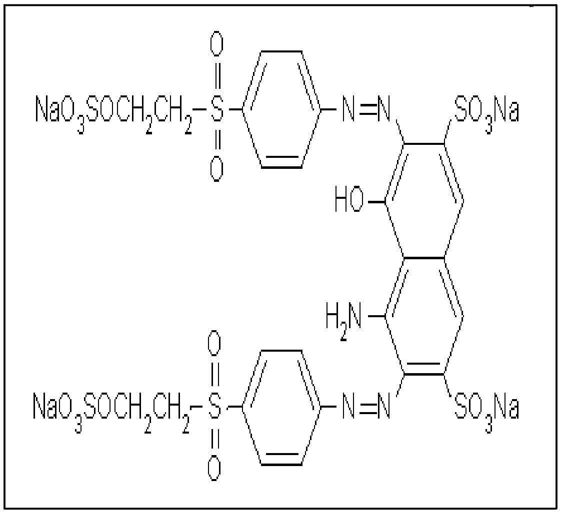

Figure 5.1: Structure of Reactive Black 5

5.1.2 Instruments Used:

a) pH meter: pH of the solution was monitored by pH meter from the company EU-Tech instrumentation and adjusted with the help of NaOH and H_2SO_4. Instrument was calibrated by freshly prepared buffer solution (pH 4 to 9) time to time throughout the study. (Fig 5.2)

b) Spectrophotometer: The spectrum was taken with UV-visible Spectrophotometer by Hitachi V-500 UV/VIS (Japan) double-beam spectrophotometer. (Fig 5.3)

Figure 5.2: pH meter

Figure 5.3: Spectrohotometer

c) Photo reactor: Comprising of a glass having three concentric cylinders, having outer ground glass jacket of borosil glass having socket and cone fitted with inlet and outlet tubes. And a cooling jacket of borosil glass with socket and inlet and outlet tubes is also provided; having capacity 200ml and a 125 watt UV bulb is used. (Fig 5.4 and 5.5)

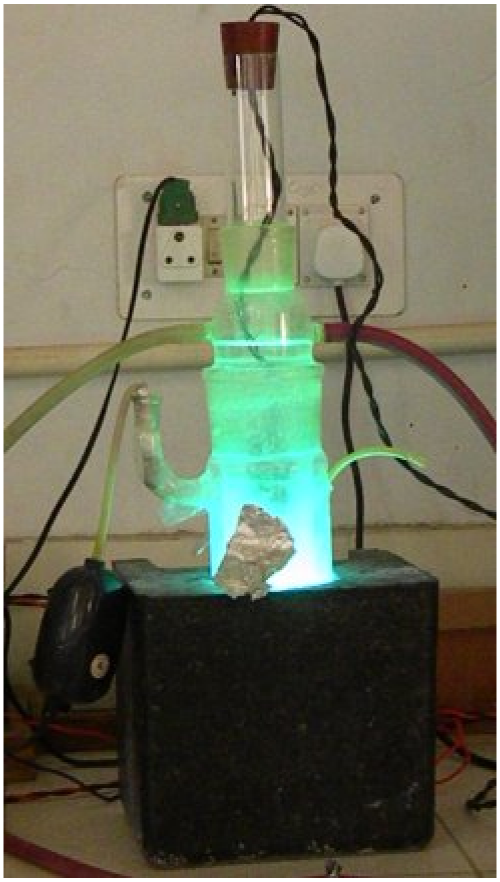

Figure 5.4: Immersion well reactor

Figure 5.5: UV bulb of 125 watts

d) Ultrasonic Bath: For Sonication ultrasonic bath is used having capacity 6.5 litre. Tank size is 12''x6"x6" (H) and U/S Power is 100 Watts U/S. Frequency is 33 + 3 KHz and its model no. is EN 60 US. (Fig 5.6)

Figure 5.6: Ultrasonicator

e) Sono Photo Reactor: The immersion type photocatalytic reactor was placed in sonicator bath thus making sonophotocatalytic reactor. (Fig 5.7)

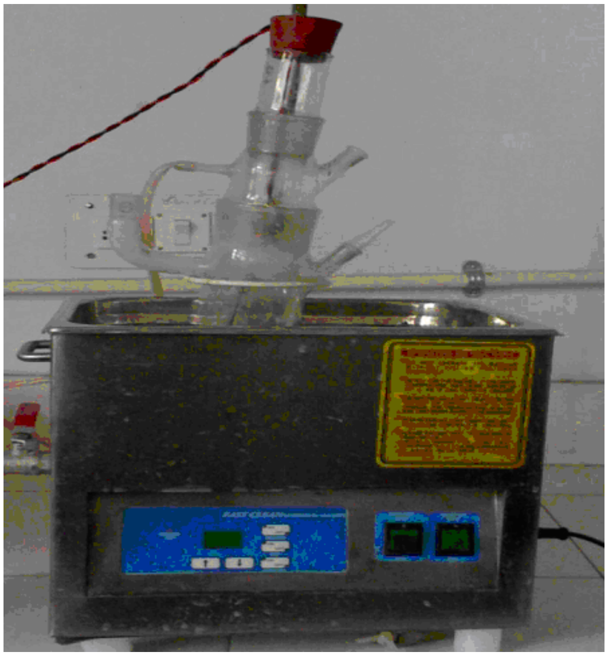

Figure 5.7: Sono photo reactor

5.2 PREPARATION OF SOLUTION

5.2.1 Compound solutions:

The stock solutions were prepared by adding a known amount of compound into a small amount of deionized water in a 1-liter volumetric flask and filling it to the mark with distilled water. Before the oxidation experiments could be performed, it was necessary to choose the appropriate concentration of compound solutions. For most of the experiments, stock solutions of 100 mg/L concentration were prepared by dissolving 100 mg RB5 in distilled water and make the solution quantity to1 L.

5.2.2 Hydrogen Peroxide:

Hydrogen peroxide (30% w/v) was obtained from Ranbaxy Laboratories, having molecular weight of 34.01. It implies that 100 ml of solution contains 30 g or 1 ml contains 300 mg. Hence for adding 4.4 mM of H_2O_2 solution, 500 µl of H_2O_2 solution was taken in 1 L of stock solution or 100 µl of peroxide solution in 200 ml of stock solution.

5.2.3 $FeSO_4$ reagent: $FeSO_4$ was obtained from having molecular weight 278 gm. For adding 0.15 mM of $FeSO_4$ in stock solution, add 41.7 mg in 1 L of stock solution or 8.4 mg in 200 ml of stock solution.

5.3 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_2SO_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
- 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 Distilled water 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 give direct pH value of the sample.

5.4 DEGRADATION OF COMPOUND

5.4.1 Photolysis: Reactive Black 5 solution of 100 mg/L was prepared by distilled water. 200 ml of sample taken in immersion well reactor, 8.4 mg of $FeSO_4$ and 100 µl of H_2O_2

were added, air was also supplied by the aerator during experiment. Sample was taken in intervals of 1 min for first 5 min and later after every 5 min for 15 min. The concentration of these samples were detected by Spectrophotometer.

5.4.2 Sonophotolysis:

The experimental condition was same as in photolysis, the only difference was ultrasonication bath. In case of sonophotolysis, complete setup (photo reactor) was placed in ultrasonicator and the sample was taken in intervals of 1 min for first 5 min and later after every 5 min for 15 min. The concentration of these samples were detected by Spectrophotometer.

CHAPTER - 6

RESULTS AND DISCUSSION

6.1 COMPOUND CHARACTERISTICS

Stock solution of sample was taken and analyzed for some initial parameters. The values of various parameters are shown in Table 6.1

Table 6.1: showing characteristics of Reactive black 5

Parameters	Value
pH of compound	8.2
COD	1600mg/l for 100ppm concentration
Maximum absorbance at visible range	595 nm
Maximum absorbance at UV range	310 nm

6.2 ABSORPTION SPECTRA OF REACTIVE BLACK 5

The absorption spectrum of Reactive Black 5 was recorded with a "UV- vis. Spectrometer (Hitachi V- 500 UV/VIS Japan double-beam spectrometer). The spectrophotometer measures the absorption spectrum using Scan software. The samples were placed in a quartz cell and the spectra were recorded in the wavelength range of 250–700 nm. Total 2 peaks were observed in absorption spectra one is at 310 nm and another is at 595 nm as shown in Fig 6.1. Compound shows maximum absorbance at 595 nm (visible range) due to presence of color and also at 310 nm (UV range) due to the presence of complex structure. Therefore Reduction of RB5 concentration is measured at both wavelength 310 nm and 595 nm.

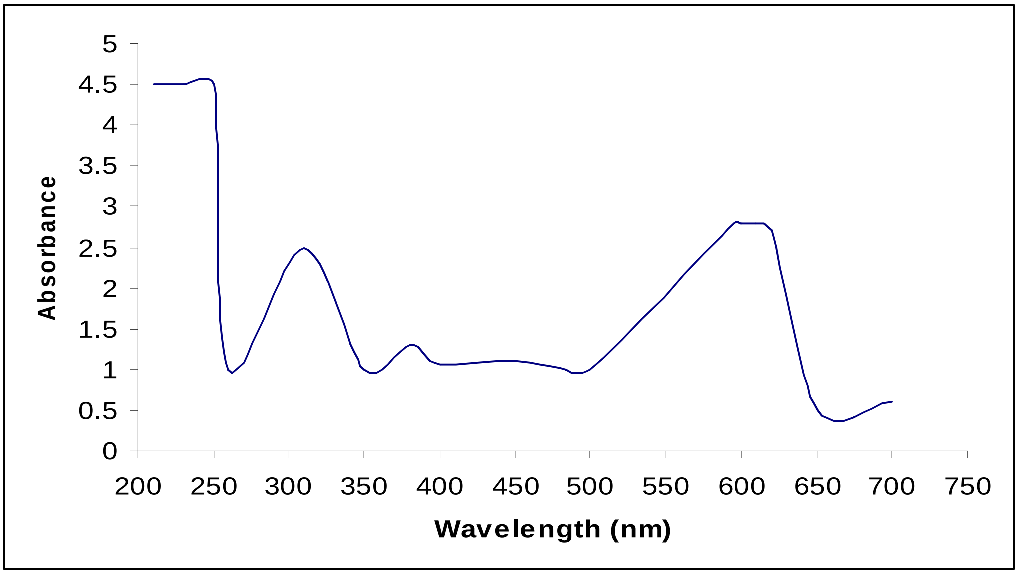

Figure 6.1: UV-Vis absorption spectrum of Reactive Black 5

6.3 STANDARD CURVE OF REACTIVE BLACK 5

Fig 6.2 and Fig 6.3 shows the standard curve for RB5 which is prepared by plotting the absorbance of sample solution of varying known concentration ranging from 10ppm to 100 ppm at 310 nm and 595 nm against concentration. From this graph we can calculate unknown concentration for RB5 solution using formula i.e. y=mx where, y is absorbance, m is slope and x is concentration. Value of R^2 is 0.9985 and slope is 0.016 at wavelength 310 nm and R^2 is 0.9981 and slope is 0.0223 at wavelength 595 nm.

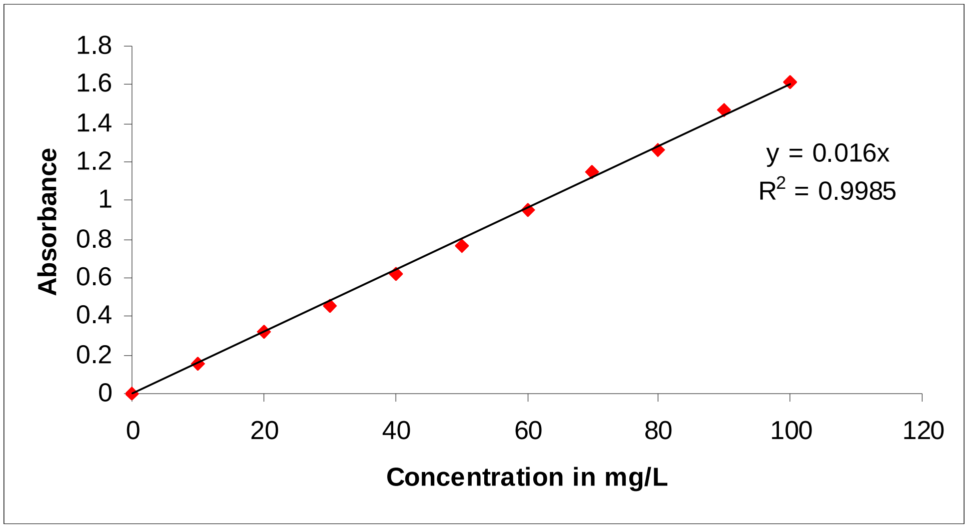

Figure 6.2: Standard curve of RB5 at wavelength 310 nm

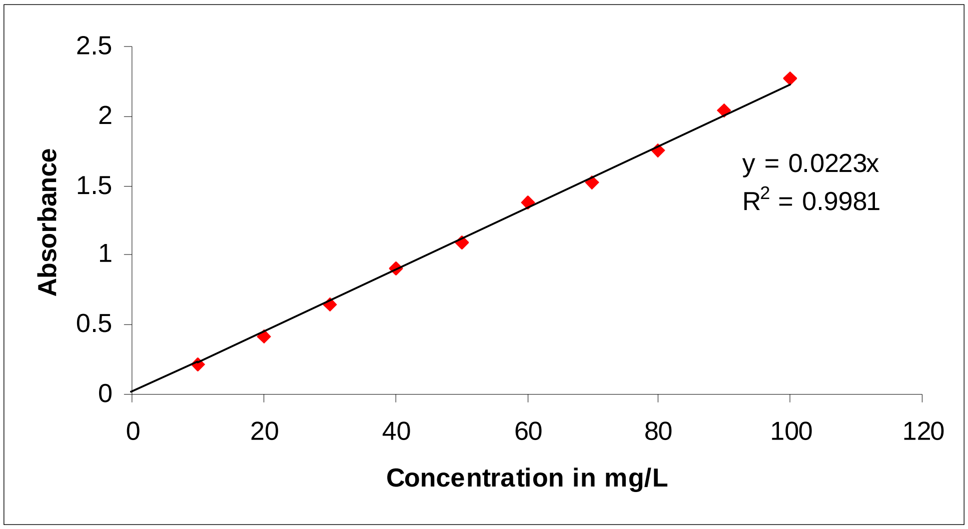

Figure 6.3: Standard curve of RB5 at wavelength 595 nm

6.4 KINETIC ANALYSIS OF PHOTO FENTON AND SONO FENTON

For more knowledge of degradation and decolourization of RB5 solution, all the oxidation processes described in terms of first order kinetics and half life time $t_{1/2}$. Table 6.2 shows the degradation and decolourization of RB5 solution in 2 min with respect to dye concentration. First order rate constant was calculated by the slope of $-\ln(C/C_0)$ *vs* t (min), where C and C_0 are the concentrations at time t and zero, respectively.

The values of k and $t_{1/2}$ was compared for different experiments and Table 6.2 depicted that dark fenton having lower value of k in comparison with photo fenton or sono fenton. This is due to the presence of additional affect sonication and UV irradiation. In case of Sono photo fenton, value of k is highest due to the presence of both sonication and UV radiation, simultaneously.

Table 6.2: Value of k and $t_{1/2}$ for first two minutes at 310 nm and 595 nm

Experiments	Value of k in min^{-1} at 310 nm and 595 nm		Value of $t_{1/2}$ at 310 nm and 595 nm	
US	0.15	0.06	4.62	11.55
UV	0.162	0.072	4.278	9.625
US+Fe^{+2}	0.126	0.54	5.5	1.283
UV+Fe^{+2}	0.138	0.072	5.022	9.625
US+H_2O_2	0.174	0.072	3.983	9.825

UV+H_2O_2	0.192	0.15	3.609	4.62
Dark Fenton	0.42	2.064	1.65	0.336
Sono Fenton	0.492	2.22	1.409	0.313
Photo Fenton	0.756	2.358	0.917	0.294
Sono photo Fenton	0.876	2.598	0.791	0.267

Rate constant and $t_{1/2}$ were calculated for 2 min data only because 1.) Degradation and decolourization capacity of RB5 increases impulsively in the presence of both UV and US process, simultaneously and individually 2.) After 2 min different intermediates are produced during the degradation of RB5 which can interfere in the reaction. This happens because sonication and UV wavelength both are important parameters can directly influence the formation of OH* for the oxidation of RB5 solution. Next step is to optimize all the parameters by fixing other values, for best oxidation process of RB5 solution.

6.5 PHOTO FENTON STUDIES

6.5.1 Effect of H_2O_2: Fig 6.4 and 6.5 shows the degradation and decolourization of RB5 at different dosage of H_2O_2. The study was conducted to determine the optimum dosage of H_2O_2 for the best oxidation process. To optimize the dosage, H_2O_2 varies from 3.5 mM to 13.2 mM into the dye solution at fixed Fe^{+2} and pH. Dye removal increases with the increasing dosage of H_2O_2 till 4.4 mM after that percentage of removal decreases or becomes constant with the increasing dosage of H_2O_2. This decrease is due to the fact of scavenging of OH* radicals by H_2O_2 **(Walling C.H., 1975)**, can be expressed by the equation:

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

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

Effective degradation (91%) and decolorization (97%) of dye solution was achieved at optimum dose 4.4 mM of H_2O_2 within 20 min of reaction after which reaction was observed to be constant.

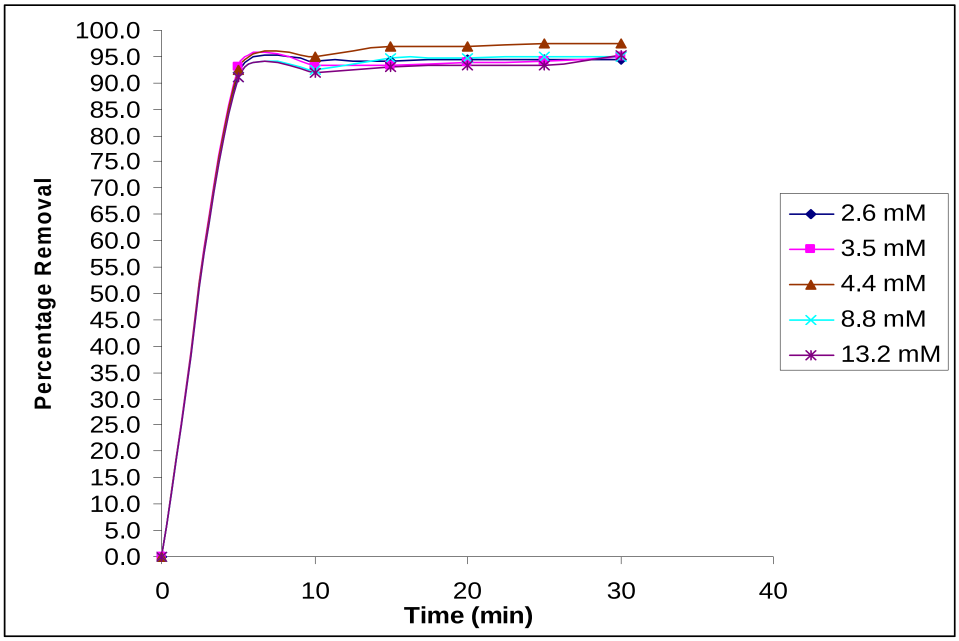

Figure 6.4: Percentage colour removal of RB5 at varying concentration of H_2O_2 at wavelength 595 nm.

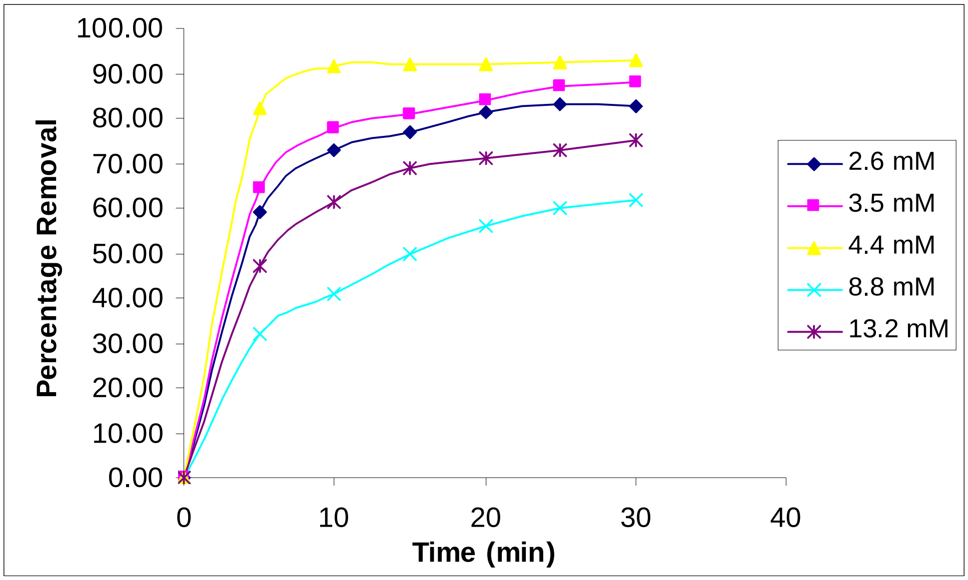

Figure 6.5 : Percentage degradation of RB5 at varying concentration of H_2O_2 at wavelength 310 nm.

6.5.2 Effect of iron dosage

Iron was used in varying concentrations ranging from 0.09 mM to 0.75 mM during the photo fenton treatment process for the optimization of the concentration while maintaining the other parameters constant. . The amount of iron in dye solution is important parameter influencing the oxidation processes. Iron dosage act as catalyst and not participate in the reaction but enhance the oxidation process. Hence with increasing iron dosage, surface of iron and simultaneously free radical production increased, so dye removal efficiency increased. The results shown in Fig 6.6 and 6.7 depicted that increased iron dosage is effective for RB5 removal up to a point. Although by increasing iron dosage from 0.09 mM to 0.75 mM, degradation and decolourization of dye decreases. It may be explained by redox reaction that OH* scavenged either by the reaction with hydrogen peroxide or by the reaction with Fe^{+2} as expressed in the equations **(Malik P.K. and Saha S.K., 2003)**:

$H_2O_2 + OH^* \rightarrow H_2O + OH_2^*$

$Fe^{+2} + OH^* \rightarrow OH^- + Fe^{+3}$

The maximum degradation of 91% and decolourization of 96% was achieved at 0.15 mM iron dosage within reaction time 20 min after which efficiency of degradation and decolourization becomes constant. The less degradation and decolourization observed at small iron dosage may be because of less production of OH* for the oxidation process. Hence, 0.15 mM dosage of iron is used as an optimum dose.

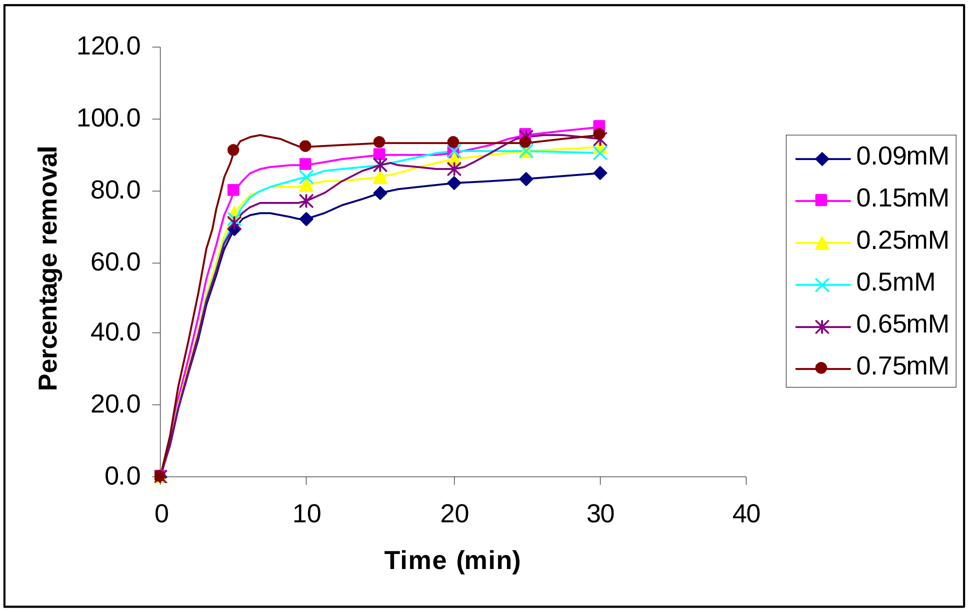

Figure 6.6: Percentage colour removal of RB5 at varying concentration of Fe^{+2} at wavelength 595 nm.

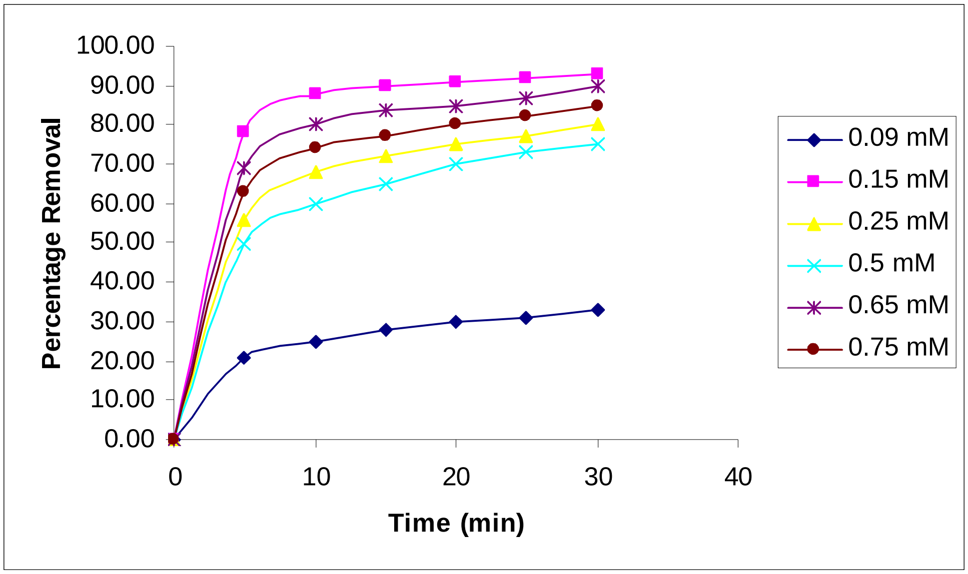

Figure 6.7: Percentage degradation of RB5 at varying concentration of Fe^{+2} at wavelength 310 nm.

6.5.3 Effect of pH

The effect of pH on the decolorization and degradation of RB5 by photo-Fenton processes is shown in Fig. 6.8 and 6.9. The results confirmed that pH significantly influences the degradation and decolourization of RB5. The experiments were carried out at different pH that varies from 1 to 8. The reaction has completed in 30 min under controlled pH and constant dose of Fe^{+2} (0.15 mM) and H_2O_2 (4.4 mM). At low pH, 1 and 2 percentage removal of dye solution was very less and also percentage removal decreases with increasing pH i.e. 5 to 8. From the figure it can be easily depicted that maximum degradation and decolourization achieved at both pH 3 and 4 but pH=4 was used as a optimum pH because degradation and decolurization of RB5 was 2% more than pH=3 i.e. 92% and 98%. At lower pH 1 and 2, dye removal was less because reaction between hydrogen peroxide and iron is seriously affected resulting, reduction in the OH* radical production. At lower and higher pH dye removal was less also because of hydroxyl radicals scavenging of H^+ ions **(Spinks J.W.T. and Woods R.J., 1990)**

$OH^* + H^+ + e^- \rightarrow H_2O$

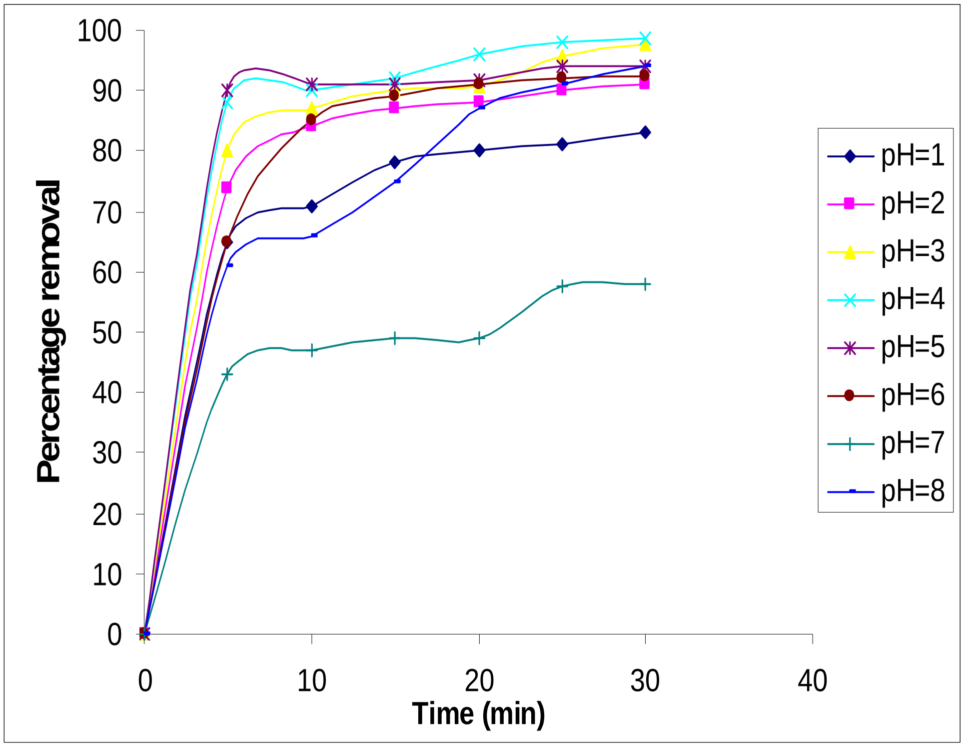

Figure 6.8: Percentage colour removal of RB5 at varying of pH at wavelength 595 nm.

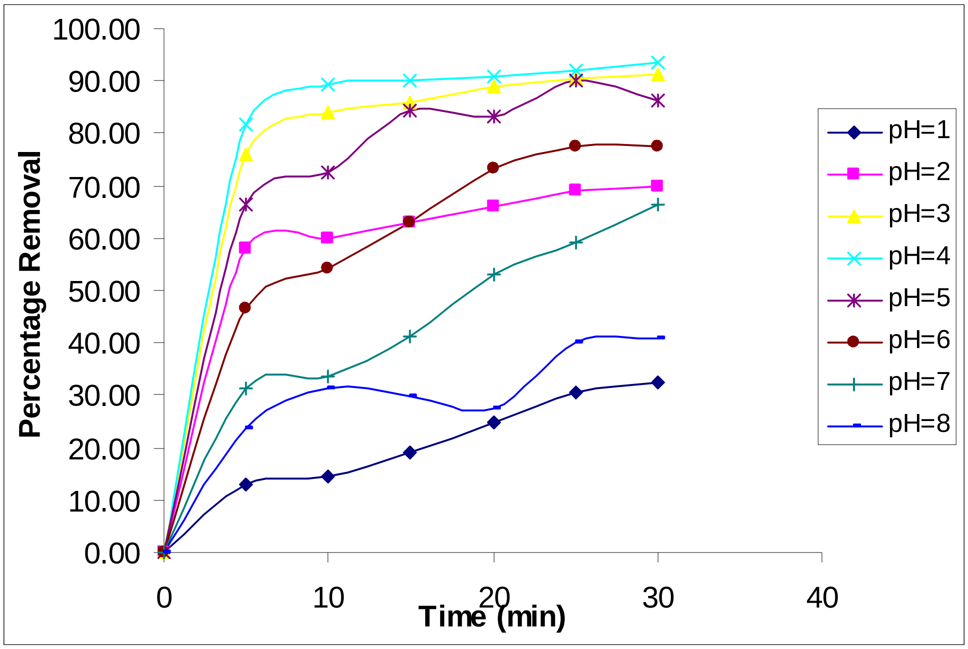

Figure 6.9: Percentage degradation of RB5 at varying of pH at wavelength 595 nm.

6.5.4 Effect of dye concentration

6.5.4 Effect of initial dye concentration

The effect of initial dye concentration on aqueous solution of RB5 on the photo-Fenton processes was investigated, since pollutant concentration is an important parameter in wastewater treatment. The influence of the concentration is shown in Figs. 6.10 and 6.11. From these figures it is possible to see that the extent of decolourization and degradation decreases with the increase in the initial dye concentration. Increase of dye concentration from 50mg/L to 200mg/L, decreases the decolorization from 98% to 90% and decreases the degradation from 92% to 80% within 30 min after which the degradation and decolourization becomes constant. It is due to the fact that; increase in dye concentration, increases the number of dye molecule but not the OH radicals. And this increasing number of dye molecule also obstructs the penetration of photons entering into the solution, therefore less production of OH* radical **(Feng J. et al., 2003)**. The maximum decolourization and degradation was achieved at dye concentration 100 mg/L. Hence, dye concentration 100 mg/L can be used as an optimum concentration.

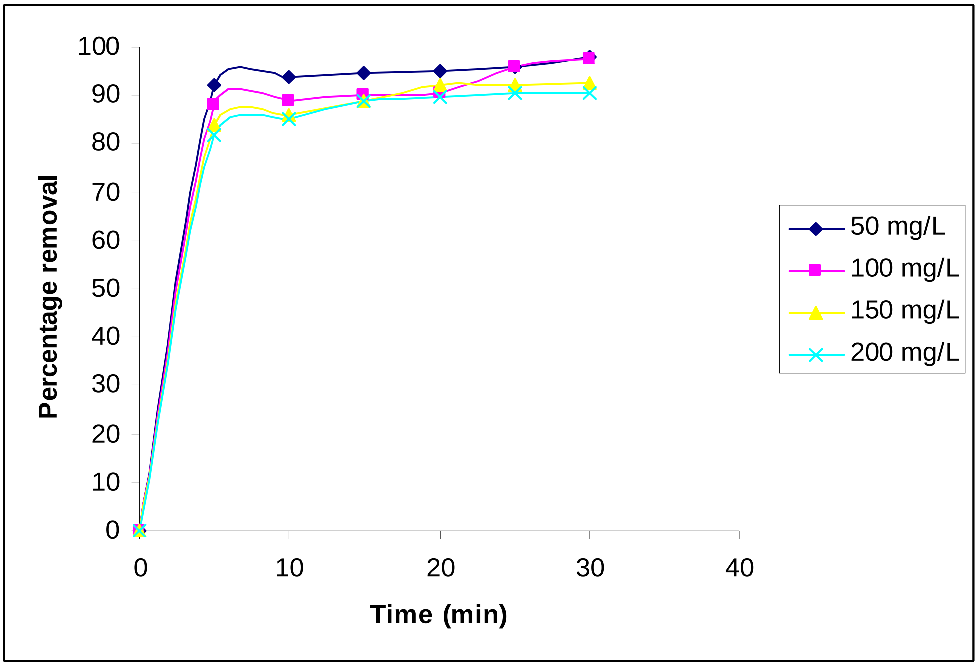

Figure 6.10: Percentage colour removal of RB5 at wavelength 595 nm at varying concentration of RB5 and other parameters were fixed.

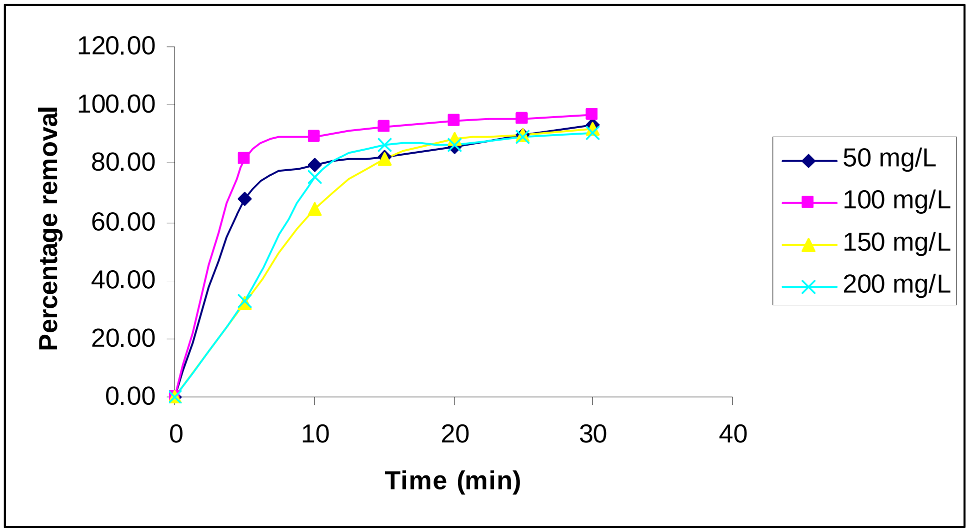

Figure 6.11: Percentage degradation of RB5 at wavelength 310 nm at varying concentration of RB5 and other parameters were fixed.

6.5.5 Comparison between UV/Dye, UV/dye/Fe^{+2} and UV/dye/H_2O_2:

To study the effect of individual parameters, preliminary studies have been done to observe the effect on the degradation and decolourization efficiency of RB5. . Figs 6.12,6.13, 6.14and 6.15 show the results of all the experiments UV/Dye, UV/dye/Fe^{+2} and UV/dye/H_2O_2. All other parameters i.e. concentration of dye, H_2O_2, Fe^{+2} and pH were same as optimized in the studies above. Different experiments were performed having reaction time 240 minutes except for UV/dye/H_2O_2 having reaction time 45 min and maximum degradation and decolourization were observed in UV/dye/H_2O_2 at pH=4 within 60 mins.

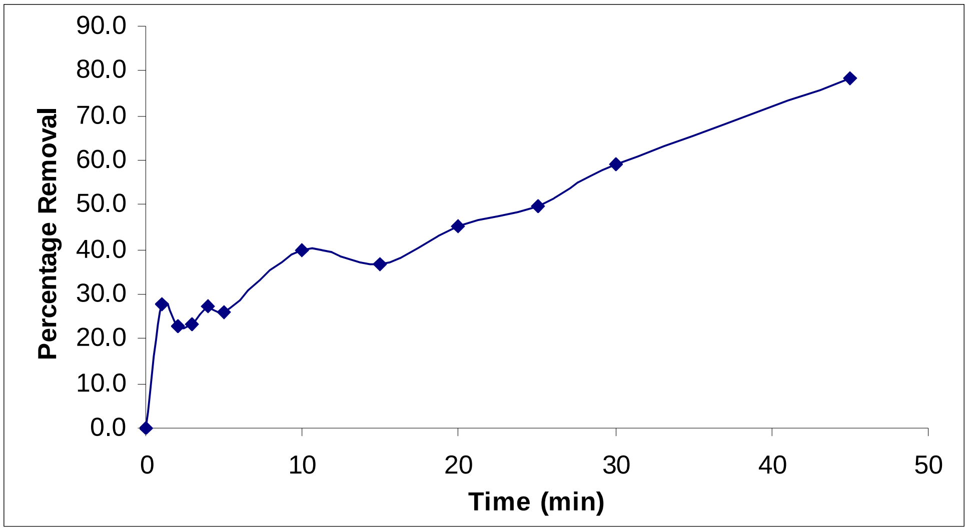

Figure 6.12: Percentage colour removal of RB5 at wavelength 595 nm in the presence of H_2O_2 and UV only.

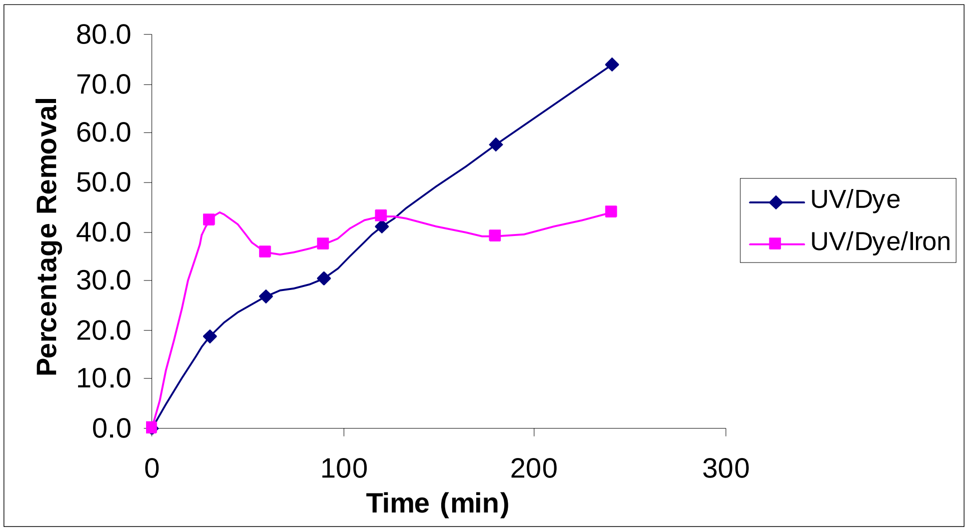

Figure 6.13: Percentage colour removal of RB5 at wavelength 595 nm in the presence of Fe^{+2}/UVand UV/Dye

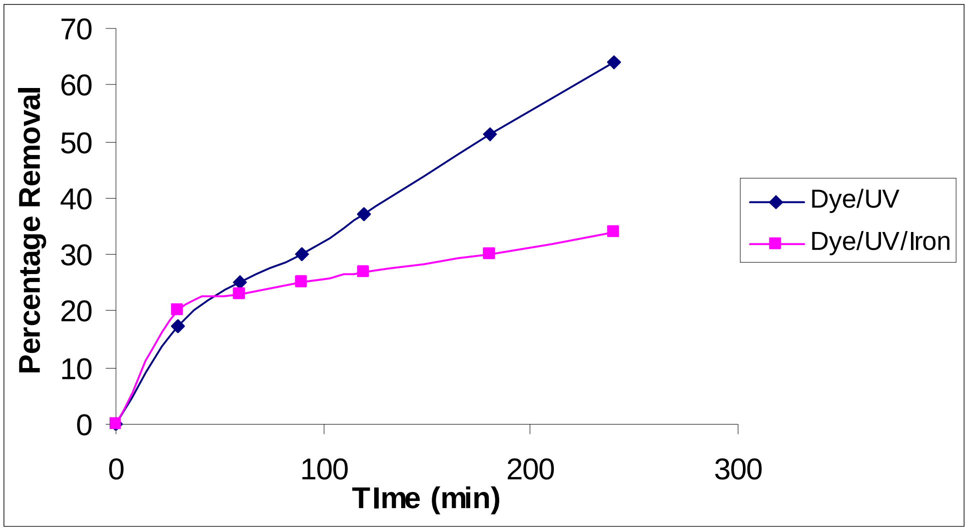

Figure 6.14: Percentage degradation of RB5 at wavelength 310 nm in the presence of Fe^{+2}/UVand UV/Dye

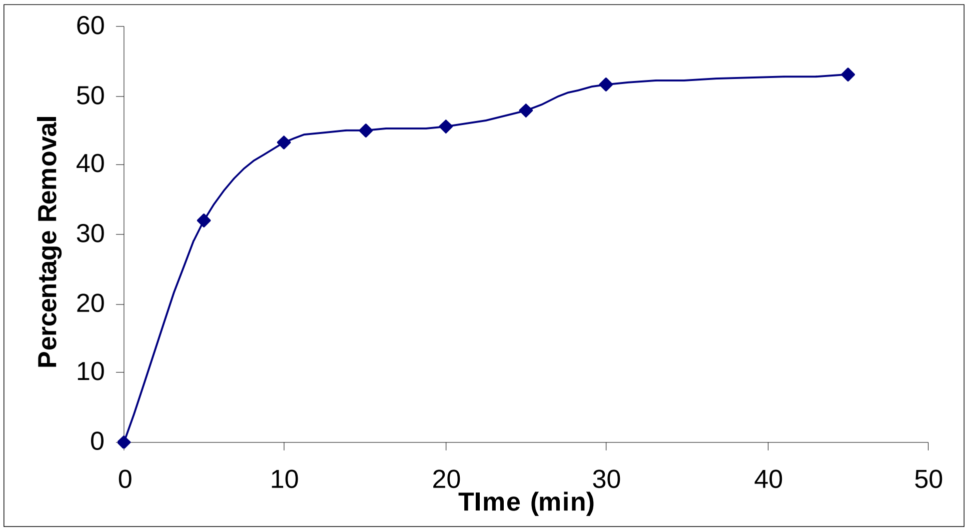

Figure 6.15: Percentage degradation of RB5 at wavelength 310 nm in the presence of H_2O_2 and UV only

6.5.6 UV-*vis* spectra analysis: To study the decolorization and degradation of RB5, UV-visible absorption spectra of 100 mg/L RB5 solution were considered before and after the treatment with photo- Fenton process where H_2O_2 4.4 mM, $FeSO_4$ 0.15 mM and pH 4 were used as observed in Fig. 6.16. Initially UV visible spectra of RB5 solution consist of two absorption band one in visible range and another in UV range. UV band having two adjacent rings while visible band ows to long conjugated п system linked by two azo groups **(Silverstein R.M.C. et al., 1991)**. Basic principle behind UV-vis absorption is that molecule of RB5 in the solution containing π electrons or non bonding electrons can absorb the energy in the form of UV or visible light to excite these electrons to higher anti-bonding molecular orbitals. More easily excited electrons, longer the wavelength of light it can absorb. Therefore, it was clearly observed from the figure that absorption peak in visible range vanish faster than that of UV range or photo fenton process partially degrade the dye solution or completely decolorize the dye solution.

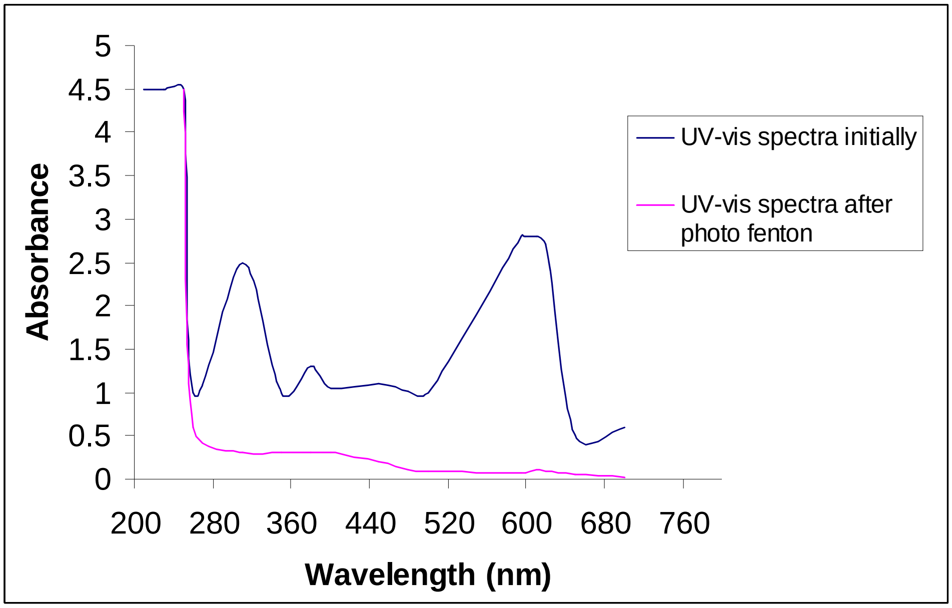

Figure 6.16: UV-vis spectra of RB5 solution before and after photo fenton degradation

6.6 ULTRA SOUND STUDIES

6.6.1 Comparison between US/Dye, US/dye/Fe^{+2} and US/dye/H_2O_2: Preliminary studies have been done to observe the effect of individual parameters on the degradation and decolourization efficiency of RB5 . Figs 6.17 and 6.18 show the result of all the experiments US/Dye, US/dye/Fe^{+2} and US/dye/H_2O_2. All the parameters i.e. concentration of dye, H_2O_2, Fe^{+2} and pH were same as optimized in photo fenton process. Sonication is used to speed dissolution, by breaking intermolecular interaction in RB5 solution. This occurs because sonication induces acoustic cavitation **(Suslick K. S. and Flannigan D. J., 2008)**; the formation, growth and collapse of bubbles in a RB5 solution having concentration 100 mg/L. Different experiments were performed having reaction time 240 minutes and maximum degradation and decolourization were observed in US/dye/H_2O_2 at pH=4.

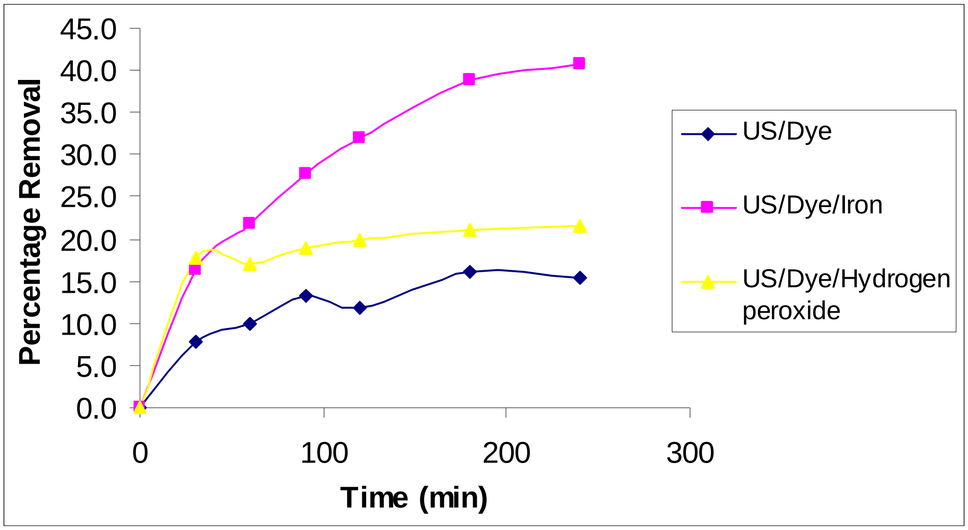

Figure 6.17: Percentage colour removal of RB5 at wavelength 595 nm in the presence of Fe^{+2}/US, US/Dye and US/Dye/H_2O_2

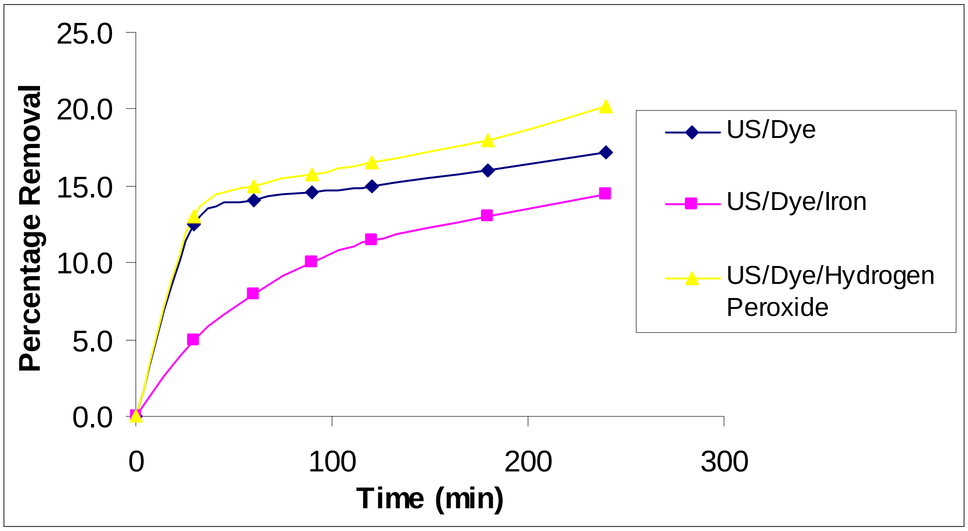

Figure 6.18: Percentage degradation of RB5 at wavelength 310 nm in the presence of US/ Fe^{+2}/UV, US/Dye and US/Dye/H_2O_2

6.6.2 Comparison between Sono fenton, Dark Fenton, Photo Fenton and Sono photo fenton

The ultrasonic wave influences the photo fenton and fenton process by increase the efficiency of degradation but decolourization was not much affected in the presence of sonication. Work on photo fenton, sono fenton and dark fenton easily appears in many literatures but sono photo fenton combination appears rarely in literatures, being ultrasound studies with photocatalysis is common. All the experiments except sono photo fenton were carried out under same optimum condition as discussed in earlier studies. In case of sono photo fenton, dosage of H_2O_2 was 2.2 mM or just half of photo fenton dosage because in sono photo fenton scavenging of OH* radicals occurs by hydrogen peroxide as explained in equation "6 and 7" **(where) (Fernandez J. et al., 1999)**. Fig 6.19 and 6.20 show the variation of H_2O_2 in the range of 1.8 mM to 3.5 mM at fixed Fe^{+2}, dye concentration and pH as discussed earlier. Maximum degradation and decolourization appears at 2.2 mM, so this can be used as optimum dose of H_2O_2 in case of sono photo fenton. Reaction time for sono photo fenton was 20 minute. Fig 6.21 and 6.22 shows the comparison between sono fenton and dark fenton while Fig 6.23 and 6.24 shows the comparison between photo fenton and sono photo fenton. From the results, it can be concluded that sonication increases the degradation efficiency over photo fenton and dark fenton.

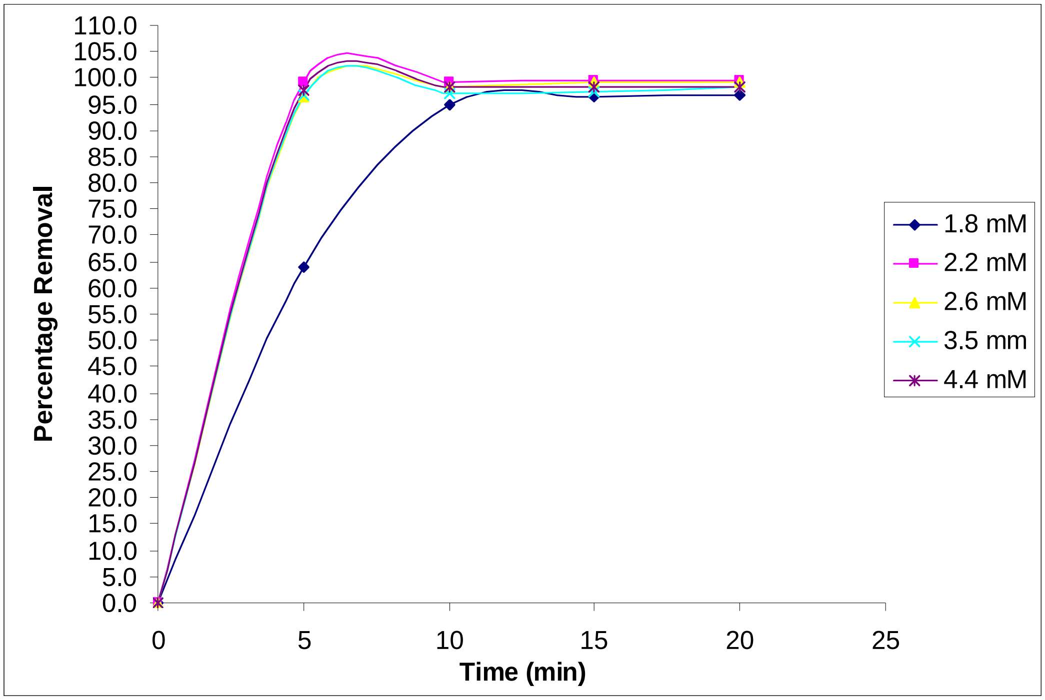

Figure 6.19: Percentage colour removal of RB5 by Sono photo fenton at varying concentration of H_2O_2 at wavelength 595 nm.

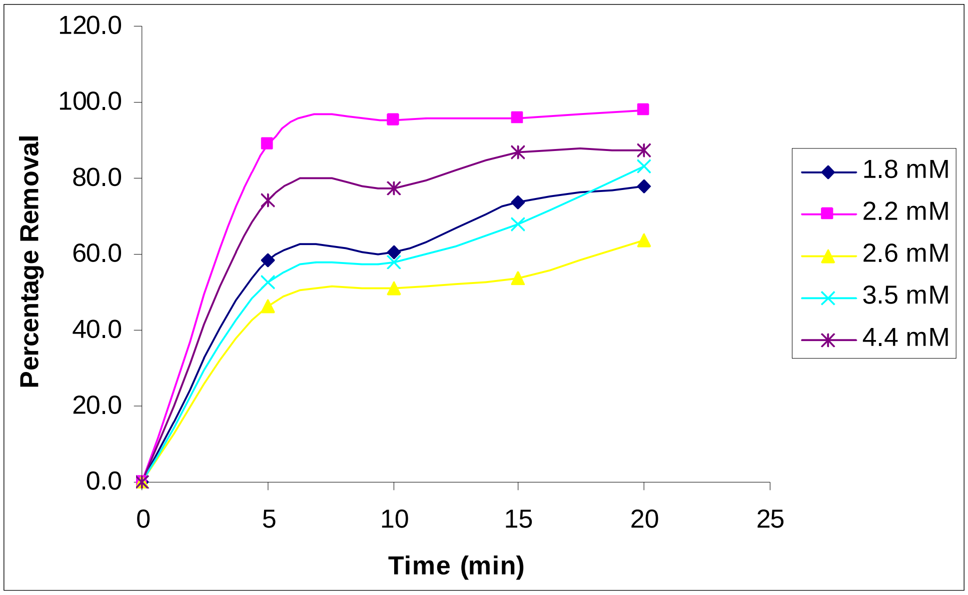

Figure 6.20: Percentage degradation of RB5 by sono photo fenton at varying concentration of H_2O_2 at wavelength 310 nm.

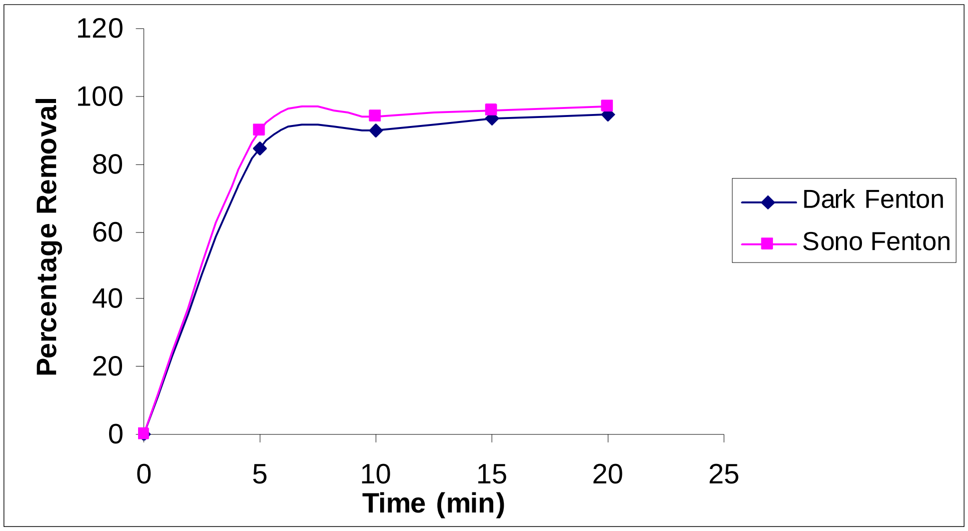

Figure 6.21: Percentage colour removal of RB5 by dark fenton and Sono fenton at wavelength 595 nm.

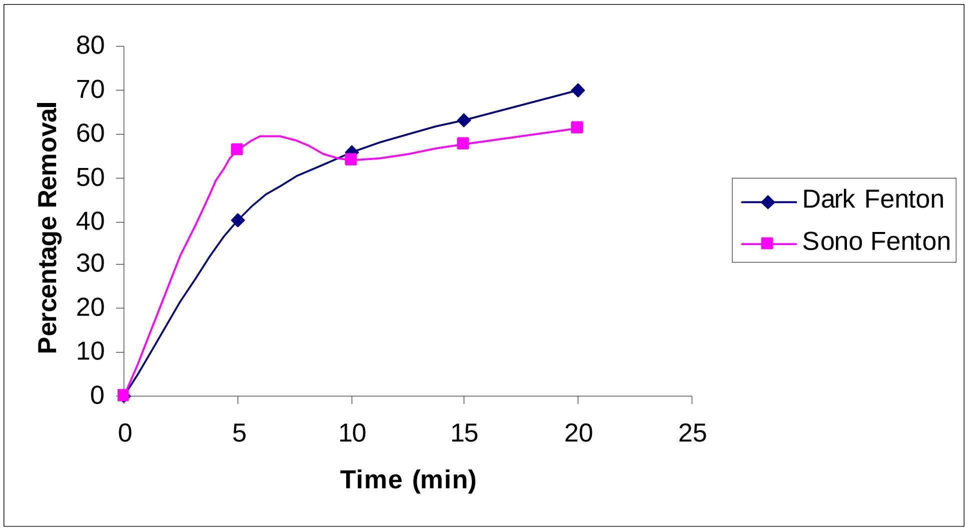

Figure 6.22: Percentage degradation of RB5 by dark fenton and sono fenton at wavelength 310 nm.

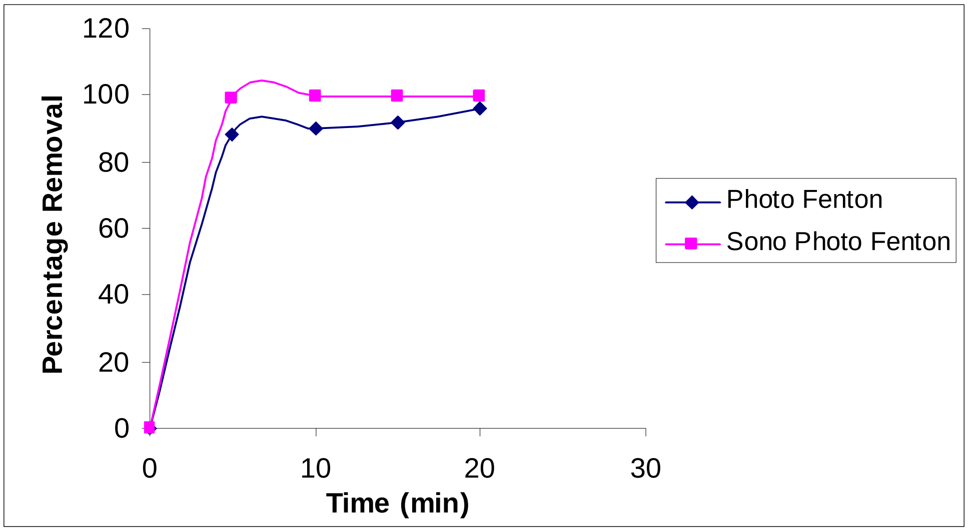

Figure 6.23: Percentage colour removal of RB5 by photo fenton and sono photo fenton at wavelength 595 nm.

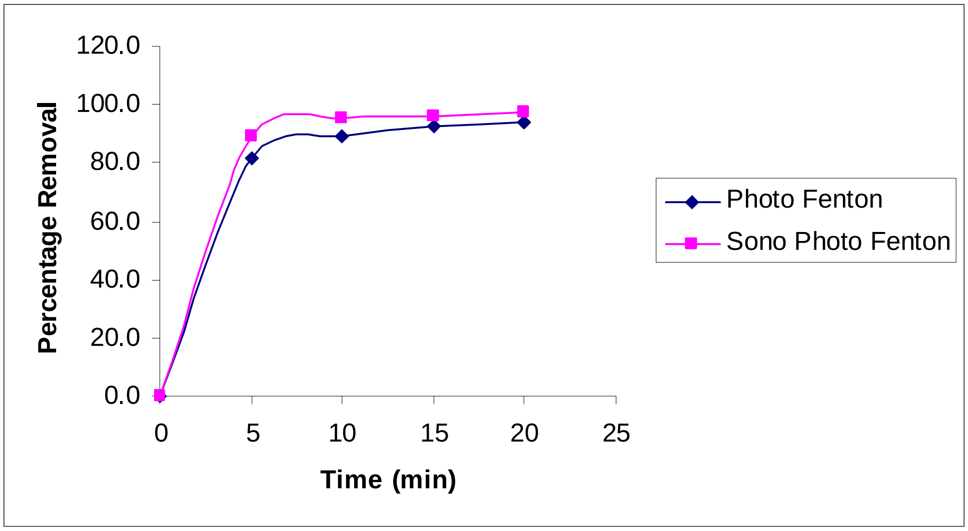

Figure 6.24: Percentage degradation of RB5 by photo fenton and sono photo fenton at wavelength 310 nm.

6.6.3 Sequential Sono fenton and Photo fenton processes

To the best of our knowledge, the combination of simultaneously and sequentially combined US and UV fenton processes has not yet been deeply addressed in literature. Moreover, sequentially coupled sono and photo fenton systems for the degradation of RB5 has not been previously reported. Hence, this new processes encouragingly provides a viable alternative to existing oxidation technologies. The coupling system was sequentially combined, applying firstly 10 min of UV–visible light followed by 10 min of ultrasound (denoted as UV→US) and vice versa (US→UV). Results of RB5 decolourization and degradation by sequential combination systems are shown in Fig 6.25 and 6.26. Maximum degradation and decolourization were observed in UV→US process as compared to US→UV process because the photo-fenton process alone provides a better activity, the beneficial effects due to sonication make the performance of ultimate photo-fenton process even more active. On the contrary, when photo-Fenton was applied during the first 10 min of reaction (UV→US), the homogeneous catalyst $FeSO_4$ was more vigorous than in the later system, and the benefits induced by ultrasound cannot be used by the photo-Fenton reaction, so giving a better performance than US→UV combination process while in case of US→UV process; the ultrasonic irradiation reduce the effect of homogeneous catalysts $FeSO_4$, leading to increased surface areas that would promote a higher amount of available active sites and decreases the degradation and decolourization efficiency.

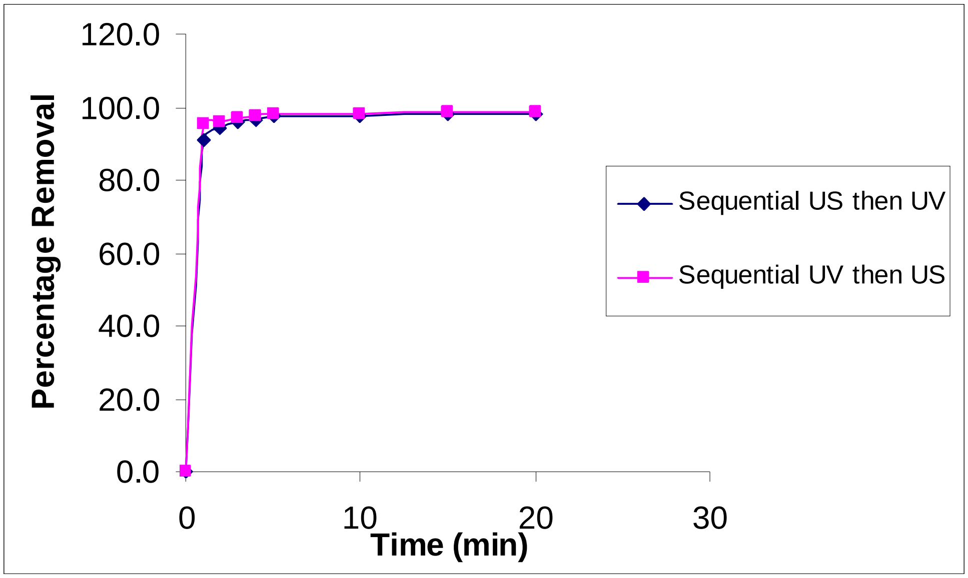

Figure 6.25: Percentage colour removal of RB5 by Sequential sono photo fenton at wavelength 595 nm.

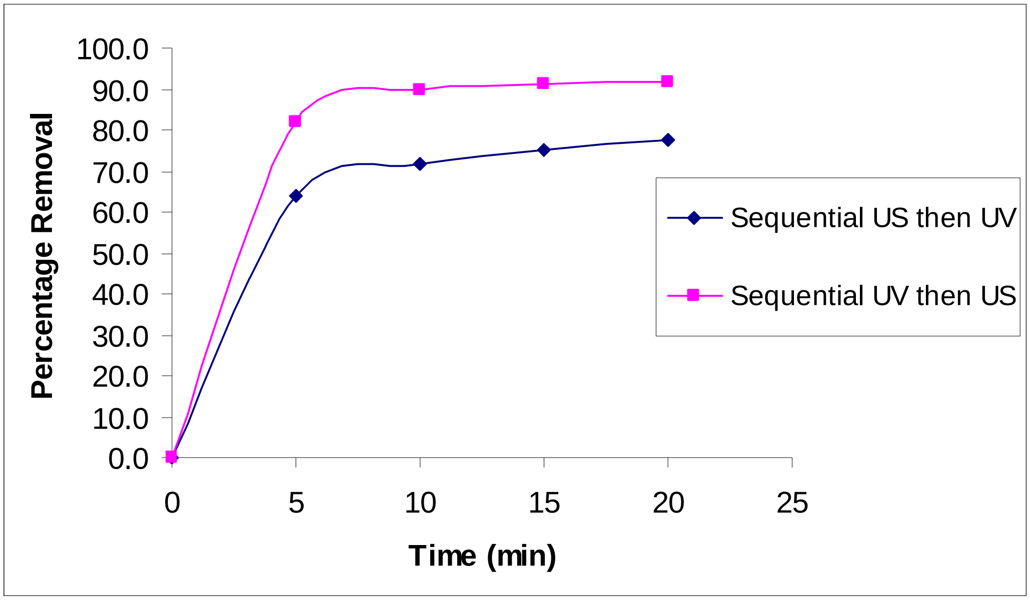

Figure 6.26: Percentage degradation of RB5 by Sequential sono photo fenton at wavelength 310 nm.

6.6.4 Absorbance spectra after Sono photo fenton:

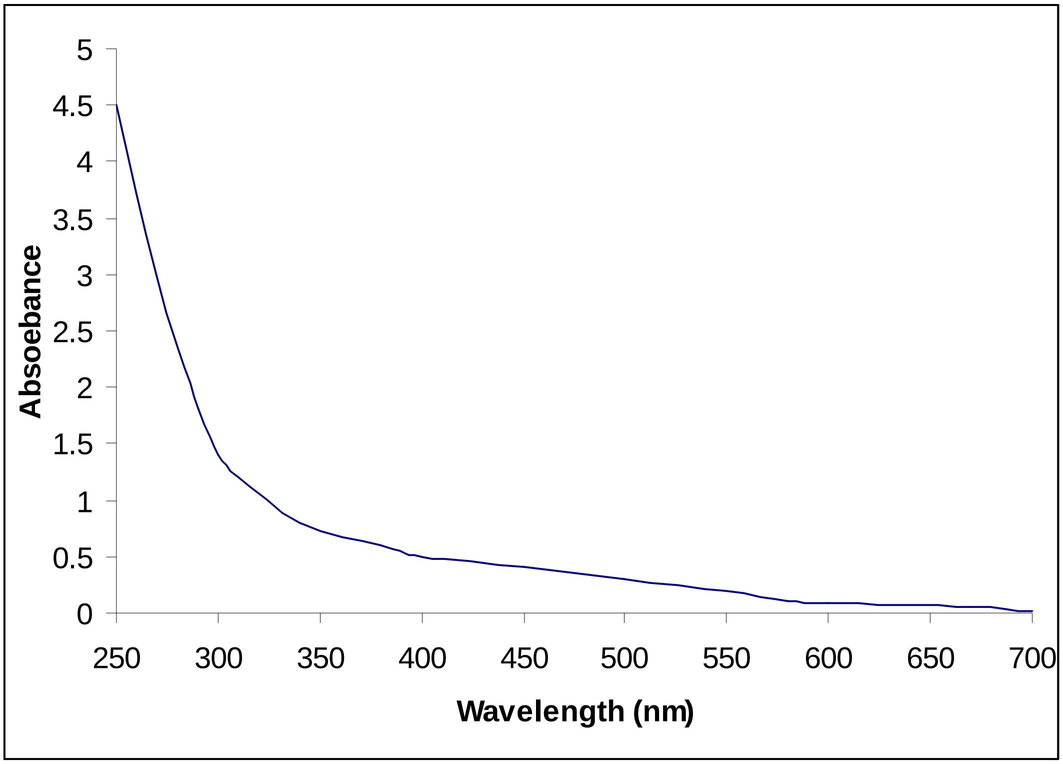

Figure 6.27: Absorption spectra of RB5 solution after sono photo fenton treatment

The primary absorption peaks of the RB5 solution were at 310 nm and 595 nm. As the reaction proceeds, the peaks disappear gradually as shown in Fig 6.27 and the full scanning spectrum pattern changes obviously after 20 min. At the end of the 20 min of reaction time, there is no evident peak observed. It proves that compound is fully decomposed under UV + US + Fe^{+2} + H_2O_2 system.

CHAPTER – 7

CONCLUSION

Sono Photo Fenton processes are eco-friendly way to degrade and decolourize the dye containing wastewater. This process has proved its superiority to other conventional methods of wastewater treatments. These processes differ from the other treatments processes because dyes are degraded rather than concentrated or transferred into a different phase. So this is one of the best techniques, for the treatment of various types of dyes.

This is a homogeneous process using ultrasound technique with UV-visible light in the presence of H_2O_2/Fe^{2+} catalyst.

The effective degradation of sequential sono–photo-Fenton process seem to be related to the benefits of ultrasound for the partial degradation of many pollutants towards further oxidized by-products along with the fragmentation of catalyst to finer particles that produces more activity in photo-Fenton systems. Besides, a simplified energy cost assessment indicated that the sequential US → UV process also shows the best cost-effective ratio for mineralization of organic compounds. Accordingly, this system can be considered as a promising and effective alternative for the destruction of dyes present in aqueous streams.

Sono Photo Fenton process is the most suitable method than Dark Fenton and Photo-Fenton, to achieve the effective results and can be suitable for the degradation of dye/colour containing wastewater with little or more retention time.

The results show that the degradation of RB5 after 20 min reaction time follows the decreasing order: $US/UV/Fe^{2+}/H_2O_2 > UV/Fe^{2+}/H_2O_2 > US/Fe^{2+}/H_2O_2 > UV \rightarrow US/Fe^{2+}/H_2O_2 > US \rightarrow UV/ Fe^{2+}/ H_2O_2 > dark/ Fe^{2+}/ H_2O_2$. While the colour removal rate of RB5 after 20 mins reaction time follows the different order i.e. $US/UV/Fe^{2+}/H_2O_2 = UV/Fe^{2+}/H_2O_2 > US/ Fe^{2+}/ H_2O_2 = UV \rightarrow US/Fe^{2+}/H_2O_2 = US \rightarrow UV/ Fe^{2+}/ H_2O_2 = dark/ Fe^{2+}/ H_2O_2$.

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