PHOTOCATALYSED DEGRADATION OF FEW SELECTED TEXTILE DYE DERIVATIVES IN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE

ABSTRACT

THESIS
SUBMITTED FOR THE AWARD OF THE DEGREE OF
Doctor of Philosophy
IN
CHEMISTRY

BY
MOHD SAQUIB

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)
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ABSTRACT

Water contamination is caused by various sources such as industrial effluents, agricultural runoff and chemical spills. Industrial effluents contain several non-biodegradable substrates that can be harmful to the environment. One major source of these effluents is the waste arising from the industrial process, which utilizes dyes to colour paper, plastic, natural and artificial fibers. A substantial amount of dyestuff is lost during the dyeing process in the textile industry, which poses a major problem for the industry as well as a threat to the environment. Decolourization of dye effluents has therefore acquired increasing attention. The photocatalytic process involving TiO₂ semiconductor particles under UV light irradiation has been shown to be potentially advantageous and useful in the treatment of wastewater pollutants. The photocatalyst on excitation generates \((e^- - h^+)\) pair with free electrons produced in the nearly empty conduction band leaving the +ve hole in the valence band. These electron and hole are capable of initiating a series of chemical reactions that eventually can mineralize the organic compounds. More over the formation of harmless end product represents another attractive feature of this process.

This study involves the photocatalytic degradation of aqueous solution of commonly used textile dyes utilizing titanium dioxide catalyst in the presence of light.

The thesis entitled "Photocatalysed degradation of few selected textile dye derivatives in aqueous suspension of titanium dioxide" is divided into three Chapters.

The Chapter 1 of the thesis deals with the photocatalysed degradation of three selected textile anthrquinone dye derivatives such as alizarin red S (1), acid green 25 (2) and remazol brilliant blue R (3) in aqueous suspension of titanium dioxide in the presence of oxygen. The
degradation was studied under a variety of conditions such as type of photocatalyst, pH, substrate and catalyst concentration and in the presence of different electron acceptors in addition of molecular oxygen. The irradiation experiments were carried out using the "Pyrex" filtered output of a 125 W medium pressure mercury lamp in an immersion well photochemical reaction vessel. The degradation was studied by monitoring the change in substrate concentration employing UV spectroscopic analysis and decrease in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of the dye derivative 3 was also investigated under sunlight and efficiency of degradation was compared with that of the artificial light source.

The degradation rates for the decomposition and mineralization of the dye was determined from the linear regression of plot of the natural logarithm of TOC and the dye concentration as a function of irradiation time, i.e. first order kinetics. The rate was calculated in terms of mole L⁻¹ min⁻¹ employing the following equations;

\[-d \left[ \text{TOC} \right]/ dt = kc^n\]

\[-d \left[ \text{A} \right]/ dt = kc^n\]

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of pollutant, n = order of reaction

The degradation rates were found to be strongly influenced by all the parameters studied.

An attempt was made to identify the intermediate products formed during the photooxidation process of all the dyes under investigations through GC/MS analysis technique. The products were characterized based on their molecular ion and mass spectrometric fragmentation pattern. Irradiation of an aqueous solution (250 mL) of alizarin red S (1, 0.35 mM) in the presence
of TiO$_2$ (1 gL$^{-1}$) for 1 h followed by GC/MS analysis of the chloroform extract gave benzene-1,2-dicarboxylic acid (8) as the only identified degradation product. The GC/MS analysis of the irradiated mixture of acid green 25 (2) under analogous conditions for 1 h also gave rise to benzene-1,2-dicarboxylic acid (8) as one of the degradation product. Similarly, irradiation of the dye derivative 3 showed the formation of 1-aminoanthraquinone (26), 3,6-diaminobenzene-1,2-dicarboxylic acid (27), 3-aminobenzene-1,2-dicarboxylic acid (28), 1,4-dihydroxyanthraquinone (34) and 1-hydroxyanthroquinone (35).

The Chapter 2 of the thesis deals with the photocatalysed degradation of three selected azo dye derivatives, acid red 29 (1), acid red 88 (2) and acid orange 8 (3) in aqueous suspension of titanium dioxide using different parameters. The decomposition and mineralization of the dye was monitored by measuring the change in substrate concentration and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of the dye was found to be strongly influenced by all the parameters studied such as type of photocatalyst, pH, catalyst and substrate concentration and in the presence of electron acceptors. For example, the photocatalyst, Degussa P25 was found to be more efficient for the degradation of the dye as compared with other commercially available TiO$_2$ samples from Milenium inorganic, Travancore titanium product and Hombikat UV100.

The GC/MS analysis of an irradiated mixture of dye derivative 1-3 in aqueous suspension of titanium dioxide showed the formation of several intermediate products. 4-amino-1-naphthalenesulphonic acid (6) was identified as one of the intermediate product in the photocatalytic degradation of acid red 88 (2). A probable pathway for the formation of product
involving electron transfers reaction and reaction with hydroxyl radical and superoxide radical anions has been proposed.

The Chapter 3 of the thesis deals with photocatalysed degradation of two selected triphenylmethane dye, gentian violet (1), p-rosaniline (2) and a xanthene dye derivative eosine yellowish (3) in aqueous suspension of titanium dioxide under varying conditions. As usual the decomposition and mineralization was studied UV spectrosopically and using TOC analyzer. Interestingly, the photocatalyst Degussa P25 was found to be more efficient for the degradation of triphenylmethane dye derivatives 1 and 2, whereas Hombikat UV100 was better for the photocatalytic degradation of the xanthene dye derivative 3. The degradation products formed during the photooxidation process of all the dye under investigation was analysed through GC/MS analysis technique. Analysis of an irradiated mixture of gentian violet (1) in the presence of Degussa P25 showed the formation of N-methylaniline (10) and p-aminobenzoic acid (16), whereas the dye derivative 2 gave rise to 4,4'-diaminobenzophenone (18) and benzophenone (22). These products have been proposed based on their molecular ion and mass fragmentation peaks.

Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of different dyes listed under Chapters 1-3.

Note: The numbers of the various compounds given in parentheses corresponds to those under the respective chapters.
List of Publications

1. Photocatalytic degradation of the textile dye, Alizarin Red S, in aqueous suspensions of titanium dioxide
   M. Saquib and M. Muneer

1. Photocatalytic degradation of CI Acid Green 25 and CI Acid Red 88 in aqueous suspensions of titanium dioxide
   M. Saquib and M. Muneer

3. Semiconductor mediated photocatalysed degradation of an anthraquinone dye, Remazol Brilliant Blue R under sunlight and artificial light source
   M. Saquib and M. Muneer

4. TiO₂-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions
   M. Saquib and M. Muneer

5. Titanium dioxide mediated photocatalysed degradation of a textile dye derivative, acid orange 8 in aqueous suspensions
   M. Saquib and M. Muneer
   *Desalination*, (in press)
6. Semiconductor mediated photocatalytic degradation of a textile dye in water: case study of acid red 29

M. Saquib and M. Muneer

_Color. Technol., (communicated)_

7. Photocatalytic degradation of two selected textile dye derivatives, eosine yellowish and p-rosaniline in aqueous suspensions of titanium dioxide

M. Saquib and M. Muneer

_J. Environ. Sci. Health A, (communicated)_
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Dedicated

To

My Parents
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CERTIFICATE

Certified that the work embodied in this thesis entitled "PHOTOCATALYSED DEGRADATION OF FEW SELECTED TEXTILE DYE DERIVATIVES IN AQUEOUS SUSPENSION OF TITANUM DIOXIDE" has been carried out by Mr. Mohd Saquib under my supervision and same has not been submitted elsewhere for a degree.

M. Muneer
(M. MUNEER)
Supervisor
STATEMENT

I hereby declared that the matter embodied in this thesis is the result of investigations carried out by me in the Department of Chemistry, Aligarh Muslim University, Aligarh, India, under the supervision of Dr. M. Muneer.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made wherever the work described is based on the findings of other investigators.

(MOHD SAQUIB)
ACKNOWLEDGEMENT

It is with great pleasure that I express my deep sense of gratitude to Dr. M. Muneer for suggesting the research problem and for encouraging me to a successful completion of this work.

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I do not find suitable words to express my feelings to my friends like Mr. M. Faisal, Messrs M. Saquib Kharme nd N. Hoda for being my side, whenever I needed them.

Last but not least with a deep sense of love and requital, I wish to thank my parents, brother and sisters whose love and affection has been constant source of inspiration to me.

The award of Junior Research Fellowship by the Department of Science and Technology (DST), GoWt, of India, New Delhi is gratefully acknowledged.

(MOHD SAQUIB)
PREFACE

The thesis entitled “Photocatalysed degradation of few selected textile dye derivatives in aqueous suspension of titanium dioxide” is divided into three Chapters.

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For example the photocatalyst, Degussa P25 was found to be more efficient for the degradation of the dye as compared with other commercially available TiO₂ samples from Milenium inorganic, Travancore titanium product and Hombikat UV100.

The GC/MS analysis of an irradiated mixture of dye derivatives 1-3 in aqueous suspension of titanium dioxide showed the formation of several intermediate products. 4-aminonaphthalene sulphonatic acid (6) was identified as one of the intermediate product in the photocatalytic degradation of acid red 88 (2). A probable pathway for the formation of product involving electron transfers reaction and reaction with hydroxyl radical and superoxide radical anions has been proposed.

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Reasonable mechanisms have been suggested to account for the formation of the various products in the reaction of different dyes listed under Chapters 1-3.

Note: The numbers of the various compounds given in parentheses corresponds to those under the respective chapters.
Chapter 1

PHOTOCATALYSED DEGRADATION OF THREE SELECTED ANTHRAQUINONE DYE DERIVATIVES, ALIZARIN RED S, ACID GREEN 25 AND REMAZOL BRILLIANT BLUE R IN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE

1.1 Abstract

The photocatalysed degradation of three selected anthraquinone dye derivatives, such as alizarin red S (1), acid green 25 (2) and remazol brilliant blue R (3) have been investigated in aqueous suspension of titanium dioxide (TiO₂) under a variety of conditions. The degradation was studied by monitoring the change in substrate concentration employing UV Spectroscopic analysis and decrease in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of the dye was studied under different conditions such as different types of TiO₂, pH, catalyst concentration, substrate concentration and in the presence of electron acceptors besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The degradation of remazol brilliant blue R (3) was also investigated under sunlight and the efficiency of degradation was compared with that of the artificial light source. The photocatalyst, Degussa P25 was found to be more efficient for the degradation of all the dyes under investigation under UV light, whereas Hombikat UV100 was better for the degradation of the dye 3 under sunlight source. The degradation products were analysed by GC/MS analysis technique and probable pathways for the formation of different products have been proposed.
1.2 Introduction

Water contamination is caused by various sources such as industrial effluents, agricultural runoff and chemical spills. The industrial estate in India is presently accommodating 48 small and medium scale dyeing and printing synthetic textile units. The industrial units are scattered and these units are producing large quantities of wastewater, which are highly polluting in nature. The consumption of water for processing one kg of textile goods varies from 10 to 300 liters, depending on the nature of the fiber, form of textile goods and processing. Taking a conservative figure of 100 liters of water per kg the amount of wastewater generated by the textile industry works out to a gigantic 4500 million kiloliters. Handling of such a huge quantity of wastewater is not only a difficult task but also a highly significant risk in maintaining the supply of safe drinking water. About 10,000 different dyes and pigments exist and over $7 \times 10^5$ tonnes of these are produced annually worldwide. An estimated 10-15% of these dyes are lost in effluents during dyeing process, that poses a major problem for the industry as well as threat to the environment.

Decolourization of dye effluents has therefore acquired increasing attention. A few dyes are known to undergo degradation via anaerobic reduction. Decolourization of dye effluent by bisulfite-catalysed borohydride reduction has also been reported earlier. During the past two decades, photocatalytic processes involving TiO$_2$ semiconductor particles under UV light illumination have been shown to be potentially advantageous and useful in the treatment of waste water pollutants. Earlier studies have shown that a wide range of organic substrates such as
alkanes, alkenes, aromatics, surfactants, herbicides, pesticides, fungicides and insecticides can be completely photomineralized in the presence of TiO$_2$ and oxygen.

1.2.1 Mechanism of photocatalysis

A Semiconductor is commonly characterized by energy gap between its electronically populated valence band and its largely vacant conduction band.$^{19}$ Irradiation of semiconductor particles with light of energy greater than or equal to the band-gap of the semiconductor promotes an electron from valence band to the conduction band.$^{19}$ The conduction band electron and the valence band electron hole may either undergo electron transfer reactions with the adsorbed substrate or recombine.$^{20}$ The electron transfer processes on irradiated TiO$_2$ surface are illustrated in Fig. 1.1 with oxygen and water being electron acceptor and donor respectively.

![Figure 1.1](image_url)
If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, $h^+_{vb}$ may react with surface-bound $H_2O$ or $OH^-$ to produce the hydroxyl radical and $e^-_{cb}$ is picked up by oxygen to generate superoxide radical anion ($O_2^-$), as indicated in the following equations 1-3:

$$TiO_2 + hv \rightarrow e^-_{cb} + h^+_{vb} \quad [1]$$

$$O_2 + e^-_{cb} \rightarrow O^-_2 \quad [2]$$

$$H_2O + h^+_{vb} \rightarrow OH + H^+ \quad [3]$$

It has been suggested that the hydroxyl radicals ($OH^-$) and superoxide radical anions ($O_2^-$) are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the bleaching of the dye. Alternatively, direct absorption of light by the dye, can lead to charge injection from exited state of the dye to the conduction band of the semiconductor as summarized in the following equations;

$$Dye_{ads} + hv \rightarrow Dye^{*}_{ads} \quad [4]$$

$$Dye^{*}_{ads} + TiO_2 \rightarrow Dye_{ads}^{*} + TiO_2 (e^-) \quad [5]$$

The ability of a semiconductor as a photocatalyst for a redox reaction is governed by the position of its conduction and valence bands (band-edge positions). For a desired electron transfer reaction to occur, the relevant potential of the electron acceptor should be below (more positive than) the conduction band of the semiconductor, while the relevant potential of the electron donor is preferred to be above (more negative than) the valence band of the semiconductor. For an organic synthesis via organic photocatalysis, the substrate must have a potential more negative
than the valence band of the semiconductor used. For a reductive synthesis, it is vice versa. A number of semiconductors have been investigated for their ability to photocatalyzed organic functional group transformations. Their band-gap and band edge positions have been summarized in several well-known reviews.\textsuperscript{20-24}

Titanium dioxide has a valence band potential of +3.1V (vs. SCE) and a conduction band potential of −0.1 V (vs. SCE). Many organic compounds have a potential above that of the TiO\textsubscript{2} valence band and therefore can be oxidized. In contrast, fewer organic compounds can be reduced since a smaller number of them have a potential below that of the TiO\textsubscript{2} conduction band.\textsuperscript{25} The other criteria for the selection of a semiconductor include its chemical and photochemical stability and environmental impact. An important factor for TiO\textsubscript{2} being the most popular semiconductor is its resistivity to strong acids and bases and its stability under illumination.\textsuperscript{26}

There are several classes of dyes, which do not favour donation from the excited states, such as anthrquinone dyes because of the presence of two electron-withdrawing carbonyl groups, which are susceptible to accept an electron rather than donate an electron. Earlier studies\textsuperscript{27-43} have shown that heterogeneous photocatalytic oxidation processes can be used for the decolourization of dye effluent in the presence of light. It has been reported\textsuperscript{44} that anthraquinone sulphonate dye, which is difficult to degrade biologically can effectively degraded in the presence of TiO\textsubscript{2} and O\textsubscript{2}. The photocatalytic degradation of few anthrquinone dyes such as reactive blue 4, acid blue 40 and alizarin red S have also been reported\textsuperscript{45-47} earlier in aqueous suspension under different conditions. In spite of these studies, no major efforts have been made to look into the detailed degradation kinetics and identification of intermediate products formed during the
photooxidation process under these conditions. With this view, we have studied the degradation of three selected anthrquinone dye derivatives such as alizarin red S (1), acid green 25 (2) and remazol brilliant blue R (3) shown in Chart 1.1, in aqueous suspension of TiO₂ under a variety of conditions and an attempt has been made to identify the intermediate products formed during the photooxidation process through GC/MS analysis technique.

1.3 Experimental

1.3.1 Reagent and chemicals

Alizarin red S (1), acid green 25 (2) and remazol brilliant Blue R (3) were obtained from Aldrich and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, Degussa P25 (Degussa AG),⁴⁸ was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH),⁴⁹ PC500 (Milenium inorganic chemicals)⁵⁰ and TTP (Travancore titanium products, India)⁵¹ were used for the comparative studies. Degussa P25 consist of 75% anatase and 25% rutile with a specific BET-surface area of 50 m²g⁻¹ and primary particle size of 20 nm.⁵² Hombikat UV100 consist of 100% anatase with a specific BET-surface area >250 m²g⁻¹ and primary particle size of 5 nm.⁵³ The photocatalyst PC500 has a BET-surface area of 287 m²g⁻¹ with 100% anatase and primary particle size of 5-10 nm,⁵⁴ whereas, TTP has a BET-surface area of 9.82 m²g⁻¹. The other chemical used in this study such as sodium hydroxide (NaOH), nitric acid (HNO₃), ammonium persulphate (NH₄)₂S₂O₈), hydrogen peroxide (H₂O₂) and potassium bromate (KBrO₃) were obtained from Merck.
Chart 1.1

1. (Alizarin red S)

2. (Acid green 25)

3. (Remazol brilliant blue R)
1.3.2 Procedure

The solutions of the dye with desired concentrations were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass equipped with a magnetic stirring bar, water circulating jacket and an opening for the supply of molecular oxygen was used. A simplified diagram of the reactor system is shown below;

![Diagram of the reactor system]

Figure 1.2

For irradiation experiment, the aqueous solution of the dye with desired concentration was taken into the photoreactor and required amount of photocatalyst was added, the solution was stirred and bubbled with molecular oxygen for at least 15 minutes in the dark to allow equilibration of the system so that the loss of compound due to adsorption can be taken into account. The pH of the reaction mixture was adjusted by adding a dilute aqueous solution of HNO₃ or NaOH. The zero
time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp (Philips). IR-radiation and short-wavelength UV-radiation were eliminated by water circulated in a Pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during irradiation and analysed after centrifugation.

The sunlight experiments were carried out in a round bottom flask made of Pyrex glass. Aqueous solution (250 mL) of desired concentration of the model compound containing required amount of photocatalyst was taken and stirred for 15 min in the dark in presence of oxygen for equilibration. The solution was then placed on flat platform with continuous stirring and purging of molecular oxygen. Samples (10 mL) were collected before and at regular intervals during illumination and analysed after centrifugation.

1.3.3 Analysis

1.3.3.1 Photomineralization of the dye

The photomineralization of the dye was measured using Total Organic Carbon Analyzer (Shimadzu TOC 5000 A). The main principle of TOC analyzer involves the use of carrier gas (oxygen), which is flow-regulated (150 ml / min) and allows to flow through the Total Carbon (TC) combustion tube, which is packed with catalyst, and kept at 680 °C. When the samples enter the TC combustion tube, TC in the sample is oxidized to carbon dioxide. The carrier gas containing the combustion products from the TC combustion tube flows through the Inorganic Carbon (IC) reaction vessel, dehumidifier, halogen scrubber and finally reaches the sample cell of the nondispersive
infrared (NDIR) detector which measures the carbon dioxide content. The output signal (analog) of the NDIR detector is displayed as peaks. The peak areas are measured and processed by the data processing unit. Since the peak areas are proportional to the total carbon concentration, the total carbon in a sample may be easily determined from the calibration curve prepared using standard solution of known carbon content. Total carbon is the sum of TOC (Total Organic Carbon) and IC (Inorganic Carbon).

1.3.3.2 Photodegradation of the dye

The photodegradation of the dye was measured using UV Spectroscopic analysis technique (Shimadzu 1601 and Systronics 118). The double beam spectrophotometer has an in-built tungsten and deuterium lamps, which provide the measurement of optical density (OD) in the range 200-1000 nm (near UV and visible regions). The samples were analysed using quartz cuvette, as it has zero absorption in the above wavelength regions.

The absorbance of the dye derivatives 1 and 3 were followed at 556 nm and 592 nm respectively and the degradation rates were calculated in terms of mole L⁻¹ min⁻¹.

1.3.3.3 Characterization of intermediate products

For the characterization of intermediate products, aqueous solutions (250 mL) of the dye containing TiO₂ (1 gL⁻¹) was taken in an immersion well photochemical reactor made of Pyrex glass. The mixture was irradiated with a 125 W medium pressure mercury lamp for a required period of time under oxygen atmosphere. The photocatalyst was removed through filtration and the filtrate was extracted with chloroform, which was subsequently dried over anhydrous sodium
sulphate. The solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC/MS analysis technique. For GC/MS analysis a Hewlett Packard Gas chromatograph and mass spectrometer (G1800 A) equipped with a 30 m HP-1 (d = 0.25 mm) capillary column, operating temperature programmed (injection temperature 100 °C which is raised to 250 °C at the rate of 10 °C min⁻¹ which is further raised to 280 °C at the rate of 30 °C min⁻¹) in splitless mode injection volume 0.5 μL with helium as a carrier gas was used.

1.3.3.4 Calculation of percentage mineralization and decomposition of the dye

The percentage mineralization and decomposition of the dye was calculated employing the following expression.⁵⁷

\[
\% \text{ Mineralization or Decomposition} = \left( \frac{C_0 - C_t}{C_0} \right) \times 100
\]

\[ C_0 = \text{initial absorbance or TOC of the dye} \]
\[ C_t = \text{absorbance or TOC remaining after irradiation of time } t. \]

1.4 Results and Discussion

1.4.1 Photolysis of aqueous solution of dye in the presence of TiO₂

Fig. 1.3 shows the change in absorption intensity at 556 nm and depletion in TOC as a function of irradiation time for an aqueous solution of alizarin red S (1, 0.35 mM) in the presence and absence of the photocatalyst (Degussa P25, 1 g L⁻¹) by the "Pyrex" filtered output of a 125 W medium Pressure mercury lamp. It was observed that 85% mineralization and 99% decomposition of the dye takes place after 90 min of irradiation. Both the curves can be fitted reasonably well by
Figure 1.3: Depletion in TOC and change in absorption intensity at 556 nm as a function of irradiation time for an aqueous solution of alizarin red S (1) in the presence and absence of photocatalyst. Experimental conditions: dye concentration (0.35 mM), V=250 mL, immersion well photoreactor, 125 W medium pressure Hg lamp, Photocatalyst: TiO$_2$ (Degussa P25, 1 gL$^{-1}$), cont. O$_2$ purging and stirring, irradiation time= 90 min.
an exponential decay curve suggesting the first order kinetics. For each experiment, the rate constant was calculated from the plot of the natural logarithm of TOC and the dye concentration as a function of irradiation time. The degradation rate for the mineralization and decomposition of the dye was calculated using formula given below,

\[-\frac{d[TOC]}{dt} = k c^n\] [7]

\[-\frac{d[A]}{dt} = k c^n\] [8]

TOC = Total Organic Carbon, A = absorbance, k = rate constant, c = concentration of the pollutant, n = order of reaction

The irradiation of aqueous suspension of the dye derivatives, acid green 25 (2, 0.25 mM) and remazol brilliant blue R (3, 0.25 mM) under analogous conditions lead to depletion in TOC and decrease in absorption intensity as a function of irradiation time respectively.

The degradation of the dye derivative 3 was also carried out under sunlight and the efficiency of degradation was compared with that of the UV light source. The degradation of the dye was better under UV light as compared with sunlight.

Blank experiments were carried out by irradiating the aqueous solution of the dye in the absence of TiO₂, where no observable loss of the dye was observed. The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.
1.4.2 Comparison of different photocatalysts

Titanium dioxide is known to be the semiconductor with the highest photocatalytic activity, is non-toxic, relatively inexpensive and stable in aqueous solution. Several reviews have been written, regarding the mechanistic and kinetic details as well as the influence of experimental parameters. It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation technique.58

We have tested the photocatalytic activity of four different commercially available TiO$_2$ powders (namely Degussa P25, Hombikat UV100, TiO$_2$ sample from Milenium Inorganic and Travancore Titanium Product) on the degradation kinetics of all the dyes under investigation. The degradation rate obtained for the decomposition and TOC depletion of 1-3, in the presence of different types of TiO$_2$ powders is shown in Fig. 1.4-1.6 respectively. It has been observed that the degradation of dye proceeds much more rapidly in the presence of Degussa P25 as compared with other TiO$_2$ samples under UV light source, whereas Hombikat UV100 was slightly better under sunlight in the photocatalytic degradation of the dye derivative 3.

The differences in the photocatalytic activity are likely to be due to differences in the BET-surface, impurities, lattice mismatches or density of hydroxyl groups on the catalyst’s surface. Since they will affect the adsorption behavior of a pollutant or intermediate molecule and the lifetime and recombination rate of electron-hole pairs. Earlier studies59 have shown that Degussa P25 owes its high photoreactivity due to slow recombination between electron and holes whereas Sachtleben Hombikat UV100 has a high photoreactivity due to fast interfacial electron transfer rate.
Figure 1.5: Comparison of degradation rate for the mineralization of acid green 25 (2) in the presence of different photocatalysts. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalysts: Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹), PC500 (1 gL⁻¹) and TTP (1 gL⁻¹), irradiation time=240 min.
Figure 1.6: Comparison of degradation rate for the decomposition of remazol brilliant blue R (3) in the presence of different photocatalysts under sunlight and UV light source. Experimental conditions: a) UV Light: dye concentration (0.25 mM), V=250 mL, Photocatalysts: Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹) and PC500 (1 gL⁻¹), irradiation time=120 min. b) Sunlight: dye concentration (0.25 mM), V=250 mL, Photocatalysts: Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹) and PC500 (1 gL⁻¹), irradiation time=120 min.
Earlier studies have shown that Degussa P25 was found to show better activity for the photocatalytic degradation of a large number of organic compounds. On the hand Lindner et al. showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. Also Hombikat UV100 was found to be better for the degradation of benzidine and 1,2-diphenyl hydrazine as shown in a recent study. These results indicate that the activity of the photocatalyst also depends on the type of the model pollutant. In all following experiments, Degussa P25 was used as the photocatalyst, since this material exhibited the highest overall activity for the degradation of the dye.

1.4.3 pH Effect

An important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Employing Degussa P25 as photocatalyst the decomposition and mineralization of alizarin red S (1) in the aqueous suspensions of TiO$_2$ was studied in the pH range between 3-11. The degradation rate for the TOC depletion and for the decomposition of the dye, as a function of reaction pH is shown in Fig. 1.7. It was observed that the degradation rate for the TOC depletion and decomposition of the dye decreases with the increase in pH from 3 to 11 and highest efficiency was observed in acidic pH.

The degradation rate for the TOC depletion of acid green 25 (2) as a function of reaction pH is shown in Fig.1.8. The mineralization of dye derivative 2 increases with the increase in pH from 3 to 9 and a further increase in pH from 9 to 11 leads to slight decrease in the degradation rate.
Figure 1.7: Influence of pH on the degradation rate for the decomposition and mineralization of alizarin red S (1). Experimental conditions: dye concentration (0.35 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), reaction pH (3, 5, 9 and 11), irradiation time=90 min.
Figure 1.8: Influence of pH on the degradation rate for the mineralization of acid green 25 (2). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), reaction pH (3.3, 6.4, 9 and 11), irradiation time=240 min
The degradation rate for the decomposition of the dye derivative 3 as a function of reaction pH employing Degussa P25 and Hombikat UV100 in the presence of UV light and sunlight source is shown in Fig. 1.9. It was observed that under sunlight the highest efficiency for the degradation of the dye was observed at pH 3, which slowly decreases with the increase in pH of the reaction mixture. On the other hand, when the reaction was carried out under UV light, higher efficiency was observed at pH 9, whereas the efficiency for the degradation of the dye at pH 3, 5.2 and 11 was similar within the experimental error limits.

The adsorption of the dye derivatives 1-3 at pH values between 3 to 11 on the surface of the photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h in a round-bottomed flask containing varying amount of photocatalyst such as 0, 0.5, 1, 2 and 5 g L⁻¹. Analysis of the dye after centrifugation indicate no observable loss of the dye in the case of acid green 25 (2), whereas some observable loss of the dye was observed in the case of alizarin red S (1) and remazol brilliant blue R (3).

In this study it has been shown that the degradation rate for the TOC depletion and decomposition of the dye derivatives under investigation is highly influenced by the reaction pH. In the case of Degussa P25 photocatalyst, the zero point of charge (pH_{zpc}) is at pH 6.25. Hence, at more acidic pH values, the particle surface is positively charged, while at pH values above 6.25, it is negatively charge. Due to the low pKa value of the sulfonic acid group, with increasing pH, the negative charges on TiO₂ are expected to repel the dye and a decrease in efficiency of degradation with increasing pH is expected. The results are in agreement with the assumption for the photocatalytic degradation of the dye derivative 1 under UV light and the degradation of 3 under
Figure 1.9: Influence of pH on the degradation rate for the decomposition of remazol brilliant blue R (3). Experimental conditions: a) UV Light: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), reaction pH: 3, 5.2, 9 and 11, irradiation time=120 min. b) Sunlight: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 g L⁻¹), reaction pH 3, 5.2, 9 and 11, irradiation time=120 min.
sunlight source. In contrast, in the degradation of the dye derivative 2, the rate has been found to increases with the increase in pH. This effect may be attributed to more efficient generation of hydroxyl radicals by TiO$_2$ with increasing concentration of OH$^-$. At the alkaline pH values, the hydroxyl radicals have to diffuse away and degrade the dye in the bulk solution. Similar results were reported earlier for acetate ion and acid blue 40.$^{43,66}$

1.4.4 Effect of substrate concentration

It is important both from mechanistic and from application point of view to study the dependence of substrate concentration on the photocatalytic reaction rate. As oxidation proceeds, less and less of the surface of the TiO$_2$ particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing irradiation time.

Effect of substrate concentration on the degradation of the dye derivatives 1-3 was studied at varying concentrations from 0.125 to 0.75 mM. The degradation rate for the TOC depletion and decomposition of 1 as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Fig. 1.10. Where it has been found that the rate decreases with the increase in substrate concentration from 0.25 to 0.75 mM.

The degradation rate for the TOC depletion of 2 as a function of substrate concentration is shown in Fig. 1.11. Here it is interesting to note that the degradation rate increases with the increase in substrate concentration from 0.125 to 0.25 mM and a further increase in the substrate concentration from 0.25 to 0.5 mM leads to decrease in the degradation rate of the dye.
Figure 1.10: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of alizarin red S (1). Experimental conditions: dye concentrations (0.25, 0.35, 0.5 and 0.75 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), irradiation time=90 min.
Figure 1.11: Influence of substrate concentration on the degradation rate for the mineralization of acid green 25 (2). Experimental conditions: dye concentrations (0.125, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), irradiation time=240.
The rate for decomposition of the dye derivative 3, as a function of substrate concentration employing Degussa P25 and UV100 under UV light and sunlight sources respectively is shown in Fig. 1.12. The degradation rate for the decomposition of 3 under UV light source showed similar trend as observed in the case of 2. On the other hand when the reaction was carried out under sunlight, highest efficiency was observed at 0.125 mM, which slowly decreases with the increase in substrate concentration as shown in the Figure.

Earlier studies on the photocatalytic degradation of colorless organic pollutants indicate that the degradation rate increases with the increase in substrate concentration. In contrast, our studies on the photocatalytic degradation of dyes indicate that the degradation rate increases with the increase in substrate concentration from 0.125 to 0.25 mM and a further increase in substrate concentration lead to decrease in the degradation rate. This may be due to the fact that as the initial concentrations of the dye increases, the colour of the irradiating mixture becomes more and more intense which prevents the penetration of light to the surface of the catalyst. Hence, the generation of relative amount of OH and O2 on the surface of the catalyst do not increase as the intensity of light and irradiation time are constant. Conversely, their concentrations will decrease with increase in concentration of the dye as the light photons are largely absorbed and prevented from reaching the catalyst surface by the dye molecules. Consequently, the degradation efficiency of the dye decreases as the dye concentration increases.

1.4.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of dyes under investigation was studied employing different concentrations of Degussa P25 and Hombikat UV100
Figure 1.12: Influence of substrate concentration on the degradation rate for the decomposition of remazol brilliant blue R (3). Experimental conditions: a) UV Light: Substrate Concentrations (0.125, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), irradiation time=120 min. b) Sunlight: Substrate Concentrations (0.125, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 g L⁻¹), irradiation time=120 min.
varying from 0.5 to 5 gL\(^{-1}\). The degradation rate for the TOC depletion and decomposition of the dye derivatives 1-3 as function of catalyst loading is shown in Fig. 1.13-1.15 respectively. As expected, the degradation rate was found to increase with the increase in catalyst concentration, which is the characteristic of heterogeneous photocatalysis.

Whether in static, slurry, or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, it was observed that above a certain concentration, the reaction rate decreases and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO\(_2\) in which all the particles, i.e., surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration \(\left[(\text{TiO}_2)_{\text{OPT}}\right]\) has to be found, in order to avoid excess catalyst and insure total absorption of efficient photons. Our results, on the effect of catalyst concentration on the degradation rate for the TOC depletion and decomposition of 1-3 as shown in Fig. 1.13-1.15 are in agreement with numerous studies reported in the literature\(^{60-62,64,67}\).

1.4.6. Effect of electron acceptors

Since hydroxyl radicals appear to play an important role in the photocatalytic degradation, electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the electron/hole \((e^-/h^+)\) pair recombination. One practical problem in using TiO\(_2\) as a photo
Figure 1.13: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of alizarin red S (1). Experimental conditions: dye concentration (0.35 mM), V=250 mL, Photocatalyst: P25 (0.5, 1, 2 and 5 gL⁻¹), irradiation time= 90 min.
Figure 1.14: Influence of catalyst concentration on the degradation rate for the mineralization of acid green 25 (2). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 3 gL⁻¹), irradiation time=240 min.
Figure 1.15: Influence of catalyst concentration on the degradation rate for the decomposition of remazol brilliant blue R (3). Experimental conditions: a) UV Light: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 gL⁻¹), irradiation time = 120 min. b) Sunlight: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (0.5, 1, 2 and 5 gL⁻¹), irradiation time = 120 min.
catalyst is the undesired electron / hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient and thus represent the major energy - wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron - hole pair recombination is to add other (irreversible) electron acceptors to the reaction. They could have several different effects such as, i.e., 1) to increase the number of trapped electrons and, consequently, avoid recombination, 2) to generate more radicals and other oxidizing species, 3) to increase the oxidation rate of intermediate compounds and 4) to avoid problems caused by low oxygen concentration. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of electron acceptors to enhance the degradation rate may often be justified. The degradation rate for the mineralization and decomposition of the dye derivatives 1-3 in the presence of different electron acceptors are shown in Fig. 1.16-1.18.

Hydrogen peroxide, bromate and persulphate ions are known to generate hydroxyl radicals by the mechanisms shown in Eqns 9-13;

\[
\begin{align*}
\text{H}_2\text{O}_2 + e^-_{cb} & \rightarrow \text{OH}^* + \text{OH}^- \quad \text{[9]} \\
\text{BrO}_3^- + 2\text{H}^+ + e^-_{cb} & \rightarrow \text{BrO}_2^* + \text{H}_2\text{O} \quad \text{[10]} \\
\text{BrO}_3^- + 6\text{H}^+ + 6 e^-_{cb} & \rightarrow \text{[BrO}_2^-, \text{H}_2\text{O}_2] \rightarrow \text{Br}^- + 3\text{H}_2\text{O} \quad \text{[11]} \\
\text{S}_2\text{O}_8^{2-} + e^-_{cb} & \rightarrow \text{SO}_4^{2-} + \text{SO}_4^{2-} \quad \text{[12]} \\
\text{SO}_4^{2-} + \text{H}_2\text{O} & \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{H}^+ \quad \text{[13]}
\end{align*}
\]
Figure 1.16: Comparison of degradation rate for the decomposition and mineralization of alizarin red S (1) in the presence of different electron acceptors. Experimental conditions: dye concentration (0.35 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L\(^{-1}\)), Electron Acceptors: KBrO\(_3\) (5 mM), H\(_2\)O\(_2\) (10 mM) and (NH\(_4\))\(_2\)S\(_2\)O\(_8\) (5 mM), irradiation time=90 min.
Figure 1.17: Degradation rate for the mineralization of acid green 25 (2) in the presence of different electron acceptors. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), Electron Acceptors: KBrO₃ (5 mM), H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (5 mM), irradiation time=240 min.
Figure 1.18: Photocatalytic degradation rate for the decomposition of remazol brilliant blue R (3) in the presence of different electron acceptors: Experimental conditions: a) UV Light: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), Electron Acceptors: KBrO₃ (5 mM), H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (5 mM), irradiation time=120 min. b) Sunlight: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 g L⁻¹), Electron Acceptors: KBrO₃ (5 mM), H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (5 mM), irradiation time=120 min.
The respective one-electron reduction potentials of different species are: \( E (O_2/O_2^-) = -155 \text{ mV}, \ E (H_2O_2/OH) = 800 \text{ mV}, \ E (BrO_3^-/BrO_2^-) = 1150 \text{ mV}, \text{ and } E (S_2O_8^{2-}/SO_4^-) = 1100 \text{ mV}. \) From the thermodynamic point of view all employed additives should therefore be more efficient electron acceptors than molecular oxygen. All the electron acceptors showed a beneficial effect on the degradation kinetics of the dye derivative 1-3 except hydrogen peroxide in the case of 3 under UV light source. The effective electron acceptor ability of KBrO₃ has been observed in number of studies before.61, 62,69 One possible explanation might be a change in the reaction mechanism of the photocatalytic degradation of dye, since the reduction of bromate ions by electrons does not lead directly to the formation of hydroxyl radicals, but rather to the formation of other reactive radicals or oxidizing reagents, e.g., Br₅₂ and HOBr. Furthermore, bromate ions by themselves can act as oxidizing agents.

1.4.7 Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye derivatives 1-3 in aqueous suspensions of titanium dioxide through GC/MS analysis technique.

The GC analysis of an irradiated mixture of 1 showed the formation of several products. The photoproducts benzene-1,2-dicarboxylic acid (8) appearing at retention times \( (t_R) \) 17.02 min was identified as one of the intermediate based on their molecular ion and mass spectrometric fragmentation peaks, which are given below;

**Compound 8:** 166 \((M^+)\), 149, 132, 104, 93, 70 and 57.
A plausible mechanism for the formation of 8 involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic process is proposed in Scheme 1.1. The model compound 1 upon the transfer of an electron can form to the radical anion 4, which may undergo addition of a hydroxyl radical followed by ring cleavage to give the keto acid 5. This intermediate on further addition of an electron and hydroxyl radical with subsequent ring cleavage will give the observed product 8.

The irradiation of an aqueous solution of the dye derivative 2, also showed the formation of benzene-1,2-dicarboxylic acid (8) appearing at retention time (tR) 24.86 min.

A mechanism for the formation of 8 involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic process is proposed in Scheme 1.2. An alternative route for the formation of 8 has also been proposed in Scheme 1.3 and 1.4 respectively, which in turn outlines the structures of other probable intermediate products. The model compound 2 upon the transfer of an electron can form to the radical anion 10, which may undergo addition of a hydroxyl radical followed by ring cleavage to give the keto acid 11. This intermediate on further transfer of an electron followed by hydroxyl radical addition with subsequent ring cleavage will give the observed product 8 as shown in Scheme 1.2. An alternative route for the formation of 8 could similarly be understood in terms of the pathways shown in Scheme 1.3 and 1.4 respectively. The intermediate 12 may undergo ring cleavage followed by abstraction of a proton to give the keto acid 15. This product on transfer of an electron followed by addition of a hydroxyl radical may loose the phenyl ring to give the dicarboxylic acid 16 as shown in Scheme 1.3. The product 16 upon the transfer of an electron can form to the radical cation 18, which may undergo cleavage to
Scheme 1.1

1. $hv/\text{TiO}_2 \rightarrow +e^-$

2. $+\text{OH}^-$

3. $+\text{H}^+$

4. $\text{SO}_3\text{Na}$

5. $\text{CO}_2\text{H}$

6. $\text{OH}$

7. $\text{SO}_3\text{H}$

8. $\text{CO}_2\text{H}$

9. $\text{SO}_3\text{H}$
Scheme 1.2

\[ \text{hv} / \text{TiO}_2 \]

\[
\begin{align*}
\text{2} & \quad \text{NaO}_2\text{S} \\
\text{NaO}_2\text{S} & \quad \text{hv} / \text{TiO}_2 \\
\text{3} & \quad \text{OH}^- \\
\text{4} & \quad \text{H}_2\text{O} \\
\text{5} & \quad \text{NaO}_2\text{S} \\
\text{6} & \quad \text{H} \\
\text{7} & \quad \text{CO}_2\text{H} \\
\text{8} & \quad \text{H} \\
\text{9} & \quad \text{H} \\
\text{10} & \quad \text{NaO}_2\text{S} \\
\text{11} & \quad \text{NaO}_2\text{S} \\
\text{12} & \quad \text{NaO}_2\text{S} \\
\text{13} & \quad \text{NaO}_2\text{S} \\
\text{14} & \quad \text{NaO}_2\text{S} \\
\end{align*}
\]
Scheme 1.3

[Chemical structures and reactions are depicted graphically.]
Scheme 1.4

\[ \text{hv/TiO}_2 \quad -e^- \]

16 \[ \overset{+H^+}{\text{hv/TiO}_2} \]

18

19

20

21

22

8
give other probable fragmentation products along with 8 as shown in Scheme 1.4.

The GC/MS analysis of an irradiated mixture of the dye derivative 3, showed the formation of five products (26, 27, 28, 34 and 35) appearing at retention times (tR) 9.23, 9.28, 9.70, 11.13 and 11.19 min, respectively. These products were identified based on their molecular ion and mass fragmentation peaks, which are given below;

**Compound 26**: 223 (M+), 205, 167, 149, 132, 121, 104, 76 and 57.

**Compound 27**: 197 (M+), 183, 169, 155, 141, 127, 112, 113, 99, 84, 71 and 57.

**Compound 28**: 183 (M+), 168, 154, 140, 126, 113, 103, 97, 85, 71 and 57.

**Compound 34**: 240 (M+), 197, 183, 168, 154, 141, 127, 113, 99, 85, 71 and 57.

**Compound 35**: 224 (M+), 196, 179, 175, 154, 141, 126, 113, 85, 71 and 56.

A plausible mechanism for the formation of different products involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme 1.5 and 1.6 respectively. The model compound 3 upon the transfer of an electron can form the radical cation 23, which may undergo loss of aminophenyl moiety followed by abstraction of a proton leading to the formation of the observed product 1-aminoanthraquinone (26). This product undergoes addition of hydroxyl radical followed by ring cleavage leading to the formation the observed product 3-aminobenzene-1,2-dicarboxylic acid (28). The dicarboxylic acid derivative 3,6-diaminobenzene-1,2-dicarboxylic acid (27) may be arising through a similar pathway as shown in the Scheme.
Scheme 1.5

[Diagram showing chemical reactions and structures labeled 3, 23, SO₂(CH₂)₂O₅H, 24, 25, 26, 27, 28, 29.]
The formation of mono and dihydroxy derivative such as 1,4-dihydroxyanthraquinone (34) and 1-hydroxyanthraquinone (35) could be understood in terms of the pathways shown in Scheme 1.6. The dye derivative 3, upon the addition of a hydroxyl radical may lead to the formation of the radical species 30 which may undergo loss of ammonia followed by an electron transfer to give the radical cation 33. This intermediate may undergo loss of aminophenyl group followed by abstraction of a proton to give the monohydroxy derivative 35. The formation of dihydroxy derivative 34 may similarly be formed through the addition of a hydroxyl radical to the radical derivative 30 with subsequent loss of ammonia and aminophenyl moiety.
Scheme 1.6

Scheme 1.6
References:


48. The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

49. The photocatalyst Hombikat UV100 was a gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fur Technischer Chemie, Universitat Hannover, Callinstrasse, Hannover, Germany.

50. The photocatalyst PC500 was a gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fur Technischer Chemie, Universitat Hannover, Callinstrasse, Hannover, Germany.

51. The photocatalyst TTP was obtained from Travancore Titanium Products, Kerala, India.


55. The Total Organic Carbon Analyzer was a gift equipment from Alexander von Humboldt-Stiftung, Bonn, Germany.

56. GC/MS analysis was carried out from Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Mumbai, India.


Chapter 2

PHOTOCATALYSED DEGRADATION OF THREE SELECTED AZO DYE DERIVATIVES, ACID RED 29, ACID RED 88 AND ACID ORANGE 8 IN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE\textsuperscript{1-3}

2.1 Abstract

The photocatalysed degradation of three selected azo dye derivatives, such as acid red 29 (1), acid red 88 (2) and acid orange 8 (3) have been investigated in aqueous suspension of titanium dioxide under a variety of conditions. The degradation was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis and depletion in Total Organic Carbon (TOC) content as a function of irradiation time. The degradation of dyes were studied under different conditions such as different types of TiO\textsubscript{2}, pH, catalyst concentration, substrate concentration and in the presence of electron acceptors such as hydrogen peroxide, ammonium persulphate and potassium bromate besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the degradation of all dyes under investigation. An attempt was made to identify the degradation products through GC/MS analysis technique and probable mechanism for the formation of product has been proposed.

2.2 Introduction

Another class of dye, which is used extensively in the textile industry is the azo dye, which is characterized by the presence of N=N linkage. This class of dye comprise about half of all textile dyes used today.\textsuperscript{4} There are several studies related to the use of semiconductors in the
photodegradation of azo dyes. The other azo dye derivatives, which have been studied, include acid dyes, reactive dyes and related compound. Most of these studies deal with the degradation of dyes under different conditions. No major efforts have been made to identify the degradation products, which is important because of the fact that azo dyes are known to give aromatic amines, which are recognized as potent carcinogenic compounds. Therefore, the objective of the present investigation has been to study the degradation of three selected azo dye derivatives such as acid red 29 (1), acid red 88 (2) and acid orange 8 (3) (Chart 2.1) in aqueous suspension of TiO₂ under a variety of conditions and to identify the degradation products formed during the photooxidation process through GC/MS analysis technique.

2.3 Experimental

2.3.1 Reagent and chemicals

Acid red 29 (1) was obtained from Hi-Media India Ltd Bombay, acid red 88 (2) and acid orange 8 (3) was obtained from Aldrich and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst titanium dioxide, (Degussa P25) was used in most of the experiments, whereas other catalyst powders namely Hombikat UV100 (Sachtleben chemie GmbH), PC500 (Milenium inorganic chemicals) and TTP (Travancore titanium products, India) were used for comparative studies. The other chemicals used in this study such as sodium hydroxide, nitric acid, ammonium persulphate, hydrogen peroxide and potassium bromate were obtained from Merck. Irradiations were carried out in an immersion well photochemical reaction vessel made of Pyrex glass (Fig. 1.2) using 125 W medium
Chart 2.1

1 (Acid red 29)

2 (Acid red 88)

3 (Acid orange 8)
2.3.2 Analysis

The degradation of the dye derivative, 1 was followed by measuring the decrease in absorption intensity at 510 nm as a function of irradiation time after 67% dilution with doubled distilled water. The mineralization of the dye derivative 1-3 was monitored by measuring the depletion in TOC as function of irradiation time using Schimadzu 5000 A TOC Analyzer. For the characterization of degradation product, the aqueous solution of the dye was irradiated in the presence of photocatalyst using 125 W medium pressure mercury lamp. The irradiated mixture was extracted with chloroform, dried over anhydrous sodium sulphate and solvent removed under reduced pressure to give a residual mass, which was analysed by GC/MS analysis technique.

2.4 Results and Discussion

2.4.1 Irradiation of an aqueous suspension of dye containing TiO₂

The aqueous solution of desired concentration of the dye derivatives, 1-3 in the presence of photocatalyst (TiO₂, 1 gL⁻¹) was irradiated by the Pyrex filtered out put of a 125 W medium pressure mercury lamp under oxygen atmosphere. As a representative example, Fig. 2.1 shows the change in absorption intensity and depletion in TOC as a function of irradiation time in the presence and absence of the photocatalyst. It could be seen from the figure that 88% mineralization and 98% decomposition of the dye takes place in the presence of photocatalyst, whereas no change was observed in the absence of photocatalyst. Both degradation curves can be
Figure 2.1: Depletion in TOC and change in absorption intensity at 510 nm as a function of irradiation time for an aqueous solution of acid red 29 (1) in the presence and absence of photocatalyst. Experimental conditions: dye concentration (0.25 mM), V=250 mL, immersion well photoreactor, 125 W medium pressure Hg lamp, Photocatalyst: Degussa P25 (1 gL⁻¹), absorption intensity was followed at 510 nm after 67% dilution, cont. O₂ purging and stirring, irradiation time=120 min.
fitted reasonably well by an exponential decay curve suggesting the first order kinetics. The degradation rate for the mineralization and decomposition of the dye was calculated in terms of \( \text{mole L}^{-1} \text{ min}^{-1} \).

The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

### 2.4.2 Comparison of different photocatalysts

The photocatalytic activity of four different commercially available TiO\(_2\) powders (namely Degussa P25, Hombikat UV100, Milenium Inorganic PC500 and Travancore TTP) was tested on the degradation kinetics of all the dyes under investigation. The degradation rate obtained for the decomposition and TOC depletion of the dye derivatives 1-3, in the presence of different types of TiO\(_2\) powders are shown in Fig. 2.2- 2.4 respectively. It is interesting to note that the mineralization of the dye derivative 2, in the presence of Degussa P25 is faster as compared with other two dye derivatives 1 and 3 respectively. It has been observed that the degradation of all dyes proceed much more rapidly in the presence of Degussa P25 as compared with other TiO\(_2\) samples. In all following experiments, Degussa P25 was used as photocatalyst since this material exhibited the highest over all activity for the degradation of the dye.

### 2.4.3 pH Effect

The photodegradation of the azo dye derivatives 1-3 was investigated at different pH values, which is one of the most important parameter in heterogeneous photocatalysis, since it influences the surface charge properties of the photocatalyst and therefore the adsorption behavior of the pollutants.\(^{30,31}\) Employing Degussa P25 as photocatalyst the decomposition and
Figure 2.2: Comparison of degradation rate for the decomposition and mineralization of acid red 29 (1) in the presence of different photocatalysts. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalysts: Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹) and PC500 (1 gL⁻¹), absorption intensity was followed at 510 nm after 67% dilution, irradiation time=120 min.
Figure 2.3: Comparison of degradation rate for the mineralization of acid red 88 (2) in the presence of different photocatalysts. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalysts: Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹), PC500 (1 gL⁻¹) and TTP (1 gL⁻¹), irradiation time=120 min.
Figure 2.4: Comparison of degradation rate for the mineralization of acid orange 8 (3) in the presence of different photocatalysts. Experimental condition: dye concentration (0.25 mM), V = 250 mL, Photocatalysts: Degussa P25 (1 g L⁻¹), Hombikat UV100 (1 g L⁻¹), PC500 (1 g L⁻¹) and TTP (1 g L⁻¹), irradiation time = 90 min.
mineralization of acid red 29 (1) acid red 88 (2) and acid orange 8 (3) in aqueous suspension of TiO₂ was studied in the pH range between 3 to 11. The degradation rate for the TOC depletion and decomposition of the dye derivative, 1 as a function of reaction pH is shown in Fig. 2.5. The degradation rate for the mineralization and decomposition of the dye was found to increase with the increase in pH from 3 to 9 and highest efficiency was observed at pH 9.

The degradation rate for the TOC depletion of acid red 88 (2) and acid orange 8 (3) as a function of pH is shown in Fig. 2.6 and 2.7 respectively. The degradation rate for the TOC depletion of dye derivative 2, increases with the increase in pH from 3 to 5.3 and a further increase in pH from 5.3 to 11 leads to decrease in the degradation rate. Whereas in the case of dye derivative 3, the degradation rate was found to gradually increase from pH 3 to 9 followed by a sudden decrease as the pH rises to 11.

The adsorption of the dye derivatives 1-3 at pH values between 3 to 11 on the surface of the photocatalyst was investigated by stirring the aqueous solution in the dark for 24 h in a round-bottomed flask containing varying amounts of photocatalyst such as 0, 0.5, 1, 2 and 5 gL⁻¹. Analysis of the dye after centrifugation indicate no observable loss of the dye in the case of acid red 29 (1), whereas some observable loss of the dye was observed in the case of acid red 88 (2) and acid orange 8 (3) at pH values 3 and 5.3.

The results of these studies indicate that the degradation rate for the decomposition and mineralization of the azo dye derivatives 1-3 under investigation is influenced by the reaction pH. It is interesting to note that the dye derivative 2 and 3 showed lower degradation rate for the TOC depletion at pH values 3 and 5.3, where significant adsorption of the dye on the surface of the
Figure 2.5: Influence of pH on the degradation rate for the decomposition and mineralization of acid red 29 (1). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), reaction pH (3, 5.2, 7 and 9), irradiation time=120 min.
Figure 2.6: Influence of pH on the degradation rate for the mineralization of acid red 88 (2).
Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), reaction pH (3, 5.3, 9 and 11), irradiation time=120 min.
Figure 2.7: Influence of pH on the degradation rate for the mineralization of acid orange 8 (3). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), reaction pH (3, 5, 3, 9 and 11), irradiation time=90 min.
catalyst was observed in the dark. The results of these studies contradict the earlier finding, where it was stated that in heterogeneous photocatalysis, the adsorption of a pollutant molecule is a prerequisite for its efficient degradation. These observations indicate that the degradation of model compound as a function of pH also depends on the type of chromophore present in the molecule.

2.4.4 Effect of substrate concentration

Effect of substrate concentration on the degradation of the dye derivatives 1-3 was studied at different concentrations of the dye varying from 0.125 to 0.75 mM. The degradation rate for the TOC depletion and decomposition of 1 as a function of substrate concentration employing Degussa P25 as photocatalyst is shown in Fig. 2.8, where it has been found that the degradation rate decreases with the increase in substrate concentration from 0.25 to 0.75 mM.

The degradation rate for the TOC depletion of 2 and 3 as a function of substrate concentration is shown in Fig. 2.9 and 2.10 respectively. Here it is interesting to note that the degradation rate for the mineralization of the dye derivative 2 increases with the increase in substrate concentration from 0.125 to 0.25 mM and a further increase in the substrate concentration from 0.25 to 0.5 mM leads to decrease in the degradation rate. In contrast, in the case of dye derivative 3, the degradation rate was found to be more or less same with in the range of the substrate concentration studied.

2.4.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of dyes under investigation was studied employing different amounts of Degussa P25 varying from 0.5 to 5 gL⁻¹.
Figure 2.8: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of acid red 29 (1). Experimental conditions: dye concentrations (0.25, 0.35, 0.5 and 0.75 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), irradiation time=120 min.
Figure 2.9: Influence of substrate concentration on the degradation rate for the mineralization of acid red 88 (2). Experimental conditions: dye concentrations (0.125, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), irradiation time=120 min.
Figure 2.10: Influence of substrate concentration on the degradation rate for the mineralization of acid orange 8 (3). Experimental conditions: dye concentrations (0.125, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), irradiation time=90 min.
The degradation rate for the TOC depletion and decomposition of acid red 29 (1) as function of different catalyst loading is shown in Fig. 2.11. It is interesting to note that the degradation rate increases markedly on increasing the catalyst loading from 0.5 to 1 gL\(^{-1}\). A further increase in the catalyst loading did not lead to significant increase in the degradation rate.

The degradation rate for the TOC depletion of 2 and 3 as a function of catalyst concentration is shown in Fig. 2.12 and 2.13 respectively. The degradation rate for the mineralization of dye derivative 2 gradually increases with the increase in catalyst loading from 0.5 to 5 gL\(^{-1}\). In contrast in the case of the compound 3, the rate increases by increasing the catalyst loading from 0.5 to 2 gL\(^{-1}\) and a further increase in the catalyst loading leads to slight decrease in the degradation rate. This may be due to the fact that at high TiO\(_2\) concentrations, particles aggregate, which reduces the interfacial area between the reaction solution and the catalyst. Thus, they decrease the number of active sites on the surface. Light scattering by the particles and the increase in opacity may be the other reason for the decrease in the degradation rate.

2.4.6 Effect of electron acceptors

The effect of electron acceptors such as Hydrogen peroxide, potassium bromate and ammonium persulphate in addition of molecular oxygen on the degradation kinetics of the dye derivatives 1-3 has been investigated in the presence of Degussa P25 as photocatalyst. Fig. 2.14 shows the degradation rate for decomposition and mineralization of acid red 29 (1) in the presence of Degussa P25 containing hydrogen peroxide and ammonium persulphate as electron acceptors. The addition of ammonium persulphate has been found to enhance the degradation rate for the decomposition and mineralization of the dye markedly as shown in the figure.
Figure 2.11: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of acid red 29 (1). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 g L$^{-1}$), irradiation time=120 min.
Figure 2.12: Influence of catalyst concentration on the degradation rate for the mineralization of acid red 88 (2). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 3 gL⁻¹), irradiation time=120 min.
Figure 2.13: Influence of catalyst concentration on the degradation rate for the mineralization of acid orange 8 (3). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 g L\(^{-1}\)), irradiation time=90 min.
Figure 2.14: Comparison of degradation rate for the decomposition and mineralization of acid red 29 (1) in the presence of two different electron acceptors. Experimental conditions: dye concentration (0.25 mM), V=250mL, Photocatalyst: Degussa P25 (1 gL⁻¹), Electron Acceptors: H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (3 mM), irradiation time=120 min.
The degradation rate for the TOC depletion of dye derivatives 2 and 3 in the presence of different electron acceptors are shown in Fig. 2.15 and 2.16 respectively. In the case of 2, the additives showed very little effect on the degradation rate. Whereas in the case of 3 the additives such as hydrogen peroxide and potassium bromate showed beneficial effect.

The details regarding the generation of reactive species and their reduction potential have already been indicated in the Chapter 1.

2.4.7 Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye in aqueous suspension of titanium dioxide through GC/MS analysis technique. The irradiation of an aqueous suspension of acid red 88 (2, 0.25 mM) in the presence of Degussa P25 (1 gL⁻¹) for 1 h followed by the GC/MS analysis of the mixture showed the formation of 4-amino-1-naphthalenesulphonic acid (6) appearing at (tₘ) 16.60 min. The product was identified based on their molecular ion and mass spectrometric fragmentation peaks, as shown below;

\[ \text{Compound 6: } 223 (M^+) , 205, 189, 167, 149, 132, 121, 104, 93, 76, 57, 43 \text{ and } 41. \]

The formation of 4-amino-1-naphthalenesulphonic acid (6) could be understood in terms of the pathways shown in Scheme 2.1. The dye 2, on transfer of an electron can give the radical cation 4, which upon the addition of a hydroxyl radical followed by cleavage will give the observed product 6.
Figure 2.15: Comparison of degradation rate for the mineralization of acid red 88 (2) in the presence of different electron acceptors. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L⁻¹), Electron Acceptors: KBrO₃ (5 mM), H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (5 mM), irradiation time=120 min.
Figure 2.16: Degradation rate for the mineralization of acid orange 8 (3) in the presence of two different electron acceptors. Experimental condition: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), Electron Acceptors: KBrO₃ (5 mM) and H₂O₂ (10 mM), irradiation time=90 min.
Scheme 2.1

\[
\begin{align*}
\text{2} & \xrightarrow{hv/ TiO_2} \text{4} \\
\text{5} + \text{6} & \xrightarrow{H^+} \text{7}
\end{align*}
\]
The GC/MS analysis of the irradiated mixture of acid red 29 (1) and acid orange 8 (3) in aqueous suspension of titanium dioxide indicate the formation of several intermediate products as shown in Fig. 2.17 and 2.18 respectively. The molecular ion and mass spectrometric peaks of these intermediate did not give any conclusive evidence for the identification of the product.
Figure 2.17: GC/MS spectra of an irradiated mixture of acid red 29 (1) in aqueous suspension of titanium dioxide.
Figure 2.18: GC/MS spectra of an irradiated mixture of acid orange 8 (3) in aqueous suspension of titanium dioxide.
References:


24. The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

25. The photocatalyst Hombikat UV100 was a gift sample Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fuer Technischer Chemie Universitat, Callinstrasse, Hannover, Germany.
26. The photocatalyst PC500 was a gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fuer Technischer Chemie Universität, Callinstrasse, Hannover, Germany.

27. The photocatalyst TTP was obtained from Travancore Titanium Products, Kerala, India.

28. The Total Organic Carbon Analyzer was a gift equipment from The Alexander von Humboldt-Stiftung, Bonn, Germany.

29. GC/MS analysis was carried out from The Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Mumbai, India


Chapter 3

PHOTOCATALYSED DEGRADATION OF TWO SELECTED TRIPHENYL METHANE DYE AND A XANTHENE DYE IN AQUEOUS SUSPENSION OF TITANIUM DIOXIDE

3.1 Abstract

The photocatalysed degradation of two selected triphenylmethane dyes such as gentian violet (1) and p-rosaniline (2) and a xanthene dye derivative, eosine yellowish (3) have been investigated in aqueous suspension of titanium dioxide under a variety of conditions such as different types of TiO₂, reaction pH, catalyst loading, dye concentration and in the presence of different electron acceptors besides molecular oxygen. The degradation of the dye was investigated by monitoring the change in substrate concentration employing UV spectroscopic analysis technique and depletion in TOC content as a function of irradiation time. The degradation rate for the decomposition and mineralization of the dye was found to be strongly influenced by all the above parameters. The photocatalyst Degussa P25 was found to be more efficient for the degradation of gentian violet (1) and p-rosaniline (2), whereas Hombikat UV100 was found to be better in the case of eosin yellowish (3). The degradation products were analysed by GC/MS analysis technique and probable pathways for the formation of products have been proposed.

3.2 Introduction

Triphenylmethane and xanthene dye derivatives have also been used extensively in the textile industry and also as a biological stain and paper printing. There are few studies on the degradation of these related systems reported in the literature. For example, Mathews and
coworkers\textsuperscript{3} have reported the photocatalytic degradation of rhodamine B using TiO\textsubscript{2} coated sand in a flat bed configuration. The kinetic study on bleaching of rhodamine 6G photosensitized by titanium dioxide has also been reported earlier by Mills and coworkers.\textsuperscript{4} The photocatalytic degradation of erythrosine, rhodamine B and eosine using TiO\textsubscript{2} has been reported by Ma et al. and Hidaka and coworkers.\textsuperscript{5,7} Zhao et al. has reported the photocatalytic degradation of cationic dye, rhodamine B using TiO\textsubscript{2} in the presence of anionic surfactant.\textsuperscript{8} The photocatalytic degradation of acid green 16 using ZnO has also been reported under different conditions by Sakthivel et al.\textsuperscript{9}

We have studied the degradation of two selected triphenylmethane dyes, gentian violet (1) and p-rosaniline (2) and a xanthene dye derivative eosine yellowish (3) (Chart 3.1) sensitized by TiO\textsubscript{2} in aqueous solution under varying conditions. An attempt has also been made to identify the intermediate products formed during the photooxidation process through GC/MS analysis technique.

3.3 Experimental

3.3.1 Reagent and chemicals

Gentian violet (1) from BDH, Poole, England, p-rosaniline (2) from Ottoic Kemi India Pvt, Ltd and eosine yellowish (3) from Johnson & Sons Hindan London were obtained and used as such without any further purification. The water employed in all the studies was double distilled. The photocatalyst, titanium dioxide samples such as Degussa P25,\textsuperscript{10} Hombikat UV100 (Sachtleben
Chart 3.1

1

2

(Gentian violet)

(p-rosaniline)

3

(Eosine Yellowish)
chemie GmbH) and PC500 (Milenium inorganic chemicals) were used for the degradation studies. The other chemical used in this study such as NaOH, HNO₃, (NH₄)₂S₂O₈, H₂O₂ and KBrO₃ were obtained from Merck.

Irradiations were carried out in an immersion well photochemical reaction vessel made of Pyrex glass (Fig. 1.2) using 125 W medium pressure mercury lamp.

3.3.2 Analysis

The degradation of the dye derivatives 1-3 was followed UV Spectroscopically by measuring the decrease in absorption intensity at 536 nm, 518 nm and 544 nm after 80%, 83% and 80% dilution with doubled distilled water as function of irradiation time. The mineralization of the dyes under investigation was monitored by measuring the depletion in TOC as function of irradiation time using Schimadzu 5000 A TOC Analyzer. For the characterization of the degradation product, the aqueous solution of the dye was irradiated in the presence of photocatalyst using 125 W medium pressure mercury lamp. The irradiated mixture was extracted with chloroform after removed the photocatalyst, dried over anhydrous sodium sulphate and the solvent was removal under reduced pressure to give a residual mass, which was analysed by GC/MS analysis technique.

3.4 Results and Discussion

3.4.1 Irradiation of an aqueous solution of the dye in the presence of TiO₂

The aqueous solution of desired concentrations of the dye derivatives, 1-3 in the presence of photocatalyst (TiO₂, 1 gL⁻¹) was irradiated by Pyrex filtered out put of a 125 W medium pressure
mercury lamp under oxygen atmosphere. As a representative example, the change in absorption intensity and depletion in TOC content as function of irradiation time in the presence and absence of the photocatalyst is shown in Fig. 3.1 for the photocatalytic degradation of gentian violet (1). It could be seen from the figure that 85% mineralization and 99% decomposition of the dye takes place in the presence of photocatalyst, whereas no change was observed in the absence of photocatalyst. Both the curves can be fitted reasonably well by an exponential decay curve suggesting the first order kinetics. The degradation rate for the mineralization and decomposition of the dye was calculated in terms of mole L$^{-1}$ min$^{-1}$.

The zero irradiation time reading was obtained from blank solutions kept in the dark, but otherwise treated similarly to the irradiated solutions.

3.4.2 Comparison of different photocatalysts

We have tested the photocatalytic activity of three different commercially available TiO$_2$ powders (namely Degussa P25, Hombikat UV100, PC500) on the degradation kinetics of 1-3. Fig. 3.2-3.4 shows the degradation rate obtained for the TOC depletion an decomposition of 1-3, in the presence of different types of TiO$_2$. It has been observed that the degradation of triphenylmethane dyes 1 and 2 proceed much more rapidly in the presence of Degussa P25, whereas the degradation of xanthene dye, 3 is faster in the presence of Hombikat UV100 as compared with other TiO$_2$ samples. It is interesting to note that the photocatalyst Degussa P25 was found to be more efficient for the degradation of all the compounds studied in Chapter 1 and 2, when irradiated with UV light source. In contrast the photocatalyst Hombikat UV 100 was found to be more effective for the photocatalytic degradation of this particular xanthene dye derivative 3.
Figure 3.1: Depletion in TOC and change in absorption intensity at 536 nm as a function of irradiation time for an aqueous solution of gentian violet (1) in the presence and absence of photocatalyst. Experimental conditions: dye concentration (0.18 mM), V = 250 mL, immersion well photoreactor, 125 W medium pressure Hg lamp, Photocatalyst: Degussa P25 (1 gL⁻¹), absorption intensity was followed at 536 nm after 80% dilution, cont. O₂ purging and stirring, irradiation time=90 min.
Figure 3.2: Comparison of degradation rate for the decomposition and mineralization of gentian violet (1) in the presence of different photocatalysts. Experimental conditions: dye concentration (0.18 mM), V = 250 mL, Photocatalysts: Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹) and PC500 (1 gL⁻¹), absorption intensity was followed at 536 nm after 80% dilution, irradiation time=90 min.
Figure 3.3: Comparison of degradation rate for the decomposition and mineralization of p-rosaniline (2) in the presence of different photocatalysts. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalysts; Degussa P25 (1 gL⁻¹), Hombikat UV100 (1 gL⁻¹) and PC500 (1 gL⁻¹), absorption intensity was followed at 544 nm after 80% dilution, irradiation time=90 min.
Figure 3.4: Comparison of degradation rate for the decomposition and mineralization of eosine yellowish (3) in the presence different photocatalysts. Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalysts: Degussa P25 (1 g L⁻¹), Hombikat UV100 (1 g L⁻¹) and PC500 (1 g L⁻¹), absorption intensity was followed at 518 nm after 83% dilution, irradiation time=30 min.
Although the photocatalyst Degussa P25 is lower in anatase content, specific BET-surface area and primary particle size with that of Hombikat UV100, this photocatalyst has been found to be more efficient for the degradation of majority of organic compounds studied earlier\textsuperscript{15-18} and in this thesis. These results indicate that the efficiency of photocatalyst for the degradation of organic pollutants depends upon the types of chromophore present in the molecule and other reaction parameters.

### 3.4.3 pH Effect

Employing Degussa P25 and Hombikat UV100 as photocatalyst the degradation rate for the TOC depletion and decomposition of the dye derivatives 1-3 was studied in the pH range between 3 to 11 and the results are shown in Fig. 3.5-3.7. The efficiency of degradation rate for the decomposition of dye 1 was better at pH 3 and 11, whereas it was lower at pH values 5.8 and 9. In contrast, the rate for the mineralization of the dye was found to decrease with the increase in pH from 3 to 9 and a further increase in pH leads to increase in the rate. The degradation rate for the TOC depletion and decomposition of the dye derivative 2 was found to be highest at pH 3.3, which slowly decreases with the increase in pH. Similarly, in the case of 3 highest efficiency was observed at pH 5, which decreases with increase in pH.

The adsorption of dye on the surface of the photocatalyst was investigated by stirring their solution in dark for 24 h in a round-bottomed flask containing varying amounts of Degussa P25 (dye 1 and dye 2) and Hombikat UV100 (dye 3) at different pH values. Analysis of the sample after centrifugation indicate some observable loss of gentian violet (1) at pH 3 and 4.6, whereas no observable loss of the dye was seen in the case of p-rosaniline (2) and eosine yellowish (3) in the
Figure 3.5: Influence of pH on the degradation rate for the decomposition and mineralization of gentian violet (1). Experimental conditions: dye concentration (0.18 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), reaction pH (3, 4, 6, 9 and 11), irradiation time=90 min.
Figure 3.6: Influence of pH on the degradation rate for the decomposition and mineralization of p-rosaniline (2). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), reaction pH (3, 5, 7 and 9), irradiation time=90 min.
Figure 3.7: Influence of pH on the degradation rate for the decomposition and mineralization of eosine yellowish (3). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 gL\(^{-1}\)), reaction pH (5.3, 7, 9, 11), irradiation time=30 min.
pH range studied (3 to 11).

3.4.4 Effect of substrate concentration

The effect of substrate concentration on the degradation of 1-3 has been investigated at varying concentrations of the dye. Fig. 3.8-3.10 shows the degradation rate for the TOC depletion and decomposition of the dye derivatives 1-3 as a function of dye concentration employing Degussa P25 and UV100 as photocatalyst. It has been observed that in the case of 1, the degradation rate increases with the increase in substrate concentration from 0.18 to 0.25 mM and a further increase in the substrate concentration from 0.25 to 0.5 mM leads to slight decrease in the degradation rate of the dye as shown in Fig. 3.8. In the case of dye derivatives 2 and 3 the rate has been found to decrease with the increase in substrate concentration from 0.25 mM to 0.75 mM. The reason for lower rates for the degradation of dyes at higher substrate concentrations has already been discussed in Chapter 1.

3.4.5 Effect of catalyst concentration

The effect of photocatalyst concentration on the degradation kinetics of 1-3 were investigated employing different catalyst loading of Degussa P25 in the case of 1 and 2 and UV100 for the dye derivative 3 varying from 0.5 to 5 gL⁻¹. As expected, the degradation rate for the TOC depletion and decomposition of the dye was found to increase with the increase in catalyst concentration as shown in Fig. 3.11, 3.12 and 3.13 respectively.
Figure 3.8: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of gentian violet (1). Experimental conditions: dye concentrations (0.18, 0.25, 0.35 and 0.5 mM), V=250 mL, Photocatalyst: Degussa P25 (1 gL⁻¹), irradiation time= 90 min.
Figure 3.9: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of p-rosaniline (2). Experimental conditions: dye concentrations (0.25, 0.35, 0.5 and 0.75 mM), V=250 mL, Photocatalyst: Degussa P25 (1 g L\(^{-1}\)), irradiation time=90 min.
Figure 3.10: Influence of substrate concentration on the degradation rate for the decomposition and mineralization of eosine yellowish (3). Experimental conditions: dye concentrations (0.25, 0.35, 0.5 and 0.75 mM), V=250 mL, Photocatalyst: Degussa UV100 (1 gL⁻¹), irradiation time=30 min.
Figure 3.11: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of gentian violet (1). Experimental conditions: dye concentration (0.18 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 gL⁻¹), irradiation time=90 min.
Figure 3.12: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of p-rosaniline (2). Experimental condition: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Degussa P25 (0.5, 1, 2 and 5 gL⁻¹), irradiation time=90 min.
Figure 3.13: Influence of catalyst concentration on the degradation rate for the decomposition and mineralization of eosine yellowish (3). Experimental conditions: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (0.5, 1, 2 and 5 gL$^{-1}$), irradiation time=30 min.
3.4.6 Effect of electron acceptors

The effect of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate in addition to molecular oxygen on the degradation kinetics of the model compounds 1-3 were investigated as well. It was found that the model compound gentian violet (1), undergoes coagulation in the presence of ammonium persulphate and TiO₂ in the dark, which was indicated by the separation of the dye from the solution. On the other hand, the electron acceptors such as hydrogen peroxide and potassium bromate have been found to enhance the efficiency of degradation as shown by the depletion in TOC as a function of irradiation time (Fig. 3.14). It is interesting to note that when the reaction was carried out in the presence of potassium bromate using Degussa P25, the TOC depletion is very fast at the initial irradiation time, which slowly decreases with increasing irradiation time.

The degradation rate for the decomposition and mineralization of p-rosaniline (2) in the presence of potassium bromate and hydrogen peroxide containing Degussa P25 is shown in Fig. 3.15. The electron acceptor such as potassium bromate has been found to markedly enhanced the degradation rate for the decomposition of the dye as shown in the figure.

The degradation rate for the decomposition and TOC depletion of eosine yellowish (3) in the presence of hydrogen peroxide and ammonium persulphate is shown in Fig. 3.16. Both the additives showed beneficial effect on the degradation rate for the decomposition of the dye whereas the effect of these additives on the TOC depletion is not pronounced.
Figure 3.14: Effect of hydrogen peroxide and potassium bromate on TOC depletion as a function of irradiation time for the photocatalytic degradation of gentian violet (1). Experimental condition: dye concentration (0.18 mM), V=250mL, Photocatalyst: Degussa P25 (1 g L⁻¹), Electron Acceptor: H₂O₂ (10 mM) and KBrO₃ (3 mM), irradiation time=90 min.
Figure 3.15: Comparison of degradation rate for the decomposition and mineralization of p-
rosaniline (2) in the presence of different electron acceptors. Experimental condition: dye
concentration (0.25 mM), V=250mL, Photocatalyst: Degussa P25 (1 g L\(^{-1}\)), Electron Acceptors:
KBrO\(_3\) (5 mM), H\(_2\)O\(_2\) (10 mM), irradiation time=90 min.
Figure 3.16: Comparison of degradation rate for the decomposition and mineralization of eosine yellowish (3) in the presence of different electron acceptors. Experimental condition: dye concentration (0.25 mM), V=250 mL, Photocatalyst: Hombikat UV100 (1 gL⁻¹), Electron Acceptors: H₂O₂ (10 mM) and (NH₄)₂S₂O₈ (3 mM), irradiation time=30 min.
3.4.7 Intermediate products

An attempt was made to identify the intermediate products formed in the photocatalytic degradation of the dye in aqueous suspension of titanium dioxide through GC/MS analysis technique. The GC/MS analysis of the irradiated mixture of (1, 0.25 mM) for 120 min shows the formation of several degradation products. Out of which two products appearing at retention times ($t_{R}$) 8.45 min and 9.30 min could be assigned to N-methylaniline (10) and p-aminobenzoic acid (16) based on their molecular ion and mass spectrometric fragmentation peaks, as shown below;

Compound 10: 107 ($M^+$), 104, 83, 73, 71 and 51.

Compound 16: 137 ($M^+$), 121, 107, 93, 86, 73, 69, 63, 55 and 49.

A plausible mechanism for the formation of these products involving electron transfer reactions and reaction with hydroxyl radicals formed in the photocatalytic system is proposed in Scheme 3.1 and 3.2 respectively.

The model compound 1 upon the transfer of an electron can form to the radical species 4, which may undergo addition of a hydroxyl radical forming 7 which may undergo cleavage either by abstracting a hydroxyl radical to form 6 or by abstracting a proton to form 9 along with the benzophenone derivative 5. The compound 1 on further transfer of an electron can form the radical cation 8, which may subsequently undergo loss of methyl group to give the observed product 10 as shown in Scheme 3.1. The formation of p-aminobenzoic acid (16) could be understood in terms of the pathways shown in Scheme 3.2. The benzophenone derivative 5, upon the transfer of an electron can form the radical anion 11, which can undergo addition of a hydroxyl
Scheme 3.1

1. Reaction of compound 1 with electrons and photolysis of TiO₂.

2. Formation of compound 4 through the addition of OH⁻.

3. Reaction of compound 4 with oxygen and photolysis of TiO₂.

4. Formation of compound 7 through the addition of OH⁻.

5. Reduction of compound 7 to product 9.

6. Reaction of compound 9 with oxygen and photolysis of TiO₂.

7. Formation of compound 10 through the addition of CH₃⁻.
Scheme 3.2

\[ \text{hv/TiO}_2 \]

5 + e\textsuperscript{-} \rightarrow 11

12 + 9 \rightarrow 13 + H^+ \textsuperscript{+} \rightarrow 14 \rightarrow 15 + H^+ \textsuperscript{+} + CH_3 \textsuperscript{+} \rightarrow 16 \rightarrow \text{hv/TiO}_2
radical forming the anionic species 13, which upon cleavage can lead to the formation of aniline and benzoic acid derivatives 8 and 12 respectively. The compound 12 on further transfer of an electron can give rise to radical cation 14, which may subsequently undergo loss of methyl group to give the observed product 16 as shown in Scheme 3.2.

The irradiated mixture of an aqueous solution of p-rosaniline (2, 0.25 mM) for 1 h showed the formation of several intermediate products through GC/MS analysis technique. Two products 18 and 22 have been proposed based on their molecular ion and mass spectrometric fragmentation peaks as indicated below;

**Compound 18:** 212 (M⁺), 202, 191, 177, 167, 155, 139, 128, 112, 99, 91, 84, 67 and 57.

**Compound 22:** 182 (M⁺), 177, 167, 153, 149, 131, 121, 115, 104, 96, 87, 69, 62 and 55.

The formation of 18 and 22 from the dye derivative 2 could be understood in terms of pathways shown in Scheme 3.3.

The model compound 2 upon the transfer of an electron can form to the radical species 17, which may undergo addition of a hydroxyl radical to give 19. The abstraction of hydroxyl hydrogen either by superoxide radical anion or by hydroxyl radical followed by loss of an aniline moiety may lead to the formation of the observed product 4,4'-diaminobenzophenone (18). The formation of 22 could similarly be understood in terms of the pathways shown in Scheme 3.3. The compound 18 upon the transfer of an electron can lead to the radical cation 20, which may undergo loss of NH₃ to give the product 21, which may in turn undergo similar subsequent reaction leading to the formation of the observed product benzophenone (22).
Scheme 3.3

\[
\begin{align*}
\text{Scheme 3.3} & \\
\text{H}_2\text{N} & \text{C}=\text{O} \\
\text{H}_2\text{N} & \text{N}^+ \text{Cl}^{-} \\
\text{hv/TiO}_2^{-} & e^+ \\
\text{H}_2\text{N} & \text{C}=\text{O} \\
\text{O}_2^/-\text{OH}^{-} & \text{C}_6\text{H}_5\text{NH}_2 \\
\text{H}_2\text{N} & \text{C}=\text{O} \\
\text{H}_2\text{N} & \text{C}=\text{O} \\
\text{hv/TiO}_2^{-} & e^+ \\
\text{H}_2\text{N} & \text{C}=\text{O} \\
\end{align*}
\]
The GC/MS analysis of an irradiated mixture of eosine yellowish (3, 0.25 mM) for 1 h indicate the formation of several intermediate products as shown in Fig. 3.17. The molecular ion and mass spectrometric peaks of these intermediate products did not give any conclusive evidence for the identification of any product.
Figure 3.17: GC/MS spectra of an irradiated mixture of eosine yellowish (3) in aqueous suspension of titanium dioxide.
References:


10. The photocatalyst Degussa P25 was a gift sample from Degussa-Huls, Frankfurt/Main, Germany.

11. The photocatalyst Hombikat UV100 was a gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fuir Technische Chemie, Universitat, Callinstrasse, Hannover, Germany.
12. The photocatalyst PC500 gift sample from Dr. D. W. Bahnemann from Photocatalysis and Nanotechnology, Institut fur Technische Chemie, Universitat, Callinstrasse, Hannover, Germany.

13. Total Organic Carbon Analyzer was gift equipment from The Alexander von Humboldt-Stiftung, Bonn, Germany.

14. GC/MS analysis was carried out from The Sophisticated Instrumentation Center, Indian Institute of Technology, Powai, Mumbai, India.


List of Publications

1. Photocatalytic degradation of the textile dye, Alizarin Red S, in aqueous suspensions of titanium dioxide
   M. Saquib and M. Muneer

2. Photocatalytic degradation of CI Acid Green 25 and CI Acid Red 88 in aqueous suspensions of titanium dioxide
   M. Saquib and M. Muneer

3. Semiconductor mediated photocatalysed degradation of an anthraquinone dye, Remazol Brilliant Blue R under sunlight and artificial light source
   M. Saquib and M. Muneer

4. TiO₂-mediated photocatalytic degradation of a triphenylmethane dye (gentian violet), in aqueous suspensions
   M. Saquib and M. Muneer

5. Titanium dioxide mediated photocatalysed degradation of a textile dye derivative, acid orange 8 in aqueous suspensions
   M. Saquib and M. Muneer
   *Desalination*, (in press)
6. Semiconductor mediated photocatalytic degradation of a textile dye in water: case study of acid red 29

M. Saqib and M. Muneer

*Color. Technol.*, (communicated)

7. Photocatalytic degradation of two selected textile dye derivatives, eosine yellowish and p-prosaniline in aqueous suspensions of titanium dioxide

M. Saqib and M. Muneer

*J. Environ. Sci. Health A*, (communicated)
VITAE

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