DEGRADATION STUDIES OF REACTIVE BLACK 5 AND TEXTILE INDUSTRY WASTEWATER BY COMBINED PHOTO-FENTON AND BIOLOGICAL OXIDATION

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DECLARATION & CERTIFICATE

I hereby declare that the work embodied in thesis entitled **"Degradation Studies Of Reactive Black 5 and Textile industry wastewater by combined photo-Fenton and Biological oxidation"** for the award of degree of Master of Technology (EST) submitted in the **School of Energy And Environment**, Thapar University, Patiala on July 2013, is a record of the work carried out by me under the guidance of **Mr. Anoop Verma** Assistant Professor, School of Energy and Environment. 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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It is certified that the above statement made by the student is correct to the best of my knowledge and belief.

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ABSTRACT

In the present study, the photo-Fenton process was used for the pretreatment of Reactive Black 5 dye and industrial textile wastewater with the objective of improving its overall biodegradability and determining the degree of increased oxidation followed by biological process. Some parameters, like pH, temperature, initial concentrations of Fe^{2+} and H_2O_2 and the use of natural or artificial light were evaluated aiming to find the optimal conditions to promote the efficient degradation of the dyes. The experimental results showed that the photo-Fenton process run under solar light was the most effective. The degradation observed is 91% with optimal conditions of pH=4, H_2O_2=4.4 mM and Fe^{2+} =0.15 Mm with 90 mins Process under UV light alone for photo-Fenton process. The optimal time to stop the pretreatment process and introduce the effluent to the biological system was 20 min. The biodegradability of the process was checked by BOD_5/COD ratio. Results obtained from this work indicated that the photo-Fenton process could be a suitable pretreatment method in reducing toxicity of pollutants and enhancing biodegradability of textile wastewaters treated in a coupled photochemical–biological system.

KEYWORDS: Textile wastewater treatment, Photo Fenton's process; Solar photo Fenton, photochemical-biological, coupled reaction.

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CHAPTER 1

1. INTRODUCTION

One of the major threats to water quality is chemical pollution from heavy metals, solvents, dyes, pesticides, etc. Chemicals enter the aquatic medium in several different ways, either dumped directly, such as industrial effluents, or from wastewater treatment plants (WWTP) that do not fulfill their obligations. They may also enter the water indirectly through the use of plant health products, such as biocides and fertilizers, in agriculture. In general, very water-soluble substances can be transported and distributed more easily in the water cycle. Discharge resulting from lax enforcement of the rules, illegal use and inappropriate application of substances may be considerable **Oller I. et al., (2011).**

Out of these, Textile mills are major consumers of water and one of the largest sectors causing intense water pollution. The impact of textile effluents on aquatic medium has been traditionally of great concern, because they contain a large variety of raw materials and reagents: synthetic dyes, pigments, biocides, oils, heavy metals, salts, nutrients and organic compounds. Consequently, these effluents are characterized by high values of chemical oxygen demand (COD), temperature, colour, changeable pH, suspended solids and organic chlorine compounds **Blanco J. et al., (2012).** Textile industry generates highly polluting wastewater and due to high Total Dissolved Solids (TDS), presence of toxic heavy metals and non biodegradable nature of the dye stuffs present in the effluent, their treatment is a very serious problem. Many operations of textile processes are water intensive in textile production. Therefore, a purification treatment to recycle water must have much better performances than for simple discharge according to the limits imposed by legislation. There are many processes available for the removal of dyes by conventional treatment technologies including biological and chemical oxidation, coagulation and adsorption but they cannot be effectively used individually. For example, the coagulation process effectively decolorized insoluble dyes, such as disperse dyes, but does not work well for soluble dyes. The activated carbon absorbent is not suitable for insoluble dyes and the biological process does not effectively decolorize because most dyes are toxic to organisms used in the process. Most of the dye molecules are complex, particularly reactive azo dyes which cause special environmental concern due to their degradation products, such as aromatic amines which

are highly carcinogenic. The use of a variety of dyes and auxiliary chemicals result in the discharge of toxic waste into natural water bodies. More than 8000 chemically different types of dyes are currently manufactured and the biggest consumers of these dyes are the textile industries **Venkatesh S. et al., (1994)**

Textile industry is probably the most potential contributor as far as color pollution is concerned. Among the above, dyes are difficult to be decolorized due to their complex structure, synthetic origin and recalcitrant nature, which makes it mandatory to remove them from industrial effluent before being disposed into hydrological system. Another problem is the disposal of large volumes of effluents which abides by environmental standards. These are generally not agreeable to conventional biological, physical and chemical treatment processes due to their recalcitrant and complex nature **Arslan I. and Balcioglu I. A. (1999).** These dyes are difficult to breakdown biologically and cannot be treated efficiently by only conventional methods using aerobic or anaerobic processes, especially acid and reactive dye treatment has been most problematic, as they tend to pass through conventional treatment system unaffected. Advanced oxidation processes (O_3, O_3/H_2O_2, O_3/UV, UV/H_2O_2, $O_3/UV/H_2O_2$ and Fe^{2+}/H_2O_2) for the degradation of non biodegradable organic contaminants in industrial effluents are attractive alternatives to conventional treatment methods. AOPs include hydrogen peroxide (H_2O_2), ozone (O_3) and UV irradiations, which have proved to be much efficient treatment processes **Lidia S. et al., (2001)**. AOPs based on the generation of very reactive and oxidizing free radicals have been used with increasing interest due to their high oxidant power.

The main routes for destroying toxic compounds in natural water are biodegradation and photo degradation. Photo degradation, which is an important mechanism for degrading aromatic hydrocarbons, chlorinated aromatic hydrocarbons, chlorinated phenols, and many pesticides, may be by direct or indirect photolysis. In photolysis, a photo sensitizer absorbs the light and transfers the energy to the pollutants, which otherwise would not react photo chemically, since they do not absorb light in the wavelength interval of the solar photons that arrive on the Earth's surface. The most important photo sensitizers in natural water are nitrate and a type of compound known generically as humic acids. Biological degradation of a chemical refers to the elimination of the pollutant by the metabolic activity of living organisms, usually microorganisms and in particular bacteria and fungi that live in natural water and soil. In this context, conventional

biological processes do not always provide satisfactory results, especially for industrial wastewater treatment, since many of the organic substances produced by the chemical industry are toxic or resistant to biological treatment **Steber J. and Wierich P. (1986).** Therefore, the only feasible option for such biologically persistent wastewater is the use of advanced technologies based on chemical oxidation, such as the Advanced Oxidation Processes (AOPs), widely recognized as highly efficient treatments for recalcitrant wastewater. These processes degrade organic pollutants by forming hydroxyl radicals which are highly reactive and non-selective **Gogate P. R. and Pandit A. B. (2004).**

Chemical oxidation for complete mineralization is generally expensive because the oxidation intermediates formed during treatment tend to be more and more resistant to their complete chemical degradation, and furthermore, they all consume energy (radiation, ozone, etc.) and chemical reagents (catalysts and oxidizers) which increase with treatment time **Munoz I. et al., (2005)**. One attractive potential alternative is to apply these chemical oxidation processes in a pre-treatment to convert the initially persistent organic compounds into more biodegradable intermediates, which would then be treated in a biological oxidation process with a considerably lower cost. Therefore, the main role of the chemical pre-treatment is partial oxidation of the biologically persistent part to produce biodegradable reaction intermediates. The percentage of mineralization should be minimal during the pre-treatment stage in order to avoid unnecessary expenditure of chemicals and energy, thereby lowering the operating cost. This is important because electricity represents about 60% of the total operating cost of photo catalytic reactors **Bandara J. et al., (1997)** and investment costs for biological processes range from 5 to 20 times less than chemical ones such as ozone or hydrogen peroxide, while treatment cost range from 3 to 10 times less **Scott J. and Ollis D. (1996)**. However, if the pre-treatment time is too short, the reaction intermediates generated could still be structurally very similar to the original non-biodegradable and/or toxic component.

In the present work, the remediation of a real textile wastewater was carried out by means of combined processes: photo Fenton as a pre-treatment to Biological process. The effect of the key variables in the photo Fenton process ($[Fe^{2+}]$, $[H_2O_2]$ and pH) has been studied, as well as a comparison between the former and the combined process in terms of remediation effectiveness, considering the alternative of water reuse in the same textile process.

CHAPTER 2

2. OBJECTIVES OF PRESENT STUDY

Main objective of study is to treat the recalcitrant dye RB5 and real industry wastewater using homogeneous photo Fenton treatment. To increase the efficiency of degradation, photo Fenton was combined with biological.

Combining these two processes i.e., photo Fenton and biological eliminates the drawbacks of individual process and optimizes the process cost. 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 RB5 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.
- To study the degradation of real textile effluent using photo Fenton process.
- To study the degradation of real textile effluent using coupled photo Fenton and biological process.

CHAPTER 3

3. REVIEW OF LITERATURE

3.1Advanced Oxidation Processes (AOP's): -

(AOPs) were defined by **Glaze W. H. et al., (1987)** as near ambient temperature and pressure water treatment processes which involve the generation of highly reactive radicals (specially hydroxyl radicals) in sufficient quantity to effect water purification. These processes are characterized that no more toxic compound can be produced during the reaction. Also via AOP's complete organic matter mineralization could be achieved. Hydroxyl radical is specially oxidation agents that attack the majority of organic matters. The kinetic of these reactions is first order for ($^{\bullet}OH$) radical concentration, and to the species to be oxidize. The hydroxyl radical characterized by its low selectivity, but it is attractive oxidant that can be used in the wastewater treatment. Several organic compounds can be eliminated or degraded immediately by use of hydroxyl radical. However, some organic are not attacked by this action like the acetic acid, oxalic acid, chloride derivatives as chloroform and tetrachloroethane.

The variety on AOP´s comes from the fact that there are many ways for hydroxyl radical production, this permit fulfillment for the requirements of any treatment. The oxidation potential of the hydrogen peroxide and ozone has been reported to be 1.77V and 2.07V, respectively while the oxidation potential for the hydroxyl radicals is approximately 2.8V. Using H_2O_2, the production of hydroxyl radicals is enhanced by the presence and action of ferrous ion (Fe^{2+}), as a catalyst **Burbano A. et al., (2003**). In this case, hydrogen peroxide is decomposed to hydroxyl radical and hydroxyl ion, while ferrous ion (Fe^{2+}) is transformed into ferric ion (Fe^{3+}). This reaction is known as Fenton's reaction:

$$H_2O_2 + Fe^{2+} \rightarrow Fe^{3+} + {}^{\bullet}OH + OH^{-}$$

The Fenton's reaction takes place in pH values ranging between 3 and 3.5. In these pH values, the formation of the free hydroxyl radicals is activated. As a result, ferrous iron is consumed quickly and reproduced slowly.

The photo-Fenton process, as its name suggests, is rather similar to the Fenton one, but employing also radiation. Its effectiveness is attributed to the photolysis of Fe (III) cations in acidic media yielding Fe (II) cations, in conjunction with reaction between Fe (II) and H_2O_2 to yield hydroxyl radicals.

Besides Fe, other transition metals can also catalyze the reactions involved in the process, e.g. copper. In fact, the reaction system using Cu as the photo-Fenton catalyst follows a similar network as that of Fe and is referred to as a photo-Fenton like reaction.

3.2 Dyes

3.2.1 Utilization

Dyes constitute a group of organic substances that are used in different colour processes; azoic dyes are the largest chemical class of dyes used regularly for textile and paper printing dyeing **Vandevivere P. C. et al., (1998)**. Since they are persistent and highly soluble in water, reactive dyes are the most important groups in cellulose dyeing (cotton, polyesters). Other dyes with different characteristic are used for other type of applications; Acid dyes are commonly used in dying polyamide fibers (Nylanthrene dyes are ideally suited to polyamide 6 or 6.6. dyeing).

3.2.2 Environmental considerations of dye pollution

Dyes are introduced into the environment as a result of several man-made activities. Nowadays, there are more than 5000 commercial dye products, most of these dyes used in textile industry. Thus, this industry is considered as one of the major resource of highly polluted wastewater. Fixation rate of a specific dye may vary according to functional groups used to fabricate such a kind of dye. In general more than 40% of initial dye mass remains in the dye bath, and hence its wastewater highly contaminated **Galindo C. et al., (2001).** Modern commercial dyes are very stabile in water solution and they contain high composition ratio of aromatic rings. Thus, it was believed that these dye molecules are non-biodegradable and some of them are toxic to bacteria. Some studies using activated sludge suggest that bio-transformation is slow for water-soluble dyes **Yoo E. S. et al., (2002).** Reactive dyes have been reported to go through the biological treatment systems without being removed **Hu C.** and **Wang Y. (1999)**. Thus, Fenton processes are good alternatives for pre treatment of these reactive dyes and following examples provide the evidences for the same.

3.3 Fenton's process

Papadopoulos A. E. et al., (2007) had examined the effectiveness of the chemical oxidation using Fenton's reagent (H_2O_2/Fe^{2+}) for the reduction of the organic content of wastewater generated from a textile industry has been studied. 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%. In addition, the alterations observed in the organic matter during the development of the process, as indicated by the ratios of COD/TOC and BOD/COD and the oxidation state, show that a great part of the organic substances, which are not completely mineralized, are subjected to structural changes to intermediate organic by-products.

Xu X. R. et al., (2004) studied the degradation of 20 different dyes in aqueous solutions by the Fenton process. These dyes include 6 types: acidic, reactive, direct, cationic, disperse and vat dyes. The former four types of dyes were decolorized and their TOC values were decreased greatly, while the color and TOC removals of the latter two types were lower. The catalytic activities of four metal ions on the degradation efficiencies of Vat Blue BO, which was chosen as a model dye because of its lowest color and TOC removals, were compared in the dark and under the ultraviolet light irradiation. The catalytic ability of different metals was $Fe^{2+} > Cu^{2+} > Mn^{2+} > Ag^{+}$ in the dark, and the same sequence was obtained under irradiation condition with greater degradation efficiency. Furthermore, the efficiencies of three oxidation processes, including H_2O_2/UV, Fe^{2+}/H_2O_2 and Fe^{2+}/H_2O_2/UV were compared. The results showed that the oxidation by Fe^{2+}/H_2O_2/UV was the strongest, and even greater than the arithmetic sum of the other two processes, which suggests the synergistic effect of ultraviolet and ferrous ions on the degradation reaction.

Sun J. H. et al., (2007) had investigated the degradation of an azo dye Amido black 10B in aqueous solution by Fenton oxidation process. The effects of different reaction parameters such as initial pH, the initial hydrogen peroxide concentration ($[H_2O_2]_0$), the initial ferrous concentration ($[Fe^{2+}]_0$), the initial Amido black 10B concentration ($[dye]_0$) and the temperature

on the oxidative degradation of Amido black 10B have been assessed. The optimal reacting conditions were experimentally determined and it was found to be initial pH = 3.50, $[H_2O_2]_0$ = 0.50 mM, $[Fe^{2+}]_0$ = 0.025 mM for $[dye]_0$ = 50 mg/L at temperature = 25 °C. Under optimal conditions, 99.25% degradation efficiency of dye in aqueous solution was achieved after 60 min of reaction. The UV–vis spectral changes of Amido black 10B in aqueous solution during Fenton treatment process were studied. It was easier to destruct the azo linkage (–N═N–) group than to destruct the aromatic rings of Amido black 10B by Fenton oxidation. The experimental results showed that the Fenton oxidation process was an effective process for the degradation of azo dye Amido black 10B at low H_2O_2 and Fe^{2+}concentrations.

Meric S. et al., (2004) studied the removal of Reactive Black 5 (RB5) from synthetic wastewater using Fenton's oxidation (FO) process. Experiments were conducted on the samples containing 100 and 200 mg l^{-1} of RB5 to remove the dye toxicity. Seventy-five milligram per litre of RB5 caused 25% toxicity on 24-h born daphnids whereas 100 mg l^{-1} of RB5 displayed 100% toxicity on *Daphnia magna*. The study was performed in a systematic approach searching optimum values of $FeSO_4$ and H_2O_2 concentrations, pH and temperature. Optimum pH and temperature for 100 mg l^{-1} of RB5 were observed as 3.0 and 40 °C, respectively, using 100 mg l^{-1} of $FeSO_4$ and 400 mg l^{-1} of H_2O_2 resulted in 71% chemical oxygen demand (COD) and 99% color removal. For 200 mg l^{-1} of RB5, 84% COD removal was obtained using 225 mg l^{-1} of $FeSO_4$ and 1000 mg l^{-1} of H_2O_2 yielding 0.05 molar ratio at pH 3.0 and 40 °C. Color removal was also more than 99%. The optimum conditions determined in accordance with the literature data. The H_2O_2 requirement seems to be related to initial COD of the sample. $FeSO_4/H_2O_2$ ratios found were not changed for both concentrations. The temperature affected the COD removal significantly at high degrees. Toxicity was completely removed for each concentration of RB5 at optimum removal conditions.

3.4 Photo Fenton

Nunez L. et al., (2006) had investigated 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), under Fenton's and photo-Fenton's conditions. Some parameters, like temperature, initial concentrations of Fe (II) and H_2O_2 and the use of natural or artificial light were evaluated aiming to find the optimal conditions to promote the efficient degradation of the dyes. The experimental

results showed that the Fenton's process run under solar light was the most effective. Pseudo-first order degradation rate constants were obtained from batch experimental data. It is suggested that Fenton's and photo-Fenton's type reactions are viable techniques for the treatment of such types of reactive dyes, according to the high levels of colour, aromatic content (UV_{254}) and DOC removal.

Montano J. G. et al., (2006) had done an environmental study using life cycle assessment (LCA) applied to three bench-scale wastewater treatments for Cibacron Red FN-R hetero-bireactive dye removal: artificial light photo-Fenton process, solar driven photo-Fenton process and artificial light photo-Fenton process coupled to a biological treatment. The study was focused on electricity and chemicals consumption, transports and atmosphere and water emissions generated by the different processes involved. Results show that the artificial light photo-Fenton process was the worst treatment in terms of environmental impact. On the other hand, both solar driven and coupled to biological photo-Fenton processes reduce significantly the environmental damage, although none can be identified as the best in all impact categories. The major environmental impact is attributed to the H_2O_2 consumption and to the electrical energy consumption to run the UVA lamp. An economic analysis of the different photo-Fenton processes has also been performed and the results are discussed together with those obtained from the environmental assessment.

Kang S. F. et al., (1999) described the use of photo-Fenton process (fig. 3.1) for color removal from textile wastewater stream. The wastewater sample to be treated was simulated by using colorless polyvinyl alcohol (PVA) and reactive dyestuff of R94H. As a result, the hydroxyl radical ($HO^{\cdot}$) oxidation can effectively remove color, but the chemical oxygen demand (COD) was removed in a slight degree. The color removal is markedly related with the amount of $HO^{\cdot}$ formed. The optimum pH for both the $OH^{\cdot}$ formation and color removal occurs at pH 3-5. Up to 96% of color can be removed within 30 min under the studied conditions. Due to the photo reduction of ferric ion into ferrous ion, color resurgence was observed after 30 min. The ferrous dosage and UV power affect the color removal in a positive way; however, the marginal benefit is less significant in the higher range of both. PVA as the major background COD of a textile wastewater stream inhibits the color removal insignificantly as its concentration increases.

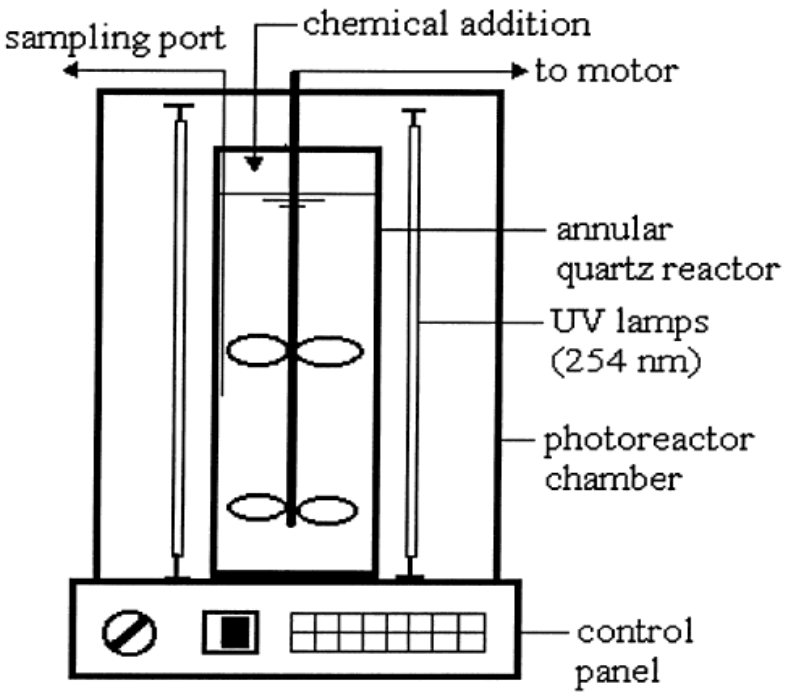


Fig.3.1: Experimental set up for photo-Fenton process for colour removal from textile wastewater

Lucas M. S. and Peres J. A. (2005) had studied the oxidative decolorization of Reactive Black 5 (RB5) in aqueous solution 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. Batch experiments were carried out to investigate the process's optimal operational conditions: pH, H_2O_2 dosage, Fe^{2+} dosage, RB5 concentration and optimal $[Fe^{2+}]_0/ [H_2O_2]_0/ [RB5]_0$ ratio, to obtain the best results at low cost, render AOP competitive with other processes. The optimal conditions found were a ratio $[H_2O_2]_0/ [RB5]_0$ of 4.9:1, a ratio $[H_2O_2]_0/ [Fe^{2+}]_0$ of 9.6:1 and pH=3.0. The decolourization 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, for optimal conditions. This small difference in dye decolourization 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 decolourization it is particularly important in dye mineralization.

Liu S. Q. et al., (2010) evaluated the Prussian blue (iron hexacyanoferrate) colloids as a heterogeneous photo-Fenton catalyst for the degradation of Rhodamine B. The emphasis is laid on the effects of alkali metal cations on the photo-Fenton process. The facts show that alkali cations strongly affect the degradation rate of organic species. The degradation rates of RhodamineB, Malachite Green, and Methyl Orange in the presence of KCl, KNO_3, andK_2SO_4, respectively, are faster than their degradation rates in the presence of the corresponding sodium salts. The average degradation rates of Rhodamine B in 0.2M KCl, NaCl, RbCl, and CsCl solution, decline in sequence, and the rate in KCl solution is greater than that without any salt added deliberately. Thus, potassium ions accelerate the degradation rate, but sodium, rubidium, and cesium ions slow the rate. The order of the rates is R_K> R >R_{Na}>R_{Rb}> R_{Cs}, which is consistent with that of the voltammetric oxidation currents of Prussian blue in the corresponding cation solutions. This phenomenon is attributed to the molecular recognition of the microstructure in Prussian blue nano particles to the alkali cations. The reaction mechanism of the photo-Fenton process has also been explored.

Punzi M. et al., (2012) had compared the efficiencies of homogeneous and heterogeneous photo Fenton oxidation for treatment of azo dye containing synthetic textile wastewater. The influence of parameters such as the presence of NaCl and starch was evaluated and optimal iron and H_2O_2 dosage determined. Complete decolorization of Remazol Red RR was achieved at all investigated NaCl and starch concentration. Mineralization, in terms of COD reduction, was 96% in the homogeneous and 93% in the heterogeneous reaction, but decreased with increasing NaCl and starch concentrations. The homogeneous oxidation showed the highest efficiency in treating synthetic wastewater containing Remazol Blue RR or a mixture of Remazol Red RR and Remazol Blue RR. Nevertheless, the mineralization was significantly lower than for Remazol Red RR, which shows the dependence on dye structure. Similar amounts of iron containing sludge were produced in the two processes, while the release of iron ions was reduced by 50% when using heterogeneous photo Fenton. Promising results were obtained when reusing the iron powder as catalyst; complete decolorization was achieved during 20 batches.

Simunovic M. et al., (2010) developed the mechanistic model describing the behavior of photo Fenton process treating the simulated industrial wastewater containing oxalates and formates. In Part I of the study, the optimal conditions for each of applied photo Fenton processes (UVC/Fe/H_2O_2 and UVA/Fe/H_2O_2) were determined and used in this study for model development and verification. The mechanistic model simulates the influence of various factors: the type of UV irradiation, the changes in concentrations of pollutants, catalysts and oxidant, on photo Fenton process performance. pH dependent equilibrium of ferrous, ferric, oxalate and formate species was simulated as well. The model was tested to evaluate its accuracy in predicting the system behavior at different pollutant concentrations. Good agreement of the data predicted by model and the empirically obtained values was confirmed by calculated standard deviation for each experimentally monitored parameter. The developed mechanistic model describing the behavior of photo Fenton process treating simulated wastewater can be characterized as interpretable, transparent, flexible and accurate. The comparison of electrical energy costs for each of the studied processes was performed. The obtained results indicate that the process using UVC source is more efficient and cheaper. However, the simulation of process effectiveness using the solar UVA irradiation recorded at annual basis for the location of proposed wastewater treatment plant speaks in the favor of solar UVA/Fe/H_2O_2 process application instead of artificial UV irradiation.

3.5 Solar Photo Fenton

Zapata A. et al., (2009) had evaluated the Photo-Fenton degradation of a mixture of commercial pesticides typically used in greenhouse agriculture, Vydate1 (10% oxamyl), Metomur (20% methomyl), Couraze (20% imidacloprid), Ditimur-40 (40% dimethoate) and Scala (40% pyrimethanil). The experiments were performed at an original dissolved organic carbon of 200 mg/L (40 mg/L of each commercial pesticide). A battery of degradation studies was carried out under sunlight at the Plataforma Solar de Almeria in a pilot plant specially developed for photo-Fenton applications. Photo-Fenton efficiency gradually rose with temperature. Nevertheless, at 50 °C there was a decrease in efficiency. The influence of Cl^- and SO_4^{2-} between 100 and 2000 and 50 and 500 mg/L, respectively, was also analyzed. A central composite experimental design and its surface response analysis were employed to study the effect of these anions.

Lapertot M. et al., (2006) presented the photo-Fenton treatment in a solar pilot-plant scale of several EU priority hazardous substances (Alachlor, Atrazine, Chlorfenvinphos, Diuron and Isoproturon) dissolved in water. The results have been evaluated not only from the point of view of contaminant disappearance and mineralization, but also of toxicity reduction and enhancement of biodegradability. Degradation was monitored by total organic carbon, pesticide concentration by HPLC–UV, inorganics released by ion chromatography, and biodegradability by the Zahn–Wellens (Z–W) test. The total volume of the solar photoreactor, composed of compound parabolic collectors with a total area of 4.16m^2, was between 70 and 82 L. The treatment was shown to be effective, mineralizing all of the pesticides tested, both alone and in mixtures. In order to find out the conditions for biocompatibility using the photo-Fenton reaction as a pre-treatment step, wastewater inoculated with unacclimated municipal sludge containing pesticides after certain degradation time was evaluated by the Z–W test. Biodegradability was enhanced (70% considered biodegradable) by the photo-Fenton treatment after 12–25 min. It may be concluded that the photo-Fenton treatment consistently enhances biodegradability of wastewater containing pesticides.

Xu X. R. et al., (2007) treated the bleaching wastewater effluent from a pulp and paper mill (located in Tianjin, China) with solar photo-Fenton process in a lab-scale reactor (22 cm×15 cm thermostatic dish). The mill used wastepaper as raw material and the effluent contained 332 mg L^{-1} of total organic carbon (TOC) and 1286 mg L^{-1} of COD. The treatment involved a constant intensity of irradiation (0.2 kW/m^2) with a solar simulator of 250 W xenon lamp and various conditions of pH, temperature, and initial concentrations of H_2O_2 and Fe (II). The better treatment conditions were searched for in the ranges of initial Fe(II) concentration from 31 to 310 mg L^{-1} (initial pH 3.0, 30°C), initial H_2O_2 concentration from 0.5 to 3 Dth (1 Dth = 1883 mg L^{-1} for TOC mineralization) (initial pH 3.0, 30 °C), initial pH from 2.0 to 6.0 (1 and 2 Dth, 10:1 of H_2O_2/Fe(II), 30°C), and temperature from 30 to 50 °C(1 Dth, 10:1 of H_2O_2/Fe(II), initial pH 2.8). TOC removal generally showed the initial fast increase stage within the first sampling time of 15 min, followed by the gradual increase stage in the remaining sampling time of 180 min experimental time course. The highest percentage of TOC removal in the first stage was about 60% when the initial pH was either 2.8 (H_2O_2=1 Dth, ratio =10:1, temperature = 30–50 °C) or 3.5 (H_2O_2 = 2 Dth, ratio = 10:1, temperature = 30 °C). Also under the latter condition, the value reached 82% at 120 min and was projected to reach 94% at 180 min. According to the positive

effect of temperature increase on TOC removal observed in this experiment, further increase above these maximum values is possible if the temperature of the above condition were increased from 30 to 40 ˚C or 50 ˚C. Furthermore, under most of the treatment conditions, the TOC removal reached or was projected to reach over 60% toward the end of the experiments. The result indicated that the solar photo-Fenton process has a potential to effectively remove TOC from the wastepaper pulp effluent on a large scale.

3.6 Biological treatment

With proper analysis and environmental control, almost all the wastewater can be treated biologically. Therefore, it is essential to understand the characteristics of each biological process to ensure that the proper environment is produced and controlled effectively.

3.6.1. Objective of biological treatment

The general objectives of the biological treatment of wastewater are to coagulate, remove the non settleable colloidal solids and to stabilize the contained organic matter**.** For domestic wastewater, the objective is simply to reduce the organic content, and in many cases, the nutrients such as nitrogen and phosphorous. However, sometimes the removal of trace organic compounds that may be toxic is also an important treatment objective. In agricultural wastewater treatment, the objective is to remove the nutrients, specifically the nitrogen and phosphorous, that is capable to stimulating the growth of aquatic plants. Beside all of that, in industrial wastewater, the objective is to remove and reduce the concentration of organic and inorganic compound.

3.6.2. Role of microorganisms

The removal of carbonaceous BOD, the coagulation of non settleable colloidal solids, and the stabilization of organic matter are accomplished biologically using of microorganisms, principally bacteria. The microorganisms are used to convert the colloidal and dissolved carbonaceous organic matter into various gases and into cell tissue. Because cell tissue has specific gravity slightly greater than that of water the resulting cells can be removed easily from treated liquid by gravity settling.

3.6.3. Introduction to microbial metabolism

Understanding of the biochemical activities of the important microorganisms is the basic information to design a biological treatment process. The two major topics considered here are (1) the general nutritional requirements of the microorganisms.

(2) The nature of microbial metabolism based on the need for molecular oxygen.

In order the microorganisms to reproduce and function properly an organism must have **Bennefield L. D. et al., (1980)**

1) A source of energy.

2) Carbon for synthesis of new cellular material.

3) Inorganic elements or nutrients.

Organic nutrients (growth factor) may also be required for cell synthesis. Carbon and energy source usually referred to as substrate. Two of the most common sources of cell carbon for microorganisms are organic matter and carbon dioxide. Organisms that use organic carbon for the formation of cell tissue are called heterotrophs. Organisms that derive cell carbon from carbon dioxide are called autotrophs. The conversion of carbon dioxide to cell tissue is a reductive process that need net input of energy. The energy needed for cell synthesis may be supplied by light or by chemical oxidation reaction (phototrophs) **Eckenfelder W. W. et al., (1963).** The principal inorganic nutrients needed by microorganisms are nitrogen (N), sulphur (S), potassium (P), magnesium (Mg), calcium (Ca)… etc. In addition to these inorganic nutrients needed, organic nutrients may also be needed by some organisms.

In order to be able to combine chemical process outlet with biological process, it is necessary to determine the variation of biodegradability as a function of the chemical reaction. Once the solution biodegradability improved it can be feed to biological treatment, else more oxidation may needed. In the last years the study has been increased in this area. It is necessary to mention as examples the effect of the AOP's in the biodegradability of organic compound **Takahashi N. et al., (1994).** Different AOP's were combined with a biological process for the treatment of textile effluents.

3.7 Coupled Fenton and biological Processes

Brosillon S. et al., (2008) tested the biodegradation of the azo dyes Reactive Black 5 and Reactive Yellow 145 and confirmed the low biodegradability of these components in the considered conditions, namely a strain of *Pseudomonas fluorescens*, cultivated at 25°C, an initial pH of 7 and in presence of a supplementary carbon source, glucose. Indeed, for an initial dye concentration of 40 ppm, the maximum yields of decolouration were 27% and 18% for the two dyes RB5 and RY145. Some tests of biological mineralisation of solutions preliminary photocatalysed demonstrate a mineralisation of the considered solutions for various irradiation times. Identification of the intermediate by-products is in progress to propose a reaction pathway

Lodha B. and Chaudhary S. (2007) evaluated the Fenton-biological (aerobic) treatment train for decolorization and mineralization of azo dyes viz. Reactive Black 5 (RB5), Reactive Blue 13 (RB13) and Acid Orange 7 (AO7). The objective of Fenton treatment was only to decolorize the dyes (breakage of -NN-), as it was considered that after breakage of -NN-, the dyes will become amenable to biodegradation and can be further treated in aerobic biological system. Hence studies were carried out to optimize the lower Fenton's doses for decolorization of dyes. The optimum doses for decolorization (>95%) of all the three dyes were found out to be 15 mgL^{-1} of Fe^{2+} (0.27 mM) and 50 mgL^{-1} (1.47 mM) of H_2O_2 dose at optimum pH 3. Further it was also investigated that at lower doses, the main problem of Fenton process (sludge generation) can also be minimized. Later the mineralization of the dye (removal of aromatic amines) was achieved in the aerobic biological treatment system. Overall reduction of 64, 89 and 75% in the aromatic amines (at 254 nm), 88, 95 and 78% in naphthalene ring associated compounds (near 310 nm) and 49, 89 and 91% reduction in benzene ring associated compounds (near 226 nm) were observed for RB5, RB13 and AO7, respectively. Thus this treatment system seems to be quite effective and economical option for the treatment of recalcitrant compounds like dyes, as the cost in the chemical treatment is considered mainly due to chemicals thus at lower doses the operational cost is saved. Further, as the sludge generation was almost negligible at lower doses, thus the savings in cost of handling and disposal of hazardous sludge also adds to economy of treatment.

Rodriguez W. et al., (2002) used the Photo-Fenton process as photochemical pre-treatment to improve the biodegradability of a wastewater coming from a textile industry located in the south

of France, which was characterized as very bio recalcitrant by means of Zahn–Wellens biodegradability test(fig 7). The effect of H_2O_2, Fe(III) and temperature on the photo-mineralization processes have been studied and the optimal conditions were found. Experiments were made to obtain information concerning the evolution of the biodegradability of the treated effluent after 40 and 70% of photo-mineralization. The photo-treated effluent is not biocompatible and its complete mineralization cannot be performed by biological means. UV–VIS and high-performance liquid chromatography (HPLC) analyses show that aromatic intermediates remain in the effluent after the photo-treatment, which have been identified as the principal reason of the bio recalcitrance**.**

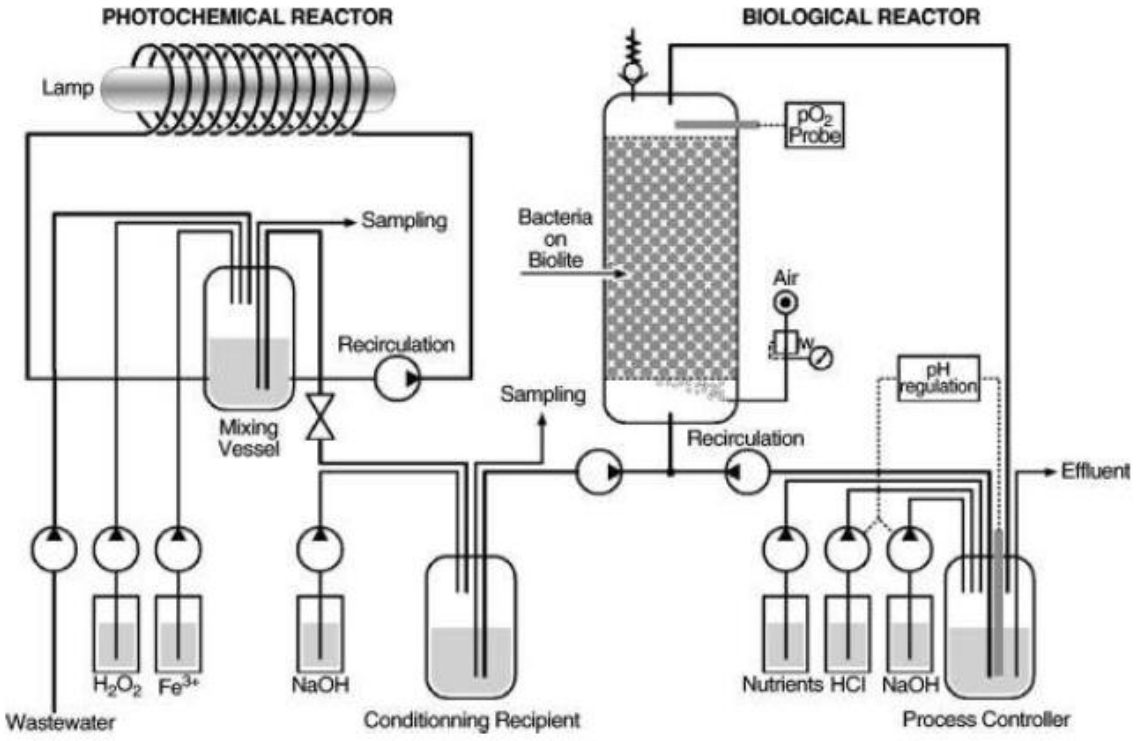


Fig. 3.2: Scheme of the photochemical-biological flow reactor.

Santos S. et al., (2010) proposed the use of the solar photo Fenton process to degrade Paracetamol in water in order to form biodegradable reaction intermediates which can be finally removed with a downstream biological treatment (by *P. putida*). Firstly, biodegradability enhancement with photo Fenton treatment time has been evaluated; the minimum mineralization level should be at least 18.6% where Paracetamol has been degraded and biodegradability

efficiency is higher than 40%. 20mgL^{-1} of Fe^{2+} and 200mgL^{-1} of H_2O_2 were selected in a lab scale study looking at Paracetamols degradation rate and organic carbon mineralization rate. As a result of scaling up the process at a pilot plant, 157.5mgL^{-1} of Paracetamol (∼1mM) was treated in 25 min of photo Fenton treatment achieving the desired biodegradability. A further economic evaluation shows how the proposed treatment strategy markedly increases plant efficiency, resulting in an 83.33% reduction in reagent cost and a 79.11% reduction in costs associated with reaction time. Total cost is reduced from 3.4502 €/m^3 to 0.7392 €/m^3.

Kajitvichyanukul P. and Suntronvipart N. (2006) had used the photo-Fenton process for the pretreatment of hospital wastewater with the objective of improving its overall biodegradability and determining the degree of increased oxidation. The chemical oxygen demand (COD), 5-day biochemical oxygen demand (BOD_5), total organic carbon (TOC) and toxicity towards the gram negative marine bioluminescent bacteria of the species *V. fischeri* were selected as the environmental sum parameters to follow the performance of this process. The enhancement of biodegradability, evaluated in terms of the BOD_5/COD ratio, increased from 0.3 to 0.52 and the oxidation degree, calculated in terms of AOS, leveled up from −1.14 to +1.58 at the optimum conditions; a dosage ratio of COD:H_2O_2:Fe(II) at 1:4:0.1, and a reaction pH of 3. The reduction in the inhibition percentage from the toxicity test indicated the safe levels for micro-organisms in degrading the residual organic substance in this method. Almost total removal percentages of COD, BOD_5, and TOC were found by a sequential activated sludge process for the pre-treated wastewater. Results obtained from this work indicated that the photo-Fenton process could be a suitable pretreatment method in reducing toxicity of pollutants and enhancing biodegradability of hospital wastewaters treated in a coupled photochemical–biological system.

Martin S. et al., (2007) had demonstrated the Biodegradability of a partially photo-oxidized pesticide mixture and the effect of photo-Fenton treatment time on growth and substrate consumption of the bacteria *Pseudomonas putida* CECT 324. Four commercial pesticides, laition, metasystox, sevnol and ultracid, usually employed in citric orchards in eastern Spain, were chosen for these experiments. The active ingredients are, respectively, dimethoate, oxydemeton-methyl, carbaryl and methidathion. Judging by biomass measurements, dissolved organic carbon measurements and biodegradation efficiency, it may be concluded that 90 min <t30W < 110 min is the critical point for the photo- Fenton treatment. *P. putida*is sensitive to

photo-produced intermediates giving rise to different kinetic behaviour: longer lag phases, slower growth rates and lower carbon uptake rates. Nonetheless, the percentage of carbon consumption was over 80%, pointing out the biodegradability of the mixture. Biodegradation efficiencies (E_f) of the photo-reaction intermediates were around 60%, in small 50-ml cultures and in a 12-l bubble column bioreactor. But with the main difference that E_f in the former took 120 h and the same biodegradation was reached in less than 30 h in the latter. Therefore, for qualitative results, experiments in flasks might be recommendable, but not for quantitative results for designing purposes.

Blanco J. et al., (2011) had investigated both Fenton oxidation and the combination of aerobic Sequencing Batch Reactor (SBR) + Fenton oxidation in a bench-scale study to degrade and reuse a real textile wastewater with a TOC=465 mg L^{-1} C, COD=2100 mg L^{-1} O_2 and *Escherichia coli*=80,000 CFU mL^{-1}, according to RD 1620/2007 (Spanish Normative for wastewater reclamation and reuse). The independent variables considered for the optimization of the oxidative process were temperature, H_2O_2 and Fe (II) concentrations. Under the best stand-alone Fenton operating conditions: T=25 °C, pH=3; [H_2O_2] =1650 mg L^{-1} and [Fe (II)] =216 mg L^{-1}, we achieved 64% TOC reduction and >99% *E. coli* removal. However, the best results were obtained when applying Fenton process with [H_2O_2] =1518 mg L^{-1} and [Fe (II)] =66.5 mg L^{-1}, as a biological polishing step. The aerobic biological treatment was conducted using a SBR with 1 day HRT. In this case 92% TOC and >99% *E. coli* removal were accomplished. The obtained results showed the feasibility of both processes to achieve suitable water qualities for internal reuse, according to RD 1620/2007.

Chen et al., (2009) analyzed the photo-Fenton coupled with a biological system for the removal of di-(2-ethylhexyl) phthalate (DEHP) in wastewater. The toxicity of DEHP-containing wastewater was found to be reduced after pre-treatment by the photo-Fenton reaction. The effect of different factors, such as DEHP, Fe^{3+} and H_2O_2 concentrations and the reaction time, on degradation efficiency was investigated. The optimal time to stop the pre-treatment process and introduce the effluent to the biological system was 60 min. The results show that effluent of DEHP-containing wastewater pre-treated by the photo-Fenton method is biodegradable and that mineralization can be completed when the wastewater is subsequently treated in a biological system. The coupled Fenton and biological treatment system for the degradation of DEHP-

containing wastewater can be successfully performed in a semi-continuous mode. These results indicate that the coupled photo-biological system is an effective and potential method for the treatment of DEHP-containing wastewater.

Liu E. S. et al., (2011) compared the treatment efficiency of aniline wastewater by single photo-Fenton; single biological oxidation and combined photo-Fenton and biological oxidation (fig. 7).The effect of different factors, such as pH, Fe^{2+} and H_2O_2concentrations on degradation efficiency were investigated. Effective degradation of aniline wastewater have been observed by photo-Fenton process, but complete mineralization of aniline wastewater need to consume large numbers of H_2O_2, so the single photo-Fenton oxidation is uneconomical technology. The aniline wastewater is less biodegradable and very toxic to microorganisms, the removal efficiency are low by direct biological oxidation. The toxicity of the aniline wastewater was found to be reduced obviously after pretreatment by the photo-Fenton oxidation.

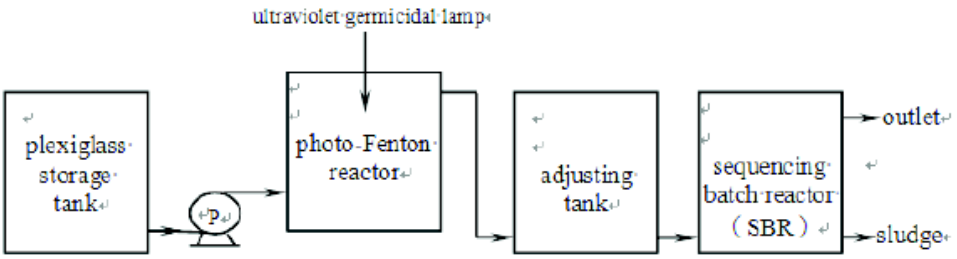


Fig. 3.3: Coupled photo-Fenton and biological oxidation

The combined photo-Fenton and biological oxidation was an effective treatment technology for toxic aniline wastewater. Experimental results showed that 62.5% of H_2O_2 were saved by combined photo-Fenton and biological oxidation processes, comparing with single photo-Fenton process.

Elmolla E. S. et al. (2011) examined the combined photo-Fenton– SBR treatment (fig. 8) of an antibiotic wastewater containing amoxicillin and cloxacillin. Optimum H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio of the photo-Fenton pre-treatment were observed to be 2.5 and 20, respectively. Complete degradation of the antibiotics occurred in one min. The sequencing batch reactor (SBR) was operated at different hydraulic retention times (HRTs) with the wastewater

treated under different photo-Fenton operating conditions (H_2O_2/COD and H_2O_2/Fe^{2+}molar ratio). The SBR performance was found to be very sensitive to BOD_5/COD ratio of the photo-Fenton treated wastewater. Statistical analysis of the results indicated that it was possible to reduce the Fe^{2+} dose and increase the irradiation time of the photo-Fenton pretreatment. The best operating conditions of the combined photo-Fenton–SBR treatment were observed to be H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 150, irradiation time 90 min and HRT of 12 h. Under the best operating conditions, 89% removal of sCOD with complete nitrification was achieved and the SBR effluent met the discharge standards.

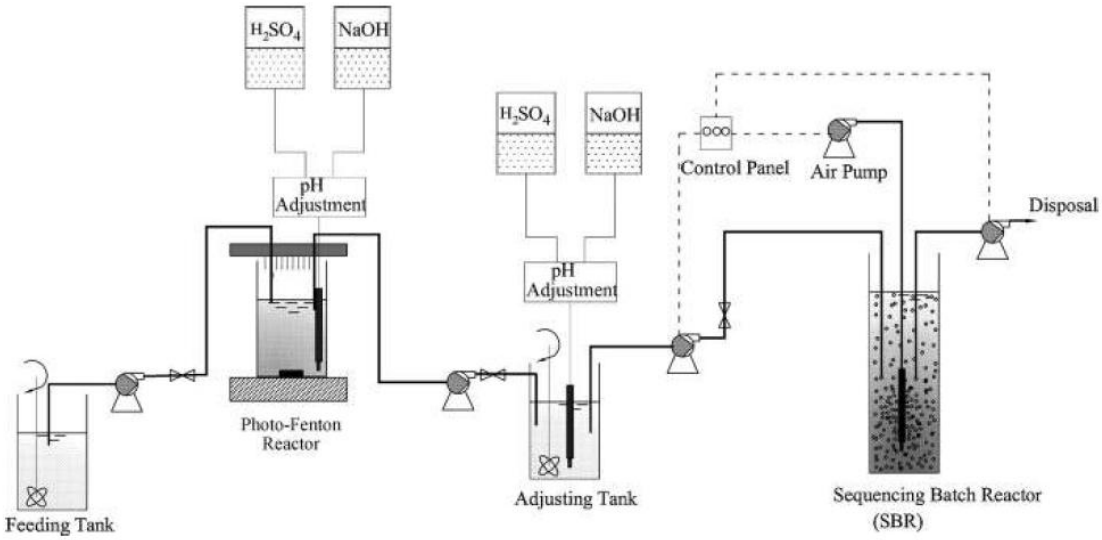


Fig. 3.4: Combined photo-Fenton–SBR process

The above cited review reports on the most recent experimental studies and developments (2002–2011) specifically combining AOPs and biological treatments (aerobic or anaerobic) for industrial wastewater decontamination not only highlights the efforts in applying AOPs as a pre-treatment, but also real cases in which the combination strategy is in the opposite direction, first eliminating the highly biodegradable part of the wastewater and then degrading the recalcitrant contaminants (non-toxic) by a post-treatment AOP.

CHAPTER 4

4. MATERIAL AND METHODS

Technical grade RB5 was procured from Sigma Aldrich, New Delhi. Raw effluent was collected from textile industry, Punjab. The sample was checked for some initial parameters and then treatment was done.

4.1 Materials

4.1.1 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 (Reactive Black 5), Molecular weight is 991.82. The structure of RB5 is shown below in fig 3.1. 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, 0.1 N H_2SO_4 and 0.1 N NaOH were used and initial pH monitored by basic pH meter from Century instrument company. Activated sludge from textile industry is used in biological treatment.

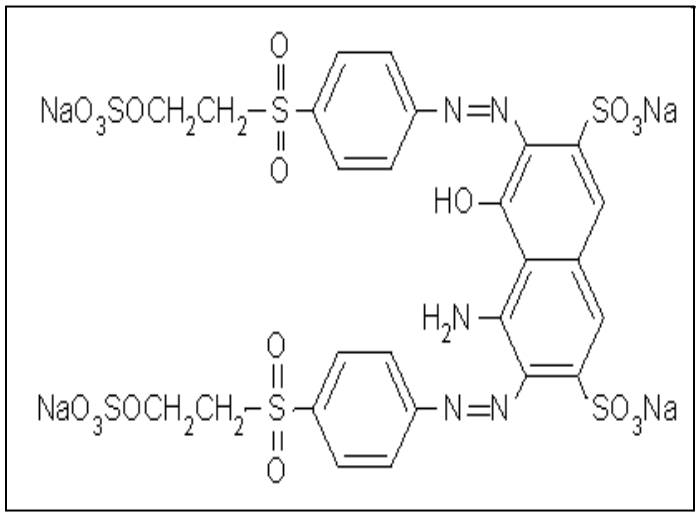


Figure 4.1: Structure of Reactive Black 5

4.1.2 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 0.1 N NaOH and 0.1 N H_2SO_4. Instrument was calibrated by freshly prepared buffer solution (pH 4 to 9) time to time throughout the study.

b) Spectrophotometer

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

c) Photo reactor

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

Figure 4.4: Photo reactor at lab scale during photocatalytic treatment

d) Reaction vessel

For the photocatalytic process, glass bowls used were both cylindrical in shape and made of borosil glass, which has a diameter 7.5 inches and is 2 inches in height with a capacity of approximately 1000 ml.

Figure 4.5: Reaction vessel in (a) In Solar light (b) In UV light

e) Electrical conductivity meter

Electrical conductivity of the samples was determined by using a deluxe conductivity meter model 601 E (Eutech, India). The Electrical conductivity in (mS/cm) of wastewater sample was estimated and before estimation Electrical conductivity meter was calibrated.

f) Turbidity meter

Turbidity of the samples was measured by using Hatch Radio turbidometer as per STANDARD METHODS for the examination of water and wastewater 1999 (20^{th} edition).

g) COD digester

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

h) Magnetic stirrer

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

i) Air sparger

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

j) Radiometer

Solar/UV Intensity was measured hourly during experimental days with Eppley (model no. 33013) radiometer. Figure 4.1 is a picture of the same radiometer.

Figure 4.6: Eppley Radiometer

j) Filter

After photo catalytic treatment by photo reactor, effluent sample were filtered through syringe filters having Millipore filters of 0.45 µm pore size.

4.2 Preparation Of Solution

4.2.1 Compound solutions

The stock solutions were prepared by adding a known amount of compound into a small amount of distilled 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.

4.2.2 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.

4.2.3 $FeSO_4$ reagent

$FeSO_4$ was obtained from Ranbaxy Laboratories 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.

4.3 Methods

4.3.1. Collection and storage of wastewater

Sample was collected from textile industry. Sampling vessel was cleaned and rinsed carefully with distilled water and then washed with sample during sample collection. Then textile effluent was stored in cold store at 4°C within 3 to 4 hrs of collection and activated sludge was stored after the addition of the nutrients in it.

4.3.2. Characterization of wastewater sample

Wastewater sample was analyzed for the COD, BOD, TDS, TSS, pH etc. The entire experimental test was repeated to get reproducibility of results. Parameters were analyzed by methods given in standard methods for the examination of water and wastewater 1999 (20^{th} edition). Reagents used for the present investigation were of AR Grade and single distilled water was used throughout the study.

4.4 Techniques

a) Estimation of COD

COD was estimated as per the standard method No. 5220 C, page No.5-14 from STANDARD METHODS for the examination of water and wastewater, 1999 (20^{th}edition).

b) Estimation of BOD

BOD was estimated as per standards method No. 5210 B, page No.5-4 from STANDARD METHODS for the examination water and wastewater, 1999(20^{th} edition). BOD was estimated by BOD bottle method.

c) Total dissolved solids (TDS)

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

d) Total suspended solids (TSS)

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

e) Analysis of chloride

Chloride was estimated as per the standards methods No.4500, page No. 4-72 of STANDARD METHODS for the examination of water and wastewater.

f) Analysis for degradation

The degradation studies were conducted by measuring absorbance in UV/VIS spectrophotometer, having a wavelength range from 190-1100 nm using a 1 cm quartz cell. All the experiments reported were carried out in a 4 ml quartz cuvette. Full scan was taken after treatment for the textile effluent.

g) Biodegradability

Due to the high cost of photochemical processes, it must be taken care that target pollutants are definitively non-biodegradable since for easily biodegradable compounds, classical biological treatments are, at present, the cheapest and the most environmentally compatible. A ratio of BOD_5/COD in wastewater is normally used to express the biodegradability of the wastewater. When the ratio of BOD_5/COD is more than 0.4, wastewater has much biodegradability, whereas if BOD_5/COD ratio is less than 0.4, wastewater is difficult to be biodegraded. To investigate the biodegradability of wastewater sample, BOD_5/COD was checked after the photo Fenton process at different time durations.

4.5 Preparation of Sample

4.5.1 For Fenton processes

200 ml of sample was taken in glass bowl (1000 ml quantity) and bowl was covered with transparent thin foil; air is also supplied by the aerator during experiments. All tests were

repeated for getting the reproducibility of results. Single distilled water was used for the all dilutions.1:1 diluted textile effluent was subjected to photo Fenton treatment. Initial pH of sample was checked and varied all the parameter to optimize the value of pH, H_2O_2, Fe^{2+} and comparison of photo Fenton in UV with solar light.

4.5.2 For Biological process

To start up aerobic biological treatment, fresh activated sludge from Textile wastewater treatment plant was added to the photo-Fenton pre-treated solution. Textile effluent with initial COD of 2000 mgL^{-1} and BOD_5/COD was 0.1 which increased to around 0.4 after the photo treatment. After neutralizing the pH of the pre treated solution with the help of 0.1 N NaOH/0.1 N H_2SO_4, the biological reaction was initiated. Nutrient supply was optimised to avoid the competitive inhibition. Air supply was continuously maintained with the help of aerators. During the biological process, daily measurements of COD, BOD and pH were performed.

4.6 Procedure

Wastewater sample was treated in the presence of UV light and natural sunlight in photo reactor for optimized hours. 200 ml of sample taken in glass bowl (1000 ml quantity) and bowl was covered with transparent thin foil; air is also supplied by the aerator during experiments. Sample was withdrawn in every 5 min. for model dye, 10 mins for textile effluent by photo Fenton process and the, respectively filtered through the syringe filter. COD of samples was measured as per the standard methods. All tests were repeated for getting the reproducibility of results. After the coupled photo catalytic and biological treatment of wastewater (with optimized conditions), sample was filtered and it has been analyzed for COD, BOD, pH etc

CHAPTER 5

5. RESULTS AND DISCUSSIONS

COMPOUND CHARACTERISTICS

The dye used was azo dye i.e. RB5 (Reactive Black 5), obtained from sigma Aldrich, Molecular weight is 991.82. 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. Stock solution of dye 500 mgL^{-1} was made and 100 mgL^{-1} was used for each batch with appropriate dilution.

5.1 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 200–1100 nm. Two significant peaks were observed in absorption spectra at 310 nm and 595 nm (Fig 5.1). Compound showed 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 degradation and decolourisation studies were performed at wavelengths 310 nm and 595 nm respectively.

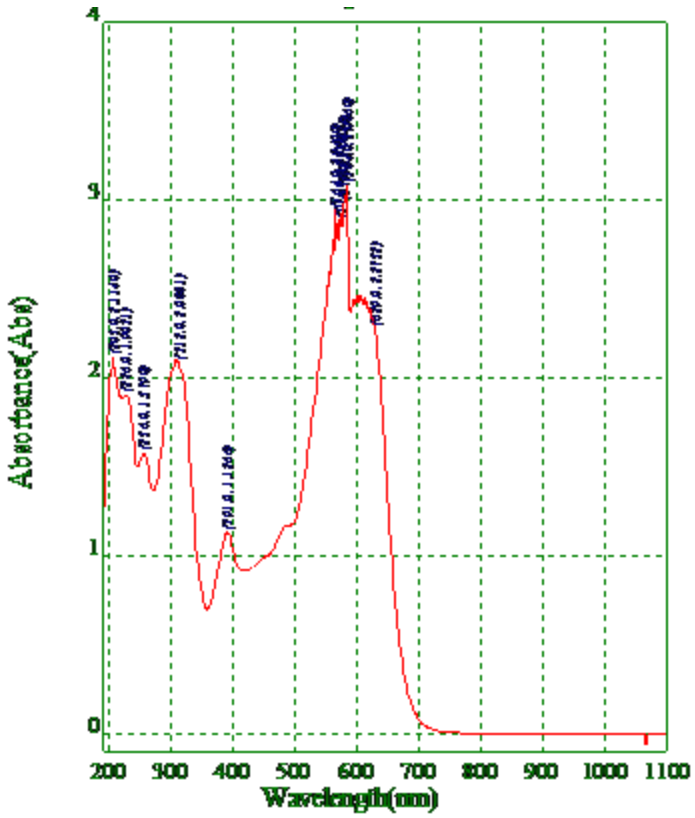


Figure 5.1: UV-Vis absorption spectrum of Reactive Black 5

5.2 Standard curve of Reactive Black 5

Fig 5.2 and Fig 5.3 shows the standard curve for RB5 which is prepared by plotting the absorbance of sample solution of varying known concentration ranging from 10 mgL^{-1} to 100 mgL^{-1} 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.

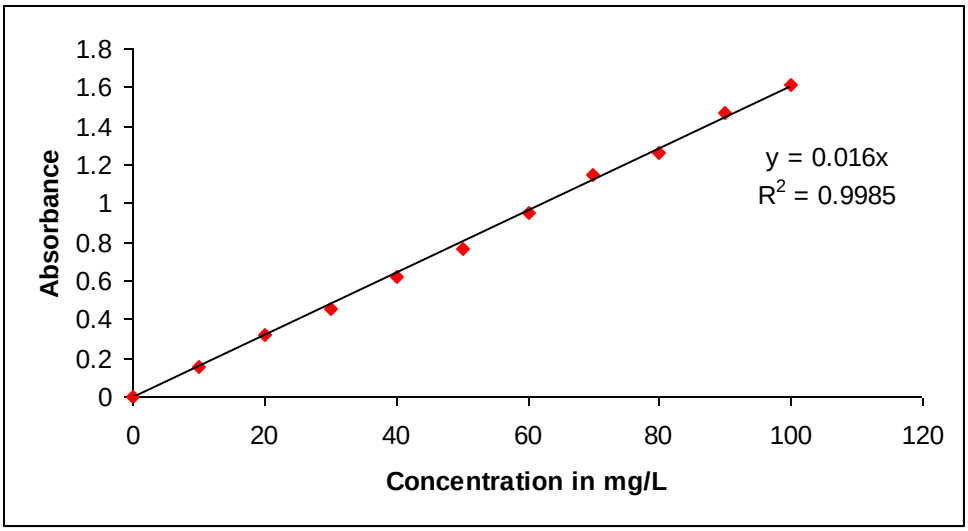


Figure 5.2: Standard curve of RB5 at wavelength 310 nm

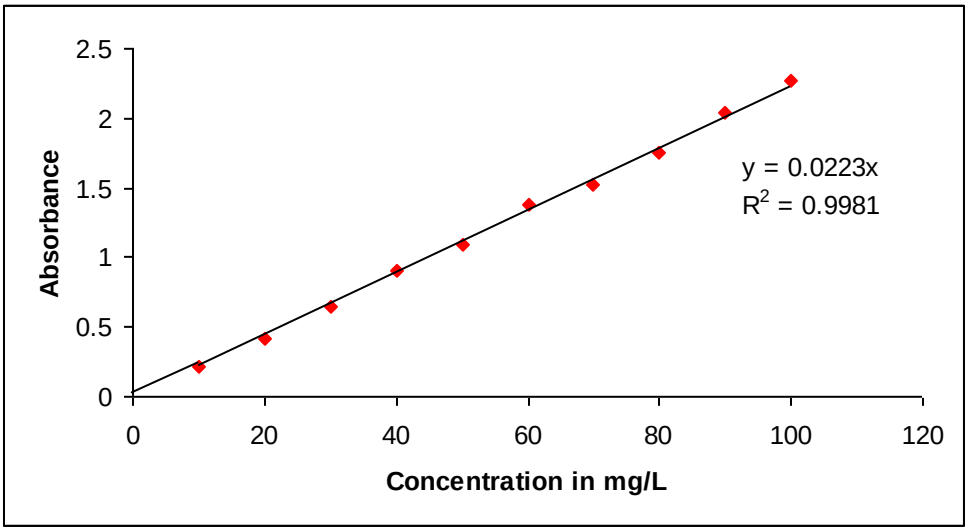


Figure 5.3: Standard curve of RB5 at wavelength 595 nm

5.3 Preliminary Studies

The degradation of RB5 dye in UV light without Fe^{2+} and H_2O_2 was very less (10%) and in absence of H_2O_2 (Fe+UV light) was observed around 12%. This can be explained as photon as well as Fenton's reagent is required for adsorption for the reaction to take place. The use of only reagent (H_2O_2) under UV light also shows very similar degradation (18%). The reason is due to

the generation of some OH* is not sufficient for reaction to take place **Pokhrel D. and Viraraghavan T. (2004).** The Fe^{2+} along with H_2O_2 in dark shows slightly better degradation (32%) as catalyst surface is required for complete reaction to take place.

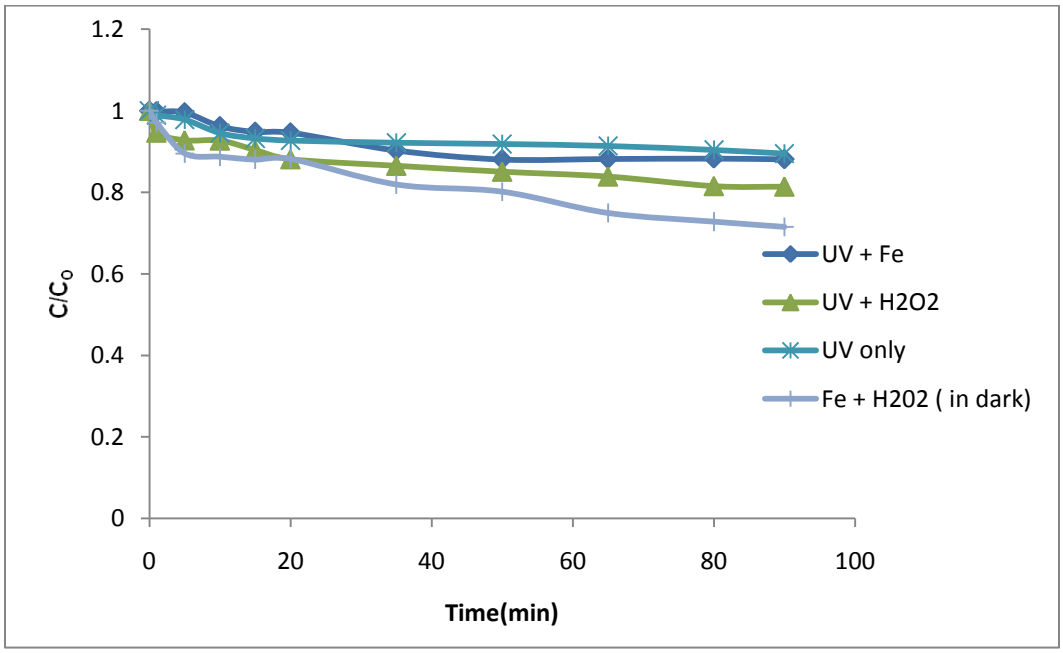


Figure 5.4 Preliminary study of RB5 dye

5.4 Photo Fenton studies

5.4.1 Effect of H_2O_2

Fig 5.4 and 5.5 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 2.6 mM to 25 mM into the dye solution at fixed Fe^{+2}(0.05 mM) and pH(3). 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. et al, (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 (99%) of dye solution was achieved at optimum dose 4.4 mM of H_2O_2 within 90 min of reaction.

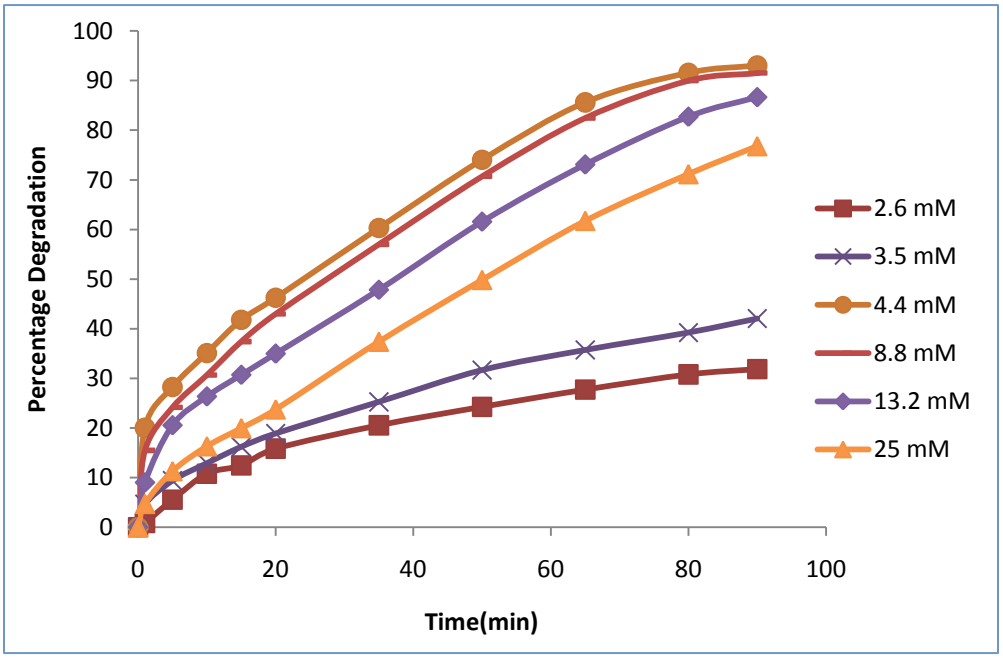


Figure 5.5 Percentage degradation of RB5 at varying concentration of H_2O_2 at wavelength 391 nm.

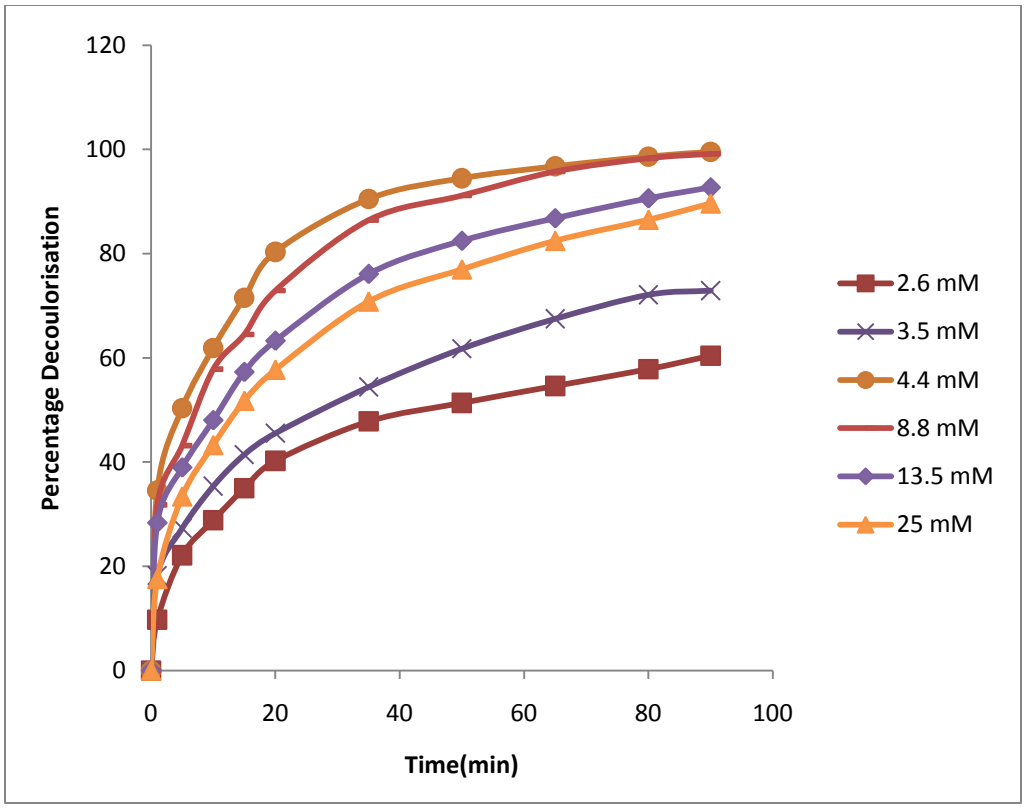


Figure 5.6 Percentage colour removal of RB5 at varying concentration of H_2O_2 at wavelength 595 nm.

5.4.2 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. Almost after 20 min the 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 dosage.

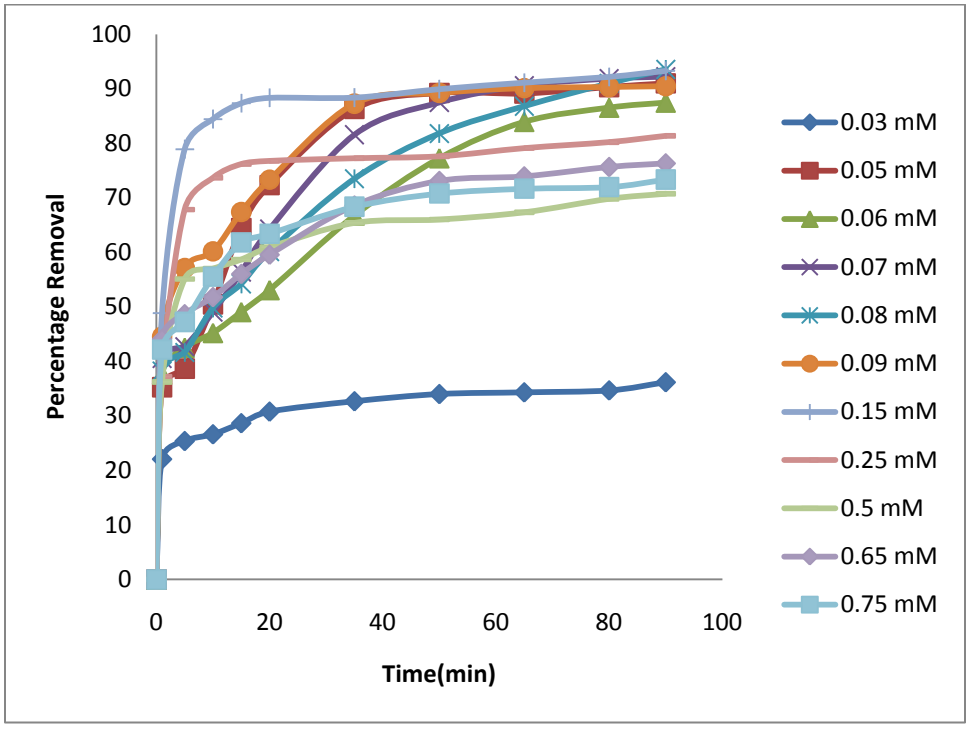


Figure 5.7 Percentage degradation of RB5 at varying concentration of Fe^{+2} at wavelength 310 nm.

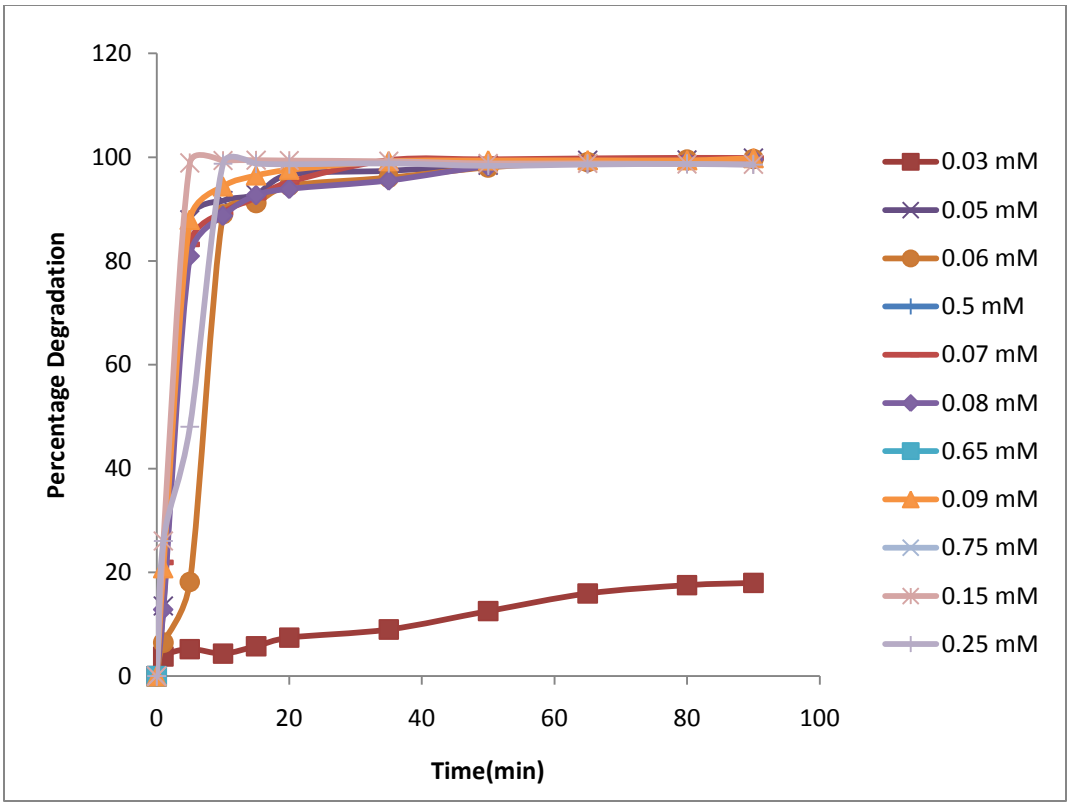


Figure 5.8 Percentage colour removal of RB5 at varying concentration of Fe^{+2} at wavelength 595 nm

5.4.3 Effect of pH

The effect of pH on the decolorization and degradation of RB5 by photo-Fenton processes is shown in Fig. 5.9 and 5.10. 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 7. 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 optimum pH because degradation and decolorization of RB5 was 2% more than pH=3 i.e. 92% and 99%. 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)**

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

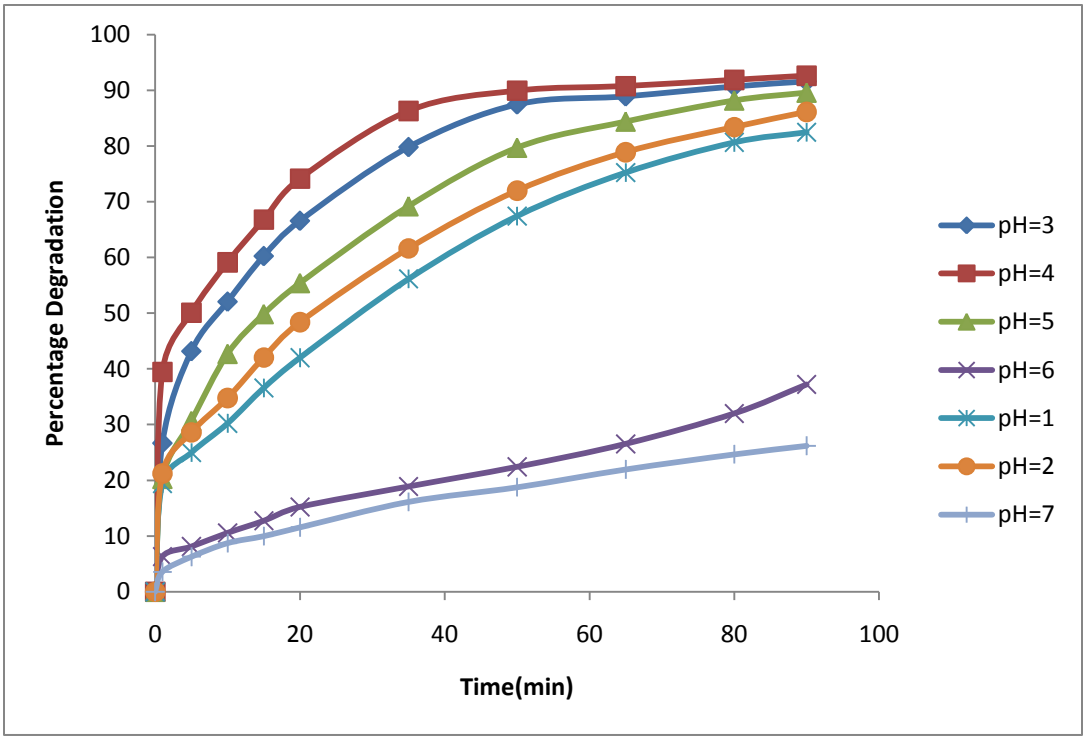


Figure 5.9 Percentage degradation of RB5 at varying of pH at wavelength 310 nm

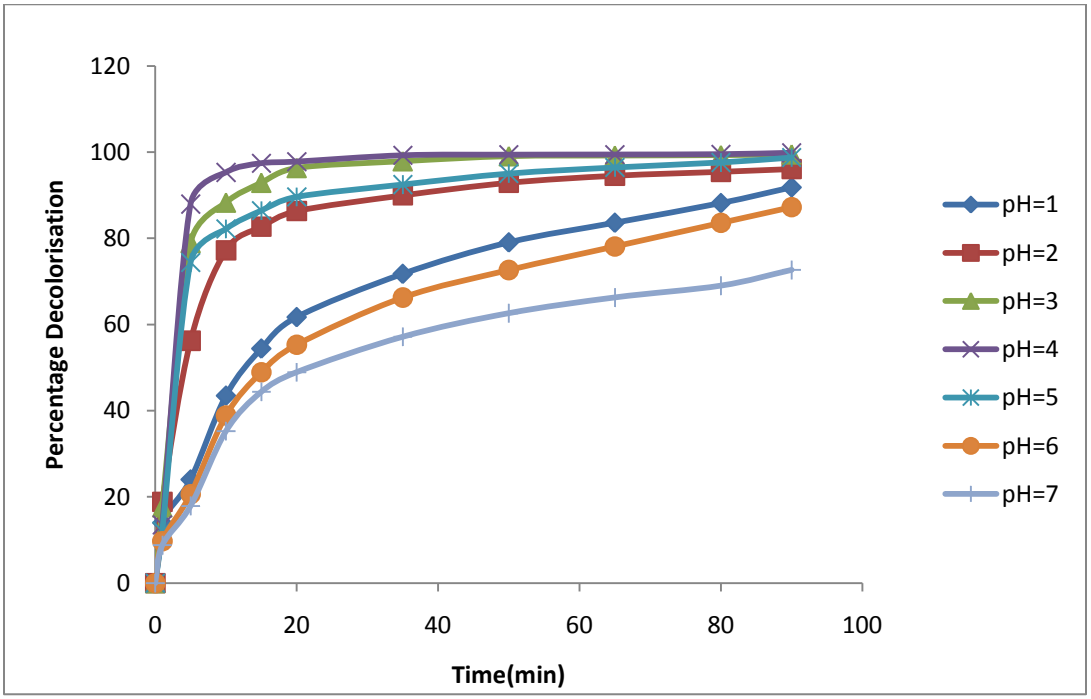


Figure 5.10 Percentage colour removal of RB5 at varying of pH at wavelength 595 nm.

5.4.4 Effect of area/volume(A/V) ratio

The ratio of Area/Volume is important as the photo catalytic oxidation reaction depends on area available for the irradiation of light. More area and less depth enhance the rate of degradation as the UV rays penetrate more into the solution **Toor A. P. et al., (2007).** The variation is done by keeping the area constant and varying the volume of the sample. 200 ml is taken as the optimum volume of sample.

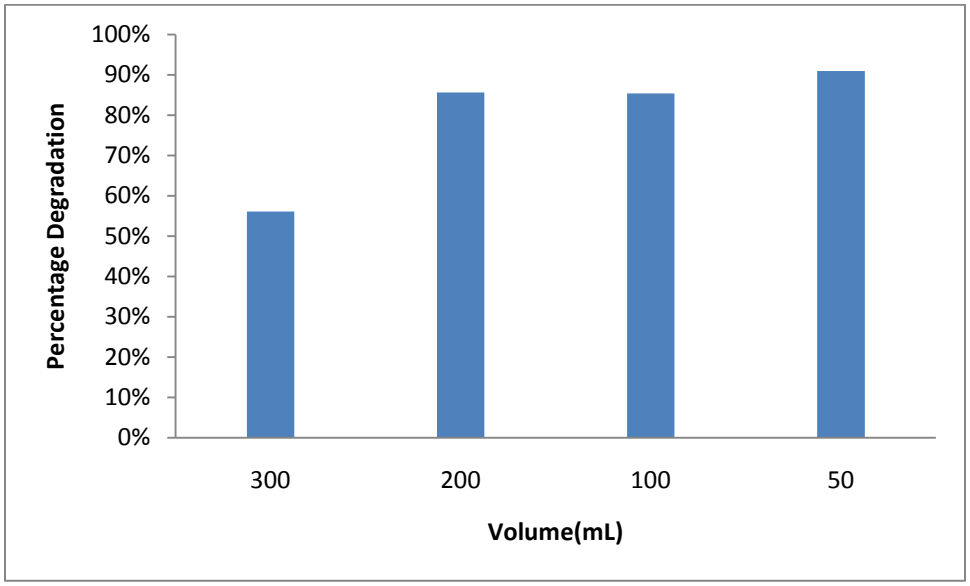


Figure 5.11 Percentage degradation of RB5 at varying area/volume at wavelength 310 nm.

5.4.5 Effect of intensity

The amount of degradation depends on the radiation intensity. Various researchers have found that the reaction rate increases with the square root of intensity at high levels, but changes to a first-order relationship at lower levels of illumination. The degradation studies of RB5 were done below 50 Wm^{-2}, thus the dependence of rate constant on intensity was of first order. The experiments were conducted with all optimum conditions in the shallow slurry pond reactor under artificial light at three different intensities of 10, 18, 27 W/m^2. The degradation rate

constant increases with increase in intensity and best results are obtained at 27 W/m^2 (Figure 5.12). At higher intensity, the electron-hole formation is predominant and hence electron-hole recombination is negligible **Bajpai P et al., (2000).** At lower intensity, electron-hole pair separation competes with recombination which decreases formation of free radicals causing lower degree of degradation.

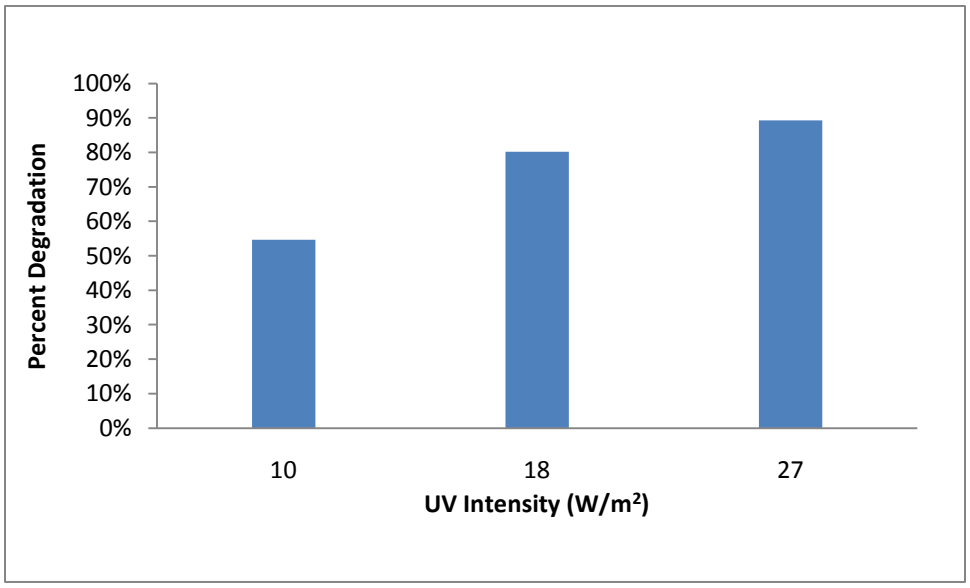


Figure 5.12 Percentage degradation of RB5 of different UV intensities at wavelength 310 nm.

5.5 SOLAR PHOTO FENTON

5.5.1 Degradation with solar/UV light

The experiments were conducted with all the optimum conditions (0.15 mM, 4.4 mM, pH 3) in shallow pond type reactor under natural light. To make the treatment economical, sunlight is preferred for the wastewater treatment **Amat A.M. et al., (2005).** The average solar UV intensity is between 25-30 Wm^{-2} as measured by radiometer. There is a free availability of sunlight as India is a tropical country. Hence, all experiments were done in the months of March, April, May between 9.30 am to 5.00 pm to harness maximum solar radiation. It was observed that the extent of degradation of the wastewater sample was more in the presence of solar light (94.6%) as compared to UV light (91%) (Figure 5.13).

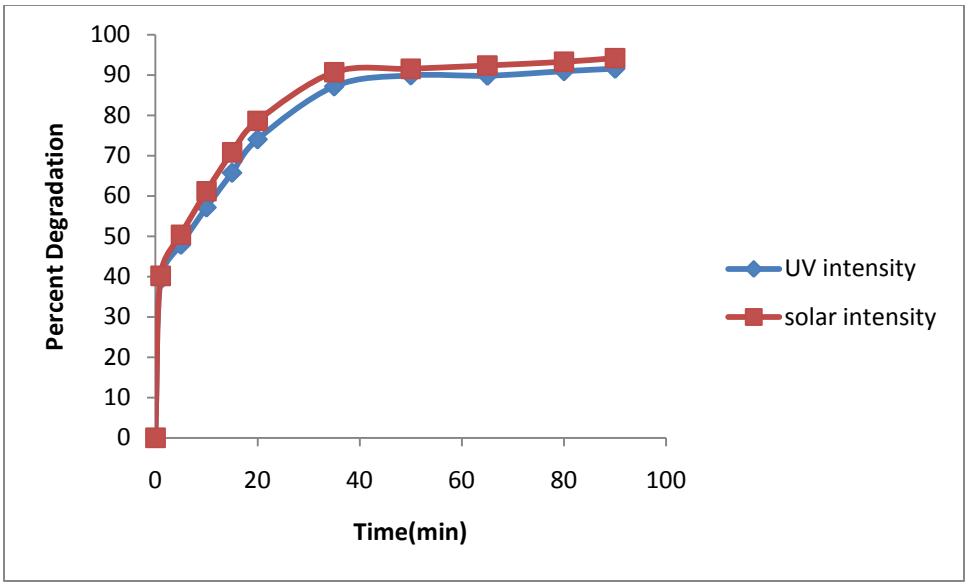


Figure 5.13 Comparison of mineralization with UV intensity and solar intensity

5.6 Biological process

The operating liquid volume of the 1 L biological vessel was 200 ml and depth 4-5cm. The vessel was equiped with a aerators for keeping DO above 3 mgL^{-1} and was kept on magnetic stirrer for proper mixing. Controlled glucose and yeast were added before adding the small amount of activated sludge. Then the pH was adjusted to neutral. The system was done in batch processes for varying period of time. 24 hours time of biological was selected as best time for degradation. At the end of the aeration-reaction period, the stirring and aeration were switched off to allow settling the activated sludge for 20 mins. Next, the corresponding volume of treated solution was decanted from the supernatant during the draw step, and for further purification the sample was filtered through the filter and checked for COD and BOD. The process was repeated to obtain repetiitive results.

5.7 Combined photo Fenton biological process

When the best photo-Fenton wastewater pretreatment for biodegradability had been determined, the combined photo Fenton biological treatment was carried out. Before performing the experiment in combined system, the biodegradability of the sample after photo Fenton process was checked by BOD_5/COD which gives 0.4 value, which means a partially biodegradable sample. Then, the effluent/sample was inoculated with 200 ml of concentrated activated sludge

from dyeing industry. The system was maintained with controlled glucose and yeast. Startup and adaptation of the biological reactor was done while simultaneously performing several runs with photo Fenton reactor in order to accumulate enough pre-treated wastewater to add to the bioreactor. The pH of different photo-Fenton runs was roughly adjusted to 7. The system was operated in batch mode. Overall mineralization efficiency of the combined Fenton and biological treatment in batch mode for the degradation of compound dye was over % of which % corresponds to solar photochemical treatment and % to the biological treatment.

5.8 Industrial Textile wastewater

The raw waste water sample was collected from equalization tank from textile industry, Punjab. The waste water was analyzed for various initial parameters such as BOD, COD and TDS etc. as shown in Table 5.2. Before photo-Fenton treatment, Textile effluent was diluted in the ratio of 1:1 with single distilled water as it was highly concentrated. All experiments were done in triplicate and mean values were recorded. The conditions were optimized by varying the operational parameters to achieve the economy of the process.

S. No.	Parameters	Textile Effluent
1.	pH	9
2.	BOD (mg/l)	196
3.	COD (mg/l)	2000
4.	TSS (mg/l)	600
5.	TDS (mg/l)	2970
6.	Chloride (mg/l)	1190
7.	Colour (Pt-Co)	167x10

Table 5.2 Characteristics of textile effluent

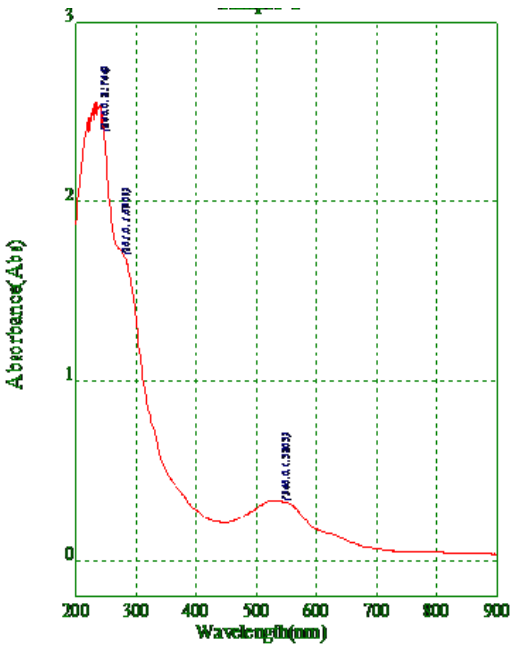
High COD levels indicate toxic state of the wastewater along with the presence of biologically resistant organic substances. Colour values indicate the large amount of dye colors present in the effluent.

5.8.1 Textile wastewater treatment

The same treatment has been applied to an industrial wastewater coming from textile industry that uses the same studied dye along with some other dyes. Clearly, this wastewater cannot be biodegraded according to its BOD_5/COD value, nearly equal to 0.1. Solar photo Fenton was used efficiently for optimum colour removal. Only little colour is left in the effluent after 20 minutes of photo Fenton process. At the same time, the COD conversion of the wastewater was 78 %. Concurrently, the ratio BOD_5/COD increased up to 0.4.

5.9 Photo Fenton treatment

Figure 5.16(a) represents the spectra of the real textile effluent and 5.16(b) represents the spectra of the treated textile wastewater with the photo Fenton treatment for the optimized time, i.e. 20 mins to feed to the treated sample to the biological treatment. The degradation is comparative less with that of RB 5 dye as many other recalcitrant and non biodegradable compounds are present in the textile effluent.



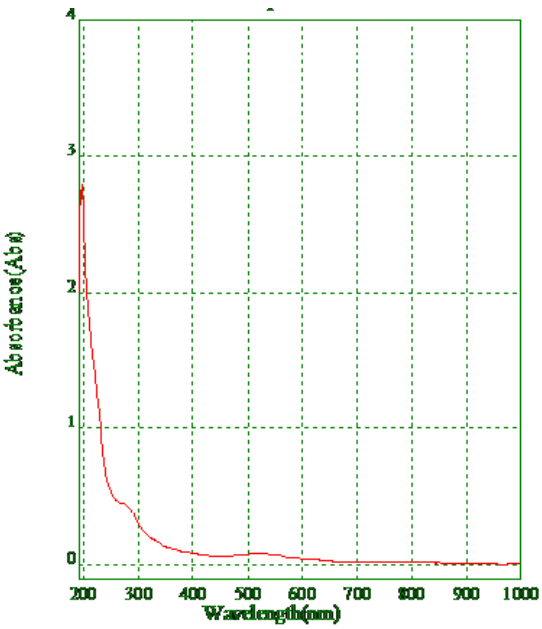


Figure 5.16 Absorption spectra of (a) Textile effluent (b) Textile waste water treated with 20 min photo Fenton.

5.9.1 Characteristics of Photo-Treated Solutions

WASTE WATER	SYNTHETIC		REAL	
	INITIAL	FINAL	INITIAL	FINAL
COD	340	90	2000	240
BOD	260	80	196	96
BOD_5/COD	.32	.5	0.098	0.4

Table 5.3 Characteristics of synthetic and real (initial and final) photo Fenton treated wastewater

The COD decrease of 76.25 % and 87 % in synthetic and real textile wastewater takes place respectively. BOD_5 may increase or decrease during Fenton's treatment. The direction of BOD_5 change may depend on initial factors of non-biodegradable and biodegradable compounds. For synthetic waste water containing RB5 dye a reduction of 69.24 % in BOD_5 was observed which is comparatively greater than the reduction in the real textile wastewater. The initial BOD_5/COD of real textile effluent was nearly 0.1. This means that waste water is easily not biodegradable. When photo Fenton treatment was applied the BOD_5/COD value increases to 0.4 which indicate the enhanced biodegrability of the waste water. Thus, photo Fenton treatment appears to be useful for increasing biodegrabality of real and synthetic wastewater containing RB5 dye.

5.10 Biological Treatment

Figure 5.17(b) shows the treated effluent with biological process for 24 hours. The peaks in the UV and visible region although diminishes but not completely removed. Thus confirming that only biological process is not sufficient to remove all non biodegradable compounds present in wastewater. The 75% reduction in COD had been observed with only biological treatment for 24 hours.

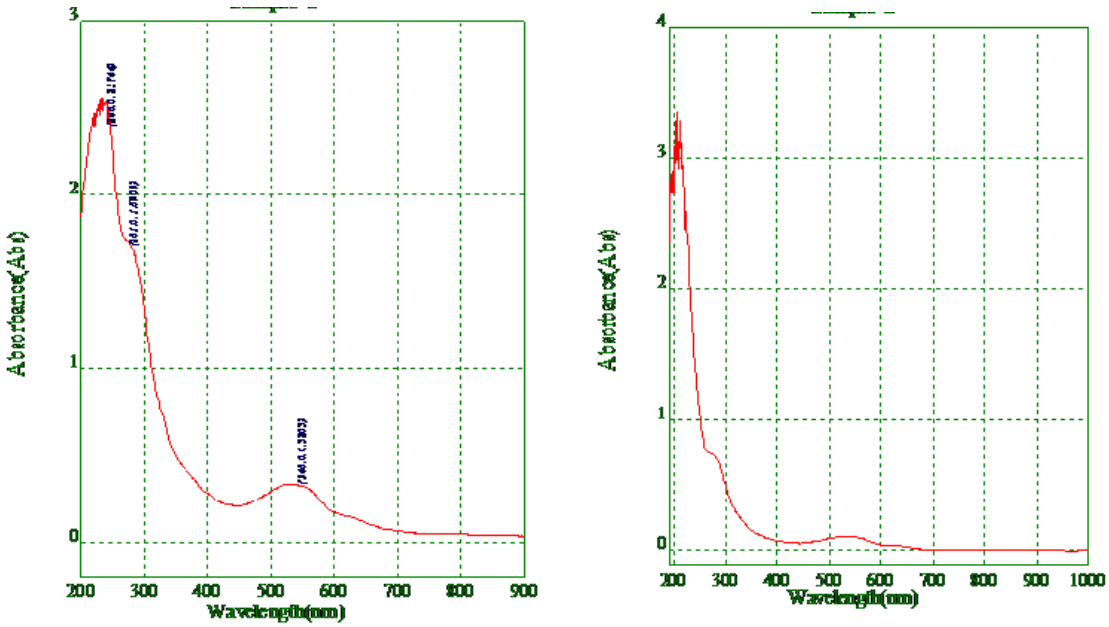


Figure 5.17 Absorption spectra of (a) Textile effluent (b) biologically treated sample of textile effluent.

COUPLED PHOTO-FENTON-BIOLOGICAL TREATMENT

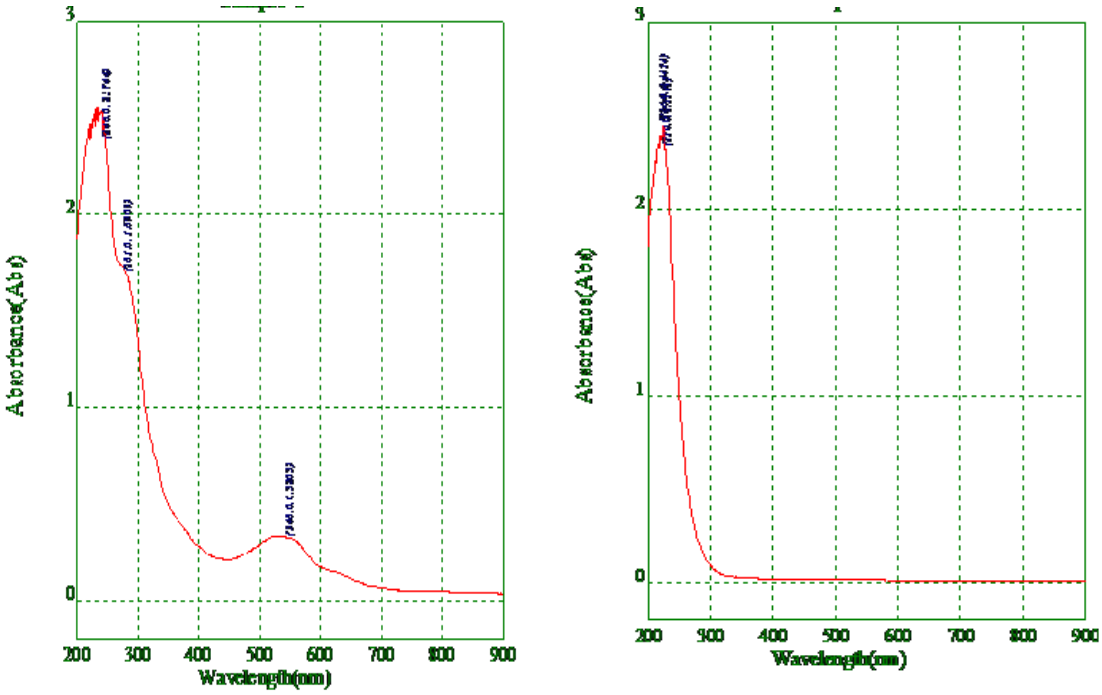


Figure 5.18 Absorption spectra of (a) textile effluent (b) biologically treated sample with pre treated photo Fenton process.

Combining both the processes i.e., photo Fenton and biological treatment shows the much better results than individual process (figure 5.18 (b)) as the spectra shows nearly zero absorbance i.e

flat nature. This shows all the recalcitrant and non biodegradable compounds present in the effluent became biodegradable after the pre treatment which further gets mineralized by biological process. The coupled Fenton process under optimal Fenton conditions gave a final COD and BOD reduction of 91% and 87%, respectively.

CHAPTER 6

CONCLUSION

In the present work, the first part of the study is to optimise the operating conditions (Fe^{2+}, H_2O_2, UV) of the photo-Fenton pretreatment of an reactive azo dye RB5(Reactive Black 5) which was usually used in the dyeing and textile effluents. Second part of the study examined combined photo-Fenton-biological treatment of the dye. Similar work was done on the textile effluent under the same set of conditions with the optimized results. A textile effluent was determined to be non-biodegradable by the ratio of BOD_5/COD which was found to be nearly 0.1 before the photo-Fenton treatment. But the BOD_5/COD was found to be near 0.4 after the 20 minute photo-Fenton process showing the sample to be biodegradable. Through this work, we have found that the optimal conditions of Fe^{2+} and H_2O_2 are 0.15 mM and 4.4 mM, respectively for the treatment of synthetic dye. Also, pH =4 was determined as the optimal pH. The main disadvantage of using only the AOP process is the high cost which can be reduced by incorporating the aerobic post treatment. Also, the efficiency of the process could be increased at low H_2O_2 dosage. Thus, combined photo Fenton biological is an effective process for treatment of textile wastewater.

In the present study, the focus was on the analysis of the each factor in the overall performance. These include the parameters like Ph, UV intensity, iron dose etc. Nevertheless, from the applied point of view one should also take in account other issues that have been discussed in detail. These include, for instance, catalyst stability. Besides, for industrial applications of AOP's, the use of continuous flow reactors should be considered, e.g. of the thin-film type, as well as possibility of using visible radiation, thus making use of wider range of solar spectrum.

Finally, in the future, special attention may be paid to the possibility of running a coupled system as biological aerobic treatment + photo-Fenton under solar radiation in an economical and environmentally friendly way. Nevertheless, the opposite assembly could also be considered where the AOP would be used as a final polishing stage.

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Conferences

- Anoop Verma, **Gurpreet Singh** and Arpita Debnath, "Degradation of Reactive Black 5 with dilution of treated RO Reject Water using Photocatalysis" A poster presented at RACES held at M.M. Modi College, Patiala, on 31st Jan 2013.
- Anoop Verma and **Gurpreet Singh Saggu**, "Treatment of textile wastewater by coupled Fenton and biological processes" A paper presented at NCRAREES 2013 held at Shoolini University, Solan, on 8th & 9th June 2013.
- Anoop Verma and **Gurpreet Singh Saggu**, "Treatment of textile wastewater by coupled Fenton and biological processes" AOP 2013 to be held at Thapar University, Patiala, on 21st-23rd November, 2013 (Accepted).

Journals

- Anoop Verma, **Gurpreet Singh** and Arpita Debnath, "Degradation of Reactive Black 5 along with dilution of RO Reject Water using Photocatalysis" Research Journal of Chemistry and Environment (communicated).
- Anoop Verma, **Gurpreet Singh** and Arpita Debnath, "Degradation and decolorisation studies of paper mill effluents by TiO_2 photocatalysis" Research Journal of Chemistry and Environment (communicated).
- Anoop Verma, **Gurpreet Singh** and Arpita Debnath, "Optimization of Fenton-biological treatment scheme for the treatment of textile effluent" Research Journal of Chemistry and Environment (communicated).

Awards

Secured 2nd position in poster presented at RACES held at M.M. Modi College, Patiala, on 31st Jan 2013.