2007

Comparison of Efficiency of an Advanced Oxidation Process for Degrading Major Classes of Dyes

Fatima Hasan Abdullah Al-Hamedi

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COMPARISON OF EFFICIENCY OF AN ADVANCED
OXIDATION PROCESS FOR DEGRADING MAJOR
CLASSES OF DYES

By

Fatima Hasan Abdullah Al-Hamedi

A thesis
Submitted to

United Arab Emirates University
In partial fulfillment of the requirements
For the Degree of M.Sc. in Environmental Sciences

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Spring 2007
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United Arab Emirates University
2006/2007
To my Father and Mother, I am proud to be your daughter.

Keep me in your thoughts and prayers.
Acknowledgement

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Fatima H Abdullah, Muhammed A Rauf, S Salman Ashraf. Kinetics and optimization of photolytic
decoloration of carmine by UV/H₂O₂. Dyes and Pigments 2007; 75: 194-198

See (Appendix ) p 118
Abstract

Synthetic dyes are a major part of our life. Products ranging from clothes to leather accessories to furniture all depend on extensive use of organic dyes.

There are numerous classes of these dyes. However, azo, anthraquinone, triarylmethane, diarylmethane, acridine, quinine, xanthane and nitro represent the major classes and are most commonly used dyes.

An unfortunate side effect of their widespread use is the fact that up to 12% of these dyes are wasted during the dyeing process, and that approximately 20% of this waste enters the environment (mostly in water supply). The effluents from these industries cause the water bodies not only to become colored, but also cause an environmental damage to the living organisms by stopping the re-oxygenation capacity of water as well as blocking sunlight. Furthermore, many of these dyes are potentially carcinogenic and can enter our drinking water supply. In fact, results from animal studies show that exposure to some can lead to cancerous and precancerous liver conditions.

Therefore, there is a need to find economical and bio-friendly methods to degrade dyes in industrial waste effluents. A number of different approaches (such as adsorption, coagulation etc.) have been developed to remove dyes from aqueous solution. However, all these methods are either costly, inefficient or result in the production of secondary waste products.
Recently a set of new approaches called advanced oxidation processes (AOP) have been developed to efficiently degrade these dye pollutants. Among the most promising of these AOP include generation of hydroxyl radicals from H$_2$O$_2$ using either:

1. UV radiation (Photolysis),
2. Fe$^{2+}$ ions (Fenton’s reagents),
3. Combination of UV and Fe$^{2+}$ (PhotoFenton) or

In comparison with other AOPs, such as Fenton, ozone, UV/O$_3$, UV/photolysis of hydrogen peroxide has the advantages such as the complete miscibility of H$_2$O$_2$ with water, the stability and commercial availability of hydrogen peroxide, no phase transfer problems, no sludge formation, simplicity of operation and lower investment costs.

Extensive work has been carried out on the use of one specific AOP a given dye. However, the efficiency of a given AOP on the different classes of dyes is not widely published. In this study, UV- H$_2$O$_2$ (UV Photolysis) was used to study the kinetics of oxidation and subsequent degradation of eight of the major dye classes. It was found that the degradation process seems to occur according to a similar mechanism for all the selected dyes and follow an apparent first order kinetics. The dye degradation was dependent on the amount of the hydrogen peroxide used and inversely proportional to the dye concentration. The optimum concentration of the UV/H$_2$O$_2$ reagent and dye
concentration was different for each dye. Furthermore, it was found that depending on the class of dye, common ions and salts that are normally part of the wastewater stream had dramatic effects on the degradation rates.

This study has shed light on whether the different classes of dyes are degraded equally well by specific AOP approach. Also, we studied the effect of salts (that are normally present in textile waste streams) on the photolytic degradation of these dyes.

Lastly, an attempt was made to identify the final degradation products of these dyes and propose degradation scheme.

A comparative analysis was done by using the data from the study. The results indicated that different classes of dyes most efficiently degraded (like diarylmethane) than other classes (like anthraquinone).

**Key words:** Textile dyes, Advanced Oxidation Processes (AOP), Hydroxyl radical, Photolytic oxidation, Hydrogen Peroxide photolysis.
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<td>Advanced Oxidation Processes</td>
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<tr>
<td>H$_2$O$_2$</td>
<td>Hydrogen Peroxide</td>
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<tr>
<td>GCMS</td>
<td>Gas Chromatography Mass Spectrometry</td>
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<tr>
<td>HPLC</td>
<td>High Performance Liquid Chromatography</td>
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<td>MG</td>
<td>Malachite Green</td>
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<tr>
<td>NY</td>
<td>Naphthol Yellow</td>
</tr>
<tr>
<td>SO</td>
<td>Safranin Orange</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet</td>
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<td>UV/Vis</td>
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1.1 Environmental pollutants:

The term ‘Environment’ is considered as a composite term for the conditions in which organisms live and thus consists of air, water, food and sunlight which are the basic needs of all living beings. The Environment also includes other living things, temperature, wind, electricity, etc. In other words, environment consists of both biotic and a biotic substances. However environment is viewed with different angles by different environmentalists. It may be concluded that, environment consists of an inseparable whole system constituted by physical, chemical, biological, social and cultural elements which are interlinked individually and collectively in myriad ways.\(^{(1)}\)

Pollution is defined as situations in which the outer ambient atmosphere and surroundings contain materials in concentrations which results in deleterious effects of such a nature as to endanger human health, harm living resources or interfere with amenities or other legitimate use of the environment. Pollution is however often associated with the release of substances into the environment which leads to an increase in concentration above the natural levels. Problems could also occur with the introduction of chemical compounds into the environment which disturbs the natural equilibrium; perhaps one of the best examples for this is emission of chlorofluorocarbons which causes depletion in the ozone layer.\(^{(2)}\)

Environmental pollutants are chemical substances of human origin found in air, water, soil, food of the human environment. These undesirable chemical substances are classified as toxic materials which enter the ecosystem in the form of solid, liquid or a gas and pose a serious threat to human being and other living organisms.\(^{(3)}\) Environmental pollutants are commonly divided into chemical and biological classes; chemical
Synthetic dye discharge to natural water sources may pose health concern to all marine as well as human life. (7) Dyestuff discharged into water bodies can chemically react in different ways depending upon whether it is acidic or basic thus the toxicity of dyestuff (i.e. mortality, genotoxicity, mutagenicity and carcinogenicity) affect aquatic organisms (fish, algae, bacteria...etc) as well as mammals. (11) Carcinogenicity is one of the more serious concerns of dyes used in textile industry. Research carried out as early as 1895 showed increased rates of bladder cancer in workers involved in dye manufacturing. (10) More recent studies have also reported increased incidences of bladder cancer in painters. Painting dyes are normally azo dyes, composed of aromatic amines-based on benzidine (such as amido black). These and other studies have clearly established a link between azo dye exposure and bladder tumor. It has been established that the toxicity and carcinogenicity of azo dyes is due to it's metabolism in the body. Azo reductions of these compounds occur due to the enzyme-mediated reaction; this enzyme called azoreductase is found in mammalian tissues especially in liver and skin. Furthermore, certain bacteria such as Staphylococcus aureus also play a major role in such metabolism reactions. (12)

Since it is well established and accepted that these chemical dyes are a major health and environmental concern, a vast amount of resources have been invested in finding ways to reduce the hazards of these dyes in waste effluents. (13)

1.2 Classification of dyes:

Until the 19th century, the primary source of dyes and pigments used to be from natural origin. However, by the end of 19th century the manufacturing of synthetic dyes started when an English chemist called W.H. Perkin attempted to prepare a synthesize quinine in 1856 to obtain alternatives for bluish substances. Perkin was successful in
obtaining a synthetic dye with excellent dyeing properties that latter became known as aniline purple, (Tyrian purple). This concept of manufacturing synthetic dyes was further followed upon by other workers and this set new trends in synthetic dyes, which became marketable goods.

In 1865, Kekule discovered the molecular structure of benzene and thus in the beginning of 20th century, synthetic dyestuff took a new turn by competing with the natural dyes. (11)

Dyes are colored, ionizing aromatic compounds based fundamentally on the structure of benzene (14) which absorb electromagnetic energy and respond over wide UV/Vis range. (11)

Dyes are classified based on their structure, source, color and method of applications in color index (C.I) which has been continuously edited since 1924. (11, 15) Dyes have chemical structures or chromophores which have joined in a sequence of alternating single and double bonds. (14) The delocalized electrons in these structures are responsible for the characteristic UV/Vis spectral properties of these dyes. Depending on the chromophores, 20-30 different groups of dyes can be considered. (11)

The present study deals with the removal of dyes from solution using advanced oxidation process (AOP). In this regard eight of the most commonly used synthetic dyes in textile industry were chosen. In addition, one of the most important and critical factor in our selection was the lack of published on the comparative efficiencies of a given AOP on degradation of diverse classes of dyes.
These dyes included acridine,azo, diarylmethane, triarylmethane, anthraquinone, nitro, xanthene and quinine-imine dyes.

1.2.1 Acridine dyes:

Acridine is a synthetic dye derived from acridine where the chromophore is quinoid ring, a positive charge noted due to the nitrogen atom attached to the quinoid ring. Acridine dyes have the general formula shown in table 1.1.

Acridine O was taken as a representative synthetic dye belonging to this group.

1.2.2 Azo dyes:

Azo dyes are defined as aromatic moieties linked together by azo (-N=N-) chromophores and represent the largest class of dyes used in textile processing. According to the number of chromophores, azo dyes are classified into four subclasses, which are monoazo dyes, disazo dyes, trisazo dyes and tetrakisazo dyes.

Amido black is a synthetic dye and is a representative synthetic dye of a disazo group of dyes. The azo dyes have the general formula is shown in table 1.1.

1.2.3 Arylmethane dyes:

Arylmethane are synthetic dyes derived from methane depending on the replacement of the hydrogen atoms. Arylmethane can be divided into diarylmethane or triarylmethane where hydrogen atoms are replaced by aryl (phenyl) rings. Diarylmethane contain two aryl rings and the dye has the general formula shown in table 1.1.
Auramine O is one of the common used dyes in this subgroup, and was thus used in this study as a representative dye for the group.

Triarylmethane dyes contain three aryl rings and these subgroup dyes contain amino groups, and that is why we sometimes identify them as aminotriarylmethane dyes. Another subgroup of arylmethane have hydroxyl groups instead of amino group, these are termed as hydroxyltriarylmethane.

Malachite green was chosen as a representative synthetic dye for aminotriarylmethane subgroup. Triarylmethane dyes have the general formula shown in table 1.1.

1.2.4 Anthraquinone dyes:

Anthraquinone is a synthetic dye derived from anthracene and is a light yellow to green crystalline substance. (17, 18) It is characterized by the general formula is shown in table 1.1 and shows that the chromophore is a quinoid ring.

Two subclasses of Anthraquinone are well known, hydroxyanthraquinone where the hydroxyl group is attached with the quinoid ring and aminoanthraquinone, where the amino group is attached with the quinoid ring.

Carmine dye which is also a hydroxyanthraquinone has been chosen to be the representative sample for this group of dyes.
1.2.5 Nitro dyes:

Nitro dyes are synthetic dyes characterized by the nitro chromopore (\(-\text{NO}_2\)). The nitro dyes have the general formula shown in table 1.1.

Naphthol Y was chosen as a representative sample of this synthetic dye group.

1.2.6 Xanthenes dyes:

Xanthenes are synthetic dyes derived from xanthene and is divided into three subgroups namely, fluorenes, fluorones and rhodols. Rodamine B, which is a member of rodamine subgroup of fluorenes, was taken as an example of xanthene synthetic dyes.

The general formula of xanthene dyes is shown in table 1.1.

1.2.7 Quinone-imine dyes:

Quinone-imines are synthetic dyes and consist of several subgroups of quinone-imine dyes. Safranin O synthetic dye is a member of azines subgroups and was chosen as a representative sample for quinone-imine synthetic dyes in this work.

Quinone-imine dyes have the general formula shown in table 1.1.
Table 1.1: Different classes of dyes and their structure

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<td>Diarylmethane</td>
<td><img src="image" alt="Diarylmethane Structure" /></td>
<td>Auramine O</td>
</tr>
<tr>
<td>Anthraquinone</td>
<td><img src="image" alt="Anthraquinone Structure" /></td>
<td>Carmine</td>
</tr>
<tr>
<td>Triarylmethan</td>
<td><img src="image" alt="Triarylmethan Structure" /></td>
<td>Malachite green</td>
</tr>
<tr>
<td>Nitro</td>
<td><img src="image" alt="Nitro Structure" /></td>
<td>Naphthol Y</td>
</tr>
<tr>
<td>Xanthene</td>
<td><img src="image" alt="Xanthene Structure" /></td>
<td>Rhodamine B</td>
</tr>
<tr>
<td>Quinone-imine</td>
<td><img src="image" alt="Quinone-imine Structure" /></td>
<td>Safranin O</td>
</tr>
</tbody>
</table>
1.3 Ways for dyes removal from wastewater:

Textile industries represent one of the major environmental contamination sources due to the large amount produced from these industries. More than 100,000 commercial dyes are known and about $450 \times 10^5$ tones per year of these are produced annually. Although small amounts of these dyes are directly discharged in aqueous effluents, but due to their high solubility in water, they are considered to be the most common water pollutants because of their toxicity and carcinogenic properties. It seems that it is difficult to treat this kind of pollutant due to its stability to light, heat and oxidizing agents. Since synthetic dyes are very harmful to the environment, it is important to remove these dyes from solution or treat them chemically so that their harmful effects are minimized.\(^{(19)}\)

Several techniques such as physical processes, biological processes, electrochemical processes and chemical processes have been applied to remove or reduce the toxicity effect of synthetic dyes from wastewater.\(^{(20)}\)

1.3.1 Physical processes:

Physical methods are the separation of dyes before it reaches the wastewater without a chemical treatment.\(^{(21)}\) Filtration (nanofiltration, ultrafiltration and microfiltration) is the one of physical methods where dyes are treated using different filters and membranes to eliminate the particles of polluted substances\(^{(20)}\) and to separate the organic compounds of low molecular weight and divalent ions from mono valent ions present in the wastewater.\(^{(6)}\)

Other physical processes use adsorption techniques (on activated carbons or biological sludge). The biotic mechanism for removing dyes from wastewater by
adsorption on sludge is well known and this is affected by sludge quality, water hardness and substance concentration. \( ^{(20)} \)

The physical methods have some disadvantages, for example the time consumed is long, the filters are blocked, and the treatment of sludge is costly and quality of treated wastewater is insufficient. \( ^{(6,13,20)} \)

\subsection*{1.3.2 Biological processes:}

Biological treatment techniques deal with the removal of dyes by using microbial biotransformation of dyes because these dyes are designed to be stable and long-lasting colorants, so they are not easily biodegraded. Many researches have demonstrated partial or complete biodegradation of dyes using pure and mixed bacteria, fungi and algae cultures. \( ^{(11)} \) In case of bacterial biodegradation the dye biodegradability is done with fungicides which degrade a wide range of aromatics due to the relatively non-specific activity of their enzymes. The catalyzing power of fungal species and the dye selectivity should be considered in fungal biodegradation. \( ^{(20)} \) Those which are using algal biodegradation involve reductive cleavage of azo linkage. Algae have been demonstrated to degrade various aromatic amines which are already formed so algal biodegradation may contribute to the removal of azo dyes and aromatic amines from the wastewater (shallow water). \( ^{(11)} \)

The biological treatment showed some disadvantages such as the biodegradability of dyes is low; in addition some biological treatment techniques are not always met with great success and the treatment is costly. \( ^{(6)} \)
1.3.3 Electrochemical processes:

Electrochemical techniques stand on the main principle that when discharge of an electric current occurs through the electrodes in the wastewater, induction of different reduction-oxidation (redox) chemical reaction takes place. \(^{(21)}\) In electrochemical processes, oxidation of organic compounds in water occurs at the anode where chlorine gas will be collected. On the other hand reduction will occur at the cathode where oxygen gas will be collected. \(^{(21)}\)

The advantages of electrochemical processes are that it has high capacity of adaptation to various volumes and different pollution loads. Several studies have shown that electrochemical methods can be successfully used to achieve decolorization of dyes solutions and dye containing wastewaters. \(^{(11)}\) Electrochemical processes are limited in use because they generate the formation of ion hydroxide sludge; \(^{(6)}\) electrochemical processes cost is high due to large energy requirements and the electrodes have limited lifetime. \(^{(11)}\)

1.3.4 Chemical processes:

The chemical process of treatment consists of coagulation, flocculation, adsorption, chlorination, reduction and bleaching with hydrogen peroxide where all the methods mentioned above cause decoloration, mineralization and degradation of dyes. \(^{(21)}\)

Recently, researchers have started considering the photochemical process as an advanced oxidation processes (AOP) due to their effectiveness. \(^{(22)}\)
1.4 Advanced Oxidation processes (AOPs):

Advanced oxidation processes are oxidation processes which are highly efficient in the removal of dyes and destroying a wide range of organic pollutants. It is based on the formation of a very reactive radical species such as hydroxyl radicals which is characterized with its higher oxidation capacity (oxidation potential $E_0 = 2.28 \text{ V}$) than any other oxidants, such as oxygen ($E_0 = 1.23 \text{ V}$), hydrogen peroxide ($E_0 = 1.78 \text{ V}$) and ozone ($E_0 = 2.07 \text{ V}$). Advanced oxidation processes involve the generation of highly reactive free radicals with the effectiveness of mineralization of various refractory and hazardous organics into $\text{CO}_2$, $\text{H}_2\text{O}$ and some anions, which are safe for the environment.

In 1970's, attempts were made where the oxidation process were improved to obtain fast and efficient ways of dye effluent treatment keeping in mind the safety of the environment so that it doesn't causes any secondary pollution. Oxidation of the waste water from photographic studies had been done by Garrison who first applied the method of advanced oxidation method for this purpose. After Garrison's attempts, advanced oxidation processes have received considerable attention due to its many observable advantages. They have been studied at ambient temperatures involving the generation of short lived highly oxidative species specially hydroxyl radicals. In principle advanced oxidation processes are characterized by high oxidation rates, flexibility, small dimension of the equipments used for water recycling processes, high reactivity and low selectivity of the reaction which enable the method to be applied to a large number of organic compounds present in the wastewater.
In summary, AOPs rely on the generated of OH radicals to degrade and breakdown organic dyes or pollutants as follows:

\[
\text{AOPs} \rightarrow \text{OH}^* \quad (1)
\]

\[
\text{RH} + \text{OH}^* \rightarrow \text{Products (P)} \quad (2)
\]

\[
\text{P} + \text{OH}^* \rightarrow \text{final Products (CO}_2, \text{H}_2\text{O)} \quad (3)
\]

The most widely used advanced oxidation processes are the following: \(^{(6)}\)

- Ozonation
- Fenton's reagent
- Heterogeneous catalysis + UV and photocatalysis
- Photolysis

1.4.1 Ozonation

The ozonation process produces hydroxyl radicals when ozone (O\(_3\)) decomposes in water.

This method is faster in alkaline solution than neutral or acidic media because ozone decolorizes water soluble dyes rapidly but in case of non-soluble dyes it reacts much slower, in addition the half life of ozone in water is less than 1 min. In addition the major operating cost for oxidation process of ozone is equal to the cost of electricity of ozone generation when air is used as a feed gas for ozone synthesis. \(^{(11, 27)}\)

Others have used peroxone where hydrogen peroxide is added to ozone because it is reductively inexpensive and available for the purpose of initiation of the decomposition cycle of ozone, thus the formation of hydroxyl radicals results. \(^{(27)}\) The combination of
different reaction steps shows that two ozone molecules produce two OH radicals as shown in the following equation. (11)

\[
2\text{O}_3 + \text{H}_2\text{O}_2 \rightarrow 2\cdot\text{OH} + 3\text{O}_2
\]

This leads to better degradation of organic compounds in wastewater compared to ozone alone. The performance of this process depends on these factors, ozone dose, contact time and alkalinity of wastewater.

Researches looking for an efficient ozone photolysis method utilize UV lamps with a radiation output at 254 nm. Many organic contaminants absorb UV energy in the range of 200-300 nm and decompose due to direct photolysis, as they become exited and react with chemical oxidants. (27) In this process (O₃/UV) ozone readily absorbs UV radiation and produces hydrogen peroxide as an intermediate which then decomposes to hydroxyl radicals (OH), which in turn causes the oxidation and degradation of organic compounds as shown in this equation. (11)

\[
\text{hv}
\text{O}_3 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{O}_2 + \text{O}_2
\]

The use of O₃/UV system depends on the molecular structure of pollutants. If wastewater contains organic compounds which strongly absorb UV light then UV radiation does not give any additional effect to ozone because of the screening of ozone from the UV by optically active compounds. (27) Ozonation can be enhanced with the use of ozone, hydrogen peroxide and ultraviolet radiation (O₃, H₂O₂, and UV). As the hydroxyl radical (OH⁻) generation rate is increased, the oxidation of organic compounds
also increases which leads to more degradation of the wastewater pollutants. Thus the efficiency of \( \text{O}_3/\text{H}_2\text{O}_2/\text{UV} \) process is higher as compared to other ozone processes.\(^{(27)}\)

The operational method considered for \( \text{UV}/\text{O}_3 \) (and/or \( \text{H}_2\text{O}_2 \)) systems depends on the rate of wastewater flow rate, types of pollutants, concentration of pollutants present and the degree of removal required.\(^{(27)}\) It is advised to run the ozonation process as a final stage (after biological treatment and filtration) for treating textile wastewater at full scale.\(^{(11)}\)

1.4.2 **Fenton's reagent/photofenton:**

They are two related techniques of advanced oxidation processes based on the presence of hydrogen peroxide.

The Fenton's reagent is a well known reaction which uses catalytic mechanism of an electron transfer between the hydrogen peroxide and a metal acting as a homogenous catalyst; the most common metal used is iron.\(^{(28)}\)

\[ \text{Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH} \]

This process is more suitable to treat wastewaters which are resistance to biological treatment; it decolorizes a wide range of dyes and industrial waste containing a range of organic compounds like phenols, formaldehyde and pesticides.\(^{(11, 28)}\) Fenton's reagent process is relatively cheap as compared to ozonation processes.\(^{(11)}\) Fenton's reagent method shows major disadvantage at higher pH and also that large volumes of waste sludge are generated by the precipitation of ferric irons salts. The process losses effectiveness because the hydrogen peroxide is catalytically decomposed to oxygen and
the process will be negatively affected by the presence of radical scavengers and strong chelating agents in wastewater. \(^{(8, 11)}\)

Photo-Fenton is one of the photo catalytic oxidation processes based on the hydroxyl free radicals formation due to ultraviolet irradiation.

\[
\text{Fe}^{3+} + \text{H}_2\text{O} \rightarrow \text{Fe(OH)}^{2+} + \text{H}^+ \\
\text{Fe(OH)}^{2+} + \text{hv} \rightarrow \text{Fe}^{2+} + \cdot \text{OH}
\]

It is described as an efficient and economically methods for wastewater treatment compared to dark Fenton's reagents. \(^{(11, 28)}\) In addition, photo Fenton process is considered as a better option to treat and eliminate textile dyes because the process has the capacity to completely decolorize and partially mineralize the textile dyes in short reaction time. \(^{(24)}\) The limitation of this method comes from the insufficient penetration of UV light in highly intense colored wastewater streams. \(^{(11)}\)

1.4.3 TiO\(_2\)-photocatalysis (UV/TiO\(_2\)):

For the environment decontamination and cleanup, photocatalysis methods are also used. TiO\(_2\) both in the anatase and rutile forms is one of the most widely used metal oxides in industry. Its high refractive index in the visible range permits preparation of thin films, thus it used as a pigment material in addition to as a catalyst support or as a photocatalyst by itself. TiO\(_2\) can be activated by UV radiation with a wavelength up to 387 nm. So in advanced oxidation photocatalysis processes, TiO\(_2\) acts as a photocatalyst of high efficiency due to its photochemical stability and non-toxic nature. \(^{(29)}\) The use of
TiO$_2$ gives extra efficient result and potential advantages if the process is done under UV light elimination and it is very useful in the treatment of wastewater pollutants such as synthetic dyes.\(^{(29, 30)}\)

In the process mentioned above, photoexitation of semiconductor leads to the formation of electron hole pair which then undergoes oxidation/reduction reactions resulting in the mineralization of the pollutants present in waste wastewater.\(^{(27, 30)}\)

1.4.4 Photolysis (UV/ H$_2$O$_2$):

In the advanced oxidation process, photolysis is the most important method that has gained attention during the last decades because it is one of the widely used chemical techniques to decolorize textile wastewater. In this method UV irradiation is combined with some powerful oxidants such as hydrogen peroxide.\(^{(31)}\)

Additionally, UV/H$_2$O$_2$ degradation is also simple to use besides being homogeneous and has also shown promising results in degrading many other organic compounds. The process in general demands the generation of OH radicals in solution in the presence of UV light. These radicals can then attack the dye molecules to undergo a series of reaction in which the organic molecules is finally destroyed or converted into simple harmless compounds.

The mechanism of photolysis can be summarized as follows.\(^{(32)}\)

a. Hydrogen peroxide photolysis to produce hydroxyl radicals

\[
\text{H}_2\text{O}_2 + \text{UV} \rightarrow 2\text{OH}^* \tag{1}
\]

b. Reaction highly reactive OH$^*$ with pollutants which gives primary products (P)

\[
\text{RH} + 2\text{OH}^* \rightarrow \text{Products (P)} \tag{2}
\]
c. Oxidation of primary products (P) with OH• in the presence of dissolved oxygen to mineral compounds

\[ P + OH\cdot \rightarrow \text{final Products (CO}_2, \text{H}_2\text{O)} \quad (3) \]

d. The reaction can also occur between OH• with excess H_2O_2

\[ 2OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O_2 \quad (4) \]

It may be noted that H_2O_2 acts as a scavenger for OH radicals hence an excessive H_2O_2 dose might actually hinder the radical degradation.\(^{32,33}\)

Experimentally, different concentration of hydrogen peroxide is tried until an optimum level of H_2O_2 dose is achieved.\(^{32}\)

The H_2O_2/UV process has several and unique advantages such as that the only reagent required is H_2O_2 which is easily available (35% solution), it can be easily stored, it is miscible in water and no mass transfer problem will occur. Also that H_2O_2/UV process is more reasonable to use with a small system which requires minimum maintenance and intermittent operation.\(^{32}\) In this process no sludge formation occurs, it is less pH-dependent,\(^{34}\) the operation can be run at ambient temperatures, also that the oxygen formed during the process is very useful for aerobic biological decay process.\(^{13}\) The process leads to complete decolorization and mineralization of sulphonated azo and anthraquinone dyes in short time.\(^{31}\) The final products in this method are H_2O, CO_2 and low molecular weight aliphatic acids.\(^{13}\)
The photolysis operating parameters (UV/H$_2$O$_2$) are feasible and economical. The process also appears to pose additional advantages such as powerful oxidation ability, high decomposition efficiency of hazardous organics and low toxic intermediates.\textsuperscript{(35)}
Chapter II

MATERIALS AND METHODS
2. MATERIALS AND METHODS:

The following sections detail the materials and methods used in the experiments outlined in this thesis. The decolorisation method using UV/H₂O₂ and the identification method using GC/MS and HPLC will also be described.

2.1 Materials and reagents:

2.1.1 Dyes:

The present study deals with the removal of eight of the most common used synthetic dyes in textile industry.

Acridine Orange (C.I name is Basic orange 14), from acridine group. It has a yellow color and a maximum absorption around 489 nm. The structure formula is shown in table 2.1.

Amido black 10B (C.I name is Acid black1), from the azo group. It has a blue black color and a maximum absorption around 618 nm. The structure formula is shown in table 2.1.

Auramine O (C.I name is Basic yellow 2), from diarylmethane group. It has a yellow color and a maximum absorption around 434 nm. The structure formula is shown in table 2.1.
Carmine (C.I name is Natural Red 4), a naturally occurring important dye. Carmine is from anthroquinone group. It has a red color and a maximum absorption around 500 nm. The structure formula is shown in table 2.1.

Malachite green (C.I name is Basic green 4), a commercial triarylmethane dye. It has a green color and a maximum absorption around 614 nm. The structure formula is shown in table 2.1.

Naphthol Yellow S (C.I name is Acid yellow 1), from nitro group. It has a yellow color and has a maximum absorption around 428 nm. The structure formula is shown in table 2.1.

Rhodamine B (C.I name is Basic violet 10), an amphoteric dye, commonly used as a fluorochrome. Rhodamine B is from Xanthene group. It has a red color and a maximum absorption around 543 nm. The structure formula is shown in table 2.1.

Safranin-O (C.I name is Basic Red 2), a histologically important dye for counterstaining cartilages, Safranin O is from quinine-imine group, it has red color and a maximum absorbance around 530 nm. The structure formula is shown in table 2.1.
Table 2.1: Different dyes classes with the structure of the represented dyes

<table>
<thead>
<tr>
<th>Dye</th>
<th>Structure</th>
<th>Class</th>
<th>$\lambda_{max}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acridine O</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Acridine</td>
<td>497 nm</td>
</tr>
<tr>
<td>Amido Black</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Azo</td>
<td>618 nm</td>
</tr>
<tr>
<td>Auramine O</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Diarylmethane</td>
<td>432 nm</td>
</tr>
<tr>
<td>Carmine</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Anthraquinone</td>
<td>500 nm</td>
</tr>
<tr>
<td>Malachite green</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Triarylmethane</td>
<td>618 nm</td>
</tr>
<tr>
<td>Naphthol Y</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Nitro</td>
<td>428 nm</td>
</tr>
<tr>
<td>Rhodamine B</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Xanthene</td>
<td>555 nm</td>
</tr>
<tr>
<td>Safranin O</td>
<td><img src="example.png" alt="Structure" /></td>
<td>Quinone-imine</td>
<td>530 nm</td>
</tr>
</tbody>
</table>
Dyes were obtained from either Fluka or Sigma and used as such. Deionized water was used for preparing solutions.

2.1.2 Other reagents:

Hydrogen peroxide (35% w/w) was obtained from Merck and was used as such in this work. Its final concentration was varied depending on the dye.

For studying the effect of pH on dye degradation, the pH of the dye solution was altered by adding incremental amounts of either concentrated HCl or concentrated NaOH.

For experiments examining the effects of different ions on the decoloration of dyes, a final concentration of 1 mg/ml of various salts was added to the dye solution before the addition of H₂O₂. Sodium salts were chosen to study the effect of ions that are normally present in textile wastewater streams.

2.2 Apparatus

2.2.1 Apparatus for dyes decoloration:

All the decoloration studies were done on a CARY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell. For photolytic experiments, the samples were irradiated with a UV lamp with an output at 254 nm at a distance of 16 cm (fig 2.1).

2.2.2 Apparatus for dyes degradation:

All the degradation studies were done on a Varian Gas chromatography (3800)-mass spectrometry (Saturn 2000), using a CP-Sil 24 CB Low Bleed/MS
Figure 2.1: Decoloration Method using UV lamp
column, operating temperature programmed (40.3-150-10.1-250-10.1) in splitless mode. An injection volume of 1 μl with helium as a carrier gas was used.

High Performance liquid chromatography (HPLC) was used using C₈-Eclipse column (Agilent) utilizing a 0 – 100% methanol (water as the base mobile phase) gradient over 30 minutes, at 1 ml/min.

2.3 Methods for studying dye decoloration/degredation:

2.3.1 UV-Visible decoloration:

Stock solutions of 1x10⁻³ M for each eight dyes were prepared in 100 mL of deionized water in a 250 mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dyes solutions with varying concentrations. A known amount of the diluted solutions was mixed with a given amount of H₂O₂ and the mixture was irradiated with UV light of 254 nm. After a given time interval, the absorbance of the solution was monitored instantaneously on CARY 50 UV/VIS spectrophotometer. The changes in absorbance value obtained in each case were plotted against time to obtain the order of apparent decoloration rate. Photolytic oxidation studies were carried out at 25 ± 2°C.

The pH effect on dye decoloration was also studied by changing the pH of the dye solution by adding incremental amounts of either dilute HCl or diluted NaOH.

For experiments examining the effects of different additives (ions) on the decoloration of these dyes, 1 mg/ml of the salt were added to the dye solution before the addition of H₂O₂. None of the salts used had any effect on the dye spectra in the
absence of UV light. The solution was then irradiated with UV light and change in absorbance value was noted to calculate the apparent decoloration rate constant.

For experiments examining the effects of different ions on the decoloration of dyes, a final concentration of 1 mg/ml of various salts were added to the dye solution before the addition of H₂O₂. The Absorbance's of solutions were monitored instantaneously on CARY 50 UV/VIS spectrophotometer.

2.3.2 HPLC

For HPLC analysis of the dye decoloration/degradation, 50 ml of dye solutions were taken either time zero (right after addition of H₂O₂ and no UV irradiation) 30 minutes of UV irradiation after addition of H₂O₂, and the organic component of the mixture was extracted using dichloromethane. The organic layer was extracted again for a second time with dichloromethane, and then dried in a rotary evaporator. The dried substance (dye and/or degraded by-products) was then dissolved in 100% dichloromethane and then used for HPLC analysis. The samples were run on C₈-Eclipse column (Agilent) using a 0 – 100% methanol (water as the base mobile phase) gradient over 30 minutes, at 1 ml/min, and analyzed by measuring the absorbance at 280 nm. A representative HPLC method profile is shown below (Fig 2.2)
Figure 2.2: Method profile showing the methanol gradient used for HPLC analyses of dyes and their degradation products.
2.3.3 GC/MS

For GC/MS analysis of the dye decoloration/degradation, 50 ml of dye solutions were taken either at time zero (right after addition of H₂O₂ and no UV irradiation) or after 30 minutes of UV irradiation after addition of H₂O₂, and the organic component of the mixture was extracted using dichloromethane. The organic layer was extracted again for a second time with dichloromethane, and then dried in a rotary evaporator. The dried substance (dye and/or degraded by-products) was then dissolved in 100% dichloromethane and then used for GC/MS analysis using Varian GC/MS system. The samples were run on CP-Sil 24 CB Low Bleed/MS column operating temperature programmed (40, 3-150-10, 1-250-10, 1) in splitless mode. An injection volume of 1 μl with helium as a carrier gas was used.
Chapter III

RESULTS AND DISCUSSION
3. Results and discussion

3.1 Decoloration studies of Acridine O in the presence of UV/H₂O₂

Photolytic decoloration of Acridine O (C.I name is Basic Orange 14) was carried out in the presence of UV light and hydrogen peroxide. The absorbance changes in the dye solution were monitored spectrophotometrically.

The present work involves the study of the kinetics of H₂O₂ assisted photochemical oxidation of Acridine O. The structure of Acridine O is shown in (table 2.1). The decoloration studies were done by observing changes in the absorbance value of Acridine O at 539 nm. Initial experiments revealed no decoloration of dye solution with either UV light or H₂O₂ alone. However, the dyes started decolorizing immediately in the presence of H₂O₂ and UV radiation. The initial investigation of the dye revealed a major peak at 539 nm as shown in (figure 3.1). Absorption spectra of the dye solution were monitored at regular intervals of time and percentage decrease in absorption was calculated as follows

\[
\% \text{ dye decoloration} = \left\{ \frac{(1 - A_t)}{A_0} \right\} \times 100
\]

where, Aₜ is the dye absorbance value at any given time, and A₀ is the initial dye absorbance value in solution. Changes in absorption value as a function of irradiation time, which is a direct measure of dye decoloration was found to fit well to a first order rate equation given by:
Figure 3.1: Time dependent degradation of Acridine O by UV/H$_2$O$_2$ within 30 minutes. [Acridine O] = 2.0µM, [H$_2$O$_2$] = 3.3mM.
\[ \ln \left( \frac{A_0}{A_t} \right) = k t \]  

where \( k \) is the apparent rate constant, \( t \) is the irradiation time and \( A_0 \) and \( A_t \) are the initial and the final absorbance values of the dye solution respectively.

Hydroxyl radicals are the main source of dye decoloration and are produced in solution due to irradiation by UV light. \(^{(36)}\)

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]  

Due to their strong oxidizing nature, hydroxyl radicals can react with the dye molecules to produce intermediates which can thus cause the decoloration of the original solution. \(^{(37)}\)

\[ \cdot \text{OH} + \text{dye} \rightarrow \text{Intermediates} \rightarrow \text{Products} \]  

The decoloration kinetics of Acridine O was carried out systematically by varying the concentration of both \( \text{H}_2\text{O}_2 \) and of the dyes. (Figure 3.2) and (table 3.1) show the effect of varying dye concentration on the kinetics of dye decoloration. The apparent rate becomes less with an increase in Acridine O concentration. Similarly, (figure 3.3) and (table 3.2) shows the apparent rate constants and percentage decoloration of Acridine O at different \( \text{H}_2\text{O}_2 \) concentrations. It can be seen that the apparent rate of dye decoloration increased with \( \text{H}_2\text{O}_2 \) concentration.
Table 3.1: Effect of Acridine O concentration on its photolytic decoloration.
\[ \text{(H}_2\text{O}_2 = 3.3 \text{ mM)} \]

<table>
<thead>
<tr>
<th>[acridine O] ( \mu \text{M} )</th>
<th>( K \times 10^{-2} \text{ (min}^{-1} )</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>1</td>
<td>6.3</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>3.7</td>
<td>0.2</td>
</tr>
<tr>
<td>3</td>
<td>2.6</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Figure 3.2: Effect of Acridine O concentration on the percent decoloration and apparent rate constant of the decoloration reaction. \([\text{H}_2\text{O}_2] = 3.3\text{mM}\).
Table 3.2: Effect of H$_2$O$_2$ concentration on Acridine O decoloration.
(Acridine O = 2.0 μM)

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] mM</th>
<th>K *10$^{-2}$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>1.67</td>
<td>4.6</td>
<td>0.6</td>
</tr>
<tr>
<td>3.34</td>
<td>6.3</td>
<td>0.2</td>
</tr>
<tr>
<td>6.67</td>
<td>8.2</td>
<td>1.1</td>
</tr>
<tr>
<td>33.3</td>
<td>7.4</td>
<td>0.1</td>
</tr>
<tr>
<td>66.6</td>
<td>5.5</td>
<td>0.2</td>
</tr>
</tbody>
</table>

Figure 3.3: Effect of Hydrogen peroxide concentration on the percent decoloration and apparent rate constant of the decoloration reaction. [Acridine O] = 2.0μM.
However, as expected, at high concentrations, the solution undergoes self quenching of •OH radicals by added amounts of H$_2$O$_2$ to produce HO•$_2$ radicals, thereby causing a decrease in % decoloration.

$$\text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}\cdot_2$$  \hspace{1cm} (4)

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways.\(^{(38)}\) Thus one can assume that H$_2$O$_2$ acts as a pseudo catalyst in this case.

In subsequent decoloration studies, the concentration of H$_2$O$_2$ was kept at an optimum level of 3.33 mM, and the Acridine O concentration was maintained at 2 μM.

Dye decoloration was also studied in various acidic or basic conditions. The pH value of was changed by adding incremental amounts of either concentrated HCl or NaOH to the dye solution and irradiating it with UV light in the presence of H$_2$O$_2$. (Table 3.3) shows the percentage change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more in basic media as compared to acidic media. This is most likely due to the fact that in alkaline pH, peroxide anions (HO$_2^-$) are produced in solution by UV radiation, which in turn can generate more •OH radicals.\(^{(39)}\)

$$\text{HO}_2^- + \text{hv} \rightarrow \cdot \text{OH} + \text{O}\cdot^-$$  \hspace{1cm} (5)
Table 3.3: Effect of pH on Acridine O decoloration.
(Acradine O = 2.0 μM; H₂O₂ = 3.33 mM)

<table>
<thead>
<tr>
<th>pH</th>
<th>K *10⁻² (min⁻¹)</th>
<th>Mean</th>
<th>STD</th>
<th>% decoloration</th>
<th>Mean</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>4.1</td>
<td>0.2</td>
<td></td>
<td>70.9</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>6.3</td>
<td>0.2</td>
<td></td>
<td>85</td>
<td>1.1</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>5</td>
<td>0.1</td>
<td></td>
<td>77</td>
<td>0.3</td>
<td></td>
</tr>
</tbody>
</table>
It has been previously noted that ions which are normally present in textile wastewater streams can have dramatic effects on the kinetics of dye decoloration. Therefore, the effects of various anions on the photolytic decoloration of Acridine O were also noted. The kinetics of dye decoloration in the presence of these ions and percentage decoloration of the dye solution in the presence of these ions is shown in (table 3.4). It can be seen from this table that most of the ions tested had little effect on dye degradation except sulfite ions which actually reduced the percent decoloration.

Under conditions where around 80% Acridine O would normally be degraded, sulphite ions reduced this to only 26%. This can be explained by the fact that sulfite anions can readily react with hydroxyl radicals as shown below.

\[ \cdot \text{OH} + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \cdot \text{SO}_3^- \quad k = 5.1 \times 10^9 \text{ (L/mol}\cdot\text{s)} \]  

In conclusion, Acridine O dye was subjected to UV light in the presence of hydrogen peroxide. The dye underwent decoloration which was observed by monitoring the changes in the absorption values of the dye solutions. The photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution. First order kinetics was found to fit well to the decoloration scheme of the dye. The decoloration of Acridine O became less in the presence of sulphite and nitrate ions. For effective decoloration of the Acridine O, sulphite ions should thus in particular be removed from the dye solution prior to its exposure to UV light.
Table 3.4: Effect of various ions on Acridine O decoloration.
(Acridine O = 2.0 μM; H₂O₂ = 3.33 mM)

<table>
<thead>
<tr>
<th>[Ions] = 1 mg/mL</th>
<th>$K \times 10^{-2}$ (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>-</td>
<td>6.3</td>
<td>0.2</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>5.2</td>
<td>0.3</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>5.4</td>
<td>0.1</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>4.9</td>
<td>0.3</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>0.6</td>
<td>0</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>6.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
3.2 Photolytic decoloration of Amido Black by UV/H$_2$O$_2$

Amido B (C.I name is Acid Black 1) was irradiated with UV light in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically.

In the present work, the kinetics of H$_2$O$_2$ assisted photochemical oxidation of Amido B was investigated. The structure of Amido B is shown in (table 2.1). The decoloration studies were attempted by observing changes in the absorbance value of Amido B at 618 nm. Initial experiments with either UV light or H$_2$O$_2$ alone did not cause any significant changes in the decoloration of dye. However, the dye started degrading immediately in the presence of H$_2$O$_2$ and UV radiation. The initial investigation of the dye revealed a major peak at 618 nm as shown in (figure 3.4). Changes in the absorption spectra of the dye solution were monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows

$$\% \text{ dye decoloration} = \{1 - \frac{A_t}{A_0}\} \times 100$$

Where, $A_t$ is the dye absorbance value at any given time, and $A_0$ is the initial dye absorbance value in solution. Changes in absorption value as a function of irradiation time, which is a direct measure of dye decoloration was found to fit well to a first order rate equation given by:

$$\ln \left(\frac{A_0}{A_t}\right) = k t \quad (1)$$
Figure 3.4: Time dependent degradation of Amido B by UV/H$_2$O$_2$ within 30 minutes. 
[Amido B] = 20 μM, [H$_2$O$_2$] = 3.3 mM.
Where $k$ is the apparent rate constant, $t$ is the irradiation time and $A_0$ and $A_t$ are the initial and the final absorbance values of the dye solution respectively.

The decoloration of the dye solution is mainly due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light.\(^{(36)}\)

\[
H_2O_2 + h\nu \rightarrow 2 \cdot OH
\] \hspace{1cm} (2)

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the decoloration of the original solution

\[
\cdot OH + \text{dye} \rightarrow \cdot P
\] \hspace{1cm} (3)

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the decoloration reaction of the dye molecule.\(^{(37)}\)

To optimize the decoloration kinetics of Amido B, we carried out a systematic study varying the concentration of both $H_2O_2$ and of the dyes. (Figure 3.5) and (table 3.5) show the effect of varying dye concentration on the kinetics of dye decoloration. The apparent rate becomes less with increase in Amido B concentration.
**Table 3.5:** Effect of Amido B concentration on its photolytic decoloration. 

\((\text{H}_2\text{O}_2 = 3.3\ \text{mM})\)

<table>
<thead>
<tr>
<th>[Amido B] µM</th>
<th>(K \times 10^{-2} \text{ (min}^{-1})</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>9.6</td>
<td>0</td>
</tr>
<tr>
<td>20</td>
<td>5.1</td>
<td>0.1</td>
</tr>
<tr>
<td>30</td>
<td>3.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

**Figure 3.5:** Effect of Amido B concentration on the percent decoloration and apparent rate constant of the decoloration reaction. \([\text{H}_2\text{O}_2] = 3.3\text{mM}\).
Similarly, (Figure 3.6) and (table 3.6) show the apparent rate constants and percentage decoloration of Amido B at different H$_2$O$_2$ concentrations. It can be seen that the apparent rate of dye decoloration increased with H$_2$O$_2$ concentration.

However, as expected, at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of H$_2$O$_2$ to produce HO$_2^-$ radicals, thereby causing a decrease in percent decoloration.

\[
H_2O_2 + \cdot OH \rightarrow H_2O + HO_2^-
\]  

(4)

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways.\(^{(38)}\) Thus one can assume that H$_2$O$_2$ acts as a pseudo catalyst in this case.

For subsequent decoloration studies, the concentration of H$_2$O$_2$ was kept at an optimum level of 3.3 mM, and the Amido B concentration was maintained at 80 µM.
Table 3.6: Effect of $\text{H}_2\text{O}_2$ concentration on Amido B decoloration. 
(Amido B = 20 $\mu$M)

<table>
<thead>
<tr>
<th>$[\text{H}_2\text{O}_2]$ mM</th>
<th>$K \times 10^{-2}$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>2.3</td>
<td>50.2</td>
</tr>
<tr>
<td>1.67</td>
<td>3.8</td>
<td>67.9</td>
</tr>
<tr>
<td>3.34</td>
<td>5.1</td>
<td>78.7</td>
</tr>
<tr>
<td>6.68</td>
<td>6.9</td>
<td>88.6</td>
</tr>
<tr>
<td>66.6</td>
<td>5.8</td>
<td>83.1</td>
</tr>
</tbody>
</table>

Figure 3.6: Effect of Hydrogen peroxide concentration on the percent decoloration and apparent rate constant of the decoloration reaction, 
$[\text{Amido B}] = 20\mu$M.
The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/ H$_2$O$_2$. (Table 3.7) show the percentage change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more in basic media as compared to acidic media. This is most likely due to the fact that in alkaline pH, peroxide anions (HO$_2^-$) are produced in solution by UV radiation, which in turn can generate more OH radicals. (39)

$$\text{HO}_2^- + \text{hv} \rightarrow \text{OH}^- + \text{O}^-$$ (5)

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye decoloration. (40) Therefore, we tested the effects of various anions on the photolytic decoloration of Amido B. The kinetics of dye decoloration in the presence of these ions and percentage decoloration is shown in (table 3.8). It can be seen from this table that carbonate and chloride ions did had a drastic effect on dye degradation. The increase in dye decoloration was due to the alkalinity of the solution not to the effect of the presence of ions. More work is needed to confirm the exact mechanism. Also surprisingly, sulfite anions did not account for a large change in % decoloration.

Under conditions where more than 50% Amido B would normally be degraded, sulphite ions reduced this to only 21%. This can be explained by the fact that sulfite anions can readily react with hydroxyl radicals as shown below. (41)

$$\cdot\text{OH} + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \cdot\text{SO}_3^-$$

$$k = 5.1 \times 10^9 \text{ (L moL}^{-1} \text{s}^{-1})$$ (6)
Table 3.7: Effect of pH on Amido B decoloration.  
(Amido B = 20 μM; H₂O₂ = 3.3 mM)

<table>
<thead>
<tr>
<th>pH value</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>2</td>
<td>57.9</td>
</tr>
<tr>
<td>7</td>
<td>78.7</td>
</tr>
<tr>
<td>11</td>
<td>74.8</td>
</tr>
</tbody>
</table>

Table 3.8: Effect of various ions on Amido B decoloration.  
(Amido B = 20 μM; H₂O₂ = 3.3 mM)

<table>
<thead>
<tr>
<th>[Ions]= 1 mg/mL</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>---</td>
<td>5.1</td>
<td>0.1</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>5.4</td>
<td>0.6</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>4.9</td>
<td>0</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>4.4</td>
<td>0.05</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>0.8</td>
<td>0.1</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>8.7</td>
<td>0.2</td>
</tr>
</tbody>
</table>
In conclusion, photolytic oxidation of Amido B was carried out in the presence of hydrogen peroxide. The decoloration of the dye solution was observed by monitoring the changes in the absorption values of the dye solutions. It was found that first order kinetics fitted well to the decoloration scheme of both the dyes. The decoloration of Amido B was pronounced in the presence of sulphite and nitrate ions. Thus for effective decoloration of the Amido B, these ions should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dyes is due to the reaction of the dye with the hydroxyl radicals generated in solution.
3.3 Decoloration studies of Auramine O in the presence of UV/H$_2$O$_2$

Photolytic decoloration of Auramine O (C.I name is Basic Yellow 2) was carried out in the presence of UV light and hydrogen peroxide. The absorbance changes in the dye solution were monitored spectrophotometrically.

The present work involves the study of the kinetics of H$_2$O$_2$ assisted photochemical oxidation of Auramine O. The structure of Auramine O is shown in (table 2.1). The decoloration studies were done by observing changes in the absorbance value of Auramine O at 430 nm. Initial experiments revealed no decoloration of dye solution with either UV light or H$_2$O$_2$ alone. However, the dyes started decolorizing immediately in the presence of H$_2$O$_2$ and UV radiation. The initial investigation of the dye revealed a major peak at 430 nm as shown in (figure 3.7). Absorption spectra of the dye solution were monitored at regular intervals of time and percentage decrease in absorption was calculated as follows

\[
\text{% dye decoloration} = \left\{ \frac{1 - A_t}{A_0} \right\} \times 100
\]

where, $A_t$ is the dye absorbance value at any given time, and $A_0$ is the initial dye absorbance value in solution. Changes in absorption value as a function of irradiation time, which is a direct measure of dye decoloration was found to fit well to a first order rate equation given by:

\[
\ln \left( \frac{A_0}{A_t} \right) = k t \quad (1)
\]
Figure 3.7: Time dependent degradation of Auramine O by UV/H$_2$O$_2$ within 30 minutes. [Auramine O] = 20 µM, [H$_2$O$_2$] = 1.7 mM.
where \( k \) is the apparent rate constant, \( t \) is the irradiation time and \( A_0 \) and \( A_t \) are the initial and the final absorbance values of the dye solution respectively.

Hydroxyl radicals are the main source of dye decoloration and are produced in solution due to irradiation by UV light. \(^{(36)}\)

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \tag{2}
\]

Due to their strong oxidizing nature, hydroxyl radicals can react with the dye molecules to produce intermediates which can thus cause the decoloration of the original solution. \(^{(37)}\)

\[
\cdot \text{OH} + \text{dye} \rightarrow \text{Intermediates} \rightarrow \text{Products} \tag{3}
\]

Decoloration kinetics of Auramine O, was also carried out systematically by varying the concentration of both \( \text{H}_2\text{O}_2 \) and of the dye. The apparent decoloration rate constant values in cases of varying dye concentration is shown in (figure 3.8) and (table 3.9). From this table on can see that decoloration became less with increasing concentration of Auramine O concentration. Similarly, (figure 3.9) and (table 3.10) show the apparent rate constants and percentage decoloration of Auramine O at different \( \text{H}_2\text{O}_2 \) concentrations. It is apparent from this data that the rate of dye decoloration was directly proportional to \( \text{H}_2\text{O}_2 \) concentration, but becomes less at very high \( \text{H}_2\text{O}_2 \) concentration, which can be attributed to self quenching of \( \cdot \text{OH} \) radicals as stated before.
Table 3.9: Effect of Auramine O dye concentration on its decoloration 
\([H_2O_2] = 1.7 \text{ mM}\)

<table>
<thead>
<tr>
<th>[Auramine O] (\mu\text{M})</th>
<th>(K \times 10^{-2} \text{ (min}^{-1})</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>6.2</td>
<td>83.7 0.5</td>
</tr>
<tr>
<td>20</td>
<td>5.5</td>
<td>80.7 0.1</td>
</tr>
<tr>
<td>30</td>
<td>2.4</td>
<td>50.2 1.4</td>
</tr>
<tr>
<td>40</td>
<td>1.5</td>
<td>35.3 2.6</td>
</tr>
</tbody>
</table>

Figure 3.8: Effect of Auramine O concentration on the percent decoloration and apparent rate constant of the decoloration reaction. 
\([H_2O_2] = 1.7 \text{ mM}\).
Table 3.10: Effect of H$_2$O$_2$ concentration on Auramine O decoloration.
(Auramine O = 20 µM)

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] mM</th>
<th>$K \times 10^{-2}$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>0.83</td>
<td>2.6</td>
<td>0.1</td>
</tr>
<tr>
<td>1.67</td>
<td>5.5</td>
<td>0</td>
</tr>
<tr>
<td>3.34</td>
<td>7.6</td>
<td>0.3</td>
</tr>
<tr>
<td>16.67</td>
<td>11.8</td>
<td>1.1</td>
</tr>
<tr>
<td>33.33</td>
<td>9.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 3.9: Effect of Hydrogen peroxide concentration on the percent decoloration and apparent rate constant of the decoloration reaction, [Auramine O] = 20µM.
However, as expected, at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of H$_2$O$_2$ to produce HO$^{\cdot}$ radicals, thereby causing a decrease in percent decoloration.

\[
H_2O_2 + \cdot OH \rightarrow H_2O + HO^{\cdot}
\]  

(4)

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways.\(^{(38)}\) Thus one can assume that H$_2$O$_2$ acts as a pseudo catalyst in this case.

In all subsequent decoloration studies, the concentration of H$_2$O$_2$ was kept at an optimum level of 1.7 mM, and the Auramine O concentration was kept constant at 20 $\mu$M.

Since pH of the solution is an important factor in determining the percentage decoloration of dye solutions, it was therefore also studied for Auramine O. The effect was studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/ H$_2$O$_2$. (Table 3.11) shows the percentage change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more in acidic media as compared to in basic media, although maximum decoloration was seen at pH 7.
Table 3.11: Effect of pH on Auramine O decoloration.
(Auramine O = 20 μM; H₂O₂ = 1.7 mM)

<table>
<thead>
<tr>
<th>pH value</th>
<th>% decoloration</th>
<th>Mean</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>46.7</td>
<td>3.6</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>80.7</td>
<td>0.1</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>13.5</td>
<td>6.4</td>
<td></td>
</tr>
</tbody>
</table>
The effect of various ions on Auramine O decoloration was also monitored. (Table 3.12) shows the percentage dye decoloration in the presence of these ions. It can be seen from this table that all the ions tested did not had a drastic effect except sulphite ions which reduced the percent decoloration to 5%. This can be explained by the fact that sulfite anions can readily react with hydroxyl radicals as shown below.\(^{(41)}\)

\[
\cdot\text{OH} + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \cdot\text{SO}_3^- \quad k = 5.1 \times 10^9 \text{ (L mol}^{-1}\text{s}^{-1})
\]  \hspace{1cm} (6)

In conclusion, Auramine O dye was subjected to UV light in the presence of hydrogen peroxide. The dyes underwent decoloration which was observed by monitoring the changes in the absorption values of the dye solutions. The photolytic oxidation of the dyes is due to the reaction of the dye with the hydroxyl radicals generated in solution. First order kinetics fitted was found to fit well to the decoloration scheme of the dyes. The decoloration of Auramine O was unchanged in the presence of the most ions tested except sulphite ions. For effective decoloration of the Auramine O, sulphite ions should thus in particular be removed from the dye solution prior to its exposure to UV light.
Table 3.12 Effect of various ions on Auramine O decoloration.
(Auramine O = 20 μM; H₂O₂ = 1.7 mM)

<table>
<thead>
<tr>
<th>Ions</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>---</td>
<td>5.5</td>
<td>0</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>4</td>
<td>0.3</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>4.2</td>
<td>0.4</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>3.6</td>
<td>0.4</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>6.6</td>
<td>0.1</td>
</tr>
</tbody>
</table>
3.4 Kinetics and optimization of photolytic decoloration of Carmine by UV/H₂O₂

Carmine (C.I name is Natural Red 4), a naturally occurring important dye, was subjected to UV radiation in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically.

In the present work, the kinetics of H₂O₂ assisted photochemical oxidation of Carmine was investigated. The structure of the dye as well as the UV-Vis spectra of the dye is given in (figure 3.10). The decoloration studies were attempted by observing changes in the absorbance value of the dye at 500 nm. Initially, experiments were carried out with either UV light or H₂O₂ alone. The results showed that mere UV light or H₂O₂ alone did not result in any significant decoloration of this dye. However when the dye solutions of various concentrations were mixed H₂O₂ prepared in aqueous media and subjected to UV light, the dye started degrading immediately in the presence of H₂O₂ and the UV radiation. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows:

\[
\% \text{ decrease in absorption} = \left\{ \frac{A \text{ (initial)} - A \text{ (final)}}{A \text{ (initial)}} \right\} \times 100
\]
Figure 3.10: Chemical structure of carmine and visible spectra showing photolytic degradation of carmine using UV/H$_2$O$_2$. Scans were taken at 0, 3, 5, 10, 15, 20, 25 and 30 minutes after photolytic treatment.

[Carminen] =80μM, [H$_2$O$_2$] =3.3mM
The change of absorption value which is a measure of its decoloration, as a function of irradiation time is depicted in (figure 3.11). The kinetics of dye decoloration with respect to its change in absorption values fitted well to a first order rate equation.

\[ \ln(A_0) - \ln(A_t) = k t \quad (1) \]

Where \( k \) is the apparent rate constant, \( t \) is the irradiation time and \( A_0 \) and \( A_t \) are the initial and the final absorbance values of the dye solution respectively. The decoloration of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light. \(^{(36)}\)

\[ H_2O_2 + hv \rightarrow 2 \cdot OH \quad (2) \]

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the decoloration of the original solution

\[ \cdot OH + \text{dye} \rightarrow \cdot P \quad (3) \]

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the decoloration reaction of the dye molecule. \(^{(37)}\)
Figure 3.11:

A) Photolytic degradation of Carmine using UV/H₂O₂. [Carmine] = 80 μM and [H₂O₂] = 3.3 mM. Scans were taken at 0, 3, 5, 10, 15, 20, 25 and 30 minutes after photolytic treatment.

B) First order curve fitting of Carmine decoloration data.
To optimize the decoloration kinetics of the dye, we carried out a systematic study varying the concentration of both $\text{H}_2\text{O}_2$ and of carmine. (Figure 3.12) and (table 3.13) show the effect of varying carmine concentration on the kinetics of dye decoloration. Unexpectedly, we found that the apparent rate of carmine decoloration appears to be the same between 20 – 80 $\mu$M concentrations of carmine. Only at carmine concentration of 160 $\mu$M a lower apparent rate of carmine decoloration and a slower apparent rate of decoloration was observed. Similarly, (figure 3.13) and (table 3.14) show the apparent rate constants and percent decoloration of carmine at different $\text{H}_2\text{O}_2$ concentrations. It can be seen that the apparent rate of dye decoloration was directly proportional to $\text{H}_2\text{O}_2$ concentration; however at high concentrations of $\text{H}_2\text{O}_2$ the increase in dye decoloration was not linear. As expected, at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of $\text{H}_2\text{O}_2$ to produce HO$_2^-$ radicals.

$$\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^-$$ (4)

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways. Thus one can assume that $\text{H}_2\text{O}_2$ acts as a pseudo catalyst in this case.

For subsequent decoloration studies, the concentration of $\text{H}_2\text{O}_2$ was kept at an optimum level of 3.3 mM, and the Carmine was maintained at 80 $\mu$M.
Table 3.13: Effect of Carmine concentration on its photolytic decoloration. 
\([\text{H}_2\text{O}_2] = 3.3 \text{ mM}\)

<table>
<thead>
<tr>
<th>[Carmine] (\mu\text{M})</th>
<th>(K \times 10^{-2} \text{ (min}^{-1})</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>2.2</td>
<td>53</td>
</tr>
<tr>
<td>40</td>
<td>2.5</td>
<td>53</td>
</tr>
<tr>
<td>80</td>
<td>2.6</td>
<td>55</td>
</tr>
<tr>
<td>160</td>
<td>1.3</td>
<td>33</td>
</tr>
</tbody>
</table>

Figure 3.12: Effect of Carmine concentration on the percent decoloration and apparent rate constant of the decoloration reaction. \([\text{H}_2\text{O}_2] = 3.3 \text{ mM}\).
Table 3.14: Effect of $\text{H}_2\text{O}_2$ concentration on carmine decoloration. (Carmine = 80 $\mu$M)

<table>
<thead>
<tr>
<th>$[\text{H}_2\text{O}_2]$ mM</th>
<th>$K \times 10^{-2}$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.83</td>
<td>1.42</td>
<td>34</td>
</tr>
<tr>
<td>1.67</td>
<td>1.9</td>
<td>44</td>
</tr>
<tr>
<td>3.32</td>
<td>2.6</td>
<td>55</td>
</tr>
<tr>
<td>6.64</td>
<td>3.0</td>
<td>59</td>
</tr>
</tbody>
</table>

Figure 3.13: Effect of Hydrogen peroxide concentration on the percent decoloration and apparent rate constant of the decoloration reaction, [Carmine] = 80$\mu$M.
The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/ H2O2. (Table 3.15) and (figure 3.14) show the percent change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more at alkaline pH, and less at acidic pH.

This enhancement in dye decoloration in basic conditions is most likely due to the fact that at alkaline pH, peroxide anions (HO2-) are produced in solution by UV radiation, which in turn can generate more OH radicals. (39)

\[ \text{HO}_2^- + \text{hv} \rightarrow \text{OH}^+ + \text{O}^- \]  

(5)

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye decoloration. (40) Therefore, we tested the effects of various anions on the photolytic decoloration of carmine (table 3.16). The kinetics of dye decoloration in the presence of these ions is also shown in (figure 3.15). It can be seen from the table and the figure that carbonate and chloride ions did not have any effect on dye degradation. Also surprisingly, nitrate and sulphate ions caused a small but significant increase in the apparent rate of dye decoloration. The increase in dye decoloration was due to the alkalinity of the solution not to the effect of the presence of ions. More work is needed to confirm the exact mechanism. Most surprising was the result we observed was the dramatic effect of sulfite anions.
Table 3.15: Effect of pH on Carmine decoloration.
(Carmine = 80 μM; H₂O₂ = 3.3 mM)

<table>
<thead>
<tr>
<th>pH value</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>10.1</td>
<td>57.17</td>
</tr>
<tr>
<td>6</td>
<td>2.6</td>
<td>55.02</td>
</tr>
<tr>
<td>10</td>
<td>4.88</td>
<td>74.48</td>
</tr>
</tbody>
</table>

Figure 3.14: Effect of pH on the decoloration of Carmine. Samples were exposed to UV/H₂O₂ for 10 minutes before measuring the resultant dye concentrations. [Carmine] = 80μM and [H₂O₂] = 3.3 mM
Table 3.16: Effect of various ions on carmine decoloration.
(Carmine = 80 μM; H₂O₂ = 3.3 mM)

<table>
<thead>
<tr>
<th>Ions</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>2.6</td>
<td>55.02</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>4.52</td>
<td>55.02</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.54</td>
<td>65.51</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>3.34</td>
<td>62.7</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.63</td>
<td>55.89</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>0.21</td>
<td>10.76</td>
</tr>
</tbody>
</table>

Figure 3.15: Effect of various ions on the decoloration of Carmine.
[Carmine] = 80μM, [H₂O₂] = 3.3 mM and [Ions] = 1 mg/ml.
Under conditions where more than 50% carmine would normally be degraded, sulphite ions reduced this to only 10%. This can be explained by the fact that sulfite anions can readily react with hydroxyl radicals as shown below.\(^{41}\)

\[
\cdot \text{OH} + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \cdot \text{SO}_3^- \quad k = 5.1 \times 10^9 \text{ (L.mol}^{-1}\text{s}^{-1})
\]

Lastly in order to confirm that the actual degradation was occurring during the photolytic treatment, samples of dye solution was taken at specific intervals and subjected to HPLC analysis. (Figure 3.16) shows the HPLC analysis of the dye solution after 30 minutes of photolytic treatment. As can be seen from this figure, a significant amount of dye was degraded within 30 minutes and additional peaks (presumably by-products) are produced. Hence, the loss of color (decoloration) we were observing was most likely due to actual dye degradation.

In conclusion, Photolytic oxidation of Carmine dye was carried out in the presence of hydrogen peroxide. The decoloration of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well to the decoloration scheme of the dye. The decoloration of the dye was less in the presence of sulphite ions. Thus for effective decoloration of the dye, this ion should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution.
Figure 3.16: HPLC analysis of the decoloration/degradation of Carmine by the UV/H$_2$O$_2$ photolytic process. Samples were taken either at 0 minutes (no UV/H$_2$O$_2$) or after 30 minutes of UV/H$_2$O$_2$ exposure. Samples were prepared and analyzed as described in Materials and Methods section.
3.5 Decoloration studies of Malachite Green in the presence of UV/H$_2$O$_2$

Photolytic decoloration of Malachite Green (C.I name is Basic green B) was carried out in the presence of UV light and hydrogen peroxide. The absorbance changes in the dye solution were monitored spectrophotometrically.

In the present work, the kinetics of H$_2$O$_2$ assisted photochemical oxidation of MG was investigated. The structure of the dye is given in (table 2.1). The initial investigation of the dye revealed a major peak at 614 nm as shown in (figure 3.17). The degradation studies were attempted by observing changes in the absorbance value of the dye at this wavelength. Initially, experiments were carried out in the absence and presence of either UV light or H$_2$O$_2$ alone. The results showed that mere UV light or H$_2$O$_2$ alone was not sufficient for degradation of this dye.

Dye solutions of various concentrations in the presence of 1.67 mM H$_2$O$_2$ were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H$_2$O$_2$ and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 614 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular

\[
\% \text{ decrease in absorption} = \left[ \frac{(A \text{ (initial)} - A \text{ (final)})}{A \text{ (initial)}} \right] \times 100
\]
Figure 3.17: Time dependent degradation of MG by UV/H₂O₂ within 30 minutes. 
\[ [\text{MG}] = 20\mu\text{M}, [\text{H}_2\text{O}_2] = 1.67\text{ mM}. \]
The change of absorption value which is a measure of its degradation, as a function of irradiation time is depicted in (figure 3.17). The kinetics of dye degradation with respect to its change in absorption values fitted well to a first order rate equation.

\[ \ln(A_0) - \ln(A_t) = k \cdot t \]

Where \( k \) is the rate constant, \( t \) is the irradiation time and \( A_0 \) and \( A_t \) are the initial and the final absorbance values of the dye solution respectively.

To optimize the degradation kinetics of the dye, we carried out a systematic study varying the concentration of both \( \text{H}_2\text{O}_2 \) and of MG. (Figure 3.18) and (table 3.17) show the rate constants and percent degradation of MG at different \( \text{H}_2\text{O}_2 \) concentrations. As can be seen the rate of dye degradation was directly proportional to \( \text{H}_2\text{O}_2 \) concentration. Similarly, (table 3.18) shows the effect of varying MG concentration on the kinetics of dye degradation. The rate of MG degradation appears to be inversely proportional to the dye concentration.

The degradation of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light. \(^{(36)}\)

\[ \text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH} \]

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the degradation of the original solution.

\[ \cdot \text{OH} + \text{dye} \rightarrow \cdot \text{P} \]
Table 3.17: Effect of H$_2$O$_2$ Concentration on the kinetics of MG Degradation (30 minutes). [MG] = 20 μM

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] mM</th>
<th>K * 10$^2$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.835</td>
<td>2.4</td>
<td>50.3</td>
</tr>
<tr>
<td>1.67</td>
<td>4.5</td>
<td>75.7</td>
</tr>
<tr>
<td>3.34</td>
<td>6.1</td>
<td>80.4</td>
</tr>
<tr>
<td>6.68</td>
<td>6.5</td>
<td>86.8</td>
</tr>
</tbody>
</table>

Figure 3.18: Effect of H$_2$O$_2$ concentration on the Kinetics of MG Degradation. [MG] = 20μM, [H$_2$O$_2$] was either 0.835, 1.67, 3.34 and 6.68mM
Table 3.18: Effect of MG concentration on the kinetics of dye degradation (30 minutes). \([H_2O_2] = 1.67\text{mM}\)

<table>
<thead>
<tr>
<th>[MG] (\mu\text{M})</th>
<th>(K \times 10^{-2} \text{ (min}^{-1}))</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>7.5</td>
<td>91.1</td>
</tr>
<tr>
<td>10</td>
<td>4.6</td>
<td>75.1</td>
</tr>
<tr>
<td>20</td>
<td>4.5</td>
<td>75.7</td>
</tr>
<tr>
<td>30</td>
<td>2.1</td>
<td>45.9</td>
</tr>
</tbody>
</table>
Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the degradation reaction of the dye molecule. The concentration of H₂O₂ was kept at an optimum level (in this case at 1.67 mM) due to the fact that at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of H₂O₂ to produce HO₂⁻ radicals.

\[ \text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]  \hspace{1cm} (4)

The peroxo radicals produced as a result of the above reaction can also enter in other reaction pathways. Thus one can assume that H₂O₂ acts as a pseudo catalyst in this case.

The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/H₂O₂. There was a significant effect on the kinetics of dye degradation appeared as shown in (table 3.19) and (figure 3.19). The rate of decoloration was very fast at alkaline pH as it became discolored within almost 15 minutes. This is contrary to what we have observed with other dyes, where photolytic dye degradation appears to be best at alkaline pH, and slowest at acidic pH. Perhaps, the well-documented pH effect on dye degradation is dye-dependent.
Table 3.19: Effect of pH on MG decoloration.

\[
\text{[MG]} = 20 \text{ \mu M; [H}_2\text{O}_2\text{]} = 1.67 \text{ mM)}
\]

<table>
<thead>
<tr>
<th>pH</th>
<th>(K \times 10^{-2} \text{ (min}^{-1}\text{)})</th>
<th>% decoloration (15 minutes)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29</td>
<td>98.7</td>
</tr>
<tr>
<td>7</td>
<td>4.5</td>
<td>49.6</td>
</tr>
<tr>
<td>12</td>
<td>14.5</td>
<td>91.4</td>
</tr>
</tbody>
</table>

Figure 3.19: Time dependent degradation of MG by UV/H\textsubscript{2}O\textsubscript{2} within 15 minutes. [MG] = 20\textmu M, [H\textsubscript{2}O\textsubscript{2}] = 1.67 mM at pH=1 (A) and pH= 12 (B)
This slight enhancement in dye degradation is most likely due to the fact that at alkaline pH, peroxide anions (HO$_2^-$) are produced in solution by UV radiation, which in turn can generate more OH radicals.$^{(39)}$

\[ \text{HO}_2^- + \text{hv} \rightarrow \text{OH}^- + \text{O}^+ \]

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye degradation. Therefore, we tested the effects of various anions on the photolytic degradation of MG as shown in (table 3.20). It can be seen from this table, that the percent degradation of the dye solution was substantially decreased in the presence of all ions. The inhibitory effect of halides on dye degradation has been previously shown and explained by us and others.$^{(40)}$

In conclusion, Photolytic oxidation of MG dye (also called as Basic green 4) was carried out in the presence of hydrogen peroxide. The degradation of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well to the degradation scheme of the dye. The degradation of the dye was less in the presence of all ions. Thus for effective degradation of the dye, these ions should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution.
Table 3.20: Effect of various ions on MG degradation (30 minutes).

[MG] = 20 μM, [H₂O₂] = 1.67 mM

<table>
<thead>
<tr>
<th>Ions</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>4.5</td>
<td>75.7</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>2.4</td>
<td>51.2</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>2</td>
<td>48.9</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>1.96</td>
<td>45.9</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.95</td>
<td>45.3</td>
</tr>
</tbody>
</table>
3.6 Photolytic decoloration of Naphthol Yellow by UV/H₂O₂

Naphthol Yellow (C.I name is Acid Yellow 1) was irradiated with UV light in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically.

In the present work, the kinetics of H₂O₂ assisted photochemical oxidation of NY was investigated. The structure of NY is shown in (table 2.1). The decoloration studies were attempted by observing changes in the absorbance value of NY at 428 nm. Initial experiments with either UV light or H₂O₂ alone did not cause any significant changes in the decoloration of dye. However, the dye started degrading immediately in the presence of H₂O₂ and UV radiation. The initial investigation of the dye revealed a major peak at 428 nm as shown in (figure 3.20).

Dye solutions of various concentrations in the presence of 6.67 mM H₂O₂ were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H₂O₂ and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 428 nm in the visible region. Changes in the absorption spectra of the dye solution were monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows

\[
\% \text{ dye decoloration} = \left\{ \frac{1 - A_t}{A_0} \right\} \times 100
\]
Figure 3.20: Time dependent degradation of NY by UV/H₂O₂ within 30 minutes. [NY] = 80 µM, [H₂O₂] = 6.67 mM.
Where, $A_t$ is the dye absorbance value at any given time, and $A_0$ is the initial dye absorbance value in solution. Changes in absorption value as a function of irradiation time, which is a direct measure of dye decoloration was found to fit well to a first order rate equation given by:

$$\ln \left( \frac{A_0}{A_t} \right) = k t$$

(1)

Where $k$ is the apparent rate constant, $t$ is the irradiation time and $A_0$ and $A_t$ are the initial and the final absorbance values of the dye solution respectively.

The decoloration of the dye solution is mainly due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light.\(^{(36)}\)

$$\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH}$$

(2)

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the decoloration of the original solution

$$\cdot \text{OH} + \text{dye} \rightarrow \cdot \text{P}$$

(3)

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they
are probably the main source of initiating the decoloration reaction of the dye molecule. (37)

The decoloration kinetics of NY was carried out systematically by varying the concentration of both \( \text{H}_2\text{O}_2 \) and of the dye. The apparent decoloration rate constant values in cases of varying dye concentration is shown in (figure 3.21) and (table 3.21).

The decoloration was systematic in nature and became less with increasing concentration of NY concentration. Similarly, (figure 3.22) and (table 3.22) show the apparent rate constants and percentage decoloration of NY at different \( \text{H}_2\text{O}_2 \) concentrations. It is apparent from this data that the rate of dye decoloration was directly proportional to \( \text{H}_2\text{O}_2 \) concentration, but becomes less at very high \( \text{H}_2\text{O}_2 \) concentration, which can be attributed to self quenching of OH radicals as stated before.

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^-
\]

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways. (38) Thus one can assume that \( \text{H}_2\text{O}_2 \) acts as a pseudo catalyst in this case.

In all subsequent decoloration studies, the concentration of \( \text{H}_2\text{O}_2 \) was kept at an optimum level of 6.67 mM, and the NY concentration was kept constant at 80 \( \mu\text{M} \).
Table 3.21: Effect of NY dye concentration on its decoloration
\( \text{\(H_2O_2\)} = 6.67 \text{mM}\)

<table>
<thead>
<tr>
<th>[NY] (\mu\text{M})</th>
<th>(K \times 10^{-2} \text{ (min}^{-1})</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>20</td>
<td>10.7</td>
<td>0.61</td>
</tr>
<tr>
<td>40</td>
<td>8.03</td>
<td>0.97</td>
</tr>
<tr>
<td>80</td>
<td>4.9</td>
<td>0.46</td>
</tr>
<tr>
<td>160</td>
<td>2.1</td>
<td>0.15</td>
</tr>
</tbody>
</table>

Figure 3.21: Effect of NY concentration on the percent decoloration and apparent rate constant of the decoloration reaction. \([\text{H}_2\text{O}_2]\) = 6.67mM.
Table 3.22: Effect of $\text{H}_2\text{O}_2$ concentration on NY decoloration.  
(NY = 80 $\mu$M)

<table>
<thead>
<tr>
<th>$[\text{H}_2\text{O}_2]$ mM</th>
<th>$K \times 10^{-2} \text{ (min}^{-1})$</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
<td>STD</td>
</tr>
<tr>
<td>1.67</td>
<td>1.63</td>
<td>0.1</td>
</tr>
<tr>
<td>3.34</td>
<td>2.87</td>
<td>0.46</td>
</tr>
<tr>
<td>6.68</td>
<td>4.9</td>
<td>0.46</td>
</tr>
<tr>
<td>33.3</td>
<td>7</td>
<td>0.46</td>
</tr>
<tr>
<td>66.6</td>
<td>5.4</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Figure 3.22: Effect of Hydrogen peroxide concentration on the percent decoloration and apparent rate constant of the decoloration reaction.  
[NY] = 80 $\mu$M.
Since pH of the solution is an important factor in determining the percentage decoloration of dye solutions, it was therefore also studied for NY. The effect was studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/H₂O₂. (Table 3.23) shows the percentage change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more in acidic media as compared to in basic media.

The effect of various ions on NY decoloration was also monitored. (Figure 3.23) and (Table 3.24) show the percentage dye decoloration in the presence of these ions. It can be seen from this table that carbonate and sulphate ions only had a slight effect on dye degradation, whereas the other ions had minimal effect. The increase in dye decoloration was due to the alkalinity of the solution not to the effect of the presence of ions. More work is needed to confirm the exact mechanism.

Under conditions where more than 40% NY would normally be degraded, sulphite ions reduced this to only 3%. This can be explained by the fact that sulfite anions can readily react with hydroxyl radicals as shown below:  

\[ \cdot \text{OH} + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \cdot \text{SO}_3^- \quad k = 5.1 \times 10^9 (\text{L mol}^{-1} \text{ s}^{-1}) \]  (6)
Table 3.23: Effect of pH on NY decoloration. (NY = 80 μM; H₂O₂ = 6.67 mM)

<table>
<thead>
<tr>
<th>pH value</th>
<th>% decoloration (10 minutes)</th>
<th>Mean</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td></td>
<td>25.7</td>
<td>0.4</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>40.9</td>
<td>5.87</td>
</tr>
<tr>
<td>11</td>
<td></td>
<td>8.78</td>
<td>0.16</td>
</tr>
</tbody>
</table>

Table 3.24: Effect of various ions on NY decoloration. (NY = 80 μM; H₂O₂ = 6.67 mM)

<table>
<thead>
<tr>
<th>[Ions]= 1 mg/mL</th>
<th>% decoloration</th>
<th>Mean</th>
<th>STD</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>40.9</td>
<td>5.87</td>
<td></td>
</tr>
<tr>
<td>Cl⁻</td>
<td>39.8</td>
<td>4.14</td>
<td></td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>32.3</td>
<td>3.23</td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>35.1</td>
<td>1.53</td>
<td></td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>8.8</td>
<td>0.21</td>
<td></td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>2.83</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>
Figure 3.23: Percent decoloration of various ions in the photolytic process of NY.
In conclusion, Photolytic oxidation of NY dye was carried out in the presence of hydrogen peroxide. The decoloration of the dye solution was observed by monitoring the changes in the absorption values of the dye solutions. It was found that first order kinetics fitted well to the decoloration scheme of the dye. The decoloration of NY became less in the presence of sulphite and carbonate ions. The overall photolytic oxidation of the dyes is due to the reaction of the dye with the hydroxyl radicals generated in solution.
3.7 Decoloration studies of Rhodamine B in the presence of UV/H$_2$O$_2$

Photolytic decoloration of Rhodamine B (C.I name is Basic violet 10) was carried out in the presence of UV light and hydrogen peroxide. The absorbance changes in the dye solution were monitored spectrophotometrically.

In the present work, the kinetics of H$_2$O$_2$ assisted photochemical oxidation of RhB was investigated. The structure of the dye is given in (table 2.1). The initial investigation of the dye revealed a major peak at 555 nm as shown in (figure 3.24). The degradation studies were attempted by observing changes in the absorbance value of the dye at this wavelength. Initially, experiments were carried out in the absence and presence of either UV light or H$_2$O$_2$ alone. The results showed that mere UV light or H$_2$O$_2$ alone was not sufficient for degradation of this dye.

Dye solutions of various concentrations in the presence of 1.67 mM H$_2$O$_2$ were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H$_2$O$_2$ and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 555 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular

\[
\text{% decrease in absorption} = \left(\left\{\text{A (initial)} - \text{A (final)}\right\}/\text{A (initial)}\right) \times 100
\]
Figure 3.24: Time dependent degradation of RhB by UV/H$_2$O$_2$ within 30 minutes. [RhB] = 10μM, [H$_2$O$_2$] = 1.67mM
The change of absorption value which is a measure of its degradation, as a function of irradiation time is depicted in (figure 3.24). The kinetics of dye degradation with respect to its change in absorption values fitted well to a first order rate equation.

\[
\ln(A_0) - \ln(A_t) = kt
\]

Where \(k\) is the rate constant, \(t\) is the irradiation time and \(A_0\) and \(A_t\) are the initial and the final absorbance values of the dye solution respectively.

To optimize the degradation kinetics of the dye, we carried out a systematic study varying the concentration of both \(H_2O_2\) and of RhB. (Figure 3.25) and (table 3.25) show the rate constants and percent degradation of RhB at different \(H_2O_2\) concentrations. As can be seen the rate of dye degradation was directly proportional to \(H_2O_2\) concentration. Similarly, (figure 3.26) and (table 3.26) show the effect of varying RhB concentration on the kinetics of dye degradation. The rate of RhB degradation appears to be inversely proportional to the dye concentration.

The degradation of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light.\(^{(36)}\)

\[
H_2O_2 + hv \rightarrow 2 \cdot OH
\]

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the degradation of the original solution

\[
\cdot OH + \text{dye} \rightarrow \cdot P
\]
Table 3.25: Effect of H$_2$O$_2$ Concentration on the kinetics of RhB Degradation (30 minutes). [RhB] = 10 μM

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] mM</th>
<th>K* 10$^{-2}$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.835</td>
<td>1.64</td>
<td>40.8</td>
</tr>
<tr>
<td>1.67</td>
<td>4.2</td>
<td>72.6</td>
</tr>
<tr>
<td>3.34</td>
<td>4.4</td>
<td>68.6</td>
</tr>
<tr>
<td>6.68</td>
<td>4.52</td>
<td>72.9</td>
</tr>
</tbody>
</table>

Figure 3.25: Effect of H$_2$O$_2$ concentration on the Kinetics of RhB Degradation. [RhB] = 10μM, [H$_2$O$_2$] was either 0.835, 1.67, 3.34 and 6.68 mM
Table 3.26: Effect of RhB concentration on the kinetics of dye degradation (30 minutes). \([\text{H}_2\text{O}_2]=-1.67\text{mM}\)

<table>
<thead>
<tr>
<th>[RhB] (\mu\text{M})</th>
<th>(K \times 10^{-2} \text{ (min}^{-1})</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5</td>
<td>10.3</td>
<td>95.9</td>
</tr>
<tr>
<td>5</td>
<td>4.1</td>
<td>69.2</td>
</tr>
<tr>
<td>10</td>
<td>4.8</td>
<td>77</td>
</tr>
<tr>
<td>20</td>
<td>2.1</td>
<td>50</td>
</tr>
</tbody>
</table>

Figure 3.26: Effect of RhB concentration on the kinetics of RhB degradation. \([\text{H}_2\text{O}_2]=-1.67\text{mM}, [\text{RhB}] \text{ was either 2.5, 5, 10, 20} \mu\text{M},\)
Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the degradation reaction of the dye molecule. The concentration of \( \text{H}_2\text{O}_2 \) was kept at an optimum level (in this case at 1.67 mM) due to the fact that at high concentrations, the solution undergoes self quenching of \( \cdot\text{OH} \) radicals by added amounts of \( \text{H}_2\text{O}_2 \) to produce \( \text{HO}_2^- \) radicals.

\[
\text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^-
\]

The peroxo radicals produced as a result of the above reaction can also enter in other reaction pathways. Thus one can assume that \( \text{H}_2\text{O}_2 \) acts as a pseudo catalyst in this case.

The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/\( \text{H}_2\text{O}_2 \). Surprisingly, the decoloration rate was slow at the alkaline pH and slightly high at acidic pH as shown in (table 3.27). This is contrary to what we have observed with other dyes, where photolytic dye degradation appears to be best at alkaline pH, and slowest at acidic pH. Perhaps, the well-documented pH effect on dye degradation is dye-dependent.
Table 3.27: Effect of pH on RhB decoloration.

\[ [\text{RhB}] = 10 \mu\text{M}; [\text{H}_2\text{O}_2] = 1.67 \text{ mM} \]

<table>
<thead>
<tr>
<th>pH</th>
<th>( K \times 10^{-2} \text{ (min}^{-1}) )</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.14</td>
<td>47</td>
</tr>
<tr>
<td>7</td>
<td>4.05</td>
<td>73</td>
</tr>
<tr>
<td>9</td>
<td>0.79</td>
<td>21</td>
</tr>
</tbody>
</table>
This slight enhancement in dye degradation is most likely due to the fact that at alkaline pH, peroxide anions (HO$_2^-$) are produced in solution by UV radiation, which in turn can generate more OH radicals.\(^{(39)}\)

\[
\text{HO}_2^- + \text{hv} \rightarrow \cdot\text{OH} + \text{O}^-
\]

HO$_2^-$ radicals work as scavenger for the decoloration process. As we mentioned previously H$_2$O$_2$ acts as a pseudo catalyst.

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye degradation. Therefore, we tested the effects of various anions on the photolytic degradation of RhB as shown in (figure 3.27). It can be seen from this figure, that the percent degradation of the dye solution was substantially decreased in the presence of all ions. The inhibitory effect of halides on dye degradation has been previously shown and explained by us and others.\(^{(40)}\)
Figure 3.27: Effect of different ions on RhB decoloration. 
\([\text{RhB}] = 10 \, \mu\text{M};\, [\text{H}_2\text{O}_2] = 1.67 \, \text{mM}\)
Lastly, in order to confirm that the decrease in absorbance of RhB after H$_2$O$_2$/UV exposure was in fact due to dye degradation, we subjected RhB samples after H$_2$O$_2$/UV to GC analysis. As can be seen in (Figure 3.28), untreated RhB dye gave a single peak at 22 minutes. However, after 30 minutes of exposure to H$_2$O$_2$/UV treatment, the dye parent peak was almost gone, and various new (break-down) peaks could be seen. We also subjected the GC samples to MS, in order to identify the breakdown products. Although the MS analysis was not conclusive (perhaps due to library limitations), we were never less able to observe signals representing small aliphatic chains as well as small chain alcohols and ketones. Thus, H$_2$O$_2$/UV treatment of RhB causes breakdown of the original toxic compound to smaller less toxic products.

In conclusion, Photolytic oxidation of RhB dye (also called as Basic violet 10) was carried out in the presence of hydrogen peroxide. The degradation of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well to the degradation scheme of the dye. The degradation of the dye was less in the presence of all ions. Thus for effective degradation of the dye, these ions should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution.
Figure 3.28: GC analysis of the decoloration/degradation of RhB by the UV/H$_2$O$_2$ photolytic process. Samples were taken either at 0 minutes (no UV/H$_2$O$_2$) or after 30 minutes of UV/H$_2$O$_2$ exposure. Samples were prepared and analyzed as described in Materials and Methods section.
3.8 Photolytic oxidation of Safranin O with H₂O₂

Safranin O (C.I name is Basic Red 2), a histological important dye for counterstaining cartilages, was subjected to UV radiation in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically.

In the present work, the kinetics of H₂O₂ assisted photochemical oxidation of SO was investigated. The structure of the dye is given in (table 2.1). The initial investigation of the dye revealed a major peak at 520 nm as shown in (figure 3.29). The degradation studies were attempted by observing changes in the absorbance value of the dye at this wavelength. Initially, experiments were carried out in the absence and presence of either UV light or H₂O₂ alone. The results showed that mere UV light or H₂O₂ alone was not sufficient for degradation of this dye.

Dye solutions of various concentrations in the presence of 1.67 mM H₂O₂ were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H₂O₂ and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 520 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows:

\[
\% \text{ decrease in absorption} = \left[ \frac{A \text{ (initial)} - A \text{ (final)}}{A \text{ (initial)}} \right] \times 100
\]
Figure 3.29: Time dependent degradation of SO by UV/H$_2$O$_2$ within 30 minutes. [SO] = 20μM, [H$_2$O$_2$] = 1.67mM
The change of absorption value which is a measure of its degradation, as a function of irradiation time is depicted in (figure 3.29).

The kinetics of dye degradation with respect to its change in absorption values fitted well to a first order rate equation.

\[
\ln (A_0) - \ln(A_t) = k \cdot t
\]

Where \( k \) is the rate constant, \( t \) is the irradiation time and \( A_0 \) and \( A_t \) are the initial and the final absorbance values of the dye solution respectively.

To optimize the degradation kinetics of the dye, we carried out a systematic study varying the concentration of both \( \text{H}_2\text{O}_2 \) and of \( \text{SO} \). (Figure 3.30) and (table 3.28) show the rate constants and % degradation of \( \text{SO} \) at different \( \text{H}_2\text{O}_2 \) concentrations. As can be seen the rate of dye degradation was directly proportional to \( \text{H}_2\text{O}_2 \) concentration. Similarly, (table 3.29) shows the effect of varying \( \text{SO} \) concentration on the kinetics of dye degradation. The rate of \( \text{SO} \) degradation appears to be inversely proportional to the dye concentration.

The degradation of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light. \(^{(36)}\)

\[
\text{H}_2\text{O}_2 + \text{hv} \rightarrow 2 \cdot \text{OH}
\]
Table 3.28: Effect of H$_2$O$_2$ Concentration on the kinetics of SO Degradation (30 minutes). [SO] = 20 μM

<table>
<thead>
<tr>
<th>[H$_2$O$_2$] mM</th>
<th>K *10$^{-2}$ (min$^{-1}$)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0.86</td>
<td>23</td>
</tr>
<tr>
<td>0.42</td>
<td>1.46</td>
<td>36</td>
</tr>
<tr>
<td>0.84</td>
<td>2.65</td>
<td>55</td>
</tr>
<tr>
<td>1.67</td>
<td>4.83</td>
<td>77</td>
</tr>
</tbody>
</table>

Figure 3.30: Effect of H$_2$O$_2$ concentration on the kinetics of SO degradation. [SO] = 20μM, [H$_2$O$_2$] was either 0.21, 0.42, 0.84 or 1.67mM
Table 3.29: Effect of SO concentration on the kinetics of dye degradation (30 min), \([H_2O_2] = 1.67mM\)

<table>
<thead>
<tr>
<th>[SO] (\mu M)</th>
<th>(K \times 10^{-2} \ (\text{min}^{-1}))</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.62</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>4.59</td>
<td>76</td>
</tr>
<tr>
<td>20</td>
<td>4.83</td>
<td>77</td>
</tr>
<tr>
<td>30</td>
<td>1.79</td>
<td>41</td>
</tr>
<tr>
<td>40</td>
<td>1.17</td>
<td>28</td>
</tr>
<tr>
<td>50</td>
<td>0.95</td>
<td>25</td>
</tr>
</tbody>
</table>
Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the degradation of the original solution

\[ \cdot \text{OH} + \text{dye} \rightarrow \cdot \text{P} \]

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the degradation reaction of the dye molecule.\(^{(37)}\) The concentration of \( \text{H}_2\text{O}_2 \) was kept at an optimum level (in this case at 1.67 mM) due to the fact that at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of \( \text{H}_2\text{O}_2 \) to produce \( \text{HO}_2^- \) radicals.

\[ \text{H}_2\text{O}_2 + \cdot \text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^- \]

The peroxy radicals produced as a result of the above reaction can also enter in other reaction pathways.\(^{(38)}\) Thus one can assume that \( \text{H}_2\text{O}_2 \) acts as a pseudo catalyst in this case.
The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/H₂O₂. Surprisingly, pH did not appear to have any significant effect on the kinetics of dye degradation shown in (Figure 3.31). This is contrary to what we have observed with other dyes, where photolytic dye degradation appears to be best at alkaline pH, and slowest at acidic pH. Perhaps, the well-documented pH effect on dye degradation is dye-dependent. We did however, see a slight increase in the degradation of SO at pH 9. This slight enhancement in dye degradation is most likely due to the fact that at alkaline pH, peroxide anions (HO₂⁻) are produced in solution by UV radiation, which in turn can generate more OH radicals.  

\[
\text{HO}_2^- + h\nu \rightarrow \text{OH}^+ + \text{O}^-
\]

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye degradation. Therefore, we tested the effects of various cations and anions on the photolytic degradation of SO shown in (Table 3.30).
Figure 3.31: Effect of pH on SO degradation. 

$[\text{SO}] = 20\mu\text{M}, [\text{H}_2\text{O}_2] = 1.67\text{mM}$
Figure 3.30: Effect of various ions on SO degradation (30min), 
[SO] = 20μM, [H₂O₂] = 1.67mM

<table>
<thead>
<tr>
<th>Ions</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% decoloration</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>5.9</td>
<td>84</td>
</tr>
<tr>
<td>Anions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>4.35</td>
<td>72</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>3.96</td>
<td>69</td>
</tr>
<tr>
<td>CO₃²⁻</td>
<td>3.7</td>
<td>68</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>2.84</td>
<td>57</td>
</tr>
<tr>
<td>Br⁻</td>
<td>2.7</td>
<td>56</td>
</tr>
<tr>
<td>CH₃COO⁻</td>
<td>1.15</td>
<td>30</td>
</tr>
<tr>
<td>SO₃²⁻</td>
<td>0.52</td>
<td>14</td>
</tr>
<tr>
<td>Cations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe³⁺</td>
<td>38.85</td>
<td>98 (10min)</td>
</tr>
<tr>
<td>K⁺</td>
<td>6.19</td>
<td>85</td>
</tr>
<tr>
<td>NH₄⁺</td>
<td>5.88</td>
<td>83</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>5.63</td>
<td>82</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>5.12</td>
<td>79</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>4.84</td>
<td>77</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>4.99</td>
<td>77</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>4.09</td>
<td>72</td>
</tr>
<tr>
<td>Cd²⁺</td>
<td>3.9</td>
<td>72</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>1.89</td>
<td>44</td>
</tr>
<tr>
<td>Ag⁺</td>
<td>0.17</td>
<td>3</td>
</tr>
</tbody>
</table>
It can be seen from this table, that the percent degradation of the dye solution was substantially decreased in the presence of bromide, chloride, bicarbonate, acetate, and sulfite ions. The inhibitory effect of halides on dye degradation has been previously shown and explained by us and others. (40) However, the effect of acetate and sulfite was unexpected. Perhaps these ions somehow scavenge the OH radicals that are produced by the photolysis of H₂O₂.

We also examined the effects of various cations on the kinetics of SO degradation. As can be seen in (table 3.30), additions of cations did not significantly effect the dye degradation, except for Cd²⁺, Cu²⁺, and Ag⁺ all of which inhibited dye degradation. The inhabitation of dye degradation by the cations could be due to either a) direct scavenge of the OH radicals and b) interaction with the dye making them less susceptible to degradation. More work is needed to confirm the exact mechanism. Addition of Fe³⁺ to the dye solution caused a very dramatic enhancement in the degradation of SO (figure 3.32, table 3.30). This is most likely due to the “photo-Fenton” mediated degradation of the dye. These significant results underscore the importance of testing the effects of various ions for effective degradation of dyes.
Figure 3.32: Photolytic (UV/H₂O₂) degradation of SO in the presence of 1 mg/ml of Fe³⁺. [SO] = 20μM, [H₂O₂] = 1.67mM.
In conclusion, photolytic oxidation of SO dye (also called as Acid Red 2) was carried out in the presence of hydrogen peroxide. The degradation of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well to the degradation scheme of the dye. The degradation of the dye was less in the presence of bromide, chloride, acetate, sulfite and bicarbonate ions. Thus for effective degradation of the dye, these ions should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution.
Chapter IV

CONCLUSION
Conclusion

This study reports on the kinetics of degradation of eight different dyes using a specific advanced oxidative process, namely, photolytic oxidation (H$_2$O$_2$/UV). The results showed that all of the eight dyes tested followed the same general trend in dye degradation. It was found that the rate and extent of dye degradation was directly proportional to the amount of H$_2$O$_2$ present and inversely proportional to the dye concentration. However, it was also found that there was an optimal concentration of H$_2$O$_2$ beyond which any increase in H$_2$O$_2$ lead to a decrease in dye degradation. Furthermore, when the effects of various ions or pH were tested, surprisingly the degradation of different dyes was affected differently. And so we were not able to come up with a general rule as to how pH or ions affect the degradation of various dyes. Therefore, this study highlights the importance of studying the kinetics and optimization of each dye, as each dye behaves differently when exposed to different ions.

Lastly, at the onset of this study, we asked ourselves a basic question: Are different classes of dyes degraded equally well by a specific AOP approach? The vast amount of data that has been generated during this study and presented here allows us to make a comparative analysis. (Table 4.1) shows the degradation rate constant as well as extent of dye degradation for six of the dyes we tested. The data shown are the results of degradation of 20 μM dye at 1.67 mM H$_2$O$_2$, and hence we can directly compare the degradation of these six dyes. (Unfortunately, for two of the dyes tested, Naphthol Y and Acridine O, we had to use higher H$_2$O$_2$ concentration or very low dye concentration, respectively. Hence they could not be used in the comparison). As can be seen from the
table. Auramine O was most efficiently degraded by the H₂O₂/UV process and Carmine was the least efficiently degraded. The relative rank order of dye degradation can be listed as follows:

Auramine O > Safranine O > Malachite G > Amido B > Rhodamine B > Carmine

It will be very useful to generalize our findings to specific classes of dyes, e.g. are diarylmethane class dyes most efficiently degraded and are anthraquinone class dyes least efficiently degraded by UV/H₂O₂ process? We believe more studies along the lines of what we have shown are needed to be able to make such general statements. Nevertheless, the results shown here clearly demonstrate that different dyes are in fact degraded differently and with different efficiencies.
Table 4.1: The degradation rate constant and the extent of dye degradation for six of the dyes we tested.

<table>
<thead>
<tr>
<th>Dye</th>
<th>[Dye] µM</th>
<th>[H₂O₂] mM</th>
<th>K *10⁻² (min⁻¹)</th>
<th>% Decoloration</th>
<th>Dye Class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Auramine O</td>
<td>20</td>
<td>1.67</td>
<td>5.5</td>
<td>81</td>
<td>Diarylmethane</td>
</tr>
<tr>
<td>Safranin O</td>
<td>20</td>
<td>1.67</td>
<td>4.8</td>
<td>77</td>
<td>Quinone-imine</td>
</tr>
<tr>
<td>Malachite green</td>
<td>20</td>
<td>1.67</td>
<td>4.5</td>
<td>76</td>
<td>Triarylmethane</td>
</tr>
<tr>
<td>Amido Black</td>
<td>20</td>
<td>1.67</td>
<td>3.8</td>
<td>68</td>
<td>Azo</td>
</tr>
<tr>
<td>Phodamine B</td>
<td>20</td>
<td>1.67</td>
<td>2.2</td>
<td>50</td>
<td>Xanthene</td>
</tr>
<tr>
<td>Carmine</td>
<td>20</td>
<td>1.67</td>
<td>2.1</td>
<td>49</td>
<td>Anthraquinone</td>
</tr>
</tbody>
</table>

* Most of the experiments were done in duplicates and triplicates and the averages did not vary more than 10%.
APPENDIX
Photolytic oxidation of Safranin-O with H₂O₂

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Abstract

Safranin-O (C.I name is Basic Red 2), a histologically important dye for counterstaining cartilages, was subjected to UV radiation in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically. The rate of degradation was calculated from the observed absorption data and was found to be first order. A systematic study of the effect of dye concentration as well as H₂O₂ concentration on the kinetics of dye degradation was carried out. Additionally, the effect of various additives on the degradation of this dye was also investigated. Most of the anions tested had a minor inhibitory effect on the degradation of the dye, with the most pronounced effect seen with Cl⁻, Br⁻, CH₃COO⁻, and SO₄²⁻ ions. Addition of cations did not significantly affect the dye degradation, except for Cd²⁺, Cu²⁺, and Ag⁺, all of which inhibited dye degradation, and Fe³⁺, which dramatically enhanced the rate of dye degradation. Examination of the effect of pH showed that the dye could be efficiently degraded over a wide pH range. A plausible explanation involving the probable radical initiated mechanism was given to explain the dye degradation.

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Keywords: Safranin; Photolysis; Degradation

1. Introduction

Dyes are an important class of chemicals which are widely used in many industrial processes in the leather, textile and printing industries. The discharge of these dyes in the effluents by these industries may cause a major environmental problem [1–4]. Many of these dyes are of major concern because of their known carcinogenic properties [5]. On passage to water bodies at large, these chemicals may pose a health concern to all forms of marine life and also to human life at the end of the food chain. Recently, many different techniques have been suggested in the literature to tackle the situation by causing the complete degradation of dyes in industrial effluents prior to entering the water bodies. These suggestions include photocatalytic, photolytic and biodegradation of various dye solutions [6–9]. Advanced oxidation process based on UV/H₂O₂ degradation is not only simple and homogeneous but has also shown promising results in degrading many other organic compounds [10–12]. The process in general demand the generation of OH radicals in solution in the presence of UV light. These radicals can then attack the dye molecule to undergo a series of reactions in which the organic molecule is finally destroyed or converted into a simple harmless compound. Safranin-O (C.I name is Basic Red 2) is a representative example of an organic dye, which belongs to the Quinone Imine Class. and is widely used for counterstaining purposes; for example, as a metachromatic method for cartilages which is stained yellow. Since the dye is known to be carcinogenic in nature, any presence of this dye in wastewater would have detrimental effects on marine life. In this paper, an attempt is made to look at the degradation of this dye in aqueous solution in the presence of H₂O₂ and UV light. The data are interpreted in terms of kinetic parameters. Furthermore, the effect of solution pH and the presence of various additives in the form of anions and cations on the degradation of the dye solution were also investigated.
**Experimental**

Safranin-O (C.I name is Basic Red 2, F. wt = 350.8) was obtained from Fluka and used as such. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck and used in this work. Its concentration in all the dye solutions for this work was kept constant at 1.67 mM unless otherwise specified. UV/VIS studies were done on a CARY 50 UV/ VIS spectrophotometer, using a 1 cm quartz cell. For photolytic experiments, the samples were irradiated with a UV lamp with an output at 254 nm.

1. Preparation of samples and degradation studies

Safranin-O stock solution of $1 \times 10^{-3}$ M was prepared in 300 mL of deionized water in a 250-mL flask. Necessary dilutions of this stock were done with deionized water to obtain the series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of H$_2$O$_2$ and the mixture was irradiated with a UV light of 254 nm. After a certain time interval, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of degradation rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

For studying the effect of pH on dye degradation, the pH of the dye solution was altered by adding incremental amounts of either concentrated HCl or concentrated NaOH. For experiments examining the effects of different ions on the degradation of Safranin, a final concentration of 0.5 mg/mL of various salts was added to the dye solution before the addition of H$_2$O$_2$. None of the salts used had any effect on the dye spectra in the absence of UV light. The solution was then subjected to UV light and change in absorbance value was noted to calculate the degradation rate constant.

2. Results and discussion

In the present work, the kinetics of H$_2$O$_2$-assisted photochemical oxidation of Safranin-O was investigated. The structure of the dye is given in Fig. 1. The initial investigation of the dye revealed a major peak at 520 nm as shown in Fig. 2. The degradation studies were attempted by observing changes in the absorbance value of the dye at this wavelength. Initially, experiments were carried out in the absence and presence of either UV light or H$_2$O$_2$ alone. The results showed that mere UV light or H$_2$O$_2$ alone was not sufficient for degradation of this dye.

Dye solutions of various concentrations in the presence of 1.67 mM H$_2$O$_2$ were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H$_2$O$_2$ and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 520 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows:

$$\% \text{ decrease in absorption} = \left(\frac{A(\text{initial}) - A(\text{final})}{A(\text{initial})}\right) \times 100$$

The change in absorption value, which is a measure of its degradation, as a function of irradiation time is depicted in Fig. 2. The kinetics of dye degradation with respect to its change in absorption values fitted well to a first order rate equation:

$$\ln(A_0) - \ln(A_t) = kt$$

where $k$ is the rate constant, $t$ is the irradiation time and $A_0$ and $A_t$ are the initial and the final absorbance values of the dye solution, respectively.

To optimize the degradation kinetics of the dye, we carried out a systematic study varying the concentration of both H$_2$O$_2$ and SO. Fig. 3 and Table 1 show the rate constants and % degradation of SO at different H$_2$O$_2$ concentrations. As it can be seen, the rate of dye degradation was directly proportional to H$_2$O$_2$ concentration. Similarly, Table 2 shows the effect of varying SO concentration on the kinetics of dye degradation. The rate of SO degradation appears to be inversely proportional to the dye concentration.
Experimental

Safranin-O (C.I name is Basic Red 2, F. wt = 350.8) was obtained from Fluka and used as such. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck and used in this work. Its concentration in all the dye solutions for this work was kept constant at 1.67 mM unless otherwise specified. UV/VIS studies were done on a CARY 50 UV/VIS spectrophotometer, using a 1 cm quartz cell. For photolytic experiments, the samples were irradiated with a UV lamp with an output at 254 nm.

1. Preparation of samples and degradation studies

Safranin-O stock solution of 1 × 10⁻³ M was prepared in 1000 mL of deionized water in a 250-mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of H₂O₂ and the mixture was irradiated with a UV light of 254 nm. After a certain time interval, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of degradation rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

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Dye solutions of various concentrations in the presence of 1.67 mM H₂O₂ were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H₂O₂ and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 520 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows:

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2.1. Preparation of samples and degradation studies

Safranin-O stock solution of 1 × 10⁻³ M was prepared in 0.00 mL of deionized water in a 250-mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of H₂O₂ and the mixture was irradiated with a UV light of 254 nm. After a certain time interval, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of degradation rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

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Keywords: Safranin; Photolysis; Degradation

1. Introduction

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2.1. Preparation of samples and degradation studies

Safranin-O stock solution of 1 × 10^{-3} M was prepared in 100 mL of deionized water in a 250-mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of H_{2}O_{2} and the mixture was irradiated with a UV light of 254 nm. After a certain time interval, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of degradation rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

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Dye solutions of various concentrations in the presence of 1.67 mM H_{2}O_{2} were prepared in aqueous media and subjected to UV light. The dye started degrading immediately in the presence of H_{2}O_{2} and the UV radiation. The rate of degradation was monitored by measuring the decrease in absorption value of the peak at 520 nm in the visible region. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows:

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To optimize the degradation kinetics of the dye, we carried out a systematic study varying the concentration of both H_{2}O_{2} and SO. Fig. 3 and Table 1 show the rate constants and % degradation of SO at different H_{2}O_{2} concentrations. As it can be seen, the rate of dye degradation was directly proportional to H_{2}O_{2} concentration. Similarly, Table 2 shows the effect of varying SO concentration on the kinetics of dye degradation. The rate of SO degradation appears to be inversely proportional to the dye concentration.
The degradation of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light \[ \text{H}_2\text{O}_2 \rightarrow 2\cdot\text{OH} \]

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates, which can cause the degradation of the original solution.

\[ \cdot\text{OH} + \text{dye} \rightarrow \cdot\text{P} \]

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the degradation reaction of the dye molecule [13]. The concentration of \( \text{H}_2\text{O}_2 \) was kept at an optimum level (in this case at 1.67 mM) due to the fact that at high concentrations, the solution undergoes self quenching of \( \cdot\text{OH} \) radicals by added amounts of \( \text{H}_2\text{O}_2 \) to produce \( \text{HO}_2 \) radicals.

\[ \text{H}_2\text{O}_2 + \cdot\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2 \]

The peroxo radicals produced as a result of the above reaction can also enter in other reaction pathways [15]. Thus one can assume that \( \text{H}_2\text{O}_2 \) acts as a pseudo catalyst in this case.

The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the dye solution in the presence of UV/H2O2. Surprisingly, pH did not appear to have any significant effect on the kinetics of dye degradation (Fig. 4). This is contrary to what we have observed with other dyes, where photolytic dye degradation appears to be best at alkaline pH, and slowest at acidic pH (manuscript submitted for publication). Perhaps, the well-documented pH effect on dye degradation is dye-dependent. We did, however, see a slight increase in the degradation of SO at pH 9. This slight enhancement in dye degradation is most likely due to the fact that at alkaline pH, peroxide anions (\( \text{HO}_2^- \)) are produced in solution by UV radiation, which in turn can generate more \( \cdot\text{OH} \) radicals [16].

\[ \text{HO}_2^- + \text{h} \nu \rightarrow \text{OH}^- + \text{O}^2- \]

We and others have previously shown that ions that are normally present in textile wastewater streams can have dramatic effects on the kinetics of dye degradation [17]. Therefore, we tested the effects of various cations and anions on the photolytic degradation of SO (Table 3). It can be seen from this table that the % degradation of the dye solution substantially decreased in the presence of bromide, chloride, bicarbonate, acetate, and sulfite ions. The inhibitory effect of halides on dye degradation has been previously shown and explained by us and by others [17]. However, the effect of acetate and sulfite was unexpected. Perhaps these ions somehow scavenge the \( \cdot\text{OH} \) radicals that are produced by the photolysis of \( \text{H}_2\text{O}_2 \).

We also examined the effects of various cations on the kinetics of SO degradation. As can be seen in Table 3, additions

---

**Table 1:** Effect of \( \text{H}_2\text{O}_2 \) concentration on the kinetics of SO degradation (30 min)

<table>
<thead>
<tr>
<th>( \text{[H}_2\text{O}_2 ) (mM)</th>
<th>( K \times 10^{-2} ) (min(^{-1}))</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21</td>
<td>0.86</td>
<td>23</td>
</tr>
<tr>
<td>0.42</td>
<td>1.46</td>
<td>36</td>
</tr>
<tr>
<td>0.84</td>
<td>2.65</td>
<td>55</td>
</tr>
<tr>
<td>1.67</td>
<td>4.83</td>
<td>77</td>
</tr>
</tbody>
</table>

\[ \text{[SO]} = 20 \mu\text{M}, \]

---

**Table 2:** Effect of SO concentration on the kinetics of dye degradation (30 min)

<table>
<thead>
<tr>
<th>( \text{[SO]} ) (( \mu\text{M} ))</th>
<th>( K \times 10^{-2} ) (min(^{-1}))</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>5.62</td>
<td>81</td>
</tr>
<tr>
<td>10</td>
<td>4.59</td>
<td>76</td>
</tr>
<tr>
<td>20</td>
<td>4.83</td>
<td>77</td>
</tr>
<tr>
<td>30</td>
<td>1.79</td>
<td>41</td>
</tr>
<tr>
<td>40</td>
<td>1.17</td>
<td>28</td>
</tr>
<tr>
<td>50</td>
<td>0.95</td>
<td>25</td>
</tr>
</tbody>
</table>

\[ \text{[H}_2\text{O}_2 \) = 1.67 mM, \]

---

**Fig. 3:** Effect of \( \text{H}_2\text{O}_2 \) concentration on the kinetics of SO degradation. \[ \text{[SO]} = 20 \mu\text{M}, \text{[H}_2\text{O}_2 \] was 0.21, 0.42, 0.84, or 1.67 mM.

**Fig. 4:** Effect of pH on SO degradation, \[ \text{[SO]} = 20 \mu\text{M}, \text{[H}_2\text{O}_2 \] = 1.67 mM,
Table 3

Effect of various ions on SO degradation (30 min)

<table>
<thead>
<tr>
<th>Ions</th>
<th>$K \times 10^{-2}$ (min$^{-1}$)</th>
<th>% Degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO$^-$</td>
<td>4.35</td>
<td>72</td>
</tr>
<tr>
<td>SO$^2-$</td>
<td>3.96</td>
<td>69</td>
</tr>
<tr>
<td>CO$^3-$</td>
<td>3.7</td>
<td>68</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>2.84</td>
<td>57</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>2.7</td>
<td>56</td>
</tr>
<tr>
<td>CH$_3$COO$^-$</td>
<td>1.15</td>
<td>30</td>
</tr>
<tr>
<td>SO$^2-$</td>
<td>0.52</td>
<td>14</td>
</tr>
<tr>
<td>Cations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe$^{3+}$</td>
<td>38.85</td>
<td>98 (10 min)</td>
</tr>
<tr>
<td>K$^+$</td>
<td>6.19</td>
<td>85</td>
</tr>
<tr>
<td>NH$_4^+$</td>
<td>5.88</td>
<td>83</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>5.63</td>
<td>82</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>5.12</td>
<td>79</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>4.84</td>
<td>77</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>4.99</td>
<td>77</td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>4.09</td>
<td>72</td>
</tr>
<tr>
<td>Cd$^{2+}$</td>
<td>3.9</td>
<td>72</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>1.89</td>
<td>44</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>0.17</td>
<td>3</td>
</tr>
</tbody>
</table>

[SO] = 20 μM, [H$_2$O$_2$] = 1.67 mM.

of cations did not significantly effect the dye degradation, except for Cu$^{2+}$, Cu$^{2+}$, and Ag$^+$, all of which inhibited dye degradation. Addition of Fe$^{3+}$ to the dye solution caused a very dramatic enhancement in the degradation of SO (Fig. 5, Table 3). This is most likely due to the “photo-Fenton” mediated degradation of the dye. These significant results underscore the importance of testing the effects of various ions for effective degradation of dyes.

4. Conclusion

Photolytic oxidation of Safranin-O dye (also called as Acid Red 2) was carried out in the presence of hydrogen peroxide. The degradation of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well to the degradation scheme of the dye. The degradation of the dye was less in the presence of bromide, chloride, acetate, sulfite, silver and bicarbonate ions. Thus for effective degradation of the dye, these ions should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution.

References

Kinetics and optimization of photolytic decoloration of carmine by UV/H$_2$O$_2$

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Abstract

Carmine (C.I. name is Natural Red 4), a naturally occurring important dye, was subjected to UV radiation in the presence of hydrogen peroxide. The photo-oxidation of the dye was monitored spectrophotometrically. The apparent rate of decoloration was calculated from the observed absorption data and was found to be of first order. A systematic study of the effect of dye concentration as well as H$_2$O$_2$ concentration on the kinetics of dye decoloration was carried out. Additionally, the effect of various additives on the decoloration of this dye was also investigated. Most of the anions tested had an inhibitory effect on the decoloration of the dye, with the most pronounced effect seen with sulfate ion as compared to carbonate, sulphate, nitrate and chloride ions. Examination of the effect of pH showed that the dye could be efficiently decolorized in a basic media. A plausible explanation involving the probable radical initiated mechanism was given to explain the dye decoloration. Lastly, we used HPLC analysis to show that the decoloration of carmine observed during the UV/H$_2$O$_2$ photolysis treatment was in fact due to the degradation of the dye.

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Keywords: Carmine; Photolytic decoloration; Hydrogen peroxide

1. Introduction

Dye degradation/decoloration has drawn considerable attention by many workers in the last few years due to the fact that dye related pollution causes many environmental problems [1–3]. Moreover these dyes are toxic in nature due to the fact that they all have aromatic groups[4]. In fact many of these dyes have been shown to have hazardous properties [5]. On passage to water bodies at large, these chemicals may pose a health concern to all marine life as well as human life at the end of the food chain. Recently, many different techniques have been suggested in the literature to address the situation by causing the complete decoloration of dyes in industrial effluents prior to their entering the water bodies.

These suggestions include photo-catalytic, photolytic and bio-decoloration of various dye solutions [6–9]. Advanced oxidation process based on UV/H$_2$O$_2$ photolytic decoloration is not only simple and homogeneous, but has also shown promising results in degrading many other organic compounds [10–12]. The process in general depends on the generation of OH radicals in solution in the presence of UV light. These radicals can then react with the dye molecules to undergo a series of reactions in which the organic molecule is finally destroyed or converted into a simple harmless compound. Carmine is a representative example of an organic dye which belongs to the “natural” class of dyes, and in food coloring, cosmetics, and paints. Since dyes are suspected to be carcinogenic in nature, any presence of them in waste water would have detrimental effects on marine and human life. In this paper an attempt is made to look at the decoloration of this dye in aqueous solution in the presence of H$_2$O$_2$ and UV light. The data are interpreted in terms of kinetic parameters. Furthermore, the effect of solution pH and the presence of various...
additives in the form of anions on the decoloration of the dye solution were also investigated.

2. Experimental

Carmine (C.I. name Natural Red 4) was obtained from Fluka and was used as such. Deionized water was used to make the dye solutions of desired concentration. Hydrogen peroxide (35% w/w) was obtained from Merck and was diluted in water right before use. UV–vis studies were done on a CARY 50 UV/VIS spectrophotometer, using a 1 cm cell. For photolytic experiments, the samples were irradiated with a UV lamp with an output at 254 nm.

2.1. Preparation of samples and decoloration studies

Carmine stock solution of $1 \times 10^{-3}$ M was prepared in 100 mL of deionized water in a 250 mL flask. Necessary dilutions of this stock were done with deionized water to obtain a series of dye solutions with varying concentrations. An aliquot of the diluted solution was mixed with a given amount of H$_2$O$_2$ and the mixture was irradiated with UV light. After a certain time interval, the absorbance of the solution was monitored instantaneously on a spectrometer. The absorbance value obtained in each case was plotted against time to obtain the order of apparent decoloration rate. Photolytic oxidation studies were carried out at 25 ± 2 °C.

For studying the effect of pH on dye decoloration, the pH of the dye solution was altered by adding incremental amounts of either dilute HCl or diluted NaOH. For experiments examining the effects of different ions on the decoloration of carmine, a final concentration of 0.5 mg/ml of various salts was added to the dye solution before the addition of H$_2$O$_2$. None of the salts used had any effect on the dye spectra in the absence of UV light. The solution was then subjected to UV light and change in absorbance value was noted to calculate the apparent decoloration rate constant.

2.2. HPLC analysis of the discolouration/degradation samples

For HPLC analysis of the dye decoloration/degradation, 50 mL of dye solutions were taken either at time zero (right after addition of H$_2$O$_2$ and no UV irradiation) or at 30 min of UV irradiation after addition of H$_2$O$_2$, and the organic component of the mixture was extracted using chloroform. The organic layer was extracted again for a second time with chloroform, and then dried in a rotary evaporator. The dried substance (dye and/or degraded by-products) was then dissolved in 100% methanol and then used for HPLC analysis. The samples were run on C$_8$-Eclipse column (Agilent) using a 0–100% methanol (water as the base mobile phase) gradient over 30 min, at 1 ml/min, and analyzed by measuring the absorbance at 280 nm.

3. Results and discussion

In the present work, the kinetics of H$_2$O$_2$ assisted photolytic oxidation of carmine was investigated. The structure of the dye as well as the UV–vis spectra of the dye is given in Fig. 1. The decoloration studies were attempted by observing changes in the absorbance value of the dye at 500 nm. Initially, experiments were carried out with either UV light or H$_2$O$_2$. The results showed that mere UV light or H$_2$O$_2$ alone did not result in any significant decoloration of this dye. However, when the dye solutions of various concentrations were mixed with H$_2$O$_2$ prepared in aqueous media and subjected to UV
light, the dye started degrading immediately in the presence of H$_2$O$_2$ and the UV radiation. The decrease in the absorption spectra of the dye solution was monitored at regular intervals of time. Percentage decrease in absorption was calculated as follows:

\[
\text{% decrease in absorption} = \left[\frac{(A_{\text{initial}}) - (A_{\text{final}})}{A_{\text{initial}}}\right] \times 100
\]

The change in absorption value which is a measure of its decoloration, as a function of irradiation time is depicted in Fig. 2. The kinetics of dye decoloration with respect to its change in absorption values fitted well into a first order rate equation.

\[
\ln(A_0) - \ln(A_t) = kt
\]

where \(k\) is the apparent rate constant, \(t\) is the irradiation time and \(A_0\) and \(A_t\) are the initial and the final absorbance values of the dye solution, respectively. The decoloration of the dye solution is due to the reaction of hydroxyl radicals generated by hydrogen peroxide in solution upon irradiation by UV light [13].

\[
\text{H}_2\text{O}_2 \rightarrow 2^{\circ}\text{OH}
\]

Since hydroxyl radicals are very strong oxidizing reagents, they can react with the dye molecules to produce intermediates which can cause the decoloration of the original solution.

\[
{\circ}\text{OH} + \text{dye} \rightarrow {\circ}\text{P}
\]

Assuming that all the hydroxyl radicals generated in solution remain in the vicinity of the dye molecule during their short lifetime, it would be safe to say that they are probably the main source of initiating the decoloration reaction of the dye molecule [14].

To optimize the decoloration kinetics of the dye, we carried out a systematic study by varying the concentration of both H$_2$O$_2$ and carmine. Fig. 3 and Table 1 show the effect of varying carmine concentration on the kinetics of dye decoloration. Unexpectedly we found that the apparent rate of carmine decoloration appears to be the same between 20 and 80 \(\mu\text{M}\) concentrations of carmine. Only at carmine concentration of 160 \(\mu\text{M}\) a lower apparent rate of carmine decoloration and a slower apparent rate of decoloration were observed. Similarly, Fig. 4 and Table 2 show the apparent rate constants and % decoloration of carmine at different H$_2$O$_2$ concentrations. It can be seen that the apparent rate of dye decoloration was directly proportional to H$_2$O$_2$ concentration; however, at high concentrations of H$_2$O$_2$ the increase in dye decoloration was not linear. As expected, at high concentrations, the solution undergoes self quenching of OH radicals by added amounts of H$_2$O$_2$ to produce HO$_2^*$ radicals [15].

\[
\text{H}_2\text{O}_2 + {\circ}\text{OH} \rightarrow \text{H}_2\text{O} + \text{HO}_2^*
\]

For subsequent decoloration studies, the concentration of H$_2$O$_2$ was kept at an optimum level of 33.2 mM, and the carmine was maintained at 80 \(\mu\text{M}\).

The effect of pH value was also studied by adding incremental amounts of either concentrated HCl or NaOH to the
dye solution in the presence of UV/H$_2$O$_2$. Table 3 and Fig. 5 show the % change in decoloration of the dye at three different pH values. The photolytic dye decoloration appears to be more at alkaline pH and less at acidic pH. This enhancement in dye decoloration in basic conditions is most likely due to the fact that at alkaline pH, peroxide anions (HO$_2^-$) are produced in solution by UV radiation, which in turn can generate more OH radicals [16]

\[
\text{HO}_2^- + \text{hv} \rightarrow \text{OH}^+ + \text{O}^- \quad (5)
\]

We and others have previously shown that ions that are normally present in textile waste-water streams can have dramatic effects on the kinetics of dye decoloration [17]. Therefore, we tested the effects of various anions on the photolytic decoloration of carmine (Table 4). The kinetics of dye decoloration in the presence of these ions is also shown in Fig. 6. It can be seen from the table and the figure that carbonate and chloride ions did not have any effect on dye degradation. Also surprisingly, nitrate and sulphate ions caused a small but significant increase in the apparent rate of dye decoloration. Most surprising result we observed was the dramatic effect of sulphite ions. Under conditions where more than 50% carmine would normally be degraded, sulphite ions reduced this to only 10%. This can be explained by the fact that sulphite ions can readily react with hydroxyl radicals as shown below [18].

\[
\text{OH}^- + \text{SO}_3^{2-} \rightarrow \text{H}_2\text{O} + \text{SO}_4^{2-} \quad k = 5.1 \times 10^9 \text{ (L mol}^{-1}\text{s}^{-1})
\quad (6)
\]

Lastly in order to confirm that the actual degradation was occurring during the photolytic treatment, samples of dye solutions were taken at specific intervals and subjected to HPLC analysis. Fig. 7 shows the HPLC analysis of the dye solution after 30 min of photolytic treatment. As can be seen from this figure, a significant amount of dye was degraded within 30 min and additional peaks (presumably by-products) were produced. Hence, the loss of color (decoloration) we were observing was most likely due to actual dye degradation.

### 4. Conclusion

Photolytic oxidation of carmine dye was carried out in the presence of hydrogen peroxide. The decoloration of the dye solution was observed by monitoring the absorption values of the solution. It was found that first order kinetics fitted well into the decoloration scheme of the dye. The decoloration of the dye was less in the presence of sulphite ions. Thus for effective decoloration of the dye, this ion should be removed from the dye solution prior to its exposure to UV light. The overall photolytic oxidation of the dye is due to the reaction of the dye with the hydroxyl radicals generated in solution. Lastly, HPLC analysis of the reaction mixture showed that the decoloration observed during the photolytic oxidation process was in fact due to carmine degradation.
Fig. 7. HPLC analysis of the decoloration/degradation of carmine by the UV/H₂O₂ photolytic process. Samples were taken either at 0 min (no UV or H₂O₂) or after 30 min of UV/H₂O₂ exposure. Samples were prepared and analyzed as described in Section 2.

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ARABIC SUMMARY
الهيدروكسيد بيروكسيد بكميات كبيرة، عدم وجود تغيير للحالة، كذلك لا يتشكل رواسب وساطة العملية ورخص التكلفة. وتتم عملية التكسير وفق آلية عمل بسيطة لجميع الصبغات المختارة وكلها تتبع القانون الأول للحركة.

هذه الدراسة سيتسلم الضوء على إذا كانت جميع الأصناف المختلفة للأصباغ مستكشرون بنفس الفعالية باستخدام طريقة واحدة. كذلك سيتم دراسة تأثير الأملاح (التي عادة توجد في مخلفات مصانع الأنسجة) على التكسير الضوئي لثمانية أصناف من الأصباغ.

وأخيراً، هناك محاولة للتعرف على نواتج التكسير ووضع مخطط لعملية التكسير.
من المحاليل المائية. ولكن كل هذه الطرق إما إنها غير فعالة وتكلفتها عالية أو أنها تؤدي إلى إنتاج مخالفات ثانوية ضارة. وحديثا تم ايجاد مجموعة من الطرق الجديدة سميّت بالعملية الحديثة للأكسدة (AOPs)، وقد تم تطويرها بحيث تقوم بتكسير الأصباغ بشكل فعال.

ومن بين هذه الطرق الفعالة والوا عدة طريقة تعتمد على إنتاج شق الأيون الهيدروكسيلي من الهيدروجين بروكسيد ($H_2O_2$) وذلك باستخدام إحد الطرق التالية:

1. الإشعاع فوق البنفسجية (Photolysis)
2. أيون الحديد الثنائي (Fenton’s reagents) ($Fe^{2+}$)
3. الاتحاد بين الإشعاع فوق البنفسجية وأيونات الحديد الثنائي (PhotoFenton)
4. باستخدام مركب متوسط (Photocatalysis) $TiO_2$

وما هو واضح حاليا أن هناك القليل من الدراسات التي ركزت على استخدام طريقة واحدة من الطرق الحديثة للأكسدة واستخدامها على أنواع مختلفة من الأصباغ. وفي هذه الدراسة سيتم التركيز على استخدام الأشعة فوق البنفسجية وحلول الهيدروجين بروكسيد ($H_2O_2$) لدراسة قوانين الحركة الأكسدة وتتبع سير التكسير لثمانية أنواع من الأصباغ الرئيسية. وبالمقارنة مع طرق أخرى من الطرق الحديثة للأكسدة مثل (Fenton, Ozone, UV/O_3, UV/TiO_2) نلاحظ أن عملية استخدام الأشعة فوق البنفسجية وحلول الهيدروجين بروكسيد (UV photolysis) لها بعض المميزات مثل الاندماج الكامل بين الماء وحلول الهيدروجين بروكسيد، ثبات وتوفر محلول
المخلص العربي

تعتبر الأصباغ الصناعية جزء رئيسي في حياتنا حيث تدخل في صناعة المنتجات من الملابس وإلى المصنوعات الجلدية إلى الأثاث، وكلها تعتمد على الاستعمال الشامل للأصباغ العضوية.

وهي هناك أصناف عديدة من هذه الأصباغ ومن أهم الأصناف الرئيسية وأكثرها استخداما هي:

azo, anthraquinone, triarylmethane, diarylmethane, acridine, quinine, xanthane and nitro

ولكن تبين لاحقا أن هناك أثرا جانبيا سيئا للاستخدام الواسع الانتشار لهذه الأصباغ، حيث أن 12% منها تهدد أثناء عملية الصباغة، وما يقارب 20% من هذه الخسارة تدخل النظام البيئي (المصادر المائية). والمخلفات من هذه الصناعات لا تجعل المياه ملونة وحسب بل تسبب أضرارا بيئية للكائنات الحية وذلك بايقاف قدرة الماء لإعادة اضافة الأوكسجين، بالإضافة إلى حجب اشعة الشمس. علاوة على كل ذلك تعتبر هذه الأصباغ أحد العوامل المسرطنة حينما تدخل في مصادر مياه الشرب. وهناك العديد من الدراسات على الحيوانات أكدت أن التعرض لبعض هذه الصبغات يؤدي إلى إصابة الحيوانات بالسرطان وخاصة سرطان الكبد.

لذلك كان هناك حاجة ملحه لإيجاد طرق اقتصادية وصديقة للبيئة لتلك صبغات المخلفات الصناعية. وقد كان هناك طرق مختلفة مثل (الاندماج، والتجدد..الخ) قد طورت لازالة الأصباغ
مقارنة كفاءة العملية الحديثة للأكسدة لتكسير المجموعات الرئيسية للصبغات

رسالة مقدمة من
فاطمة حسن عبد الله الحامدي

مقدمة إلى
جامعة الإمارات العربية المتحدة

استكمالاً لمتطلبات الحصول على درجة الماجستير في علوم البيئة

2007