STUDIES ON DEGRADATION OF DYES PRESENT IN THE INDUSTRIAL EFFLUENTS

BY
MD. AHSAN HABIB

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DEPARTMENT OF CHEMISTRY
BANGLADESH UNIVERSITY OF ENGINEERING AND TECHNOLOGY
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Md. Ahsan Habib

TO
My Beloved Mother

DECLARATION

This thesis work has been done by the candidate himself and does not contain any material extracted from elsewhere or from a work published by anybody else. The work for this thesis has not been presented elsewhere by the author for any degree or diploma.

Md. Ahsan Habib
(Candidate)
M. Phil Student
Roll No. 040003212 (F)
Session: April' 2000.
Department of Chemistry
BUET, Dhaka
Bangladesh.

CERTIFICATE

This is to certify that the research work embodying in this thesis has been carried out under my supervision. The work presented herein is original. This thesis has not been submitted elsewhere for the award of any other degree or diploma in any University.

Dr. Md. Rafique Ullah
(Supervisor)
Professor & Head
Department of Chemistry
BUET, Dhaka
Bangladesh.

Bngladesh University of Engineering and Technology, Dhaka

Department of Chemistry

Certification of Thesis

A thesis on

"Studies on degradation of dyes present in the industrial effluents"

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MD. AHSAN HABIB

has been accepted as satisfactory in partial fulfilment of the requirements for the degree of Master of Philosophy (M. Phil) in Chemistry and certify that the student has demonstrated a satisfactory knowledge of the field covered by this thesis in an oral examination held on September 29, 2001.

Board of Examiners

1. Dr. Md. Rafique Ullah
   Professor & Head
   Department of Chemistry
   BUET, Dhaka.

   Supervisor & Chairman 29.9.2001

2. Dr. A.J. Mahmood
   Professor
   Department of Chemistry
   University of Dhaka.

   Co-Supervisor

3. Dr. Al-Nakib Chowdhury
   Associate Professor
   Department of Chemistry
   BUET, Dhaka.

   Member

4. Dr. Tajmeri S.A. Islam
   Professor
   Department of Chemistry
   University of Dhaka.

   Member (External)

Abstract

Brilliant Golden yellow, BGY, a textile dye, has been chosen for studying its degradation characteristics. Two methods of degradation have been tried. These methods are Fenton and mediated photodegradation. Two semiconducting oxides have been chosen as mediators. These are TiO_2 (rutile) and ZnO. BGY solution shows absorption peak at $\lambda=415\pm2$ nm with $\varepsilon=7.81\times10^{3}$ $Lmol^{-1}cm^{-1}$ at 29°C.

The concentrations of BGY was about $5.10\text{x}10^{-5}$M to $3.00 \text{ x } 10^{-4}$ M, the solution initial pH varied beltween 2.50 to 6.20. The concentration of H_2O_2 was between $8.00 \text{ x } 10^{-4}$M to $5.00 \text{ x } 10^{-3}$M, the concentration of Fe (III) $2.00 \text{ x } 10^{-5}$M to $1.00 \text{ x } 10^{-4}$M. The amount of TiO_2 per 50 ml solution was $1.00 \text{ x } 10^{-3}$ to $4.50 \text{ x } 10^{-3}$ g and the amount of ZnO per 50 ml. was $2.50 \text{ x } 10^{-3}$ to $10.00 \text{ x } 10^{-3}$g .

The Fenton degradation of the BGY was complete within 10 minutes and so long H_2O_2 was in sufficiently large amount. The other parameters did not affect the % degradation of the dye, which was about 93% even in the presence 410 nm light.

In the oxide mediated photodegradation 100% degradation of the BGY could be achieved by using 320 nm light. ZnO mediated degradation appeared to be faster. TiO_2 mediated degradation appeared to be dependent on the amount of TiO_2, other parameters hardly affected the photodegradation process.

Langmuir-Hinshelwood kinetic model has been applied to the mediated degradation. It gives some idea why ZnO is a better mediator for photodegradation of BGY.

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CHAPTER 1

GENERAL INTRODUCTION

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1.1.0 Photochemistry

1.1.1 Status and prospect of photochemistry

Man has been aware from the earliest times of the influence that the sun's radiation has on matter. However, it is during the last seventy years or so that a systematic understanding of photochemical process has developed. A logical pattern to the interaction between light and matter emerged only after the concept of the quantization of energy was established.

The significance of photochemistry is by no means limited to the use that nature and man make use of it. Rather, the chemistry itself is of profound interest at the most fundamental level. The study of photochemistry embraces all of the phenomena associated with the absorption and emission of radiation by chemical systems. It includes phenomena that are mainly spectroscopic, such as fluorescence and phosphorescence, luminescencet chemical reactions, such as flames and the gleam of the firefly; and photostimulated reactions, such as photographic, photosynthetic, and photolytic reactions of various kinds. For every atom and molecule known to us in the ground state, there are likely to be one or more excited states and their chemistry is almost inevitably distinct from that of the ground-state species. Whole new fields of Chemistry are thus opened up by allowing light to interact with the elements and their compounds.

'Photochemistry' is a term, rather loosely applied, is concerned with the 'bimolecular' interaction of light quantum and a molecule and the subsequent chemical and physical changes which result from this interaction. The radiations of photochemical importance lie, however, almost exclusively in the visible and ultra violet regions, i.e., from about 200nm to 800nm wave length.

The essential feature of photochemistry is probably the way in which 'exited states' of atoms or molecules play a part in the processes of interest. Apparently that absorption or emission of radiation to or from these states is the concern of the spectroscopist as well as of the photochemist. The photochemist must have at least a background knowledge of spectroscopy. At the same time, the photochemist is frequently interested in the rates at which processes occur, so that the concepts of reaction kinetics can be employed.

1.1.2 Absorption of light

A photochemical reaction is produced by the absorption of electromagnetic radiation by a molecule. According to Planck's quantum theory, this energy absorption takes place by steps, each step or transition corresponding to the absorption of a 'quantum' of energy (photon). The energy E of this quantum is given by Planck's equation:

$$E = h\nu \qquad (1.1)$$

Where h is the Planck's constant and ν is the frequency of the absorbed radiation. Planck's equation can also be written as follows

$$E = \frac{hc}{\lambda} \qquad (1.2)$$

where c is the velocity of light and λ is the wavelength of the radiation.

1.1.3 Fundamental laws of photochemistry

First law (Grotthus, 1817; Draper, 1943):
"The light absorbed by a molecule is the only light which can produce photochemical changes in the molecule"
Second law (Stark- Einstein, 1913):
"The absorption of light by a molecule is a one- quantum process in which the sum total of primary quantum yields must be equal to unity," that is,

$$\Sigma\varphi_i = 1 \qquad (1.3)$$

where φ_i is the quantum yield of *ith* primary process, which may include dissociation, isomerization, fluorescence, phosphorescence, radiationless transitions, and all other reaction paths that lead to the destruction or deactivation of the excited molecule.

1.1. 4 Excitation by Absorption

A molecule that has absorbed a quantum of radiation becomes 'energy-rich' or 'excited' in the absorption process. Absorption in the wavelength region of photochemical interest leads to electronic excitation of the absorber. Absorption at longer wavelengths usually leads to the excitation of vibrations or rotations of molecules in its ground electronic state. Although it would be a mistake to suppose that the only form of excitation that could lead to photochemical change is electronic, it is generally true that electronically excited states are involved in photochemical processes.

1.1. 5 Fates of electronically Excited Species

Photochemical processes involving the absorption of light can be divided into the act of absorption, which falls within the domain of spectroscopy, and the subsequent fate of the electronically excited species formed. It has been implied that there are several such fates. Let us consider a general scheme:

$AB + h\nu \rightarrow AB^*$

Fig.1.1.0: represents, in simplified form the various paths by which an electronically excited species (AB^*) may lose its energy.

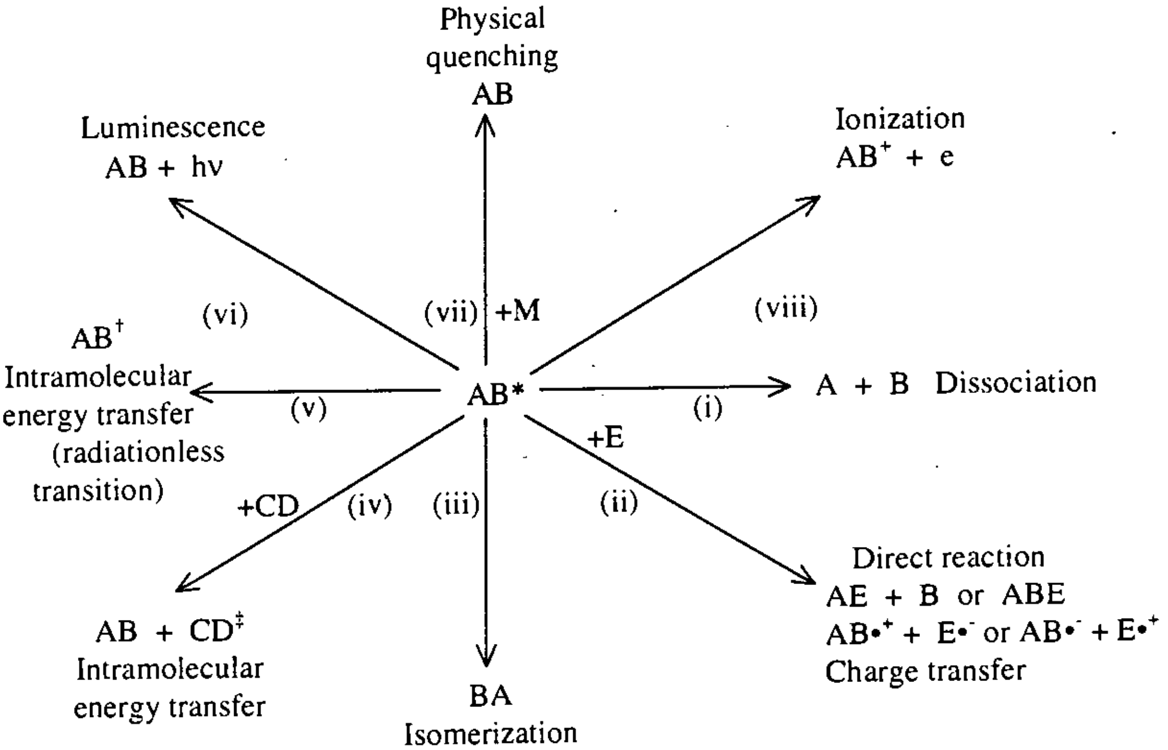


Fig. 1.1. 0: The several routes of loosing electronic excitation. The use of symbols *,† and ‡ is only intended to illustrate the presence of electronic excitation and not necessarily differences in states. One or both of products of process (I)-(iii) may be excited.

Different paths by which an electronically excited species may lose its energy are as follow:

i) Chemical change comes about as a result of dissociation of the absorbing molecule into reactive fragments.

ii) Chemical change comes about as a result of direct reaction of the electronically excited species.

iii) Electronically excited species may also undergo spontaneous isomerization.

iv) & (v) Energy transfer, leads to excited species, which can then participate in any of the general processes.

vi) Radiative loss of excitation energy gives rise the phenomenon of luminescence.

vii) Physical quenching. In this process an atom or molecule M can relieve AB* of its excess energy.

viii) Several mechanisms for dissociation are recognized. A special case of dissociation in that of ionization is shown.

1.1. 6 The Beer-Lambert Law

The absorption of a monocromatic beam of light by a absorbing system is described by the familiar combined Beer-Lambert law. One form of the law, commonly employed in photochemical studies, is

$$A = \log \frac{I_0}{I_t} = \in [J]\, l \qquad (1.4)$$

Where,

I_0 = intensity of the light incident upon the sample cell

I = intensity of the light leaving the sample cell

A = optical density or absorbance

[J] = molar concentration (mol L^{-1}) of absorbing species J

l = length of sample cell (cm)

and $\in$, molar absorption coefficient or molar extinction coefficient or molar absorptivity, is a constant for a given pure absorbing species at a given wavelength. The unit of $\in$ is L mol^{-1} cm^{-1}.

1.1.7. 0 Quantum Yield

The quantum yield of formation (or disappearance) of a product as a result of a photochemical reaction is defined as the number of molecules of this product which are formed (or which disappear) per quantum of light absorbed. Quantum yield Φ is given by,

$$\Phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light aborbed in the same time}}$$

$$\Phi = \frac{\text{No of moles of reacting molecules involved in a given time}}{\text{No.of Einstein absorbed in the same time}}$$

$$\Phi = \frac{\text{Rate of reaction due to the light absorption}}{\text{Intensity of the light.}} \qquad (1.5)$$

1.1.7.1 Types of quantum yield: Several types of quantum yields are used in photochemistry: *primary quantum yield, product quantum yield, quantum yields of fluorescence, decomposition, rearrangement,* etc. To avoid confusion one should always indicate the type of quantum yield which is given. It is highly important to distinguish between the primary quantum yield φ and the product quantum yield Φ. The former is the quantum yield of the product formed as a result of the primary process, while the latter is calculated by determining the total number of molecules formed at the end of the reaction, i.e., it includes products formed in secondary processes. Let a molecule M undergoes a photochemical reaction to form the radical M· in the primary process; let this radical then react to yield products A, B, C The primary quantum yield of M· will then be defined by the relationship

$$\varphi_{M\cdot} = \frac{d[M\cdot]/dt}{I_a} \qquad (1.6)$$

Where I_a is the radiation intensity absorbed by M, that is:

$$\varphi_{M\cdot} = \frac{\text{No. of M radicals formed per cm}^3\text{ per second}}{\text{No. of quanta absorbed by M per cm}^3\text{ per second}} \quad (1.7)$$

The quantum yield of the final product A will be

$$\Phi_A = \frac{d[A]/dt}{I_a} = \frac{\text{No. of A molecules formed per cm}^3\text{ per second}}{\text{No of quanta absorbed by M per cm}^3\text{ per second.}} \quad (1.8)$$

1.1.7.2 Significance of quantum yield: The quantum yield is in one of the most useful and fundamental quantities in the study of photochemical reactions. The quantum yield indicates the extent of side reactions and the ultimate efficiency of conversion of starting materials into products, irrespective of the number of quanta absorbed.

Measurement of quantum yield is well documented in mechanistic studies of photochemical reactions. Measurements of quantum yields provide information about the nature of the excited states and energies in determining of kinetic parameters such as life times of excited states and quenching rate constants.

Small quantum yields of all decomposition products ($\varphi<<1$) indicate important deactivation, fluorescence, or other process that lead to net chemical change.

Large product quantum yields of all decomposition products ($\varphi>>1$) indicate the involvement of dark or even chain reaction. As for example, the photochemical reaction between hydrogen and chlorine, quantum yield ≈ 10^6, indicates that the reaction proceeds through chain reaction mechanism.

The quantum yields of some photochemical reactions in gas phase and in liquid phase are given in Table 1.2. In most cases, the quantum yield of photochemical reaction will be less in the liquid phase than in the gas phase. A very important factor in the differing photochemical behaviour in the gas phase and in the solution is the occurrence of 'case effects' in the latter phase. This is because in liquid phase, an active molecule or atom may readily be deactivated by frequent collisions with other molecules, or with the solvent. Moreover, because of the short mean free path in the liquid phase, free radicals or atoms, when formed photochemically, will tend to recombine before they have a chance to go very far from each other. Therefore the net effect of these processes will give low quantum yield.

The 4 th reaction in Table 1 shows the reverse result. This reverse result may be due to the formation of intermediates of kinetic energy sufficiently high to separate them rapidly, thereby preventing their recombination.

Table-1.1.0: Quantum yields of different reactions under different conditions.

Reaction	Wave length nm	Quantum Yield.		
		Gas phase	Remarks	Liquid phase
$2NH_3=N_2+3H_2$	210	0.25 (0.14-0.32)	Depends on pressure	0 (Liquid NH_3)
$CH_3COOH = CH_4+ CO_2$	<230	1	-	0.45 (water)
$NO_2 = NO + 1/2\ O_2$	405	0.50	-	0.03 (CCl_4)
$Ni\ (CO)_4 = Ni + 4\ CO$	301-313	0	-	2.8 (CCl_4)
$2HI= H_2+ I_2$	207-282	2	Constant over wide range of T and P	-
$H_2 + Br_2= 2HBr$	Below 600	2	Near 200°C very small at 25° C	-
$H_2 + Cl_2 = 2HCL$	400-430	Up to 10^6	varies with P_H2and impurities	-

T = Temperature, P = Pressure

1.1. 8.0 Photochemical Reaction

There are two types of photochemical reaction,

i) Direct reaction

and ii) Sensitized reaction.

In a direct photochemical process, one or more of the reactants absorbs the incident light and is consumed in the subsequent chemical reactions that captures the light energy. Schematic representation of this process is

$$\begin{aligned} A + h\nu &\rightarrow A^* \\ A^* &\rightarrow \text{products (unimolecular)} \\ \text{or } A^* + B &\rightarrow \text{products (bimolecular)} \qquad (1.9) \end{aligned}$$

In a photo sensitized process, on the other hand, a mediator, that is not itself involved in the ensuring chemical reaction, transfers the absorbed light energy to another reactant that is consumed in the subsequent chemical reactions. A schematic example of this process is,

$$\begin{aligned} S + h\nu &\rightarrow S^* \\ S^* + A &\rightarrow S + A^* \\ A^* &\rightarrow \text{products (unimolecular)} \\ \text{or } A^* + B &\rightarrow \text{products (bimolecular)} \qquad (1.10) \end{aligned}$$

Where A and B are reactants, S is a sensitizer, and A* and S* represent excited electronic species. It is thus possible, in sensitized photochemical reactions, to utilize wavelengths of light which might otherwise be inaccessible to the reactants.

1.1.8.1 Heterogeneous photolysis: The Photochemical reactions involving two or more different phases are called heterogeneous photolysis. Sensitized reactions are the most usual reactions in heterogeneous system. It is very important in natural environment. Photodegradation of organic pollutants, e.g. chlorinated phenol or some chlorinated organics involving metal oxides with semiconductor properties is an example of heterogeneous photolysis.

1.1.8.2 Kinetics of photochemical processes: The ratio of overall to primary quantum yields, Φ/ϕ, is analogous to the kinetic chain length, γ, determined in studies of thermal chain reactions. The quantities may be expressed in terms of rate constants for the several secondary reactions, and their variation with concentrations of various species may lead to confirmation of a hypothetical reaction mechanism and evaluation of rate constants.

In thermal reactions, γ is defined by the relation,

$$\gamma = \frac{\text{rate of reactant disappearance}}{\text{rate of initiation}} \qquad (1.11)$$

Quantum yields may also be defined in terms of rates, rather than numbers of molecules and photons. An intensity of radiation, I, refers to an energy per unit time, and it is frequently convenient to express the absorption intensity, I_{abs}, as the energy absorbed in unit time by unit volume: it is then in the same form as a rate expressed in terms of concentration units, with energies (number of photons) replacing number of molecules. Hence for a process

$$A + h\nu \longrightarrow \text{products} \qquad (1.12)$$

$$\Phi = \frac{-d[A]/dt}{I_{abs}} \qquad (1.13)$$

Furthermore, if we assume that the primary quantum yield, ϕ, is for formation of reactive intermediates, then $\phi\, I_{abs}$ is the rate of initiation in the photochemical system, and

$$\frac{\Phi}{\phi} = \frac{\text{rate of reactant disappearance}}{\text{rate of initiation}} \equiv \gamma \qquad (1.14)$$

In fact, initiation by photochemical means is often the best way in which to study the kinetics of radicals or energy-rich species. The rate of initiation can be measured accurately. In addition by using sufficiently low temperature of experiment a plethora of confusing processes, often found is thermal reactions initiated at high temperature can be avoided.

1.1.8.3 Reactions studied by Photochemical means: The reactions studied in various phases which have been fruitfully studied by photochemical means may include:

a) Unimolecular dissociation and rearrengement

b) Acid-base equilibria

c) Bimolecular addition reaction

d) Photoreduction and photo-oxidation

e) Substitution reaction

f) Electron transfer reaction

g) Decomposition and polymerization reactions.

1.1.9.0 Radiation sources

Since light must be absorbed to effect a photochemical change, the choice of light is dictated by the absorption spectrum of the reactant to be studied. Thus the first step in any photochemical study should be the determination of the ultraviolet and visible absorption spectra of the reactant, preferably in the same physical state in which its photochemical properties are to be studied.

1.1.9.1 The mercury arcs: The most widely used source of ultraviolet and visible light for conventional photochemical study using steady illumination are the mercury arcs. Three basic types of arcs are as follow:

a) the low pressure or 'resonance' lamp,

b) the medium pressure arc, and

c) the high pressure mercury arcs.

A) Low pressure mercury arc lamps (resonance lamps): In such lamps the pressure of mercury is 0.005 to 0.1 mm. Two main lines are emitted: 253.7nm and 184.9nm. Low pressure lamps work at low current intensities, under fairly high voltages and their power demand is low (less than 100 w); their lifetimes are long (about 10,000 hours).

B) Medium pressure mercury arc lamps: In these lamps the pressure of mercury is about one atmosphere. These lamps can accordingly be used in conjunction with filters or monochromators. The power demand of these lamps can be very high (several thousands of watts) and their useful service life usually does not exceed 1000 hours.

C) High pressure mercury arc lamps : The pressure of mercury in these lamps is more than 10 atm. These lamps are the most useful sources of UV radiation, but their emission mostly lies beyond 300nm. The power demand of lamps of this kind may be as high as 400,000 W. Their useful service life is quite short (100-200 hrs).

1.1.9.2 Resonance lamp: Cd-vapour resonance lamp has been used for used for the photosensitized luminescence of many substances [4]. This source emits radiation mainly at 326.1 and 228.8 nm. Sodium vapour resonance lamps are available commercially, and lamps using the other alkali metals can be either purchased or constructed easily. They usually offer little interest for photochemical use since the electronic transition involved are of such small energy. Zinc[5] resonance lamps and inert-gas resonance lamp have been built and used successfully.

1.1.9.3 Discharge lamps: Various ingenious designs of discharge lamps for short-wavelength ultraviolet are described in the current literature. A windowless source from a low pressure discharge in hydrogen has been found to be very rich in the 800-200 nm region [6]. High-intensity noble-gas discharges have been described using low pressures of Krypton (116.5, 123.6 nm)[6]. Hot-cathode low pressure discharges using hydrogen, helium, argon, or nitrogen provide radiation in the 50-165 nm region[6].

1.1.9.4 Lasers: Laser is another important source in photochemical study. The characteristics of laser radiation are:

a) High monochromiticity

b) Possibility of very short pulses,

c) High peak power resulting from short pulse duration,

d) High peak beam density

1.1.9.5 The vacuum ultraviolet region: It is an important one, at least for gas-phase photochemistry, because many highly energetic processes can occur, including those involving higher excited states and photoionization. Light sources for this region are generally synchrotron radiation. The radiation is also produced in bursts, with pulse lengths as short as 100 ps, so that time-resolved experiments are possible.

1.1.9.6 Flash photolysis: Flash photolysis is a powerful tool for the study of the primary processes in photochemical systems. Of the various types of flash system the electrical discharge between inert metal electrodes in a gas at low pressure has been most widely used. Three basic types of flash systems most widely used today are as follow:

a) the electrical discharge between inert metal electrodes in a gas at low pressure,

b) the high energy spark discharge between magnesium or other relatively volatile metal electrodes,

c) the 'exploding wire' flash.

1.1.10.0 Actionometry

The measurement of the intensity of radiation is inevitable to determine the quantum yields. The quantum yield of a transformation that takes place in a good chemical actinometer under irradiation should not significantly change in the experimental conditions; the analysis of the transformation thus produced must be simple and accurate. Now-a-days photochemists use mainly three methods of light-intensity determination, which are:

a) the thermopile-galvanometer system,
b) the chemical actinometer, and
c) the phototube.

Amongst these, the thermopile-galvanometer is sufficiently versatile to be useful for absolute light-intensity measurements over the entire spectral range from visible to far ultraviolet.

1.1.10.1 Types of chemical actinometer:

A) *Vapour - phase actionometry:*

250 - 320 nm: acetone or diethyl ketone

180 - 250 nm: hydrobromic acid

B) *Solid phase actionometry:*

The only system currently in use is the isomerization of o-nitro benzaldehyde to o-nitrosobenzoic acid in a solid medium (a KBr capsule or a polymer film).

C) *Liquid phase actinometry:*

The most frequently used system is the potassium ferrioxalate actinometer of Hatchard and Parker[1-2]. Its effective range is very wide: between 250-480 nm. The useful range of uranyl oxalate is between 208-435 nm; this compound is also frequently used, but is much less sensitive than potassium ferrioxalate. The characteristic features of potassium tris-(oxalato)Ferrate(III), $K_3Fe(C_2O_4)_3$, system are as follow:

a) High sensitivity. It is about 100 times sensitive than that of uranyl oxalate actinometer normally employed.

b) The quantum yield for Fe^{2+} formation is substantially constant over the wavelength range 254-579 nm.

c) The quantum yield for Fe^{2+} formation is virtually insensitive to temperature, solution composition, and light intensity.

d) Great stability of photolyzed products

e) Simplicity of operation

f) Applicability to the measurement of a wide range of values of a total light intensity.

g) Quantum efficiency is not critically dependent on the solution composition nor does it vary significantly over the temperatuer range 22-33^{0}C.

Irradiation of tris (oxalato) ferrate (III) in acid solution such as sulphuric acid results in reduction of Fe^{3+} to Fe^{2+}, and simultaneous oxidation of the $C_2O_4^{2-}$ ion. The quantum yield of the photoreduction of the ferric complex has been accurately determined. The light absorption by reactant in the region of 254- 480 nm was measured at definite intervals. The product ferrous ion and its oxalate complex in these solution do not absorb the incident radiation measurably during the photolysis, but after the exposure the ferrous ion is converted into highly absorbing and easily analyzable red coloured 1,10-phenanthroline complex. The quantum yield increases with the decrease in wavelength of the radiation.

1.1.10.2 Actionometric determination of the intensity of the absorbed radiation: Substance A, which is utilized in the photoconversion, is irradiated for a given length of time under the same conditions as the sample to be irradiated. The light intensity absorbed per unit time will be:

$$I_0^i = \frac{n}{\Phi_A . t . (1 - 10^{-\varepsilon[A]l})} \quad \text{quanta sec}^{-1} \qquad (1.15)$$

Where, n = number of species formed during the time of irradiation, t.

Φ_A = absolute quantum yield of the product.

The expression $(1-10^{\epsilon[A]l})$ is the fraction of the incident light absorbed by the actionmeter.

I_0^i = intensity of the light beam on the inner side of the first window of the cell.

1.1.11. 0 Importance of photochemistry.

Photochemistry is basic to the world we live in. The relevance of photochemistry also lies in its varied applications in science and technology. Photochemistry has seen an enormous increase of research activity in all areas over the past twenty years, particularly in the field of utilization of solar energy through photochemical reactions[3.4] and in the study of kinetics and mechanism of photochemical reactions[5-7]. There is also increasing interest in elucidating the mechanism of storage of solar energy in the biological systems[8]. The most important fields in which photochemistry plays a vital role are

a) Atmospheric photochemistry
b) Photosynthesis
c) Vision
d) Photoimaging
e) Photochromism
f) Solar energy storage
g) Photochemistry in synthesis
h) Photomedicine
i) Removal of environmental pollutants

1.2.0 Free Radical

Chemical bonds are usually formed from the sharing of two electrons, whereas a free radical is a species with one unparied electron. This makes many, but not all, free radicals chemically quite reactive, as the species seek to find another electron to pair up with. However, the definition includes common chemicals such as oxygen. Not surprisingly, therefore, oxygen is a common reactant in free-radical processes, having a propensity to take part in single -electron transfer or free- radical addition reactions in which electrons become paired. Another common gaseous chemical which is a free radical is nitric oxide.

Ionizing radiation ejects single electrons from molecules, and so the radiolysis of water, for example, generates free radicals at a rate readily controlled by manipulating the radiation source. By adding suitable solutes, specific free radicals identical to those the body produces naturally can be generated. Thus techniques originally developed to help study the reactive intermediates in chemical events following radiolysis have proven to be powerful methods of characterzing the reactions of natural free radicals in predominantly aqueous meida such as the bulk of the cellular environment. In fact, the rates of several of the most important reactions of natural free radicals were first measured in this way, and the tools of radiation chemistry provide important information concerning free radical reactions of biological importnace. Radiation chemistry is therefore becoming increasingly important in this much wider context.

Oxidation and reduction are chemical terms which describe the loss or gain of electrons by molecules, respectively. Thus ferrous iron, Fe(II) is oxidiized to ferric iron Fe(III) by the loss of a single election, the charge on the ion changing from +2 to +3 in the process. Hydroxide ions in water ($^{-}$OH) can be ionized, losing an electron, to give hydroxyl free radicals ($^{\cdot}$OH); the unparied electron in $^{\cdot}$OH is denoted by the radical 'dot' and such species have a strong tendency to restore the electron pair by pulling a hydrogen atom, complete with a single unpaired electron, from C-H bonds in Brilliant Golden Yellow for example. An oxidizing agent in thus a molecule, atom or radical fragement which likes to gain an electron. (In fact, radiation chemistry has provided us with a versatile and powerful method of quantifying the propensity to electron gain or loss involving short-lived free radicals, where conventional electrochemical methods fail.)

1.2.1 Fenton's reagent and Fenton reation

H.J.H Fenton first reported in 1894 that malic acid was rapidly oxidised by hydrogen peroxide in presence of ferrous ion. Later it was confirmed that in presence of Fe(II) or Fe(III), H_2O_2 generate hydroxl free radicals ($^{\cdot}OH$). These radicals are strongly reactive intermediates. The mixture of Fe(II) or Fe(III) with H_2O_2 commonly is called Fenton's reagent.
The mechanism of generation of hydroxyl free radicals[43] :

In presence of ferrous ion
$H_2O_2 + Fe(II) \rightarrow {}^{\cdot}OH + {}^{-}OH + Fe(III)$ (1.16)

In presence of ferric ion
$H_2O_2 + Fe(III) \rightarrow HO_2{}^{\cdot} + H^+ + Fe(II)$ (1.17)

The perhydroxy radicals ($HO_2{}^{\cdot}$) are very unstable and converted into hydroxyl free radicals ($^{\cdot}OH$).
$2HO_2{}^{\cdot} \rightarrow 2{}^{\cdot}OH + O_2$ (1.18)

The dydroxyl radicals are strong oxidizing agent and oxidize the organic compunds by generating new organic free radicls ($R^{\cdot}$).
$RH + HO^{\cdot} \rightarrow R^{\cdot} + H_2O$ (1.19)

The free radical R. scavenge oxygen molecule from the environment and form perhydroxy radical ($RO_2{}^{\cdot}$)[44] which is very reactive and in presence of Fe(II), they are converted into stable products (H_2O, CO_2, HNO_3 etc.).

$R. + O_2. \rightarrow RO_2.$ (1.20)

$RO_2{}^{\cdot} + Fe(II) \rightarrow$ degraded products. (1.21)

1. 3.0 Semiconducting oxides as a photocatalyst

Aqueous toxic waste is an important international problem. Processes are needed to be developed for the detoxification of various classes of chemical wastes. The photoassisted detoxification processes can be developed that are industrially and economically feasible. During the last two decades, extensive research programmes have been persuade in the area of heterogeneous photocatalyis with semiconducting particulate systems for the photodecomposition of liquid waste and polluted water. Most of the work found in the literature regarding heterogeneous photocatalytic processes deals with aqueous suspensions. Semiconductors used as photo-catalysts include TiO_2 [8-23], ZnO[24], CdS [25-26] and Fe_2O_3[27-29].

1.3.1 TiO_2 - Nature, Structure and Energetics

Titanium dioxide or titania is a non-stoichiometric transition metal oxide. The approximate composition range for oxygen in TiO_2 is 1.998-2.000[30].Accordingly TiO_2 behaves as n-type semiconductor. It occurs in nature in three crystalline forms that are rutile, anatase and brookite. Rutile is thermodynamically more stable than anatase at room temperature. The free energy change for anatase to rutile is -5.4kJ/mol [31]. The band gap energy of TiO_2 ranges from 3.0 to 3.2 eV depending on its nature. The equivalent wavelength ranges from 376 to 410 nm.

Ultraviolet radiation below 390nm stimulates valence-band electrons in TiO_2 particles in aqueous suspension. These electrons are promoted to the conduction band (e^-_{cb}) creating holes in the valence band (h^+_{vb}). These electron/hole pairs can either recombine, producing thermal energy, or interact with the external environment to perform oxidation and reduction reactions. Thus reaction (21) initiates hosts of other chemical reactions.

$$TiO_2 + h\nu \rightarrow TiO_2\,(e^-_{cb}, h^+_{vb}) \qquad (1.22)$$

1.3.2 Surface charge on aqueous TiO_2 photocatalyst dispersions during illumination : The pH of zero zeta potential (p.z.z.p.) for the n-type TiO_2 particles results at pH 5 [32]. At pH < p.z.z.p. protonation of the surface creating -Ti-O-H groups, produces a net positive charge, and at pH>p.z.z.p., deprotonation produces a negative surface charge.

Examination reveals that in the absence of any hole scavengers, such as Cl^- ions, TiO_2 valence band holes are, thermodynamically sufficiently energetic to oxidize either H_2O or OH^- to generate adsorbed OH radicals, and this has been well established experimentally [33]. At neutral and basic pHs, the reactions may be written as:

$h^+_{vb} + (H_2O)_{ads} \rightarrow (\cdot OH)_{ads} + H^+_{(aq)}$ (1.23)

$h^+_{vb} + (OH^-)_{ads} \rightarrow (\cdot OH)_{ads}$ (1.24)

Alternately the holes may oxidize Ti-O-H surface groups via

$h^+_{vb} + \text{-Ti-O-H}_{(aq)} \rightarrow \text{-Ti-O-H}^+_{(aq)}$ (1.25)

or, in base,

$h^+_{vb} + \text{-Ti-O}^-_{(aq)} \rightarrow \text{-Ti-O}\cdot_{(aq)}$ (1.26)

Illumination of TiO_2 dispersions at pH< p.z.z.p. (pH ≈ 5) with ultra-band gap energy photons produced an increase in positive surface charge. This is explained by the following sequence of reactions

$(\text{-Ti-O-Ti-})_{(s)} + e^-_{cb} \rightarrow (\text{-Ti-O}^-\text{-Ti-})_{(s)}$ (1.27)

and then

$(\text{-Ti-O}^-\text{-Ti-})_{(s)} + H^+_{(aq)} \rightarrow (\text{-Ti-(O}^-\text{-H}^+\text{)-Ti-})_{(s)}$ (1.28)

1.3.3 Behaviour of TiO_2 surface during photolysis: Ultraviolet radiation below 390nm stimulates valence-band electrons in TiO_2 particles that are suspended is contaminated water. These electrons are promoted to the conduction band (e^-_{cb}), creating holes is the valence band (h^+_{vb}).

The holes in the TiO_2 valence band can migrate to the surface and can either oxidize an adsorbed species directly or can react with water and adsorbed

OH^- to produce hydroxyl radicals that are powerful oxidizers capable of attacking dissolved organics. For both the cases of oxidative pathways, the final products are reported to be water, carbon dioxide and other simple and harmless inorganic products.

$$TiO_2 + h\nu \rightarrow TiO_2\ (e^-_{cb}, h^+_{vb}) \qquad (1.29)$$

$$\text{Organic} + h^+_{vb} \rightarrow \text{Organic}^+ \qquad (1.30)$$

$$(H_2O)_{ads} + h^+_{vb} \rightarrow (\cdot OH)_{ads} + H^+_{(aq)}\ \text{(acidic media)} \qquad (1.31)$$

$$(OH^-)_{ads} + h^+_{vb} \rightarrow (\cdot OH)_{ads}\ \text{(alkaline media)} \qquad (1.32)$$

$$\text{Organic} + (\cdot OH)_{ads} \rightarrow \text{products} \qquad (1.33)$$

$$\text{Organic}^+ \rightarrow \text{products} \qquad (1.34)$$

The electrons , in turn, react with dissolved oxygen to form superoxide anions, $(\cdot O_2)$, which combine with protons to form $\cdot OOH$ radicals that also form hydroxyl radicals after further reactions [9,11,15,34-37].Particularly in acidic media, the $(\cdot OOH)$ radicals can be one of the predominant oxidants in the initial photodegradation stages.

$$O_2 + e^-_{cb} \rightarrow \cdot O_2^- \qquad (1.35)$$

$$\cdot O_2^- + H^+ \rightarrow \cdot OOH \qquad (1.36)$$

$$\cdot OOH + \cdot OOH \rightarrow H_2O_2 + O_2 \qquad (1.37)$$

$$\cdot O_2^- + \cdot OOH \rightarrow OOH^- + O_2 \qquad (1.38)$$

$$OOH^- + H^+ \rightarrow H_2O_2 \qquad (1.39)$$

$$H_2O_2 + e^-_{cb} \rightarrow (\cdot OH)_{ads} + OH^- \qquad (1.40)$$

$$H_2O_2 + \cdot O_2^- \rightarrow (\cdot OH)_{ads} + OH^- + O_2 \qquad (1.41)$$

$$H_2O_2 + h\upsilon \rightarrow 2(\cdot OH)_{ads} \qquad (1.42)$$

$$\text{Organic} + (\cdot OH)_{ads} \rightarrow \text{products} \qquad (1.43)$$

1. 4. 0 Review of the literature.

The term "degradation" usually used to refer complete oxidation mineralization, that is the conversion of organic compounds to CO_2, H_2O, NO_3, SO_4^{2-} or other oxidess, halides phosphates etc.

Fenton's process has been widely studied in the past two decades for the mineralization of organic hazardous and toxic components in aqueous medium.
The kinetics of degradation of Orange (II) in the presence of sunlight by Fenton process[38] was studied by Bandara and co-worker. Light and temperature have shown to be effective in the mineralisation of Orange (II). Light accelerates the observed degradation. The results obtained in this study suggest that termodynamic potential for the redox couple in the Fenton process is not important factor controlling the degradation of this dye.

Pulgarin and has co-workers have studied the dynamics of oxidant addition as a parameter in the modeling of dye (Orange II) mineralisation via advanced oxidation technologics[39]. The processes in the light and the dark involving Fenton's reagent are effective in the degradation of OrangeII solutions. The degradation time was shown to be strongly dependant on pH of the medium. Orange II becomes significant only at pH <5. The H_2O_2 added and O_2 evolved were monitored during the degradation cycles, allowing optimization of the times for oxidant addition. About 88% dye mineralization occurred in 40 min under light irradiation. A model for the degradation has been developed from the available kinetic rates for radical reactions.

Purification of textile waste water by a combined Fenton's processes and ion exchange[40] was done by Ming and his co-wokers. The treatment system consists of the Fenton process and chemical coagulation was primarily used to remove colour, turbidity. COD, Fe (III) ions concentrations and total hardness. Results indicated that combined chemical treatment methods were very effective and capable of elevating water qulity of the treated waste water.

Mineralisation of antineoplastic agents used in hospitals has been studied[41] by M Laget. Cyclophosphamide was completely oxidised by NaClO, H_2O_2 and Fenton's reagent ($FeCl_2$+H_2O_2) but direct mutagens were generated from Fenton oxidation in the presence of dextrose.

The stoichiometry of Fenton's reagent in the oxidation of dichloroethylene (DCE), trichlorothane (TCE), tetrachloroethane (Tet.CE) and dichloroethane (DCEA) has been studied[42] by Tang. The theoretical optimal ration between H_2O_2 and Fe^{2+} was

II. However, the experimental optimal pH was 3.5. The amount of H_2O_2 required to achieve a certain percent removal follows the order of TCE> tec. CE> DCE>> DCEA.

Heterogeneous decomposition of COD components in ash filtrate samples by Fenton's reagent, TiO_2 and granite porphyry powders has been studied[43] by Moto and his co-worker.

The oxidation of COD species by treatment with heterogeneous suspensions of Fention's reagent, TiO_2 and granite porphyry along with H_2SO_4 prior to heavy metal removal improves the subsequent ferric treatment efficiency.

Destruction of TNT by Fenton's process[44] has been studied. Treating an aqueous TNT solution with Fenton's reagent on the dark resulted 100% destruction of TNT within 24 hours. This coincided with 40% mineralisation. Subsequest exposure to light resulted in>90% mineralisation. The generation of 2,4,6, trinitro benzoic acid and 2,4,6, trinitrobanzene within 15min following Fenton oxidation of TNT were also oxidation and decarboxylation. Subsequently transformation involves nitro moiety removal with ring hydroxylation and cleavage as evidenced by the stoichiometric recovery of TNT-N as NO_3^- and production of oxalic acid. Upon exposure to light, Fe(II) was formed and the oxalate produced from ^{14}C- TNT oxidation disappeared. This coincided with a decrease in solution ^{14}C activity.

An azo dye (Procaine red) has been degraded by advanced oridation (Fenton process and UV light) process[45]. At pH $\approx$ 3 and with H_2O_2/Fe(II) 79% of the dye has been degraded in 20 minutes.

p-chlorophenol has been degraded by Fenton's process[46]. For this study batch experiments were carried out to investigate the effects of pH, Fe^{2+} and H_2O_2 levels, p-chlorophenol concentration and chloride level. The decomposition proceeded rapidly only within a limited pH of 2-4. It was a typical decomposition that an initial fast decomposition rate was significantly reduced after a few minutes. The fast initial rate was first order with respect to p-chlorophenol and its rate constant was proportional to the initial level of Fe^{2+} and H_2O_2. The occurrence of the slow rate of decomposition was primarily attributed to the Fe^{2+} depletion caused by Fe-organic complex formation. The effect of chloride was pH dependent and could be significant as its concentration was increased. These observations strongly suggest that the reactions accounting for the conflicting effects of organic intermediates and products and heteroatioms should properly be included in the future models.

In the treatment of surfactant wastewater by Fenton's process[47] using anionic alkylbenzene sulfonate (ABS) and linear alkyl benzene sulfonate (LAS). A first-order kinetic model has been found to represent the Fenton oxidation of surfactant water.

Degradation of selected pesticide active ingradients and commercial formulations in water by the photo assisted Fenton reaction has been studied[48] by M.Becker. Destruction of pesticide active ingredients (AI) and compound formulations in acidic aqueous solution with the catalytic photo assisted Fenton process. The temperature rise and UV photolysis increase tha rate of mineralization of the organic compounds. In some cases, intermediate products such as formate, acetate and oxalate appeared in the early stages of degradation. The inert ingradients present in the medium had no affect for the cimpound Furadan.

Semiconductor photocatalysis can be more appealing than the more conventional chemical methods because generally semiconductors are inexpensive, non toxic and capable of extended use with out substantial loss of photocatalytic activity. Furthermore, semiconductor particles, recovered by filtration or centrifugation or when immobilized in a fluidized bed reactor, retain much of their native activity after repeated catalytic cycles.

TiO_2 has been widely used as a catalyst in the photodegradation of many compounds. Photodegradation of different types of surfactants catalyzed by TiO_2 semiconductor particles under either UV radiation or solar exposure has been published [63-66] . Evidence for the formation of OH radicals has been studied .

Photodegradation of many organic pollutants including phenol and chlorinated phenols and other chlorinated compounds have been extensively studied [67,74] in the presence of TiO_2. In most of these cases kinetics and degradation mechanism have been investigated. In the case of chlorinated phenols photodegradation follows first order kinetics up to 75% degradation. The photocatatytic degradation of phenol has been extensively studied because of its high toxicity[39-75]. With phenols and halophenols, such as 2-chlorophenol , photodegradation over $Ti0_2$ leads to rapid mineralization to CO_2 and HCl. Again, anatase showed a high photoactivity than rutile. ZnO is also an efficient catalyst for the photodecomposition of phenols[79] but unlike $Ti0_2$, ZnO shows appreciable instability during irradiation . Thus, phenol oxidation must compete with the photocorrosion of the photocatalyst.

Pyruvate has efficiently converted to lactate under illumination in aqueous suspension of TiO_2 in the presence of an electron donor[80] . It has been reported that photoconversion does not require additional catalysts and its efficiency depends on the pH and the electron donor in the solution.

Nb (V) ion, as Nb_2O_5, doped TiO_2 thin films has been used for photocatalytic degradation of formic acid[81]. Nb (V) ion doping in TiO_2 enhance n-type semiconductivity of TiO_2 . Its magnitude is dependent upon the doping level by Nb_2O_5[82] .

Photoreduction of carbon dioxide in aqueous TiO_2 suspension mixed with various metal powder has been studied [83] . CH_4 and HCHO have been found to form when Cu-TiO_2 photocatalyst is used.

Activity of chromium (III) ion doped titania as a phtocatalyst has been studied by many workers. Cr(III) doped TiO_2 has been used for various photocatalytic processes such as water splitting [84] , reduction of dinitrogen [85] , and CO_2 [86], oxidation of some organic compounds[87] and splitting of methanol [88] . All the findings agree that the doping displaces the light absorption towards the visible region of the solar spectrum , but the presence of Cr(III) ions negatively affects the photocatalytic behaviour for the investigated processes except for the reduction of dinitrogen [86] . Colloidal TiO_2 doped with Cr(III) ions and also with Pt and RuO_2 reported to have positive results for the sustained water photocleavage [89].

Metal ions doped in quantum sized TiO_2 colloids with Fe (III) , Mo(V) , Ru(III) , Os (III) , Re(V) , V(V) and Rh (III) with the range of dopants 0.1 - 0.5% has been systematically studied [90] . It has been observed that the photoreactivity for both oxidation and reductions is significantly increased . On the other hand Co(III) and Al(III) ions doping decreases the reactivity . The presence of some transition metal ions has been found to influence the photocatalytic oxidation mediated by TiO_2 [91-94].

It has been found that the rate of oxidation of toluene have increases in the presence of 10^{-5} M Cu(II), Fe(III) and Mn (II) at pH 3 . However higher concentration and pH affect this rate adversely.

Role of oxygen during photodegradation in the presence of TiO_2 has been investigated [95,96] . It has been suggested that oxygen plays an important role in the semiconductor mediated reaction by trapping the conduction band electron as superoxide ion ($\cdot O_2^-$) and thus delaying the electron hole recombination process. Superoxide ions form hydroxyl radicals that take part in subsequent degradation. It has also been suggested [86] that the degradation rate is dependent to some extent on the surface charge of the TiO_2 particle.

Photocatalytic activity of sol-gel TiO_2 and Degussa, P-25 TiO_2 has been found to be the same[97]. Both systems can be optimized in terms of the amount of TiO_2 and calcination temperature. It has been found that with the increase of TiO_2 concentration, light intensity rapidly increases first and then gradually decreases.

Quantum yield of photodegradation depends on the particle size of TiO_2 and light intensity [98]. The quantum yield increases with decreasing illumination intensity and size of the particle. It has been shown that the photooxidation of toluene by TiO_2 in acetonitrile is dramatically improved by the addition of small amount of sulphuric acid [99]. Photohydroxylation of benzoic acid[100] and photooxidation of ammonia [101] in the presence of aqueous suspension of TiO_2 have also been reported.

Sensitization of TiO_2 semiconductor with many compounds such as pthalolocyanines [102], $Ru(bpy)_3^{2+}$ complex and its derivative [103-105], chlorophyllin [106] and 8-hydroxyquinoline complexes have been reported. The mechanism [107-108] of the sensitization process involves charge injection from the excited state of the sensitizer to the conduction band of TiO_2.
This takes place in the visible light irradiation. The process is extremely sensitive to the pH of the medium[107].

Photodegradation of 3,4 - dichloropropionamide in aqueous TiO_2 suspension has been reported [109]. 100% destruction of 3,4 - DPA occurred within 5 hours when illuminated with a medium pressure lamp (λ=265nm) in the presence of TiO_2. During the photodegradation of 3,4 - DPA, formation of Cl^-, H^+, NO_3^- and CO_2 were observed. Application of solar energy instead of artificial illumination also gave successful results.

The photocatalytic oxidation of o-, m- and p- cresol was compared with ZnO and TiO_2 [110]. The same products were obtained with both ptotocatalysts. The rate of photocatalytic transformation increases with increasing pH and with the addition of small amounts of H_2O_2. The limited inhibition by ethanol suggests that hydroxyl radicals are the main but not the only oxidizing species involved.

Mineralization of organic matter and elimination of colour from the black liquor waste water, coming from wood pulping , using UV light in the presence of $ZnO-Fe_2O_3$ mixtures has been studied[111]. The results showed that CO_2 evolution was instantaneous and increased with time.

The light flux and light flux density over wide ranges on the photomineralization rates of 2,4-dichlorophenol and monochloroacetic acid by TiO_2 in aqueous suspension have been studied[112]. The photomineralization of aqueous 2,4-dichlorophenol at near uv-irradiated TiO_2 film has been monitored using an ultramicroelectrode stationed at micrometer distances from the TiO_2 film surface[113].

Not only TiO_2, other oxides have also been used as photocatalysts. A comparative photoxidation of three oligocarboxylic acids[110] have been done with TiO_2 (Degussa-25), α-Fe_2O_3, γ-Fe_2O_3, Fe_3O_4 and mixed Ti (IV)-Fe(III) oxides. TiO_2 has been found to be most effective catalyst. ZrO_2 and $ZrTiO_2$ powders have been used for the oxidation of isopropanol [101]. Photodegradation of razine over different metal oxide, such as TiO_2, ZnO, WO_3, ZnO_2 and Fe_2O_3 has also been investigated [114]. Besides Al_2O_3[115], SiO_2[116], ZnO[117] etc. have been used as photocatalyst.

1. 5. 0 Objective of the present work

Dyes are used in the textile industries and in the ball-point pen factories in Bangladesh. The unused dyes from these factories are thrown in the adjacent water way. The untreated dyes in water undergo photo- and also bio-degradation causing damages to the standing crops, fish and other aquatic lives. In order to devise ways and means to destroy the unused dyes in the effluent from different factories. We have chosen one dye, brilliant golden yellow, BGY, used in dying factories. This is known as reactive dye easily soluble in water.

Studies on degradation of dyes are not new. Two widely used methods are adopted for degrading dyes present in the effluents. One of these method is the so called "Fenton process" and the other is mediated photodegradation. In our studies we have used both of these methods. In the mediated photodegradation, we have used two semiconducting oxides, TiO_2 and ZnO.

Most of the investigators have used anatase but in our study we have used rutile as TiO_2. Moreover ZnO, mediator, has been used only in a few cases, but we have used it in our study just to see how it compares with TiO_2 (rutile) as a mediator.

CHAPTER 2

EXPERIMENTAL - GENERAL

2.1.0 Chemicals

Following materials are used without further purification.

(1) Mohr's salt, $FeSO_4.(NH_4)_2SO_4.6H_2O$ (AR.BDH)

(2) Potassium tris(oxalato)ferrate(III), $K_3[Fe(C_2O_4)_3]. 3H_2O$ (RG, BDH)

(3) 1,10-phenanthroline, monohydrate $C_{12}H_8N_2.H_2O$ (AR, E. Merck)

(4) Sodium acetate (AR, E. Merck)

(5) Hydrochloric acid (AR, BDH)

(6) Titanium dioxide (rutile, 99.99% pure, Fluka)

(7) Zinc oxide (Fluka)

(8) Ferric Nitrate ($Fe(NO_3)$. $9H_2O$) (AR, BDH)

(9) Hydrogen peroxide (H_2O_2) (BDH)

(10) Sulphuric acid (AR, BDH)

(11) Nitric acid (AR, BDH)

(12) Brilliant Golden Yellow (RG, BDH)

(13) Ferric nitrate (AR, BDH)

(14) Potassium permanganate (AR, BDH)

(15) Sodium hydroxide (AR, BDH)

(16) Buffer solution (Sodium acetate-Sulphuric acid buffer)

2.2.0 Pieces of equipment used

Equipment used for the analytical purpose were

(1) Double-beam UV-visible spectrophotometer (UV-160A, Japan)

(2) Electronic balance (FR-200, Japan)

(3) pH meter (Orion, Japan)

(4) Visible light source (410nm light)

(5) UV-light source (320nm light)

2.3.0 Preparation of solution

All the aqueous solutions were prepared with distilled water obtained from distillation plant. In addition, throughout the whole investigation distilled water was used for other purpose e.g. washing the glasswares.

2.3.1 Mohr's salt solution

This solution was prepared by dissolving 0.98g solid Mohr's salt in 0.05 M sulphuric acid solution and volume was made up to 250.0 mL.

2.3.2 Potassium tris- (oxalato) ferrate(III) solution

6.0×10^{-3} M, 500.0 mL solution was prepared by dissolving requisite amount of the solid reagent in 0.05 M sulphuric acid. The volumetric flask containing this solution was covered with black paper and was always kept in the dark.

2.3.3 1-10 Phenonthroline solution

This solution was prepared by dissolving 0.25g of the solid reagent in 250.0 mL of water.

2.3.4 Buffer solution (pH=4.5)

Buffer solution was freshly prepared by the addition of 2.5 mL concentrated sulphuric acid to a solution of 20.50g sodium acetate, the final volume of the solution being 250.0 mL.

2.3.5 Preparation of H_2O_2 solution

1.0 ml of pure $H_2O_2(l)$ was diluted to 100ml. 5ml of this solution was titrated against standard $KMnO_4$ solution in acid medium and standard H_2O_2 solution was found As it is decomposed , so it was standardized before the experimental work did .

2.3.6 Ferric nitrate solution

This solution was prepared by dissolving 0.3714 hydrated $Fe(NO_3)_3 . 9H_2O$ in dilute nitric acid and volume was made up to 100 mL. The concentration of this solution was measured by spectrophotometric method converting Fe(III) into Fe(II)-1,10 phenanthroline complex.

2.3.7 $KMnO_4$ solution

100ml $KMnO_4$ solution was prepared in dilute H_2SO_4 solution by using requisite amount of solid $KMnO_4$ and it is measured accurately by spectrophotometric method .

2.3.8 Stock solution on Brilliant Golden Yellow (BGY)

1.00×10^{-3} M 100ml BGY solution was prepared by using 0.061g of solid BGY.

2.4.0 Experimental set-up for Photodegradation

Beaker (R), made of pyrex-glass, was used the reactor . The dimensions of the beaker; the inside diameter was 3.84 cm and height was 5.36cm. The experimental set-up for the photodegradation is shown in Fig. 2.1(4)The source radiation comprised of a lamp (L), (Applied photo physics, England) which emitted steady monocromatic radiation of wavelength 410 nm and 320 nm. The reactor was placed on a stand (S) and the distance of the solution surface from the lower part of the lamp was fixed at 2.50 cm by adjusting the stand height. The total system was enclosed in a wooden box, called the lamp-house (H), and its inside surfaces were blackened. There was a small inlet (I) on one of the lamp-house walls of to let inside cold and hot gases to keep lamp-house temperature constant at 29.0^0 C. A thermometer (T) was installed inside the lamp-house to serve the purpose of observing the inside temperature

2.5.0 Spectrum of TiO_2 suspension

0.0045g TiO_2 was taken in 5.0 mL water to make a suspension. The suspension was aged over night and its spectrum was recorded in the following day after appropriate dilution with water. The spectrum shows broad band at 345nm (Fig. 2.1).

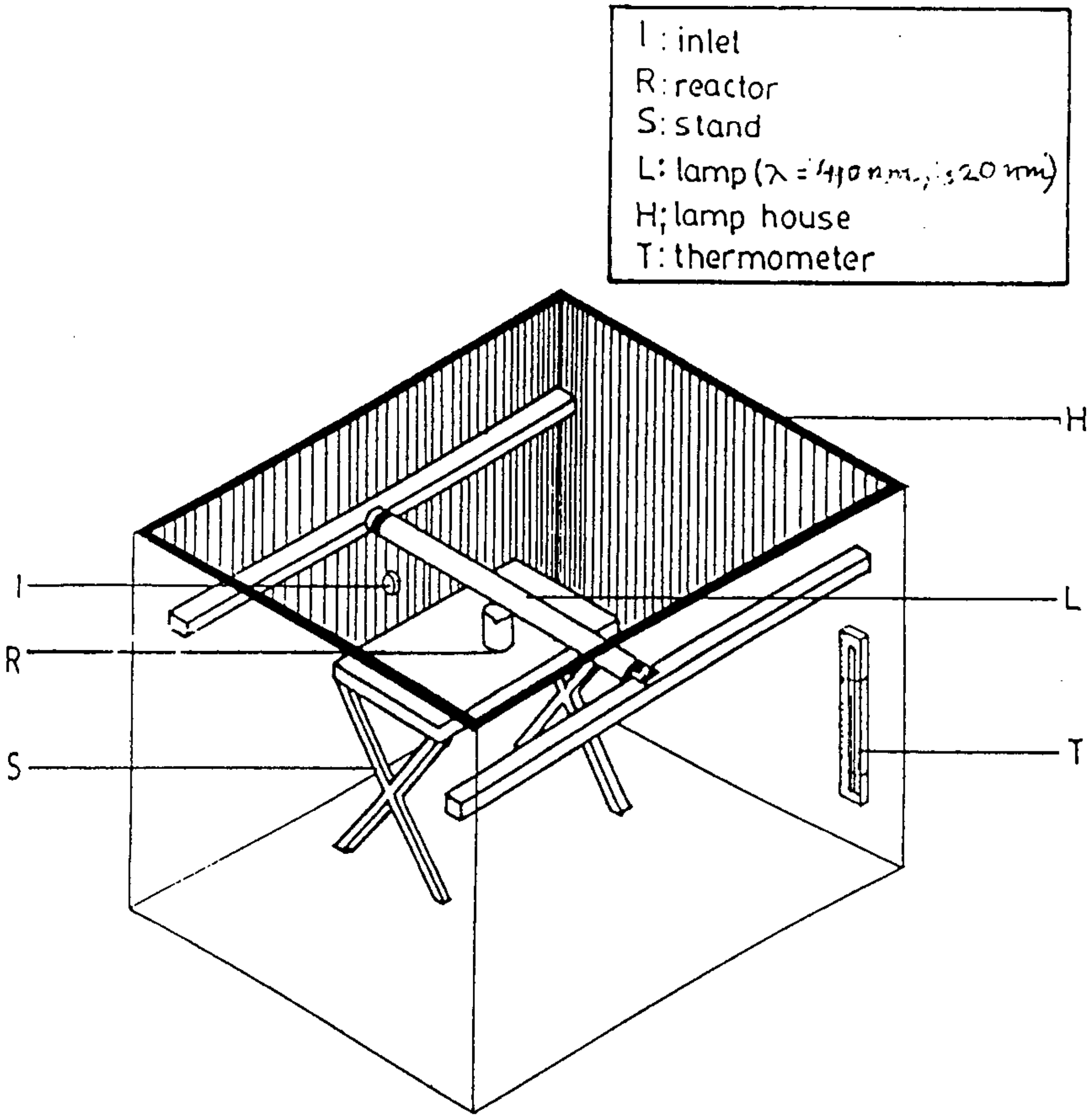


Fig 2.1(a) Experimental set-up for Photolysis.

```
        ***  PEAK-PICK  ***

   -- PEAK --            -- VALLEY --
  λ          ABS         λ          ABS
------------------------------------------
  345.0      1.144       226.0      0.848
  208.0      0.887
```

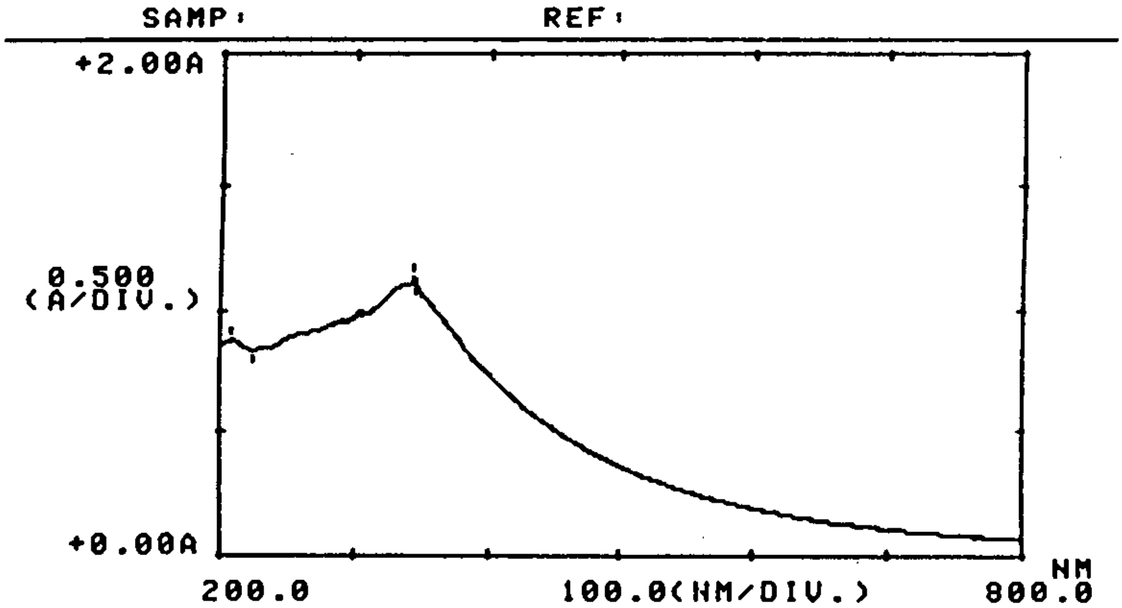


Fig.2.1 Spectrum of aqueous suspension of TiO_2 .

```
              ***  PEAK-PICK  ***

      -- PEAK --               -- VALLEY --
     λ          ABS          λ           ABS
 ------------------------------------------------
     345.0      0.501        528.0       0.444
```

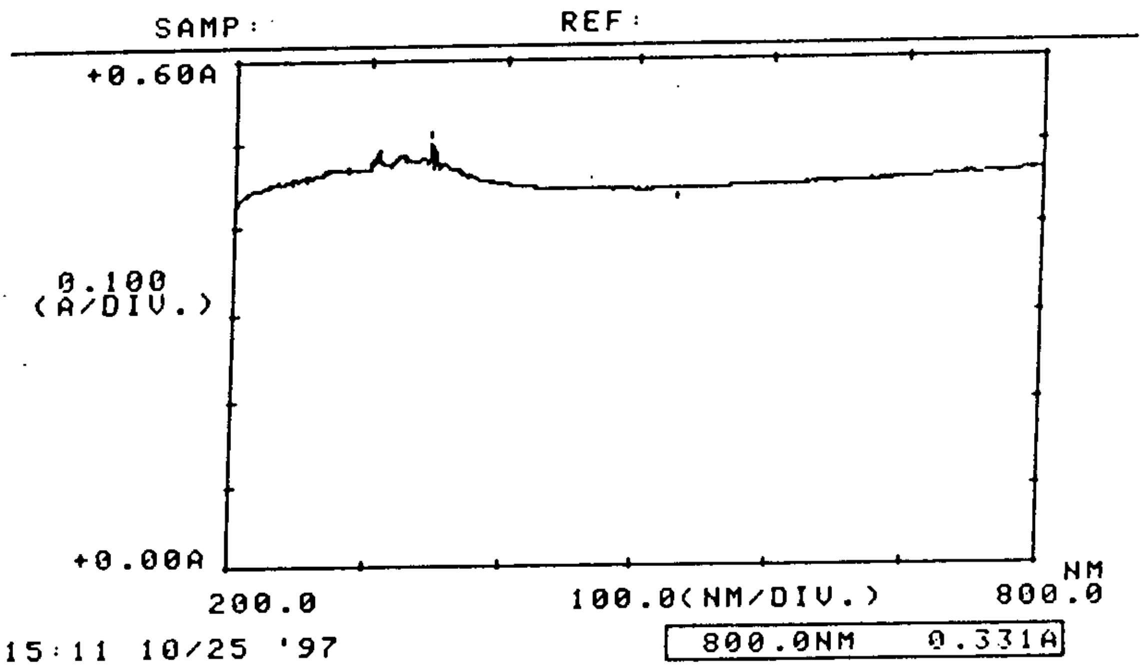


Fig. 2.2 : Spectrum of aqueous suspension of ZnO

2.6.0 Spectrum of ZnO suspension

0.01 g of ZnO was taken in 5.0ml water to make a suspension. The suspension was aged over night and its spectrum was recorded in the following day after appropriate dilution with water (Fig. 2.2)

2.7.0 Calibration curve for analysis of Fe (II)

Mohr's salt was standardized directly with standard dicromate solution using diphenylamine as the indicator in the usual way. Strength of this solution was 1.0×10^{-2} M. 2 mL of this solution was transferred to a 100.0 mL volumetric flask and the volume was made by addition of 0.05 M sulphuric acid solution and the solution was 2.00×10^{-4} M. To a series of seven 50.0 mL volumetric flasks 6.0, 8.0, 10.0, 12.0, 14.0, 16.0 and 18.0 mL of 2.00×10^{-4} M Mohr's salt solution were taken. To these flasks about 6.0 mL 0.10% 1,10-Phenanthroline solution, 10.0 mL sulphuric acid - sodium acetate buffer solution and sufficient 0.05 M sulphuric acid were added to make up the volume. These solutions were mixed well and allowed to stand for an hour in the dark for the completion of the formation of the orange-red Fe (II)-phenanthroline complex, The absorbance of each solution was measured at 510 nm [45] (λ_{max} of Fe(II)-phenanthroline complex) against a reference containing iron free solution made up of 6.0 mL 0.01% 1,10-phenanthroline, 10.0 mL buffer and 0.05 M sulphuric acid in 50.0 mL volumetric flask.

The plot of absorbance vs. molar concentrations of the complex solution was a straight line passing through the origin (Fig.2.3). From the slope of this straight line, molar extinction coefficient of Fe(II)-phenanthroline complex, $\in_{Fe(II)}$ was determined using following relationship:

$$A = \in_{Fe(II)} [Fe(II)] l \qquad (2.1)$$

where,

A = absorbance of Fe(II)-phenanthroline complex solution at 510 nm.

l = optical path length of the spectrophotometer cell
= 1.0 cm

[Fe(II)] = concentration of Fe(II) solution.

$\in_{Fe(II)} = 1.14 \times 10^4$ L mol^{-1} cm^{-1} at 29^{0}C was obtained.

Results are presented in Table 2.1

2.8.0 Results

2.8.1 Determination of molar absorption coefficient of Fe(II)-phenanthroline complex

Table 2.1: Absorbance of Fe(II)-phenanthroline complex at different concentrations.

Sample	: Mohr's salt
Temperature	: 29^0C
Reference	: Iron free solution containing phenanthroline solution buffer and 0.05 M sulphuric acid.
λ_{max} of Fe(II)-phenanthroline complex	: 510 nm

Run no.	$[Fe(II)] \times 10^5$ M	Absorbance
1	0.00	0.000
2	2.40	0.271
3	3.20	0.362
4	4.00	0.443
5	4.80	0.542
6	5.60	0.634
7	6.40	0.734
8	7.20	0.821

$\varepsilon_{Fe(II)}$ at 510nm = 1.14×10^4 L mol^{-1}cm^{-1} at 29^0C

```
            ***  PEAK-PICK  ***

   -- PEAK --              -- VALLEY --
  λ          ABS           λ          ABS
-------------------------------------------
  510.0      2.008         777.0     -0.023
                           329.0     -0.686
```

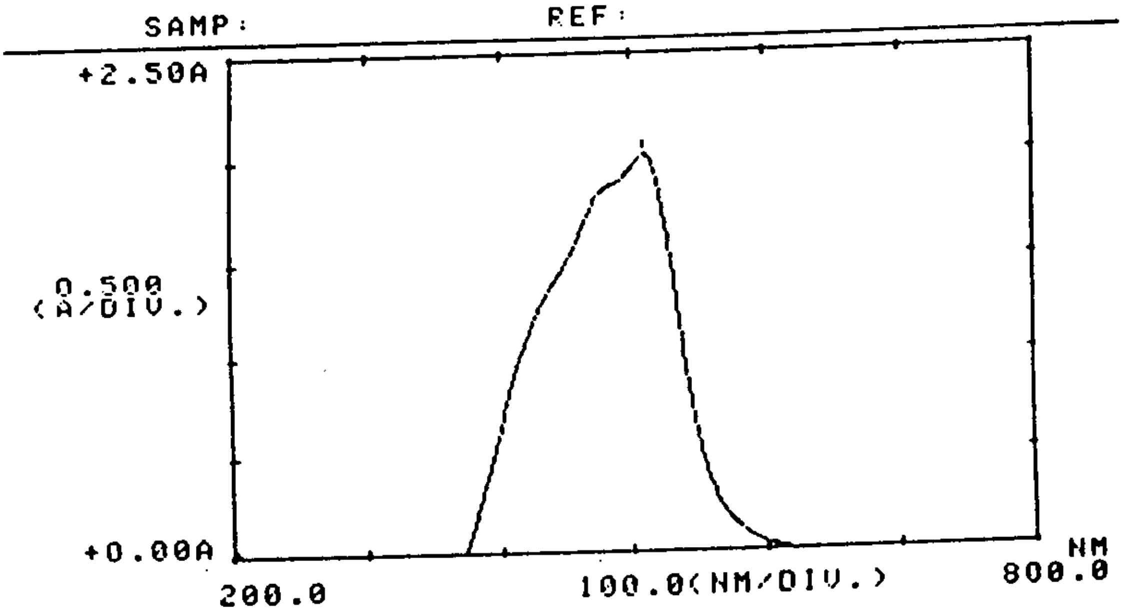


Fig.2.3Spectrum of Fe(II)-phenanthroline complex .

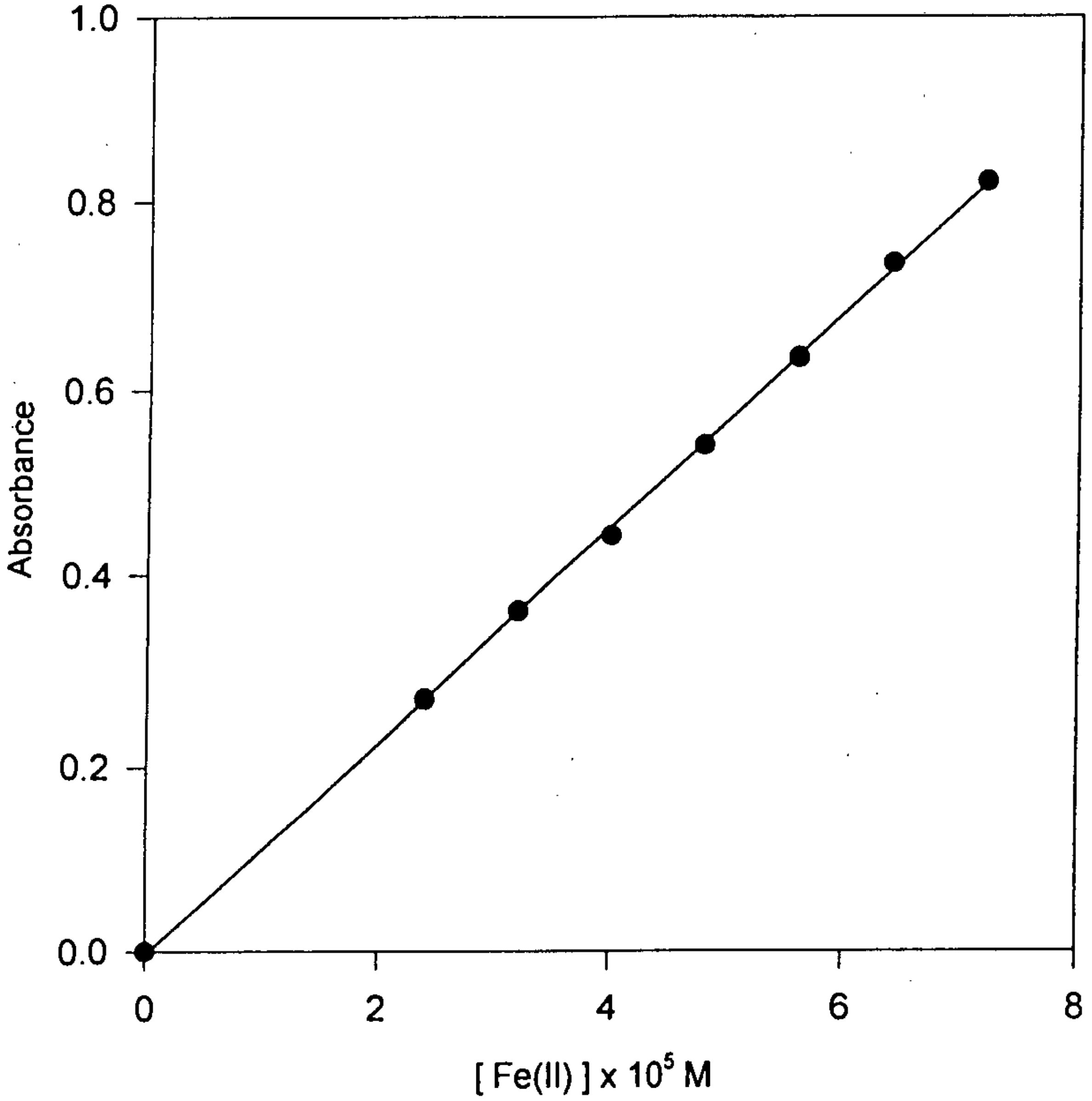


Fig.2.4: Absorbance of Fe(II)-phenanthroline complex at different concentrations at 510 nm .

CHAPTER 3

STUDIES ON BRILLIANT GOLDEN YELLOW (BGY) BY FENTON AND PHOTO-FENTON'S PROCESSES

3.1.0 Experimental

3.1.1 Spectrum of Brilliant Golden Yellow (BGY) in the aqueous solution.

The spectrum of BGY solution in the aqueous solution (Fig. 3.1) has distinguishable peaks at 416 nm and 223 nm respectively. The position of the peak at 416 nm remains almost constant at all conditions. Therefore this peak has been taken as the working wave length for the experimental measurement of degradation of BGY. The molar absorption coefficient of BGY at 416nm was found 7810 $Lmo^{-1}cm^{-1}$ at 29.0^0C (table 3.1, Fig. 3.3)

3.1.2 Degradation of BGY by Fenton's reagent

The process of degradation of BGY by Fenton's reagent was carried out both in the dark and in the presence of light. For this purpose 50mL of reaction mixture was prepared by taking requisite amount of BGY solution, Fe(III) nitrate solution, HNO_3 solution and H_2O_2 solution of known concentrations. It is to be noted that volume of deionised water was so added that when H_2O_2 solution was added the total volume was 100 mL. From this solution 50 mL solution was transferred in a parallel beam photochemical reactor for photolysis by light. The temperature of the photochemical reactor was constant at 29.0^0C. From the rest of the solution, 3 mL solution was taken in a cell and kept in the dark thermostat chamber of the UV-visible spectrophotometer, and temperature was kept constant at 29.0^0C. The chemical change (absorbance) was measured for both of the solution in the dark and in the light in 2 minutes intervals by UV-visible spectrophotometer. This procedure for the measurement of degradation was repeated for different conditions. The different conditions were

a) Variation of H_2O_2 concentration

b) Variation of Fe(III) concentration

c) Variation of H^+ ion concentration

d) Variation of BGY concentration

Data are presented in Tables 3.5, 3.6, 3.7, 3.8

3.1.3 Determination of initial rate of degradation

The initial rate of degradation was determined from the slope of the tangent drawn at the initial absorbance (of BGY) vs time profile. It was assumed that all light was completely absorbed by the system.

Initial rate of degradation

$$v = -\frac{d[BGY]}{dt} \quad \dots \quad \dots\dots \quad \dots\dots (3.1)$$

$$= -\frac{dA}{l.\varepsilon.dt} \quad \dots\dots\dots \qquad (3.2)$$

where, A= absorbance of BGY

ε = molar absorption co-efficient of BGY

l= length of the cell

3.1.4 Determination of (%) degradation

The Beer-Lambart law for dilute solution is written as-

$$A = \varepsilon[BGY]l \quad \dots\dots\dots\dots\dots \qquad (3.3)$$

Since ε and l are constant, then

$$A \propto [BGY] \quad \dots\dots\dots\dots\dots \qquad (3.4)$$

$$A_0 \propto [BGY]_0 \quad \dots\dots\dots\dots\dots \qquad (3.5)$$

$$A_t \propto [BGY]_t \quad \dots\dots\dots\dots\dots \qquad (3.6)$$

Therefore,

$$(\%)\ \text{Degradation} = \frac{A_0 - A_t}{A_0} \times 100$$

where, $[BGY]_0$ = concentration of BGY at time t =0

[BGY] = concentration of BGY at time 't'

A_0 = absorbance of BGY at time t= 0

A_t = absorbance of BGY at time 't'

```
          ***  PEAK-PICK  ***

     -- PEAK --              -- VALLEY --
   λ           ABS          λ           ABS
-----------------------------------------------
   416.0      0.755        735.0      -0.002
   224.0      1.524        328.0       0.243
```

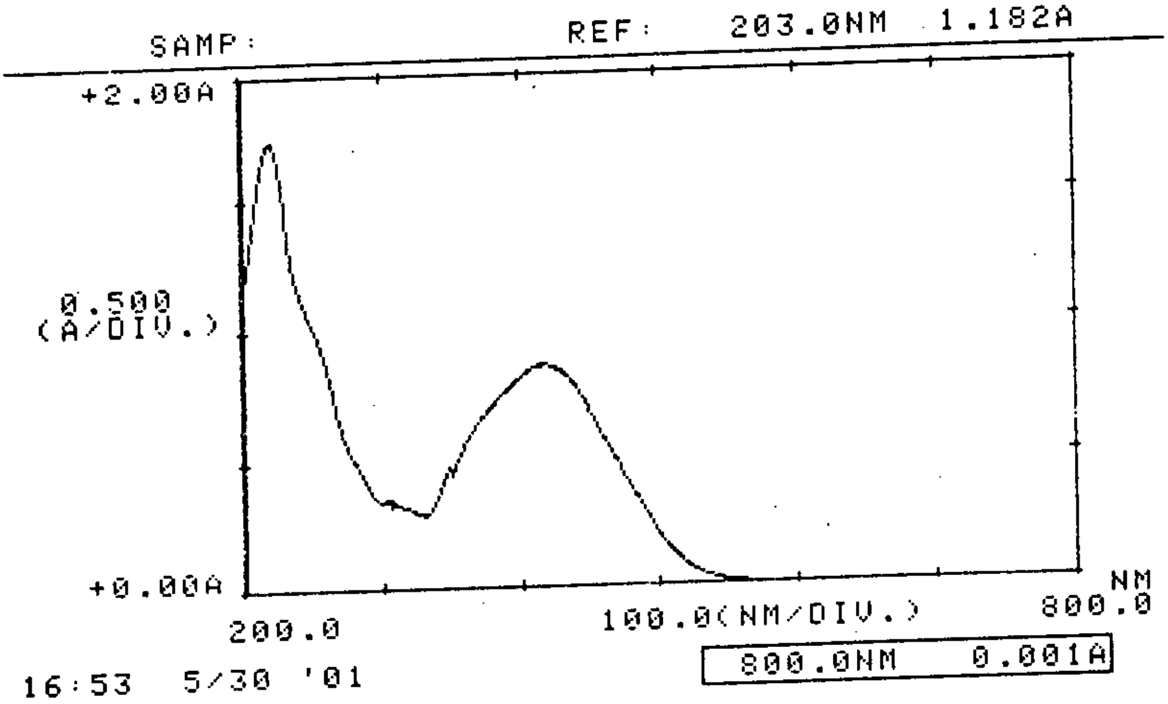


Fig. (3.1) **Spectrum of Brilliant Golden Yellow (BGY) in aqueous solution (Reference: Water).**

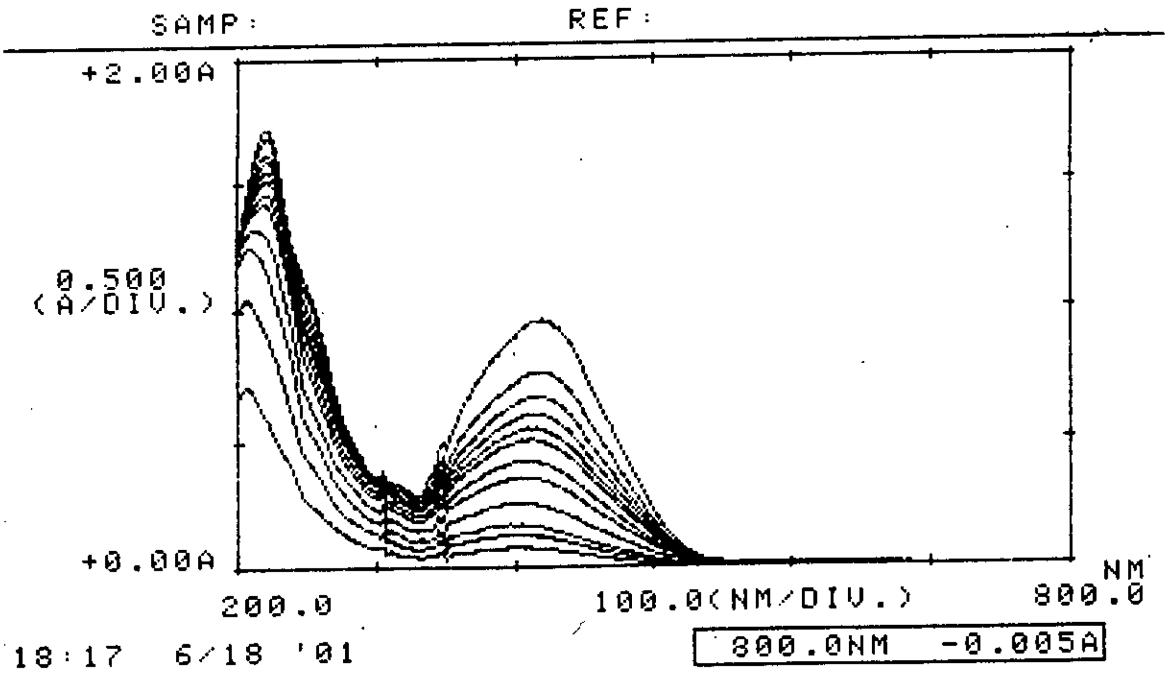


Fig. 3.2 The pattern of degradation of BGY

Ref. : Water, Temperature 29^{0}C

3.2.0 Results

3.2.1: Determination of molar absorption co-efficient of BGY

Table 3.1: Absorbance of BGY solutions at different concentrations.

Reference : water

λmax of BGY : 415 nm

Temperature : 29.0°C

Run No	$[BGY] \times 10^{-4}$ M	Absorbance at 415 nm
1	1.0	0.770
2	1.2	0.930
3	1.4	1.089
4	1.6	1.244
5	1.8	1.427
6	2.0	1.563

Molar absorption co-efficient of BGY at 416nm and 29.0°C is 7810 $Lmol^{-1}cm^{-1}$

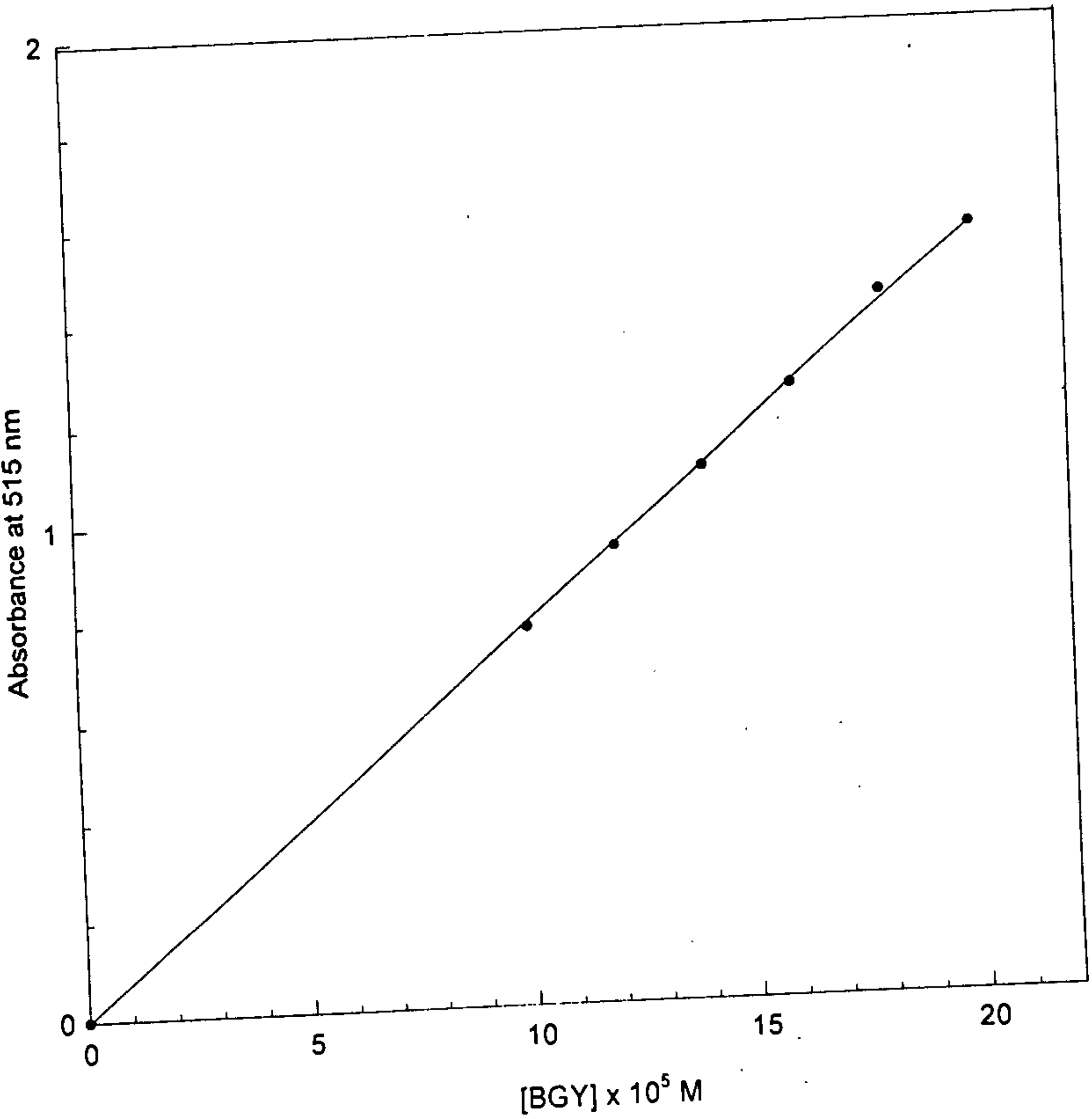


Fig.3.3 Absorbance *vs* [BGY]

3.2.2: Effect of pH on the spectra of BGY.

Table3.2: Absorbance of BGY solutions at different pH of the medium.

Reference : water

[BGY] : 2.06×10^{-4}M

Temperature : 29.0°C

Run No	pH	$\lambda_{max}(1)$ (nm)	Absorbance
1	6.0	415	1.607
2	5.0	415	1.607
3	4.0	415	1.607
4	3.0	415	1.607
5	2.0	415	1.607
6	1.5	415	1.607

3.2.3 Investigation of any complex formation by Fe(III) with BGY

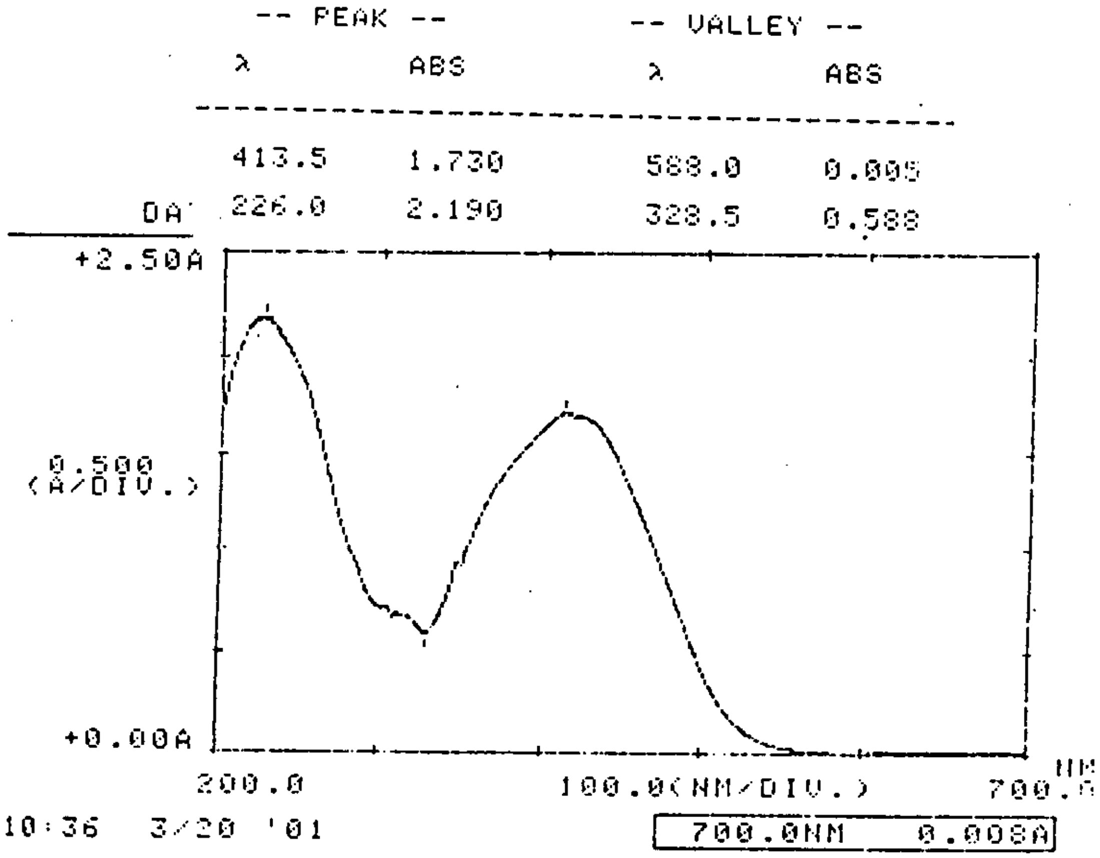
Table 3.3: Absorbance of BGY solutions in presence of Fe(III) ion.

Reference : water

pH of the medium : 2.30

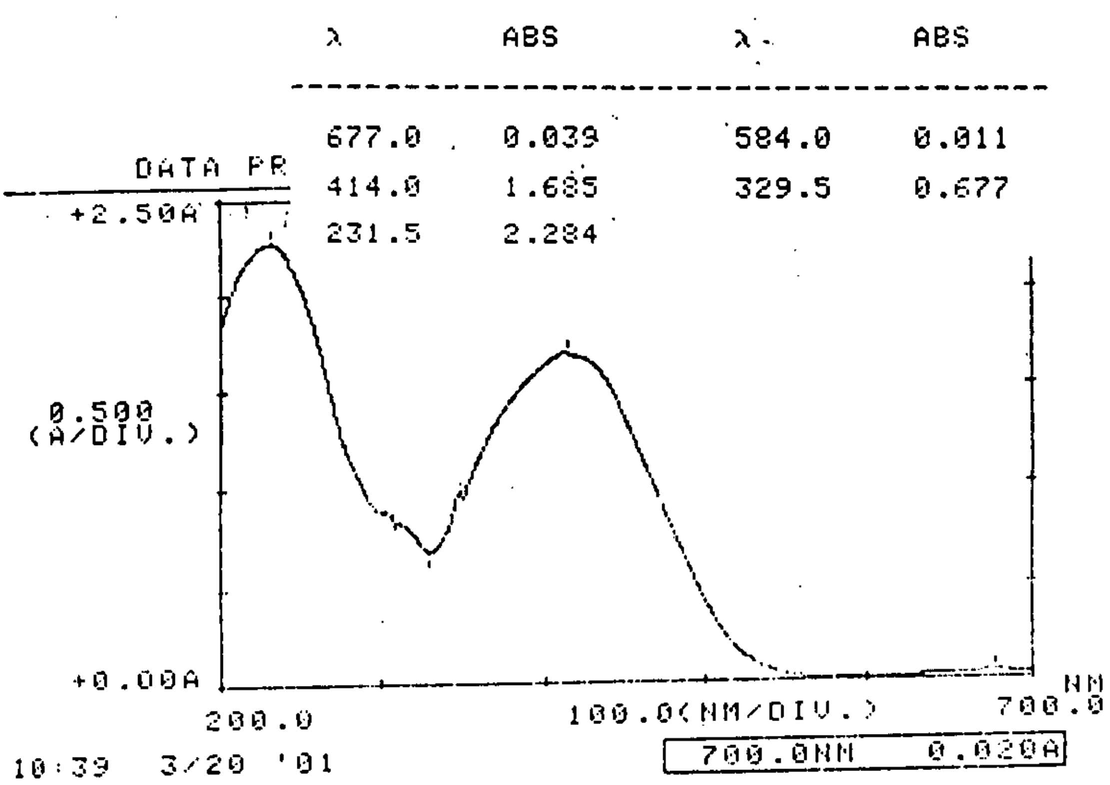
Temperature of the medium : 29.0°C

Run No	[BGY]:[Fe(III)]	Time (days)	λmax (nm)	Absorbance
1	2:1	0		
2		1	415	1.607
3		2	415	1.607
4		3	415	1.607
5		4	415	1.607
			415	1.607
1	1:1	0	415	1.607
2		1	415	1.607
3		2	415	1.607
4		3	415	1.607
5		4	415	1.607
1	1:2	0	415	1.607
2		1	415	1.607
3		2	415	1.607
4		3	415	1.607
5		4	415	1.607



```
        -- PEAK --                  -- VALLEY --
   λ              ABS            λ            ABS
---------------------------------------------------
  413.5          1.730         588.0        0.005
  226.0          2.190         328.5        0.588
```

Fig. 3.4 (a) Spectrum of Brilliant Golden Yellow(BGY) without Fe(III).



```
        -- PEAK --                  -- VALLEY --
   λ              ABS            λ            ABS
---------------------------------------------------
  677.0          0.039         584.0        0.011
  414.0          1.685         329.5        0.677
  231.5          2.284
```

Fig. 3.4 (b).Spectrum of Brilliant Golden Yellow(BGY) with Fe(III).

3.2.4:Degradation of BGY in the absence of Fenton's reagent.

Table3.4: Photolysis of BGY and measurement of absorbance at different time.

Source of emitting radiation	: 320 nm light
Reference	: water
[BGY]	: 2.06×10^{-4}M
Temperature of the medium	: 29.0°C
λmax of BGY	: 415nm

Run No	Time of photolysis (min)	Absorbance	degradation of BGY (%)
1	0	1.607	0.00
2	10	1.607	0.00
3	20	1.607	0.00
4	30	1.607	0.00
5	40	1.607	0.00
6	50	1.607	0.00
7	60	1.607	0.00

3.2.5.0 Degradation of BGY in the presence of Fe (111) and H_2O_2.

3.2.5.1. Effect of H_2O_2 concentrations on degradation of BGY.

Table: 3.5 Absorbance and (%) degradation at different time.

Reference : water
[BGY] : 2.97×10^{-4}M
[Fe(III)] : 4.00×10^{-5}M
[H^+] : 4.18×10^{-3}M
Temperature of the medium : 29.0°C
λmax of BGY : 415nm
(a) [H_2O_2] : 8.00×10^{-4}M

a-1 : Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	0.5710	15.11	49.10
3	05.00	0.2950	4.02	86.27
4	10.00	0.2100	2.72	90.84
5	15.00	0.2010	2.45	91.76
6	20.00	0.1940	2.41	91.87
7	25.00	0.1920	2.39	91.92
8	30.00	0.1900	2.39	91.94

a-2 : Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	0.5600	15.07	49.25
3	5.00	0.2860	3.66	87.68
4	10.00	0.2040	2.61	91.21
5	15.00	0.1950	2.50	91.58
6	20.00	0.1900	2.43	91.82
7	25.00	0.1880	2.41	91.89
8	30.00	0.1860	2.38	91.99

(b) $[H_2O_2]$: 1.0×10^{-3}M

b-1 : Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	0.5620	15.09	49.17
3	5.00	0.2680	3.43	88.45
4	10.00	0.2000	2.56	91.38
5	15.00	0.1950	2.50	91.58
6	20.00	0.1810	2.32	92.19
7	25.00	0.1790	2.29	92.29
8	30.00	0.1770	2.27	92.36

b-2 : Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	05530	15.04	49.36
3	5.00	0.2620	3.35	88.72
4	10.00	0.1940	2.48	91.65
5	15.00	0.1870	2.39	91.95
6	20.00	0.1770	2.27	92.36
7	25.00	0.1750	2.24	92.46
8	30.00	0.1730	2.22	92.53

(c) $[H_2O_2]$: 3.00×10^{-3}M

c-1 : Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	$[BGY]\times10^{5}$M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	0.5500	15.10	49.13
3	5.00	0.2570	3.29	88.92
4	10.00	0.1900	2.43	91.82
5	15.00	0.1800	2.30	92.26
6	20.00	0.1700	2.18	92.66
7	25.00	0.1680	2.15	92.76
8	30.00	0.1660	2.13	92.83

c-2 : Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	$[BGY]\times10^{5}$M	Degradation of BGY (%)
1	00.00	2.1380	29.70	00.00
2	02.00	0.5240	15.02	49.40
3	5.00	0.2500	3.20	89.23
4	10.00	0.1820	2.33	92.15
5	15.00	0.1720	2.20	92.59
6	20.00	0.1660	2.13	92.83
7	25.00	0.1640	2.10	92.93
8	30.00	0.1620	2.07	93.03

d) [H_2O_2] : 5.00×10^{-3}M

d-1 : Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	0.55300	15.06	49.29
3	5.00	0.2400	3.07	89.66
4	10.00	.01810	2.32	92.19
5	15.00	0.1720	2.20	92.59
6	20.00	0.1680	2.15	92.76
7	25.00	0.1660	2.13	92.83
8	30.00	0.1640	2.10	92.93

d-2 : Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3180	29.70	00.00
2	02.00	0.5110	15.01	49.46
3	5.00	0.2240	2.87	92.49
4	10.00	0.1740	2.23	92.96
5	15.00	0.1630	2.09	93.20
6	20.00	0.1580	2.02	93.33
7	25.00	0.1550	1.98	93.40
8	30.00	0.153	1.96	

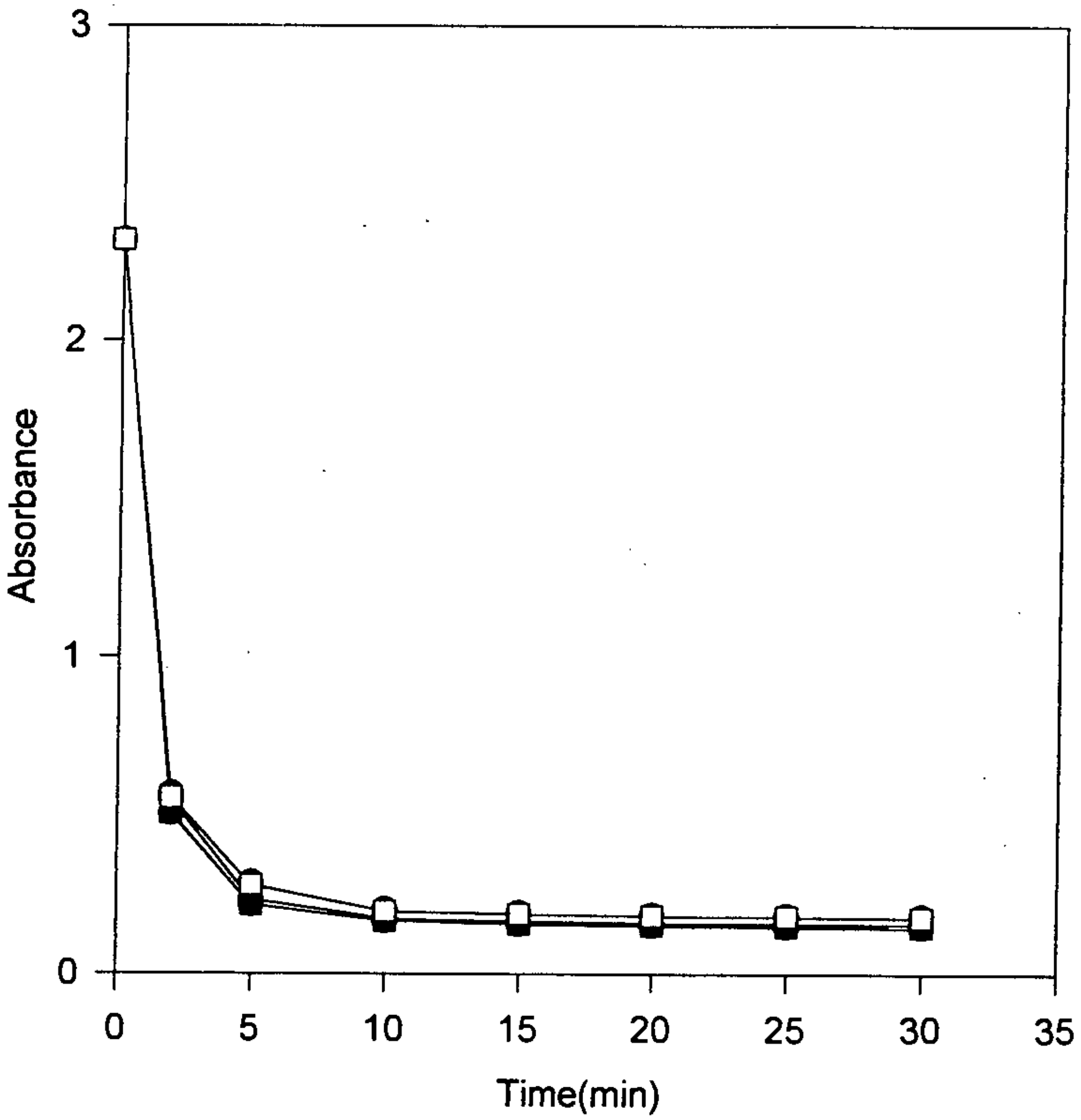


Fig. 3.5. (a):Effect of [H_2O_2] on thedegradation of BGY in dark and at 410 nm light

● ○ 1.0e-3M ■ □ 8.0e-4M

[solid symbol:reaction in dark,open symbol:reaction in visible light]

[BGY]:2.97e-4M,[Fe(111)]:4.0e-5M,[H^+]:4.18e-3M,Temp.:29.0°C

Temp. : 29.0°C

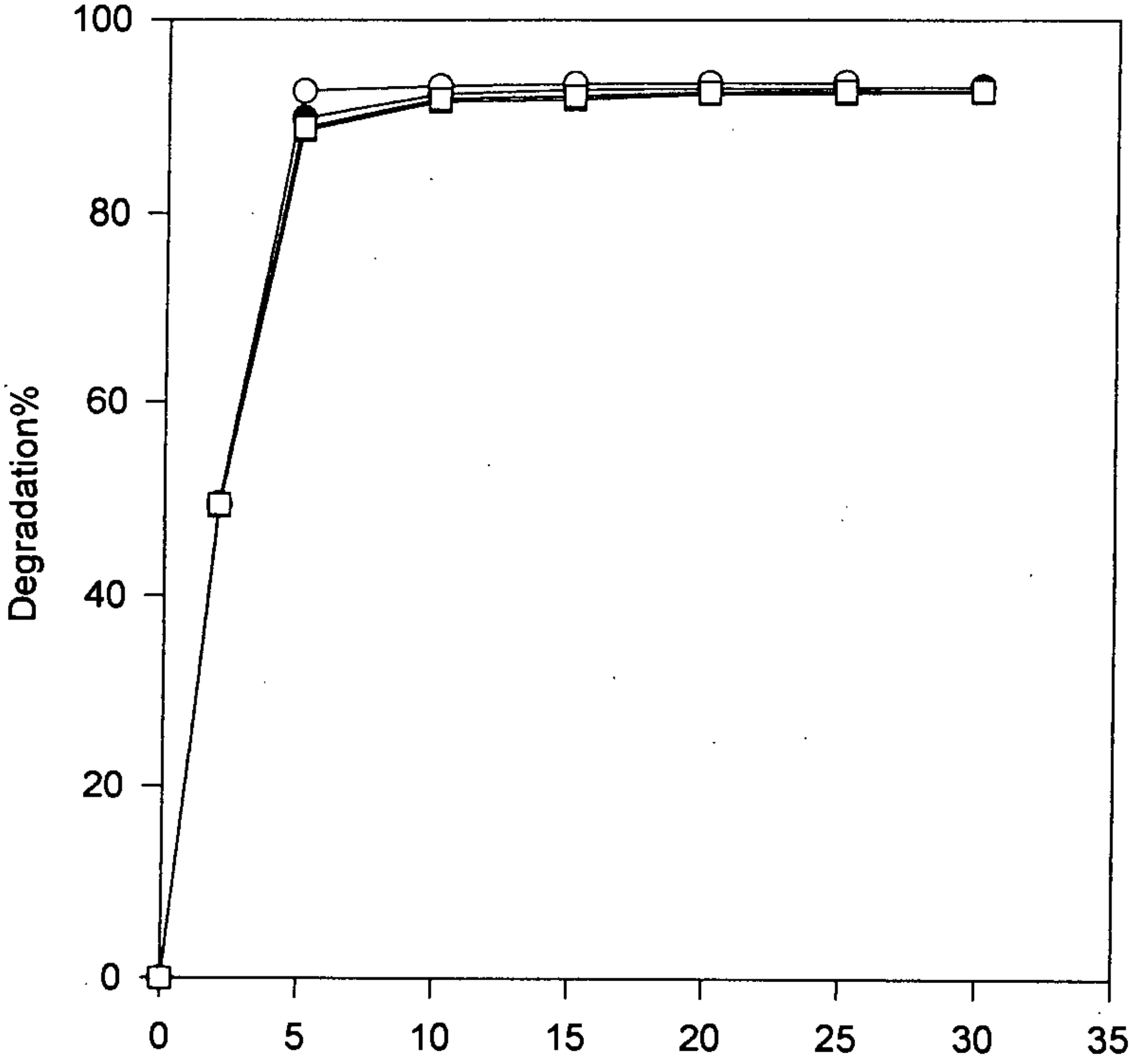


Fig. 3.5. (b) Effect of $[H_2O_2]$ on thedegradation of BGY in dark and at 410 nm light

● ○ 1.0e-3M ■ □ 8.0e-4M

[solid symbol:reaction in dark,open symbol:reaction in visible light]

[BGY]:2.97e-4M,$[Fe_{(III)}]$:4.0e-5M,$[H^+]$:4.18e-3M,Temp.:29.0^{0}C

3.2.5.2 Effect of Fe(III) ion concentrations on degradation of BGY

Table: 3.6 Absorbance and (%) degradation at different time.

Reference	: water
[BGY]	: 3.00×10^{-4}M
[H_2O_2]	: $3.00. \times 10^{-3}$M
[H^+]	: 4.18×10^{-3}M
λmax of BGY	: 415nm
Temperature of the medium	: 29.0°C
(a) [Fe(III)]	: 2.0×10^{-5}

a-1 : Degradation in dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1480	14.70	51.00
3	5.00	0.2700	3.46	88.47
4	10.00	0.1990	2.55	91.50
5	15.00	0.1840	2.36	92.13
6	20.00	0.1800	2.30	92.33
7	25.00	0.1780	2.28	92.40
8	30.00	0.1770	2.27	92.43

a-2 : Degradation in 410nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1350	14.53	51.57
3	5.00	0.2330	2.98	90.07
4	10.00	0.1840	2.36	92.13
5	15.00	0.1700	2.18	92.73
6	20.00	0.1630	2.09	93.03
7	25.00	0.1580	2.02	93.27
8	30.00	0.1570	2.01	93.50

(b) [Fe(III)] : 4.0×10^{-5}M

b-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.0	0.00
2	02.00	1.1450	14.66	51.13
3	5.00	0.2670	3.42	88.60
4	10.00	0.1980	2.54	91.53
5	15.00	0.1830	2.34	92.20
6	20.00	0.1780	2.28	92.40
7	25.00	0.1760	2.25	92.50
8	30.00	0.1730	2.22	92.60

b-2: Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.0	00.00
2	02.00	1.1300	14.47	51.77
3	5.00	0.2260	2.89	90.37
4	10.00	0.1790	2.29	92.37
5	15.00	0.1630	2.09	93.03
6	20.00	0.1540	1.97	93.43
7	25.00	0.1490	1.91	93.63
8	30.00	0.1480	1.90	93.67

(c) [Fe(III)] : 7.0x10^{-5}M

c-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1420	14.62	51.27
3	5.00	0.2650	3.39	88.70
4	10.00	0.1950	2.50	91.67
5	15.00	0.1800	2.30	92.33
6	20.00	0.1760	2.25	92.50
7	25.00	0.1740	2.23	92.57
8	30.00	0.1740	2.23	92.57

c-2: Degradation in the 410nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.0	00.00
2	02.00	1.1280	14.44	51.87
3	5.00	0.2250	2.88	90.40
4	10.00	0.1780	2.28	92.40
5	15.00	01.620	2.07	93.10
6	20.00	0.1530	1.96	93.47
7	25.00	0.1490	1.91	93.63
8	30.00	0.1480	1.90	93.67

(d) [Fe(III)] : 1.00×10^{-4}M

d-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1430	14.64	51.20
3	5.00	0.2660	3.41	88.63
4	10.00	0.1960	2.51	91.63
5	15.00	0.1810	2.32	92.27
6	20.00	0.1770	2.27	92.43
7	25.00	0.1750	2.24	92.53
8	30.00	0.1740	2.23	92.57

d-2: Degradation in the 410nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1310	14.48	51.73
3	5.00	0.2310	2.96	90.13
4	10.00	0.1830	2.34	92.20
5	15.00	0.1680	2.15	92.83
6	20.00	0.1610	2.06	93.13
7	25.00	0.1560	1.99	93.37
8	30.00	01.550	1.498	93.40

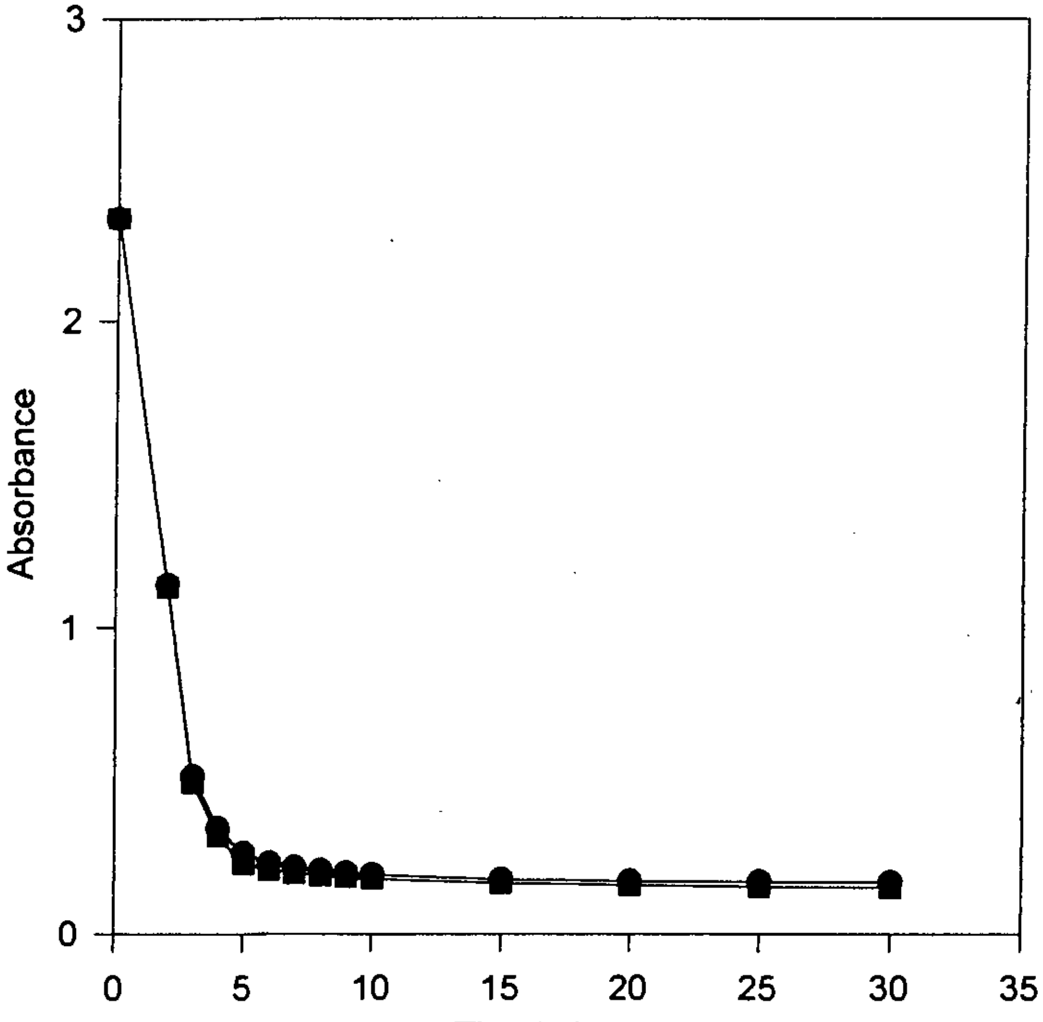


Fig. 3.6. (a) **Effect of [Fe (III)]**on the degradation of BGY in dark and at 410 nm light

■□ 7.0e-5M ● ○ 1.0e-4M

[solid symbol: reaction in dark,open symbol:reaction in visible light]

[BGY]:3.0e-4M,[H_2O_2]:3.0e-3M,[H^+]:4.18e-3M,temp.:29.0^{0}C

Temp. : 29.0^{0}C

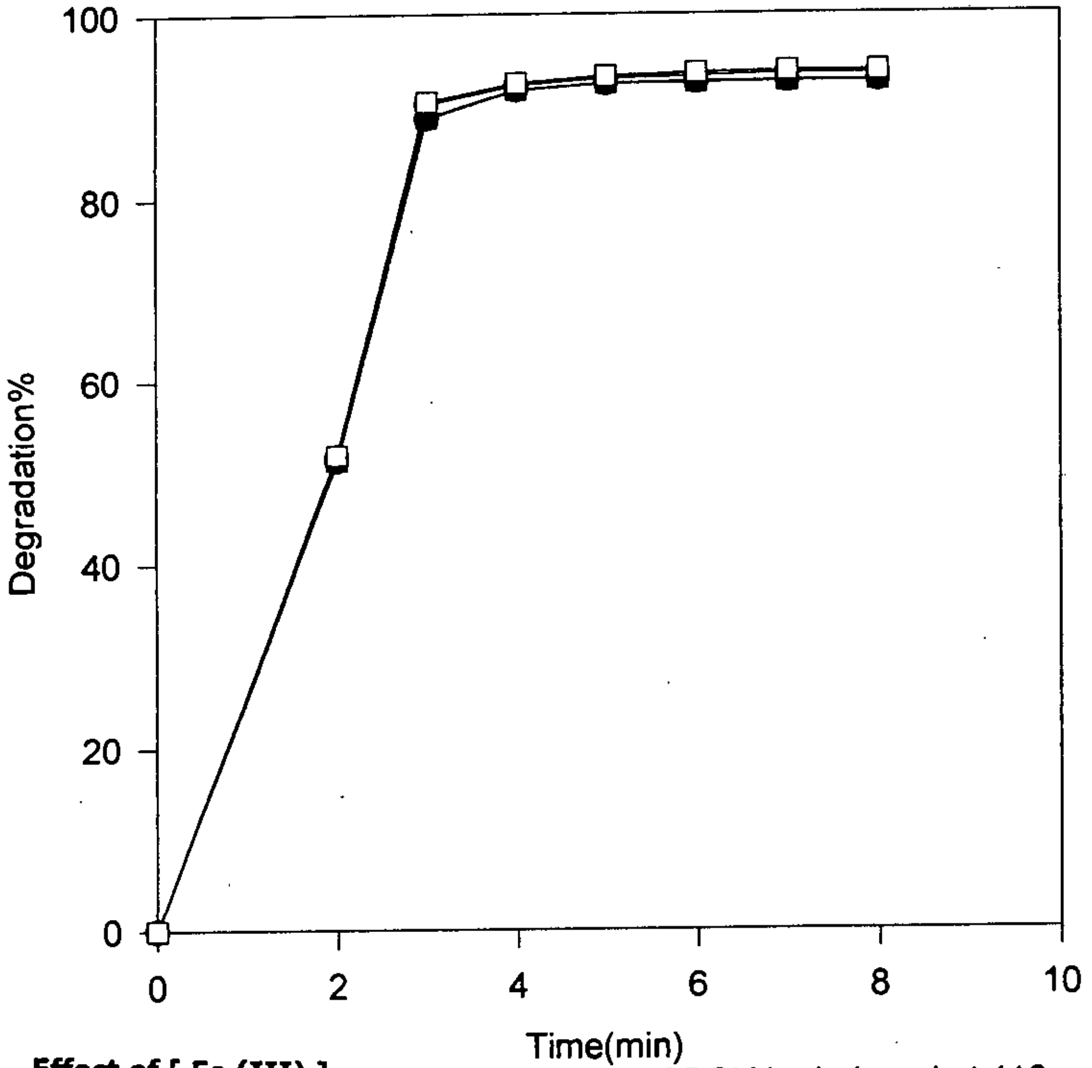


Fig. 3.6. (b) **Effect of [Fe (III)]** on the degradation of BGY in dark and at 410 nm light

■□ 7.0e-5M ● ○ 1.0e-4M

[solid symbol: reaction in dark,open symbol:reaction in visible light]

[BGY]:3.0e-4M,$[H_2O_2]$:3.0e-3M,$[H^+]$:4.18e-3M,temp.:29.0°C

3.2.5.3. Effect of H^+ ion concentrations on degradation of BGY.

Table: 3.7. Absorbance and (%) degradation at different time.

Reference : water
[BGY] : 3.00×10^{-4}M
[Fe(III)] : 4.00×10^{-5}M
[H_2O_2] : 3.00×10^{-3}M
λmax of BGY : 415nm
Temperature of the medium : 29.0°C
(a) [H^+] : 2.10×10^{-3}M

a-1 : Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1420	14.62	51.27
3	5.00	0.2600	3.33	88.90
4	10.00	0.1930	2.47	91.77
5	15.00	0.1740	2.23	92.57
6	20.00	0.1700	2.18	92.73
7	25.00	0.1670	2.14	92.87
8	30.00	0.1660	2.13	92.90

a-2 : Degradation in the 410nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1340	14.52	51.60
3	5.00	0.2500	3.20	89.33
4	10.00	0.1900	2.43	91.90
5	15.00	0.1680	2.15	92.83
6	20.00	0.1620	2.07	93.10
7	25.00	0.1590	2.04	93.20
8	30.00	0.1580	2.02	93.27

(b) $[H^+]$: 4.18×10^{-3}M

b-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1370	14.56	51.47
3	5.00	0.2580	3.30	89.00
4	10.00	0.1930	2.47	91.77
5	15.00	0.1720	2.20	92.67
6	20.00	0.1660	2.13	92.90
7	25.00	0.1630	2.09	93.03
8	30.00	0.1620	2.07	93.10

b-2: Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1300	14.47	51.77
3	5.00	0.2520	3.23	89.23
4	10.00	0.1910	2.45	91.83
5	15.00	0.1650	2.11	92.97
6	20.00	0.1580	2.02	93.27
7	25.00	0.1530	1.96	93.47
8	30.00	0.1520	1.95	93.50

(c)[H^+] :6.36×10^{-3}M

c-1: Degradation in dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1400	14.60	51.33
3	5.00	0.2610	3.34	88.87
4	10.00	0.1940	2.48	91.73
5	15.00	0.1760	2.25	92.50
6	20.00	0.1710	2.19	92.70
7	25.00	0.1670	2.14	92.87
8	30.00	0.1660	2.13	92.90

c-2: Degradation in 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1300	14.47	51.77
3	5.00	0.2560	3.28	89.07
4	10.00	0.1920	2.46	91.80
5	15.00	0.1700	2.18	92.73
6	20.00	0.1660	2.13	92.90
7	25.00	0.1620	2.07	93.10
8	30.00	0.1610	2.06	93.13

(d) $[H^+]$:8.26×10^{-3}M

d-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	$[BGY] \times 10^5 M$	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1520	14.75	50.83
3	5.00	0.1710	3.47	88.43
4	10.00	0.1980	2.54	91.53
5	15.00	0.1840	2.36	92.13
6	20.00	0.1800	2.30	92.33
7	25.00	0.1770	2.27	92.43
8	30.00	0.1760	2.25	92.50

d-2: Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	$[BGY] \times 10^5 M$	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1380	14.57	51.43
3	5.00	0.2650	3.39	88.70
4	10.00	0.1920	2.46	91.80
5	15.00	0.1770	2.27	92.43
6	20.00	0.1700	2.18	92.73
7	25.00	0.1660	2.13	92.90
8	30.00	0.1650	2.11	92.97

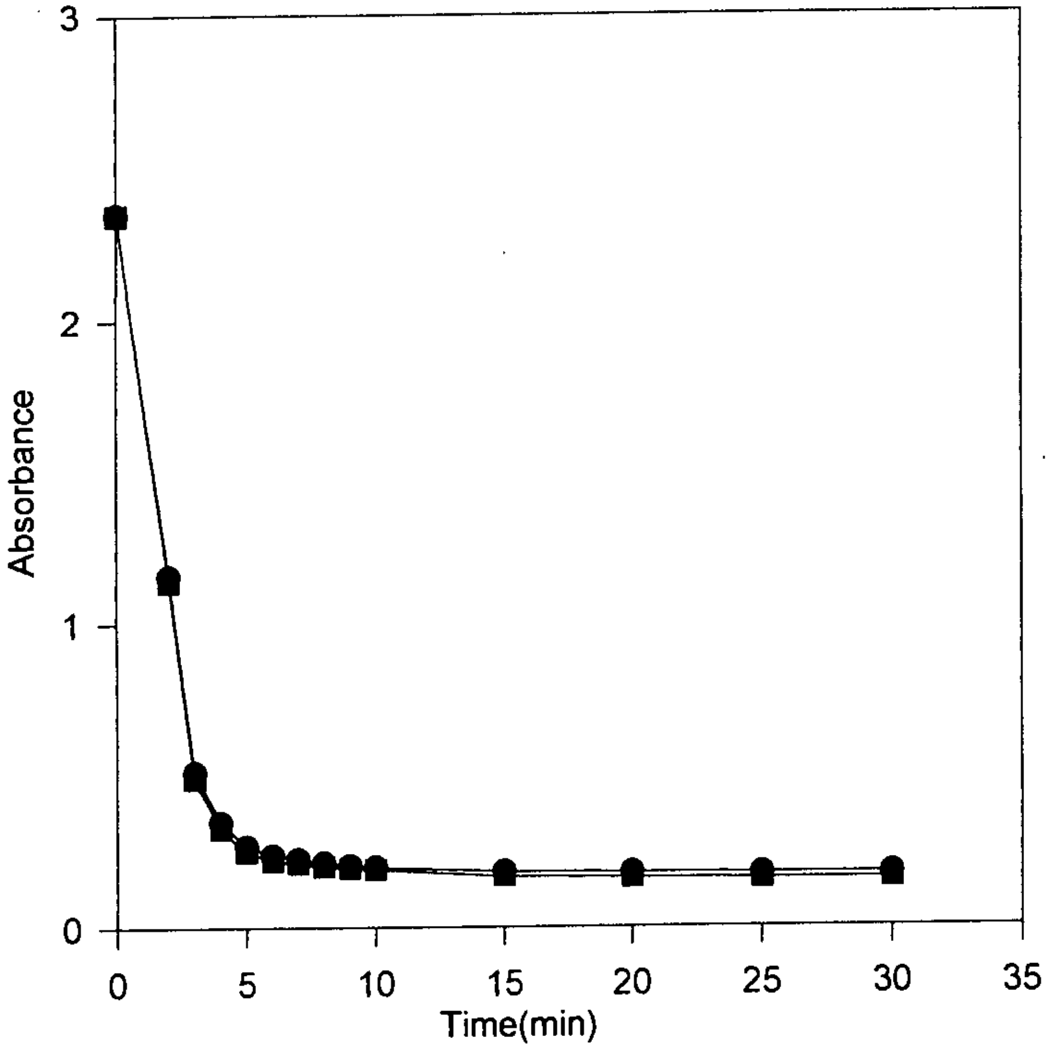


Fig. 3.7. (a) :Effect of $[H^+]$ on the degradation of BGY in dark and at 410 nm light

●○ $[H^+]$=8.26e-3M ■□ $[H^+]$=2.10e-3M

[solid symbol:reaction in dark,open symbl:reaction in visible light]

[BGY]:3.0e-4M,$[Fe_{(III)}]$:4.0e-5M,$[H_2O_2]$:3.0e-3M,Temp.:29.0^{0}C

Temp. : 29.0^{0}C

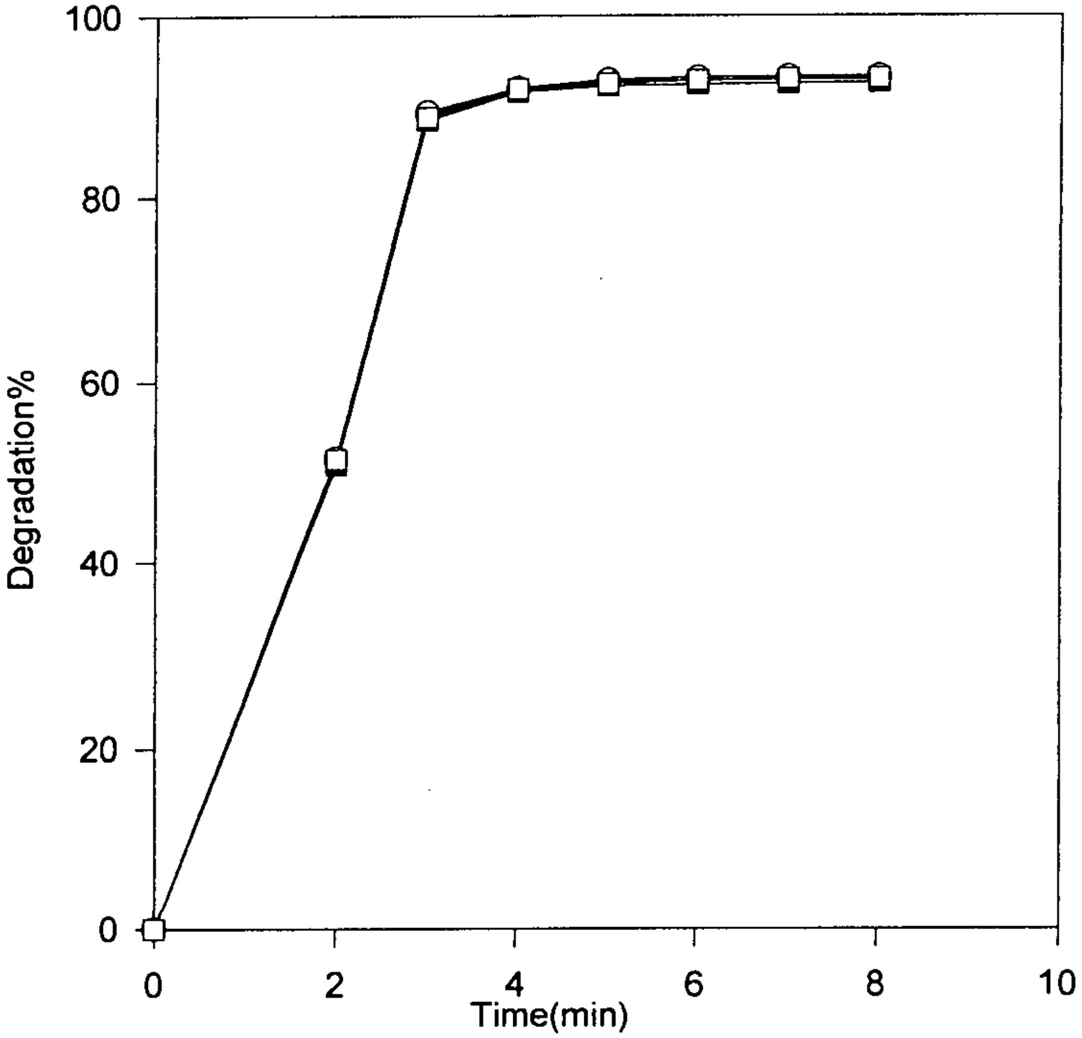


Fig. 3.7. (b) :Effect of [H$^+$] on the degradation of BGY in dark and at 410 nm light

●○ [H$^+$]=8.26e-3M ■□ [H$^+$]=2.10e-3M

[solid symbol:reaction in dark,open symbl:reaction in visible light]

[BGY]:3.0e-4M,[Fe$_{(III)}$]:4.0e-5M,[H_2O_2]:3.0e-3M,Temp.:29.0^{0}C

Temp.. : 29.0^{0}C

3.2.5.4 Effect of BGY concentrations on degradation of BGY.

Table: 3.8 Absorbance and (%) degradation at different time.

Reference : water
[Fe(III)] : 4.00×10^{-5}M
[H_2O_2] : 3.00×10^{-3}M
[H^+] : 4.18×10^{-3}M
λmax of BGY : 415nm
Temperature of the medium : 29.0°C
(a) [BGY] : 1.00×10^{-4}M

a-1 : Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.7810	10.00	00.00
2	02.00	0.3600	4.61	53.90
3	5.00	0.1010	1.29	87.10
4	10.00	0.0800	1.02	89.80
5	15.00	0.0730	0.93	90.70
6	20.00	0.0690	0.88	91.20
7	25.00	0.0680	0.87	91.30
8	30.00	0.0680	0.87	91.30

a-2 : Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.7810	10.00	00.00
2	02.00	0.3350	4.29	57.10
3	5.00	0.0920	1.18	88.20
4	10.00	0.0960	0.88	91.20
5	15.00	0.0580	0.74	92.60
6	20.00	0.0510	0.65	93.50
7	25.00	0.0480	0.61	93.90
8	30.00	0.0470	0.60	94.50

(b) [BGY] :1.75×10^{-4}M

b-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	1.3670	17.50	00.00
2	02.00	0.6800	8.71	50.23
3	5.00	0.1200	1.54	91.20
4	10.00	0.0830	1.06	93.94
5	15.00	0.0760	0.97	94.46
6	20.00	0.0700	0.90	94.86
7	25.00	0.0680	0.87	95.03
8	30.00	0.0670	0.86	95.08

b-2: Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	1.3670	17.50	00.00
2	02.00	0.6550	8.39	52.06
3	5.00	0.1010	1.29	92.63
4	10.00	0.0740	0.95	94.57
5	15.00	0.0670	0.86	95.09
6	20.00	0.0620	0.79	95.49
7	25.00	0.0600	0.77	95.60
8	30.00	0.0590	0.76	95.66

(c) [BGY] :2.25x10^{-4}M

c-1: Degradation in the dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	1.7570	22.50	00.00
2	02.00	0.8760	11.22	50.13
3	5.00	0.1740	2.23	90.09
4	10.00	0.1210	1.55	93.11
5	15.00	0.1100	1.41	93.73
6	20.00	0.1020	1.31	94.18
7	25.00	0.0980	1.25	94.44
8	30.00	0.0970	1.24	94.45

c-2: Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	1.7570	22.50	00.00
2	02.00	0.8520	10.91	51.51
3	5.00	0.1630	2.09	90.71
4	10.00	0.1140	1.46	93.51
5	15.00	0.1030	1.32	94.13
6	20.00	0.0960	1.23	94.53
7	25.00	0.0940	1.20	94.67
8	30.00	0.0920	1.18	94.76

(d) [BGY] : 3.00×10^{-4}M

d-1: Degradation in dark

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1560	14.80	50.67
3	5.00	0.2700	3.46	88.47
4	10.00	0.1960	2.51	91.63
5	15.00	0.1830	2.34	92.20
6	20.00	0.1790	2.29	92.37
7	25.00	0.1760	2.25	92.50
8	30.00	0.1750	2.24	92.53

d-2: Degradation in the 410 nm light

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	2.3430	30.00	00.00
2	02.00	1.1010	14.10	53.00
3	5.00	0.2360	3.02	89.93
4	10.00	0.1800	2.30	92.33
5	15.00	0.1680	2.15	92.83
6	20.00	0.1620	2.07	93.10
7	25.00	0.1600	2.05	93.17
8	30.00	0.1590	2.04	93.20

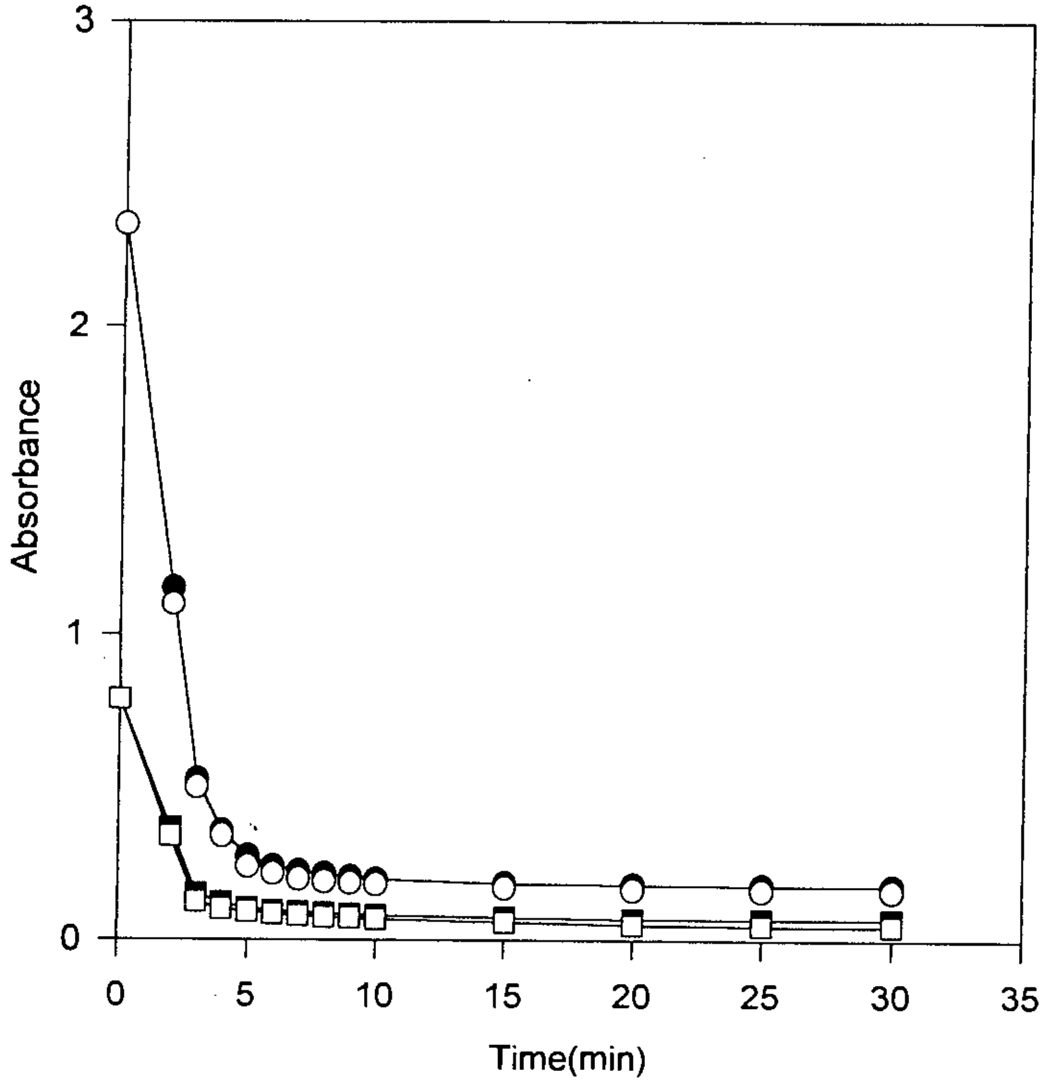


Fig. 3.8. (a) : Effect of [BGY] on the degradation of BGY in dark and at 410 nm light
[Fe$_{(III)}$]=4.0e-5M,[H_2O_2]=3.0e-3M,[H^+]=4.18e-3M,Temperature=29.0^{0}C
●○ 3.0e-5M ■□ 1.0e-5M
[solid symbol:reaction in dark,open symbol:reaction in visible light]

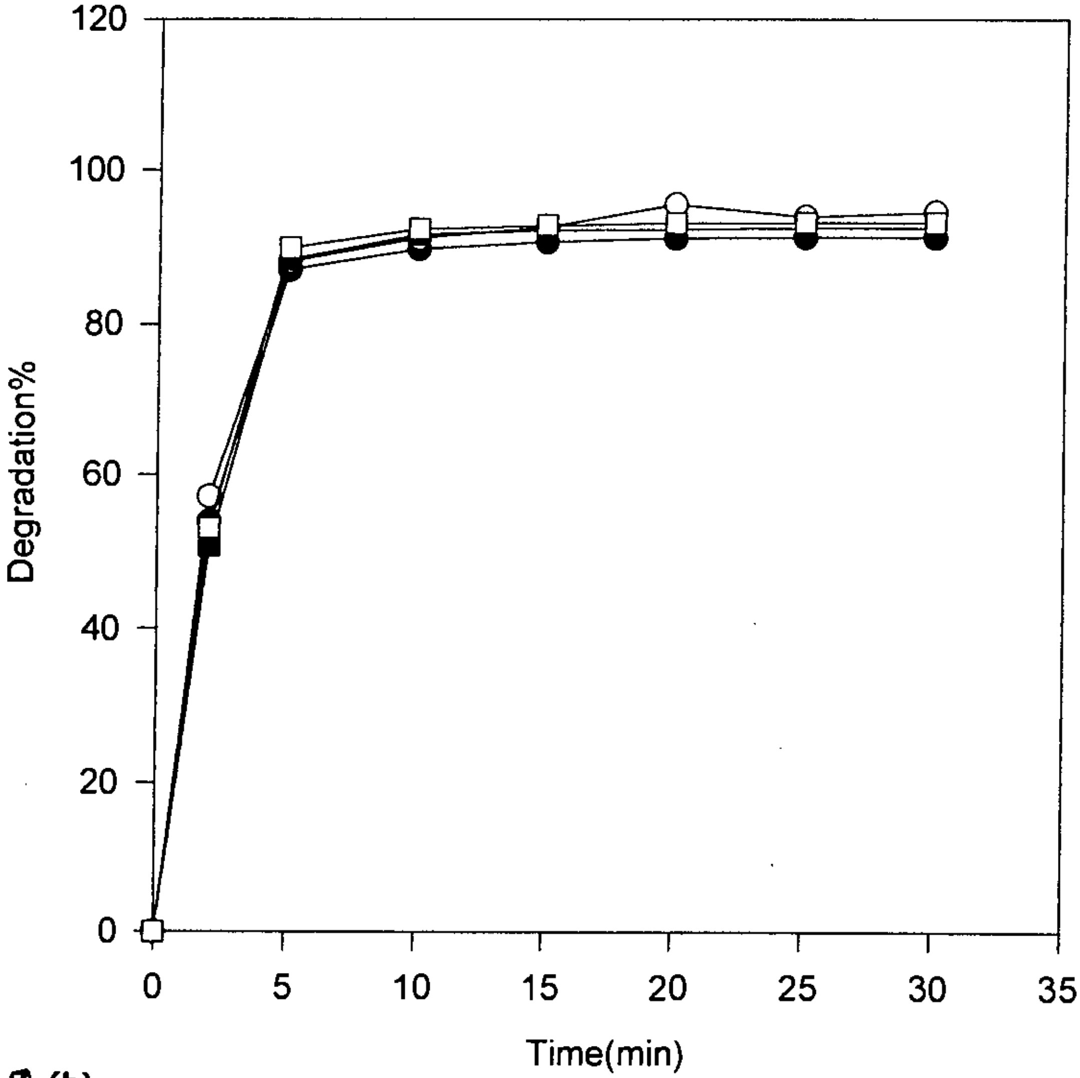


Fig. 3.8. (b) : Effect of [BGY] on the degradation of BGY in dark and at 410 nm light
$[Fe_{(III)}]=4.0e-5M, [H_2O_2]=3.0e-3M, [H^+]=4.18e-3M$, Temperature=29.0°C
●○ 3.0e-5M ■□ 1.0e-5M
[solid symbol:reaction in dark,open symbol:reaction in visible light]

CHAPTER 4

STUDIES ON BRILLIANT GOLDEN YELLOW (BGY) IN THE PRESENCE OF TiO_2

4.1.0 Experimental

4.1.1 Spectrum of Brilliant Golden Yellow (BGY) in the aqueous solution.

All the procedures were the same as those described in chapter 3.

4.1.2 Photodegradation of BGY in the absence of TiO_2

Table 4.1 : Photodegradation of BGY at different time inter vals.

Reference	: Water
Source emitting radiation	: 320 nm
Volume of solution irradiated.	: 50.0 ml
λ_{max} of BGY	: 415nm
Initial pH of the medium	: 6.20
[BGY]	: 2.33 x 10^{-4}M

Run No	Time of photolysis (min)	Absorbance	[BGY]× 10^{4} M	Degradaton of BGY (%)
1	0	1.822	2.33	0.00
2	10	1.822	2.33	0.00
3	20	1.821	2.33	0.00
4	30	1.820	2.33	0.00
5	40	1.819	2.33	0.00
6	50	1.818	2.32	0.00
7	60	1.818	2.32	0.00

4.1.3 Effect of different light sources on the photodegradation of BGY in the presence of TiO_2

Table 4.2 : Photodegradation of BGY with different light sources in the presence of TiO_2

Reference : Water

Amount of TiO_2 : 4.5×10^{-3}g

Volume of solution irradiated : 50.0 ml

λ_{max} of BGY : 415nm

Initial pH of the medium : 6.20

[BGY] : 2.57×10^{-5} M

(a) Source emitting radiation : 320 nm

Intensity : $(3.64 \pm 0.03) \times 10^{-9}$ Ein. s^{-1} cm^{-3}

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.007	2.57	0.00
2	15.00	1.525	1.95	41.28
3	30.00	1.214	1.40	55.75
4	45.00	0.934	1.09	67.95
5	60.00	0.723	0.83	76.12
6	75.00	0.574	0.66	83.42
7	90.00	0.434	0.50	90.76

(b) Source emitting radiation : 410 nm

Intensity : $(4.08 \pm 0.03) \times 10^{-9}$ Ein. s^{-1} cm^{-3}

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	2.070	2.38	0.00
2	15.00	2.006	2.31	2.94
3	30.00	1.919	2.21	7.14
4	45.00	1.849	2.13	10.50
5	60.00	1.771	2.04	14.29
6	75.00	1.702	1.96	17.65
7	90.00	1.632	1.88	21.01

4.1.4 Effect of amount of TiO_2 on the photodegradation of BGY.

Table 4.3 : Photodegradation of BGY in the presence of different amount of TiO_2

Reference	: Water
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
Initial pH of the medium	: 6.20
Source emitting radiation	320 nm
[BGY]	: 7.08×10^{-5}M
(a) Amount of TiO_2	: 1.00×10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3630	4.65	34.32
3	20.00	0.2910	3.73	47.32
4	30.00	0.2430	3.11	56.07
5	40.00	0.1980	2.54	64.12
6	50.00	0.1650	2.11	70.20
7	60.00	0.1290	1.65	76.70
8	70.00	0.1060	1.36	80.80
9	80.00	0.0750	0.96	86.44
10	90.00	0.0500	0.64	90.96

b) Amount of TiO_2 : : 2.50×10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3490	4.47	36.86
3	20.00	0.2810	3.60	49.15
4	30.00	0.2340	3.00	57.63
5	40.00	0.1900	2.43	65.68
6	50.00	0.1570	2.01	71.61
7	60.00	0.1220	1.56	77.97
8	70.00	0.1000	1.28	81.92
9	80.00	0.0690	0.88	87.57
10	90.00	0.0420	0.53	92.51

c) Amount of TiO_2 : : 3.50×10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.8	0.00
2	10.00	0.3350	4.29	39.41
3	20.00	0.2710	3.47	50.99
4	30.00	0.2250	2.90	59.04
5	40.00	0.1820	2.33	67.10
6	50.00	0.1490	1.91	73.02
7	60.00	0.1150	1.47	79.24
8	70.00	0.0940	1.20	83.05
9	80.00	0.0630	0.81	88.56
10	90.00	0.0290	0.37	94.77

d) Amount of TiO_2 : **: 4.50×10^{-3}g**

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3210	4.11	41.95
3	20.00	0.2300	2.95	58.33
4	30.00	0.1740	2.23	68.50
5	40.00	0.1410	1.81	74.44
6	50.00	0.1080	1.38	80.51
7	60.00	0.0800	1.02	85.60
8	70.00	0.0510	0.65	90.82
9	80.00	0.0210	0.27	96.19
10	90.00	0.0050	0.06	99.15

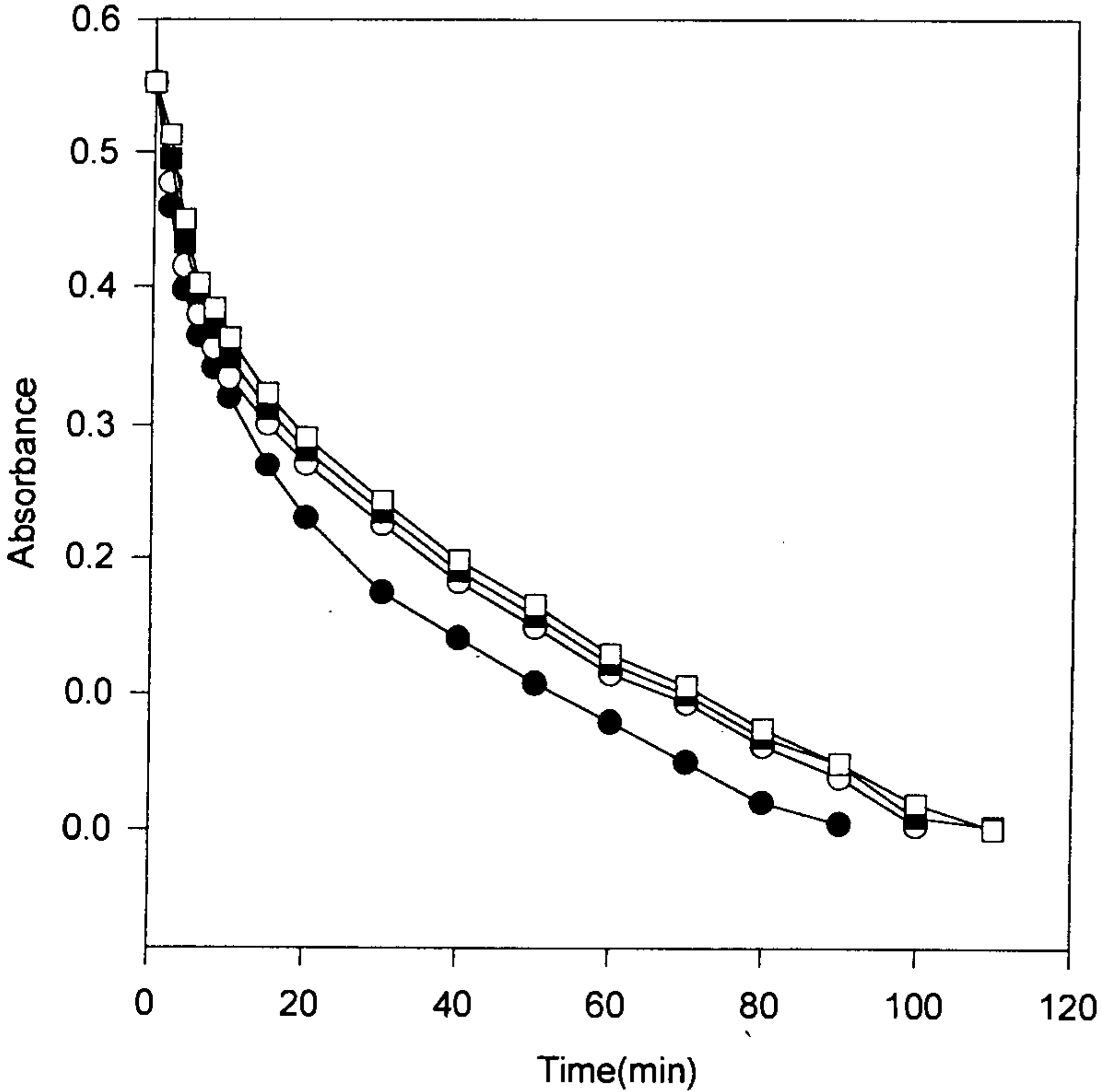


Fig. 4.1 (a). :Effect of the amount of TiO_2 on the photodegradation of BGY

● 4.5e-3g ○ 3.5e-3g ■ 2.5e-3g □ 1.0e-3g

[BGY]=7.1e-5M pH:6.20

Temp. : 29.0°C

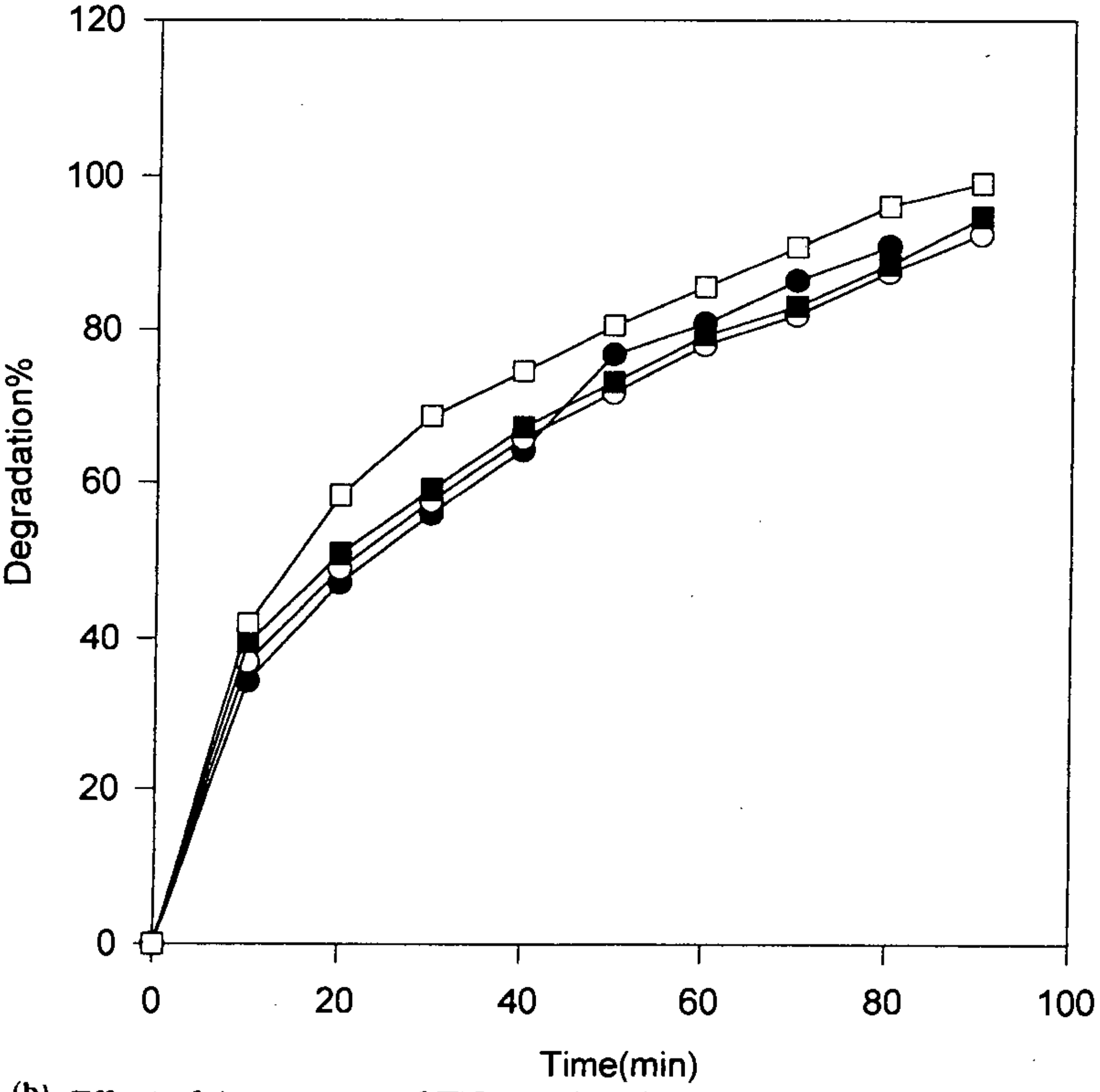


Fig. 4.1 (b). Effect of the amount of TiO_2 on the photodegradation of BGYat 320nm
1.0e-3g ○ 2.5e-3g ■ 3.5e-3g □ 4.5e-3g[BGY]=7.1e-5M

4.1.5 Effect of different initial pH of the medium on the photodegradation of BGY in the presence of TiO_2

Table 4.4 : Photodegradation of BGY in the presence of TiO_2 at different initial pH of the medium.

Reference	: Water
Amount of TiO_2	: 2.50×10^{-3}g
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
Source emitting radiation	: 3.75 nm
[BGY]	: 7.08×10^{-5}M
(a) pH of the medium	: 2.50

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3280	4.20	40.68
3	20.00	0.2660	3.41	51.84
4	30.00	0.2190	2.80	60.45
5	40.00	0.1770	2.27	67.94
6	50.00	0.1450	1.86	73.73
7	60.00	0.1100	1.41	80.08
8	70.00	0.0870	1.11	84.32
9	80.00	0.0530	0.68	90.40
10	90.00	0.0360	0.46	93.50

(b) pH of the medium : 3.75

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3230	40.14	41.53
3	20.00	0.2610	3.34	52.82
4	30.00	0.2140	2.74	61.30
5	40.00	0.1720	2.20	68.97
6	50.00	0.1410	1.81	74.44
7	60.00	0.1060	1.36	80.80
8	70.00	0.0830	1.06	85.03
9	80.00	0.0500	0.64	90.96
10	90.00	0.0330	0.42	94.07

(c) pH of the medium : 5.00

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3380	4.33	38.84
3	20.00	0.2730	3.50	50.56
4	30.00	0.2260	2.90	59.04
5	40.00	0.1830	2.34	66.95
6	50.00	0.1510	1.93	72.74
7	60.00	0.1160	1.48	79.10
8	70.00	0.0930	1.19	83.19
9	80.00	0.0620	0.79	88.84
10	90.00	0.0420	0.54	92.37

(d) pH of the medium : 6.20

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3530	4.52	36.16
3	20.00	0.2850	3.65	48.45
4	30.00	0.2380	3.05	56.92
5	40.00	0.1940	2.48	64.97
6	50.00	0.1610	2.06	70.90
7	60.00	0.1260	1.61	77.26
8	70.00	0.1030	1.32	81.36
9	80.00	0.0730	0.93	86.86
10	90.00	0.0530	0.68	90.40

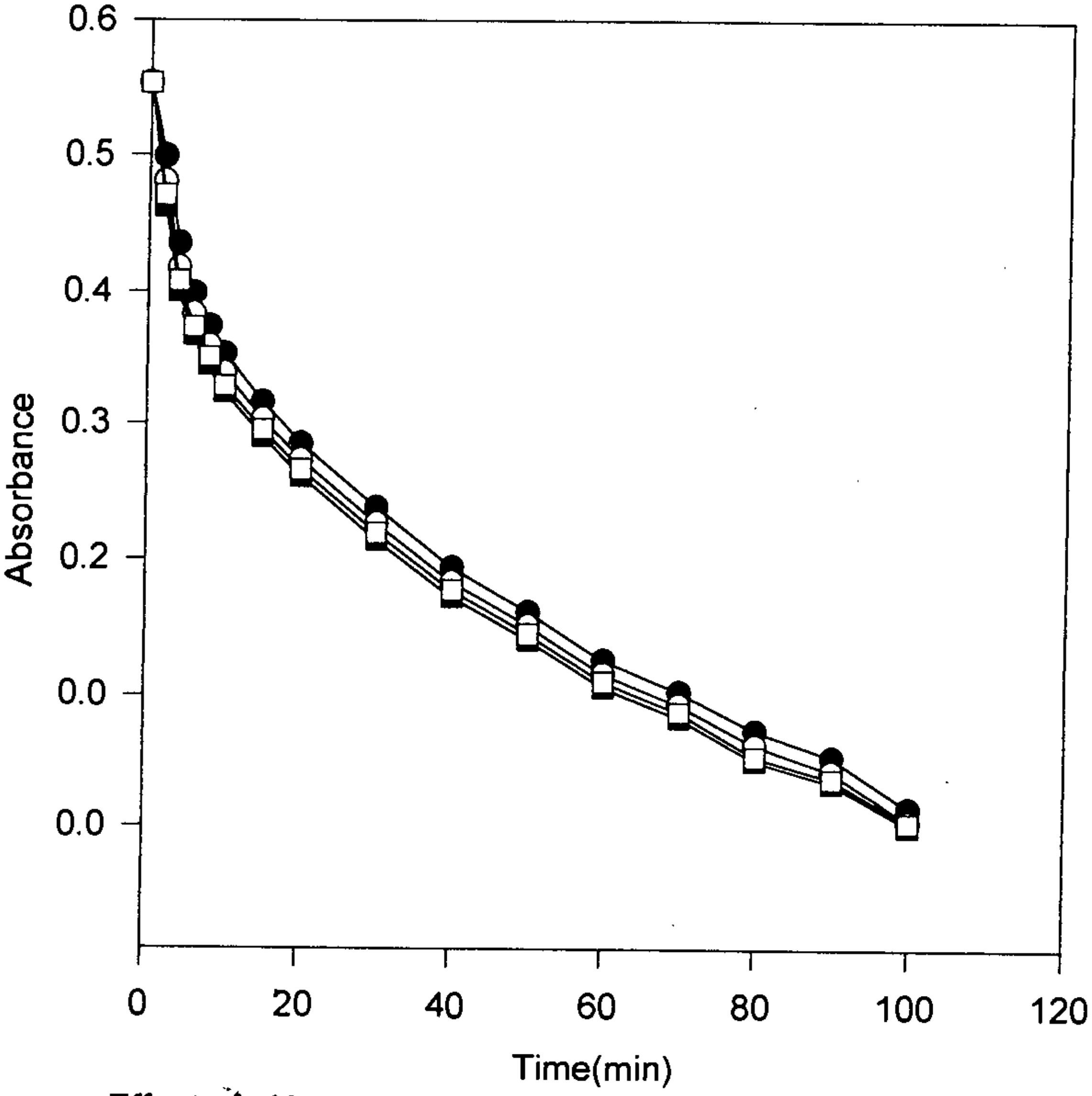


Fig. 4.2 (a). :Effect of pH on the photodegradation of BGY in the presence of TiO_2

● pH:6.20 ○ pH:5.0 ■ pH:3.75 □ pH:2.50

[BGY]=7.10e-5M TiO_2:2.50e-3g

Temp. : 29.0^{0}C

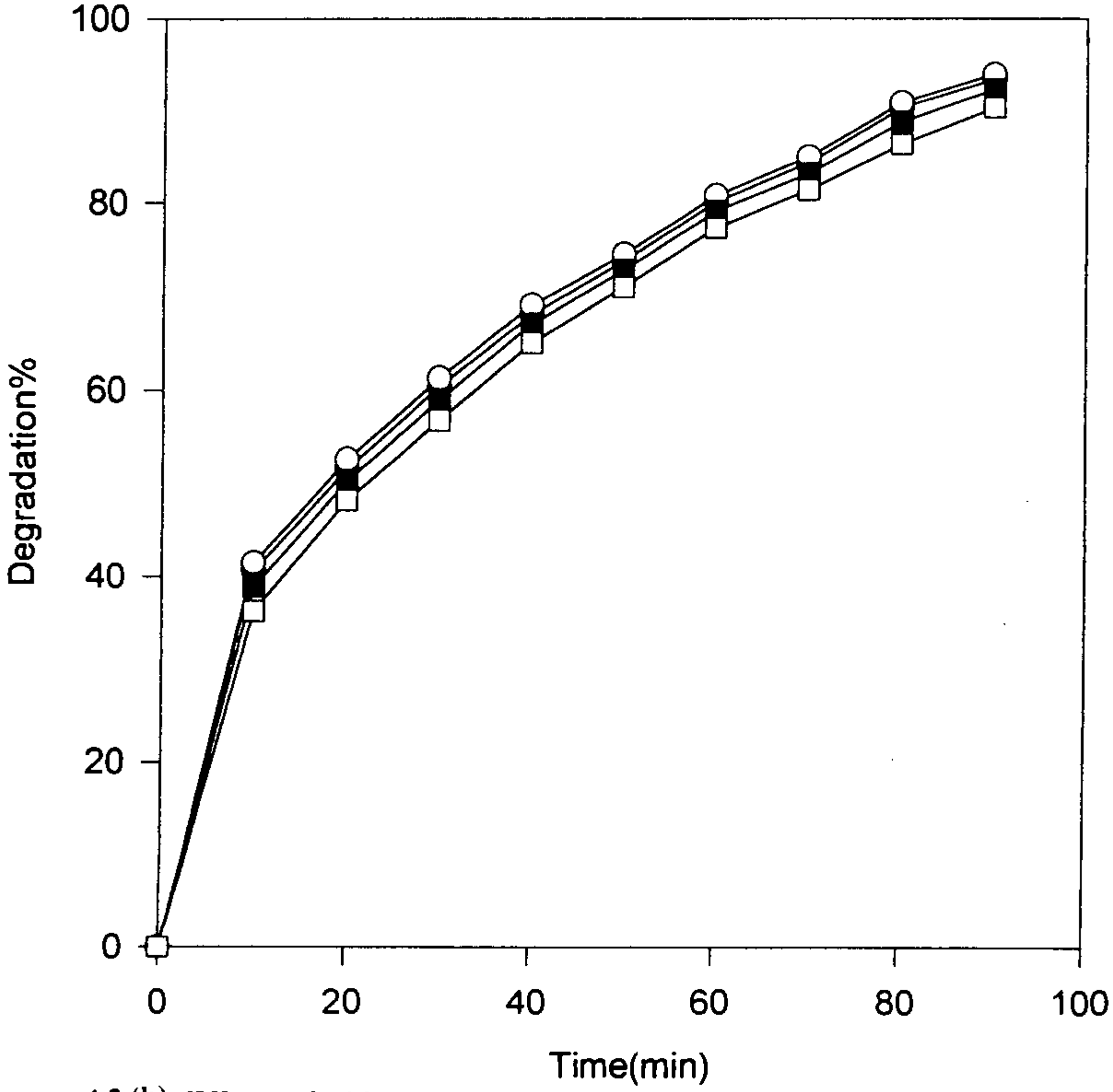


Fig. 4.2 (b):Effect of pH on the photodegradation of BGY in presence of TiO_2

pH=6.20 ○ pH=5.0 ■ pH=3.75 □ pH=2.50[BGY]=7.10e-5M

Temp. : 29.0°C

4.1.6 Effect of different initial concs. of BGY on the Photodegradation in the presence of TiO_2

Table 4.5 : Photodegradation of BGY in the presence of TiO_2 at different time intervals

Reference	: Water
Amount of TiO_2	: 2.50×10^{-3}g
Source emitting radiation	: 320 nm
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
pH of the medium	: 6.20
(a) [BGY]	: 5.16×10^{-5}M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.4030	5.16	0.00
2	10.00	0.2530	3.24	37.21
3	20.00	0.2060	2.64	48.84
4	30.00	0.1720	2.20	57.36
5	40.00	0.1310	1.68	67.44
6	50.00	0.1000	1.28	75.19
7	60.00	0.0730	0.93	81.98
8	70.00	0.0470	0.60	88.37
9	80.00	0.0290	0.37	92.83
10	90.00	0.0120	0.15	97.10

(b) [BGY] : 7.08×10^{-5}M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.5530	7.08	0.00
2	10.00	0.3490	4.47	36.86
3	20.00	0.2810	3.60	49.15
4	30.00	0.2340	3.00	57.63
5	40.00	0.1900	2.43	65.68
6	50.00	0.1570	2.10	70.34
7	60.00	0.1220	1.56	77.97
8	70.00	0.1000	1.28	81.92
9	80.00	0.0690	1.88	87.57
10	90.00	0.0500	0.64	90.96

(c) [BGY] : 8.50 x 10^{-5} M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.6640	8.50	0.00
2	10.00	0.4300	5.51	35.18
3	20.00	0.3620	4.64	45.41
4	30.00	0.3120	4.00	52.94
5	40.00	0.2710	3.47	59.18
6	50.00	0.2330	2.98	64.94
7	60.00	0.2000	2.56	69.88
8	70.00	0.1710	2.19	74.23
9	80.00	0.1440	1.83	78.47
10	90.00	0.1170	1.50	82.35

(d) [BGY] : 9.90 x 10^{-5} M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.7740	9.91	0.00
2	10.00	0.5200	6.66	32.80
3	20.00	0.4290	5.50	44.50
4	30.00	0.3790	4.85	51.06
5	40.00	0.3400	4.35	56.10
6	50.00	0.2980	3.82	61.45
7	60.00	0.2690	3.44	65.29
8	70.00	0.2300	2.94	70.33
9	80.00	0.2040	2.61	73.66
10	90.00	0.1790	2.29	77.00

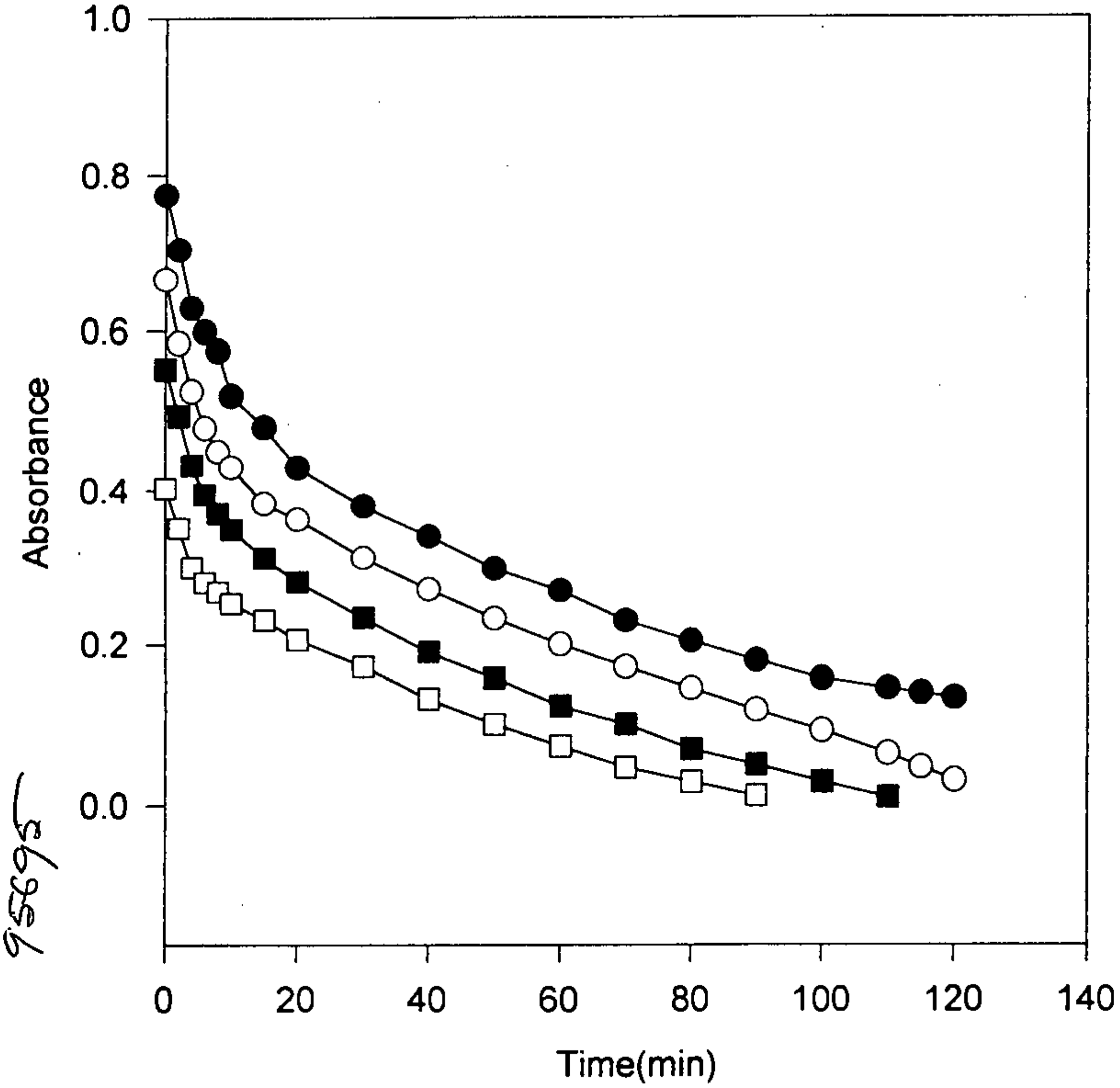


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Fig. 4.3 (a). :Photodegradation of BGY in presence of TiO$_2$(2.50e-3g)

● 9.9e-5M ○ 8.5e-5M ■ 7.08e-5M □ 5.16e-5M pH:6.20

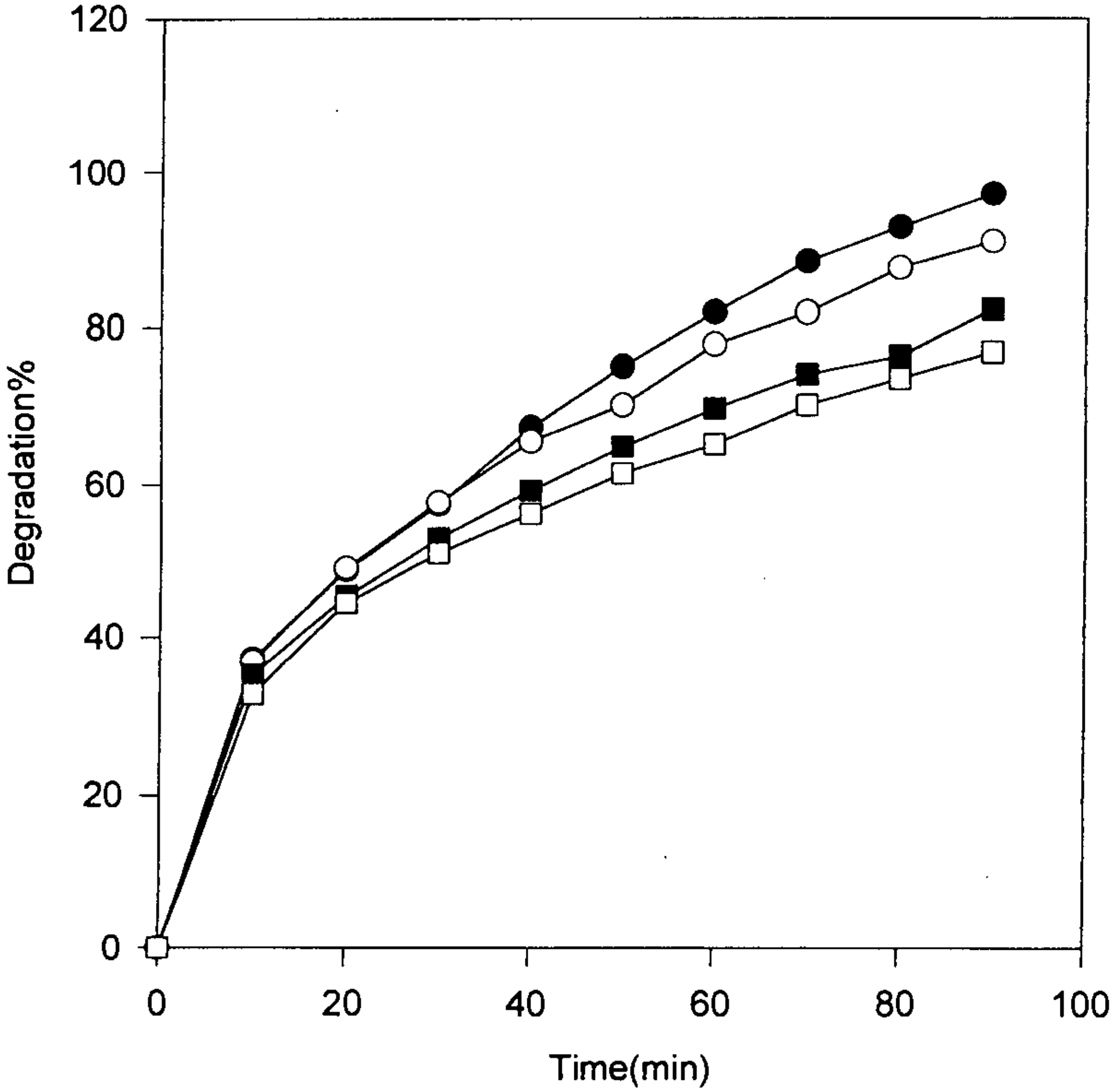
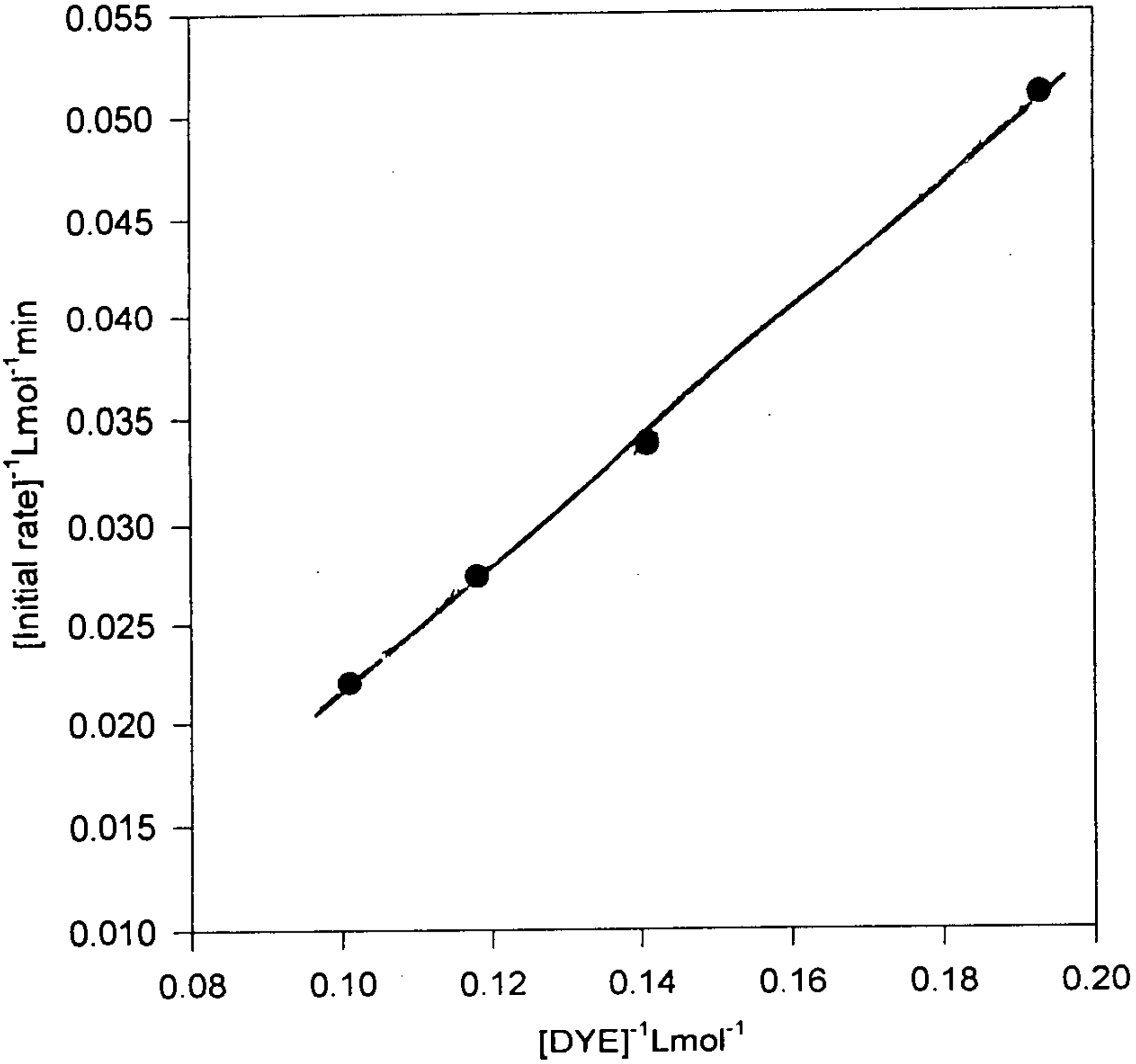


Fig. 4.3 (b). : Photodegradation of BGY in presence of TiO_2

● 5.16e-5M ○ 7.08e-5M ■ 8.5e-5M □ 9.9e-5M



Fog- 4.4 [DYE]$^{-1}$[Initial rate]$^{-1}$plot for BGY in the presence of TiO_2

CHAPTER 5

STUDIES ON BRILLIANT GOLDEN YELLOW (BGY) IN THE PRESENCE OF ZnO

5.1.0 Experimental

5.1.1 Spectrum of Brilliant Golden Yellow (BGY) in the aqueous solution.

All the procedures were the same as those described in chapter 3.

5.1.2 Photodegradation of BGY in the absence of ZnO

Table 5.1 : Photodegradation of BGY at different time inter vals.

Reference	: Water
Source emitting radiation	: 320 nm
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
Initial pH of the medium	: 6.20

Run No	Time of photolysis (min)	Absorbance	$[BGY] \times 10^4$ M	Degradaton of BGY (%)
1	0	1.92	2.46	0.00
2	10	1.92	2.46	0.00
3	20	1.92	2.46	0.00
4	30	1.91	2.44	0.00
5	40	1.90	2.43	0.00
6	50	1.90	2.43	0.00
7	60	1.89	2.42	0.00

5.1.3 Effect of amount of ZnO on the photodegradation of BGY.

Table 5.2 : Photodegradation of BGY in the presence of different amount of ZnO

Reference	: Water
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
Initial pH of the medium	: 6.20
Source emitting radiation	320 nm
[BGY]	: 11.06 x 10^{-5}M
(a) Amount of ZnO	: 2.50 × 10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.4090	5.24	52.90
3	20.00	0.2410	3.09	72.06
4	30.00	0.1350	1.73	84.36
5	40.00	0.0490	0.63	94.30
6	50.00	0.0270	0.34	96.93
7	60.00	0.0120	0.15	98.64

b) Amount of ZnO : : 5.00 x 10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^{5}M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3970	5.08	54.07
3	20.00	0.2350	3.01	72.65
4	30.00	0.1300	1.66	85.00
5	40.00	0.0440	0.56	94.94
6	50.00	0.0230	0.29	97.38
7	60.00	0.0080	0.10	99.10

c) Amount of ZnO : : 7.5 x 10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3850	4.93	55.42
3	20.00	0.2290	2.93	73.51
4	30.00	0.1250	1.60	85.53
5	40.00	0.0390	0.50	95.48
6	50.00	0.0190	0.24	97.83
7	60.00	0.0040	0.05	99.55

d) Amount of ZnO : : 10.0 x 10^{-3}g

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3730	4.78	56.78
3	20.00	0.2230	2.86	74.14
4	30.00	0.1200	1.54	86.8
5	40.00	0.0430	0.55	95.03
6	50.00	0.0150	0.19	98.28
7	60.00	0.0040	0.05	99.55

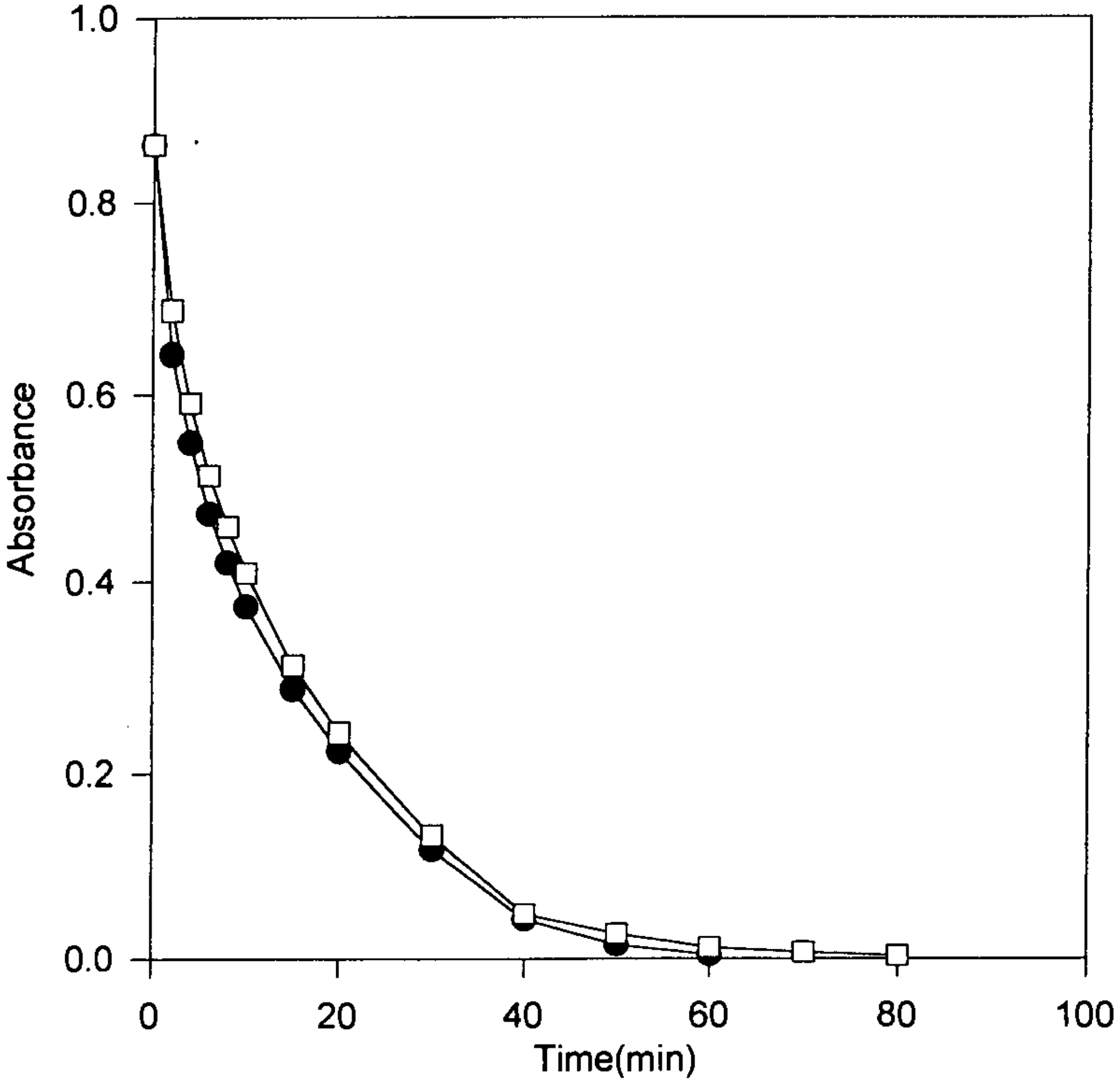


Fig. 5.1 (a). Effect of the amount of ZnO on the photodegradation of BGY

● 10.0e-3g ☐ 2.5e-3g [BGY:11.1e-5M pH:6.20

Temp. : 29.0^{0}C

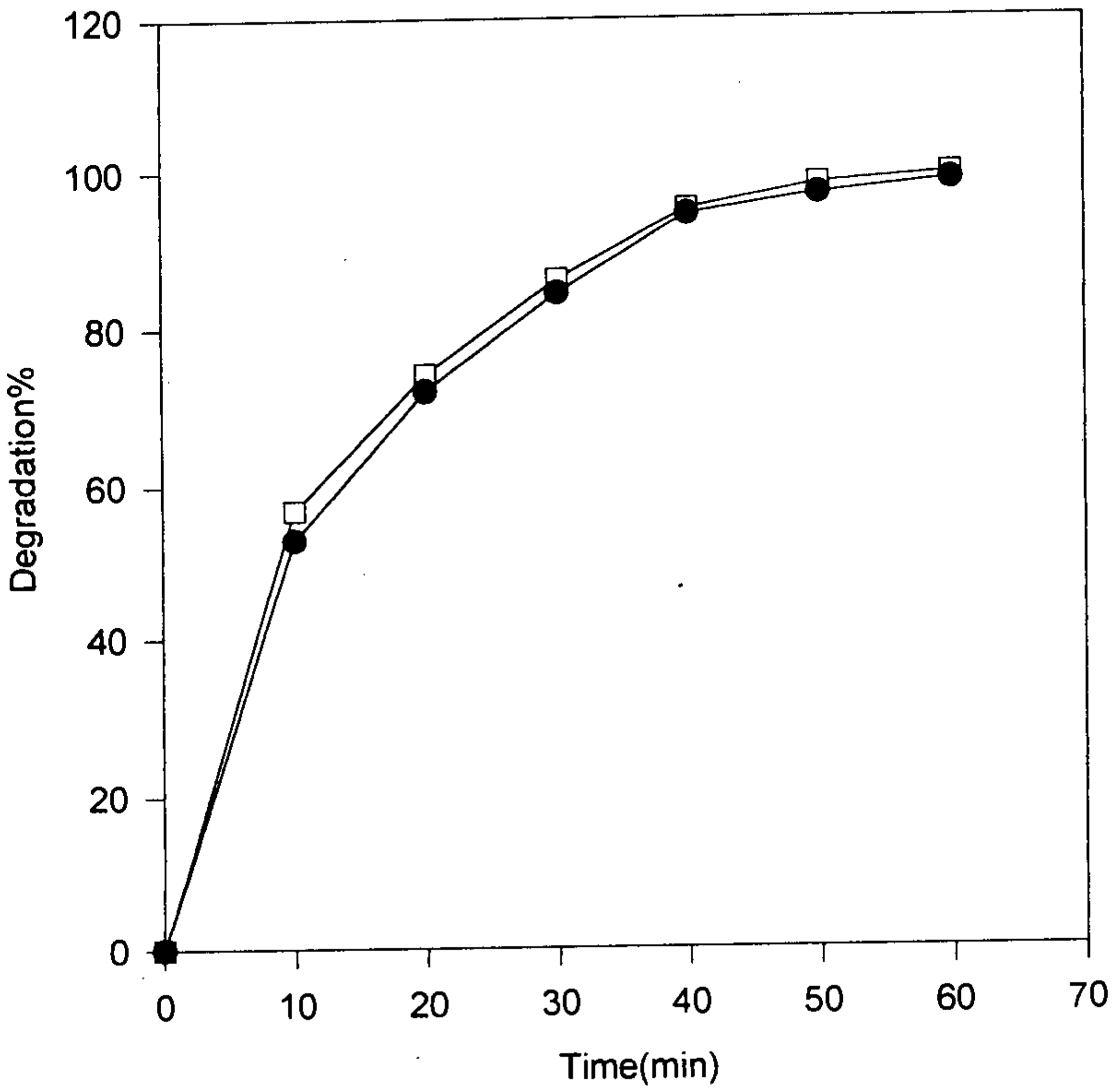


Fig. 5.1 (b).: Effect of the amount of ZnO on the photodegradation of BGY

● 10.0e-3g □ 2.50e-3g [BGY]=11.1e-5M pH:6.20

Temp. : 29.0^{0}C

5.1.4 Effect of different initial pH of the medium on the photodegradation of BGY in the presence of ZnO

Table 5.3 : Photodegradation of BGY in the presence of ZnO at different initial pH of the medium.

Reference	: Water
Amount of ZnO	: 1.00×10^{-2}g
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
Source emitting radiation	: 320 nm
[BGY]	: 11.06×10^{-5}M

(a) pH of the medium : 2.50

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3560	4.56	58.77
3	20.00	0.2770	3.55	67.90
4	30.00	0.2170	2.78	74.86
5	40.00	0.1150	1.47	86.71
6	50.00	0.0360	0.46	95.84
7	60.00	0.0040	0.06	99.46

(b) pH of the medium : 3.75

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3530	4.52	59.13
3	20.00	0.2740	3.51	68.26
4	30.00	0.2140	2.74	75.23
5	40.00	0.1130	1.45	86.89
6	50.00	0.0340	0.44	96.02
7	60.00	0.0030	0.04	99.64

(c) pH of the medium : 5.00

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3620	4.64	58.05
3	20.00	0.2790	3.57	67.72
4	30.00	0.2180	2.79	74.77
5	40.00	0.1160	1.49	86.53
6	50.00	0.0380	0.49	95.57
7	60.00	0.0020	0.03	99.73

(d) pH of the medium : 6.20

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3730	4.78	56.78
3	20.00	0.2860	3.66	66.91
4	30.00	0.2230	2.86	74.14
5	40.00	0.1200	1.54	86.08
6	50.00	0.0430	0.55	95.03
7	60.00	0.0080	0.10	99.10

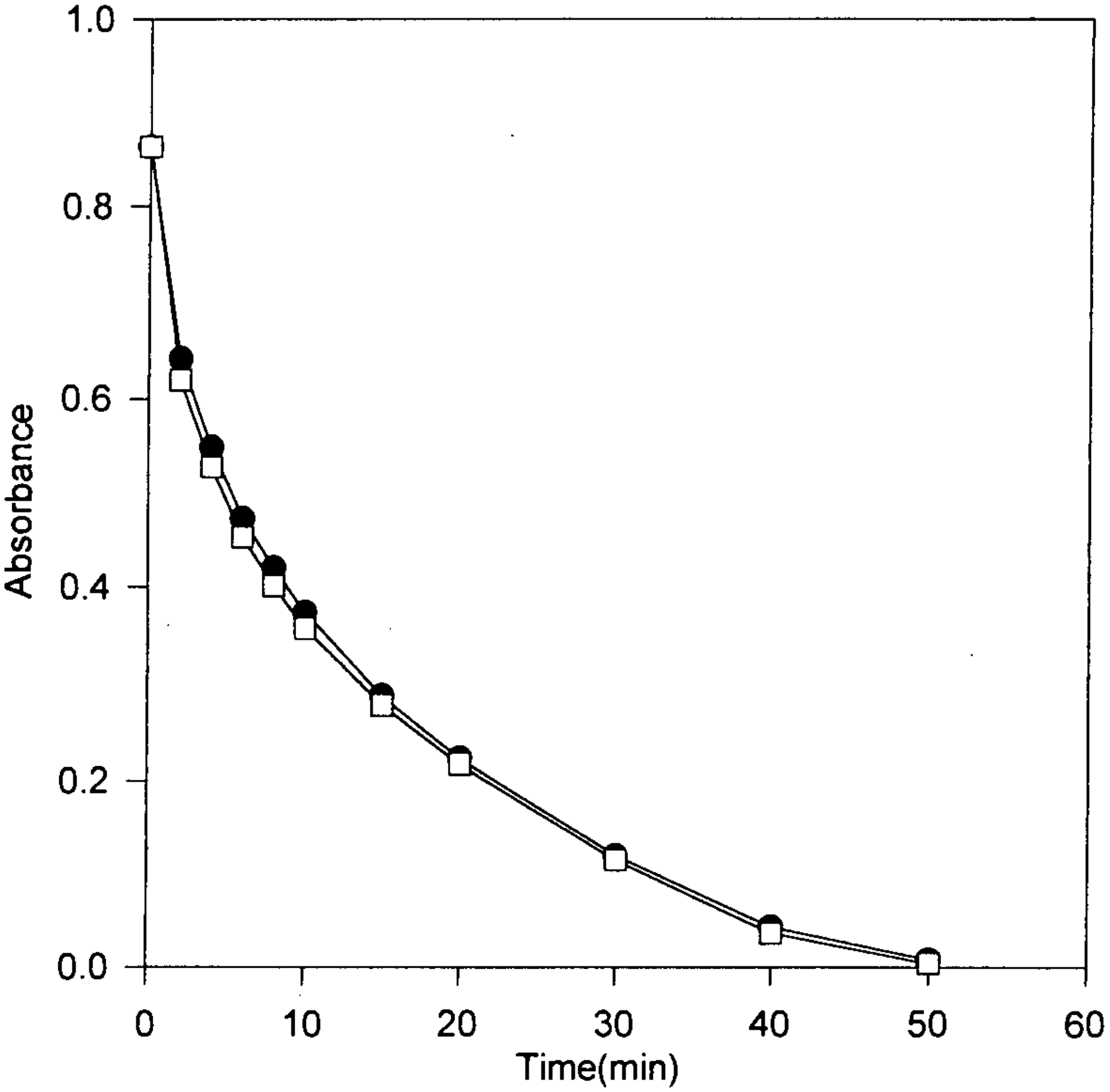


Fig. 5.2 (a).: Effect of pH on the photodegradation of BGY in presence of ZnO

● pH-6.20 □ pH-2.5 [BGY]:11.1e-5M ZnO:1.0e-2g

Temp. : 29.0^{0}C

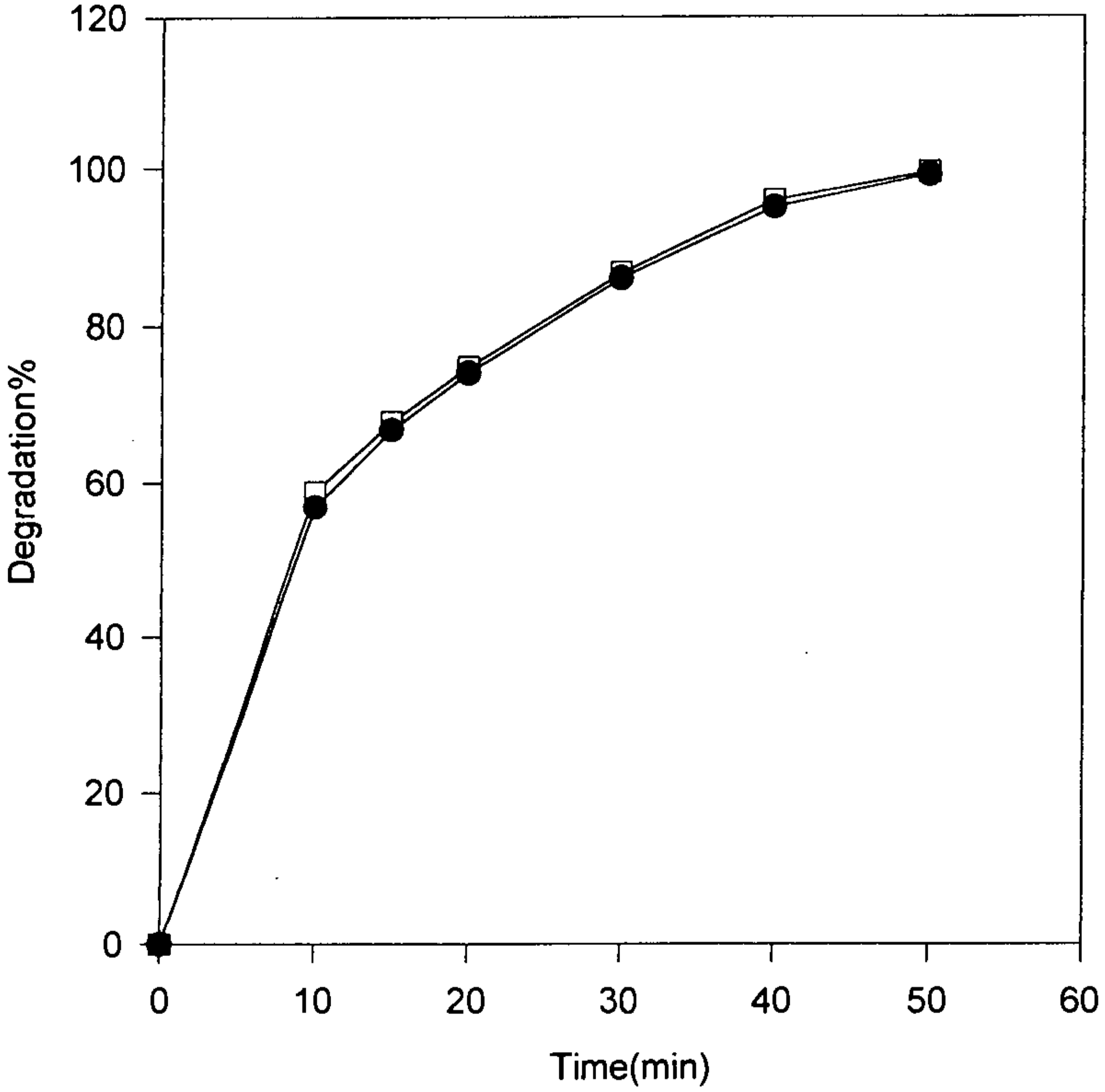


Fig. 5.2 (b).: Effect of pH on the photodegradation of BGY in presence of ZnO

● pH :6.20 □ pH:2.50 [BGY]=11.1e-5M ZnO:1.0e-2g

Temp. : 29.0^{0}C

5.1.5 Effect of different initial concs. of BGY on the Photodegradation in the presence of ZnO

Table 5.4 : Photodegradation of BGY in the presence of ZnO at different time intervals

Reference	: Water
Amount of ZnO	: 1.00×10^{-2}g
Source emitting radiation	: 320 nm
Volume of solution irradiated	: 50.0 ml
λ_{max} of BGY	: 415nm
pH of the medium	: 6.20
(a) [BGY]	: 7.82×10^{-5}M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.6100	7.82	0.00
2	10.00	0.1960	2.51	67.90
3	15.00	0.1280	1.64	79.03
4	20.00	0.0800	1.02	86.96
5	30.00	0.0030	0.04	99.49
6	40.00	0.0000	0.00	100.00

(b) [BGY] : 9.76×10^{-5}M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.7550	9.67	0.00
2	10.00	0.2810	3.60	62.77
3	15.00	0.2020	2.59	73.22
4	20.00	0.1470	1.88	80.56
5	30.00	0.0540	0.69	92.86
6	40.00	0.0020	0.03	99.69

(c) [BGY] : 11.10×10^{-5} M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.8640	11.06	0.00
2	10.00	0.3730	4.78	56.78
3	15.00	0.2860	3.66	66.91
4	20.00	0.2230	2.86	74.14
5	30.00	0.1200	1.54	86.08
6	40.00	0.0430	1.55	95.03

(d) [BGY] : 12.30×10^{-5} M

Run No	Time of Photolysis (min)	Absorbance	[BGY] x 10^5M	Degradation of BGY (%)
1	00.00	0.9630	12.33	0.00
2	10.00	0.5090	6.52	47.12
3	15.00	0.4010	5.13	58.39
4	20.00	0.3540	4.53	63.26
5	30.00	0.2480	3.18	74.21
6	40.00	0.1600	2.05	83.37

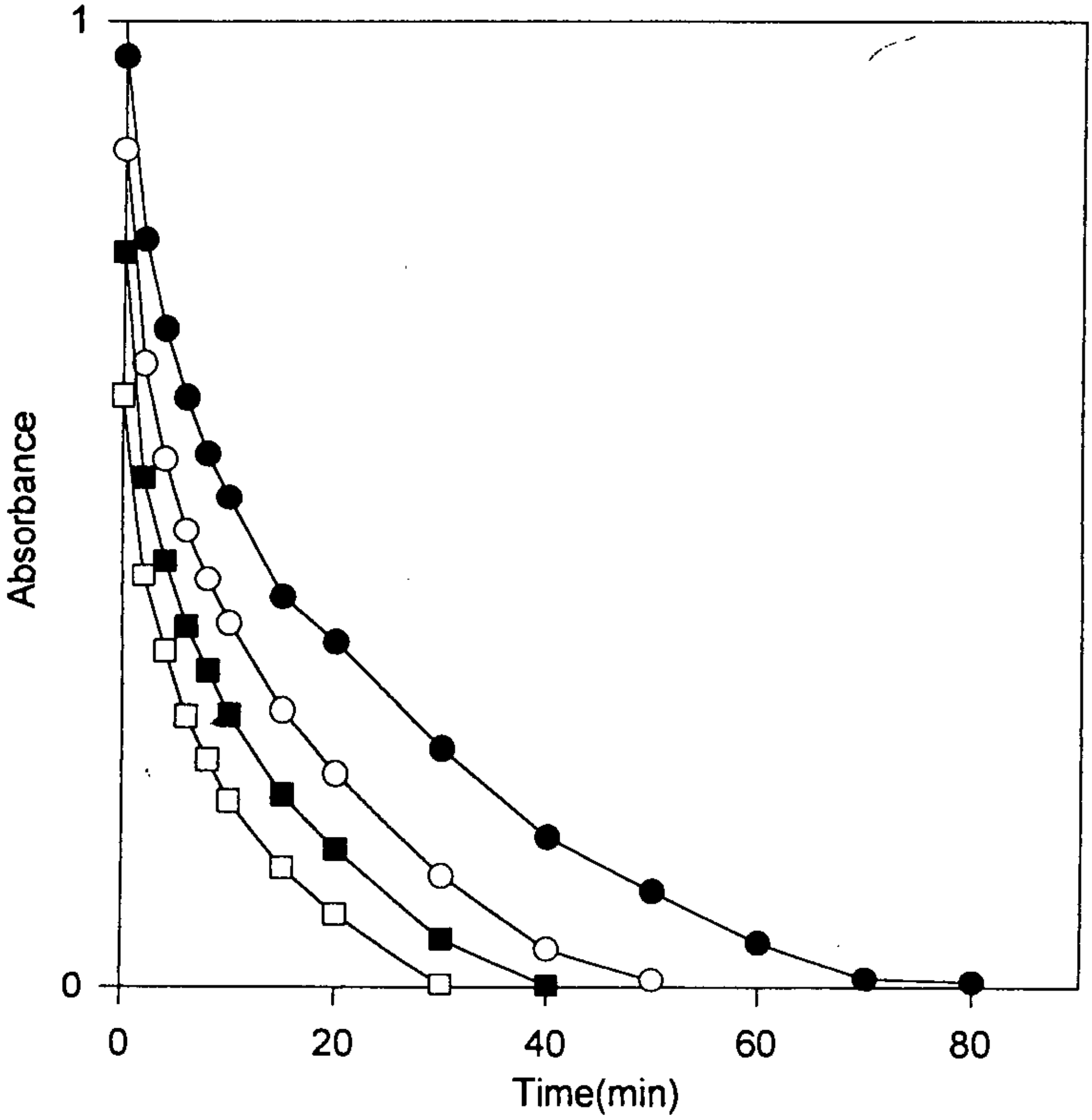


Fig. 5.3 (a). : Photodegradation of BGY in presence of ZnO(1.0e-2g)

● 12.3e-5M ○ 11.1e-5M ■ 9.67e-5M □ 7.82e-5M

Temp. : 29.0^{0}C

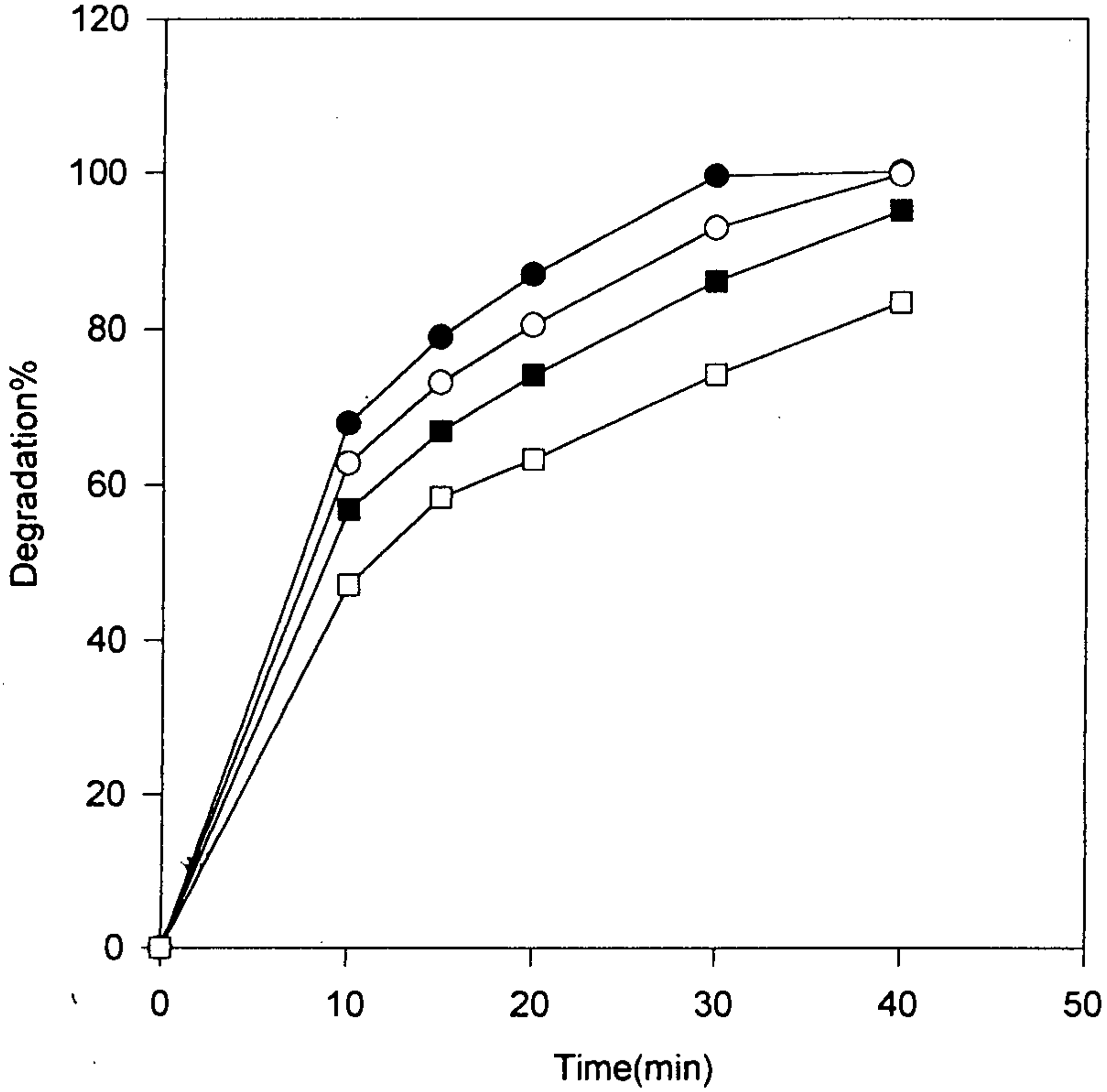


Fig. 5.3 (b). :Photodegradation of BGY in the presence of ZnO(0.01g)

● 7.82e-5M ○ 9.67e-5M ■ 11.1e-5M □ 12.3e-5M

Temp. : 29.0^{0}C

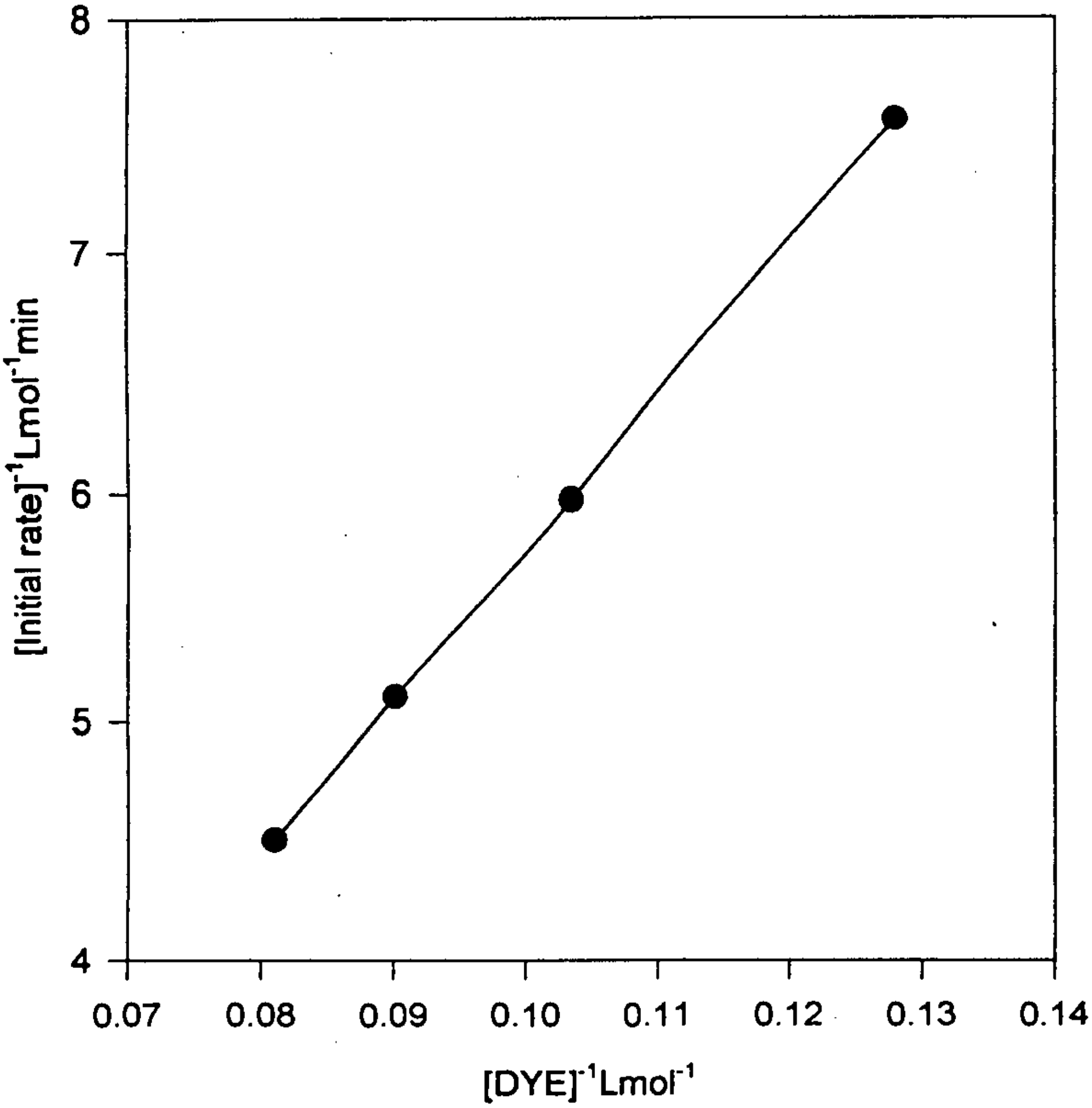


Fig.5.4: [DYE]$^{-1}$vs [Initial rate]$^{-1}$plot for photodegradation of BGY in presence of ZnO(1.0e-2g)

CHAPTER 6
RESULT AND DISCUSSION

6.1.0 Result and discussion

Brilliant golden yellow, BGY (Fig. 6.1) is an anionic azo dye. Its spectrum (Fig3.1) shows one absorption peak at 415 ± 2 nm with $\varepsilon = 7.18 \times 10^3$ L mol^{-1} cm^{-1} at 29.0°C.

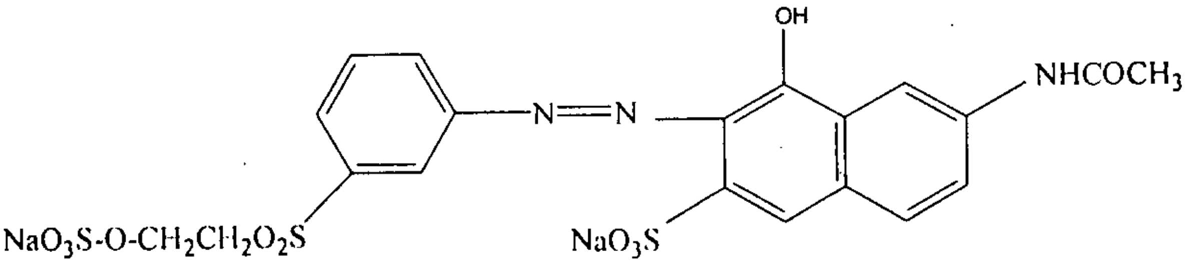


Fig. 6.1 Structure of BGY

Degradation pattern of the dye is show in Fig. 3.2. The dye seems to be completely minaralized ofter degradation. The aqueous solution after complete minaralization is expected to contain Na^+ , NO_3^{-1} and SO_4^{-2} ions. The carbon dioxide gas, one of the products of minaralization has been detected. After minaralization the only peak at about 224nm vanishes when a nitrate solution, (e.g KNO_3) is taken as reference indicating the presence of a nitrate ion the solution.

6.1.1.0 Degradation by Fenton & Photo-Fenton Process.

Experiments show that BGY is not degraded by H_2O_2 alone, or by simply Fe(III). 410 nm , light does not seem to have any immediate effect of BGY. Neither, light (410 nm) has any immediately detectable effect on BGY in the presence of H_2O_2 or Fe(III) alone. Accordingly, the agent or agents that degrade the dye may not be generated in sufficient quantities. It is known [9-10] that radicals are needed to present in the system to degrade dyes.

6.1.1.1 Effect of hydrogen peroxide. Figures 3.5(a), 3.5(b and Table 6.1 show that in the presence of Fe(III) degradation immediately starts if sufficient amount of H_2O_2 is present in the system. The degradation seems to be complete within about 10 minutes. We have found that simply by maintaining the H_2O_2 concentration about twice the concentration of BGY; this rate of degradation can be maintained. Further increase in H_2O_2 concentration, even by sixfold, does not influence the pattern of decomposition.

6.1.1.2 Effect of Fe(III) ion concentration. So long there is sufficient H2O2 in the system, the degradation of dye does not seem to be affected by the concentration of Fe(III). (Figures 3.6(a), 3.6(b) and Table 6.1).

6.1.1.3 Effect of hydrogen ion concentration. The presence of Fe(III) in the system requires that its hydrogen ion concentration should be maintained within a limit to prevent the hydrolysis of Fe(III). Accordingly, the lowest hydrogen ion concentration of the medium is 2.10 x 10^{-3}M (Table 6.1) suggest that there is a possibility that during the decomposition, the concentration of hydrogen ion should increase. Thus further increase in the in the hydrogen ion concentration will not affect the degradation that much (Figures 3.7(a), 3.7(b) and Table 6.1).

6.1.1.4 Effect of BGY concentration. The variation of BGY concentration within the range 1.00x 10^{-4} to 3.00x10^{-4} M does not seem to affect the degradation significantly (Figures 3.8(a), 3.8(b) and Table 6.1). Whatever variation is noticeable is within 2%. This is because there is too much H_2O_2 in the system. It is to be noted that use of excess of H_2O_2 in the system may help dealing with unknown concentration of the dye in a system.

6.1.1.5 Effect of light. Light promotes an extra reaction path is complementary to that represented by reaction 5.2. Consequently, some additional supply of Fe(II) should have spectacularly. However results do not show that (Table 6.1)

6.1.2.0 Photodegradation

Any degradation of BGY solution by 320 nm light alone within the duration of the experiment (about 90 minutes) was too small to be detected. However appreciable degradation was recorded when quite small quantities of TiO_2 (rutile) and ZnO were separately present in the aqueous solution of the dye. Such degradation in the presence of these (semiconducting oxides) is knoun as mediated degradation. Attempts have been made to evaluate the extent of photodegradation by varying the initial pH of the system, amounts of the mediators; that is,TiO_2 and ZnO and initial concentrates of the dye.

6.1.2.1 The effect of mediator concentration. Although the amount of ZnO does not seem to affect the degradation that much (Figures 5.1 (a), 5.1(b) and Table 6.3) the amount of TiO_2 affects the degradation appreciably (Figures 4.1(a), 4.1(b) and Table 6.3). Consequently in the subsequent experiments amount of TiO_2, and also ZnO was kept constant while other parameters were changed.

6.1.2.2 The effect of initial pH of the medium. The figures 4.2 (a), 4.2 (b), 5.2 (a) and 5.2 (b) show the effect of pH on the photodegradation of BGY. The pH of the medium does not have spectacular influence on the photodegradtion in both the cases (TiO_2 and ZnO).

6.1.2.3 The effect of concentration of the dye on its photodegradation. The similar pattern of influence of the dye concentration on the photodegradation (Fig 4.3(a), 4.3(b), 5.3(a) and 5.3(b).

6.1.3.0 Adsorption Characteristics of the dyes on the mediators.

Generally the initial rate (R_i) of mediated photadegradation of the dye or any other orgnanic substrate in aqueous solution matches Langmuir - Hinshelwood kinetic model[118-121].

$$Ri = \frac{kK\,[Dye]}{1+K\,[Dye]} \qquad \text{------------------------------} \qquad (6.1)$$

Where [Dye] is the initail concentration of the dye. K is the apparent Langmiur adsorption constant of the dye on the oxide mediator. k is the proportionality constant suggesting a measure of the intrinsic reactivity of the photoactivated surface with the dye. k is proportional to the intensity of the light. k is also proportional to the fraction of O_2 adsorbed on the surface. Adsorption coefficient for O_2 is noncompetitive as it remains exclusively adsorbed at the preferred sites on the oxide surface.

The zero-order initail rate of photodegradations (Ri) was evaluated from curves of the concentration of the dye vs time (Fig 3.2). Equation (6.1) was written in this form.

$$\frac{1}{Ri} = \frac{1}{k} - \frac{1}{1+K\,[Dye]} \qquad \text{------------------------------} \qquad (6.2)$$

k and K values were obtained from figures 4.4(c) and 5.4(c) and tabulated in Table 6.2. Although the k values for TiO_2 and ZnO are almost identical the difference in the K values is likely to be reflected in the mediated degradation of BGY. The relatively strongly bound BGY on TiO_2 makes the progress of its photodegradation comparatively slower (Table 6.3)

6.1.4.0 Tentative mechanises of mediated photodegradation.

The band gap energies for ZnO, TiO_2 (rutile) and TiO_2 (anatase) are 3.2eV, 3.00 eV. Devand 3.00 eV respectively. Most of the information involving TiO_2 as mediator is based on anatse. Very little is known about the mechanism of photodegradation involving ZnO as mediator.

Since ZnO and rutile has the identical band grape energy we assume almost identical mechanism involved in the photodegradation process involving ZnO. Simlarr mechanism should also be valid for rutile.

The degradation process, all the investigators agree, preceeds the adsorption of the dye on the oxide (MO) surface. The excitation of the adsorbed dye ($D_{ads} \rightarrow {}^{*}D_{ads}$) and genaration of electrons e^{-}_{CB} and holes (h_{VB}) due to photoexcitation of MO are the causes of generation of host of radicals OH, $O_2^{\cdot}$ etc. These radicals are ultimately responsible for photodegradation of the dye. Accordingly some important known steps in the photodegradation mediated by MO may be as follows[118-120]

$D_{ads} + h\nu \rightarrow {}^{*}D_{ads}$ -------------------------------------- (6.3)

${}^{*}D_{ads} + MO \rightarrow MO(e) + D^{+}_{ads}$ -------------------------- (6.4)

$MO(e) + O_2 \rightarrow MO + O_2$ --------------------------- (6.5)

$MO + h\nu \rightarrow e^{-}_{CB} + h_{vb}^{+}$-------- ---------------------- 6.6)

$MO + e^{-}_{CB} + \rightarrow MO(e^{-})$ ------------------------- (6.6)

$h_{vb}^{+} + H_2O \rightarrow H^{+} + OH^{\cdot}$ ------------------------------ (6.7)

$O_2^{\cdot} + H^{+} \rightarrow HO^{\cdot}_2$ ------------------------------------- (6.8)

$HO^{\cdot}_2 + H^{+} + MO(e^{-}) \rightarrow H_2O_2$ ----------------------- (6.9)

$H_2O_2 + MO(e^{-}) \rightarrow OH^{\cdot} + OH^{-}$ --------------------- (6.10)

$OH^{-} + h^{+}_{vb} \rightarrow OH^{\cdot}$ ------------------ (6.11)

$D_{ads} + + (OH^{\cdot}, O^{\cdot}_2$- and /or $O^{\cdot}_2) \rightarrow$ minaralized inducts (6.12)

election in the 0trapped on the MO surface. The generation of H_2O_2 and other radicals has been experimentally verified.

6.1.5.0 Relevance of the present work and the industrial Effluents.

It is true the development of two laboratory processes, (a) Dye degradation by Fenton process and (b) Mediated phatodegradation of the dye, are not immediately applicable to industrial effluents containg such dyes, However one can weigh in his mind which one of these processes are relevant to one's problem. Laboratory experiments can be scaled up and a few trial experiments can decide the appropriate process. The following steps can be suggested for application at the site of the factory

(i) Instead of allowing the dye containing effluent discharging in the adjacent waterbody let the effluent be accumulated in an appropriate ditch. When settled the cleaner, but coloured, effluent be allowed to drain out into a treatment ditch.

(ii) Let the concentration of the dye be known.

a) Acid, H_2O_2 and Fe(III) salt solution be charged (Fenton process), the open air treatment will provide enough light to aceelerate the minaralization process. However before discharging the treated effluent pH must be adjusted with washing soda.

b) For mediated Photodegradation we suggest to have several glass sheets covered with thin ZnO paste, Let the coated sheets be arranged in decreasing heights so that slowly flowing effluents from the setling runs over the sheets stepwise.

It is to be noted that this process of degradation will be much slower. The sunlight is being used instead of 320 nm light. The proportion of UV in sunlight is considerably low.

Table : 6.1 The effects of variables on the photodegradation of BGY by Fenton and photoFenton's processes.

$[H_2O_2]$ $\times 10^4$M	[Fe (III)] $\times 10^5$M	$[H^+]\times$ 10^3M	[BGY] $\times$ 10^4M	% Degradation			
				Dark 10 min.	Visible 10 min.	Dark 30 min.	Visible 30 min.
8.00	4.00	4.18	2.97	90.84	91.21	91.94	91.99
10.00				91.38	91.65	92.36	92.53
30.00				91.82	92.15	92.83	93.03
50.00				92.93	93.40	92.93	93.40
30.00	2.00	4.18	3.00	91.50	92.13	92.43	93.50
	4.00			91.53	92.37	92.60	93.67
	7.00			91.67	92.40	92.57	93.68
	10.00			91.63	92.20	92.57	93.40
30.00	4.00	2.10	3.00	91.77	91.90	92.90	93.27
		4.18		91.77	91.83	93.10	9350
		6.36		91.73	91.80	92.90	93.13
		8.26		91.53	91.80	92.50	92.97
30.00	4.00	4.18	1.00	89.80	91.20	91.30	94.50
			1.75	93.94	94.57	95.08	95.66
			2.25	93.11	95.51	94.45	94.76
			3.00	91.63	92.33	92.53	93.20

Table- 6.2 Parameters k and K of Langmuir - Hinshelwood Equation for Photodegradation of BGY at 320 nm.

Oxide	k ($molL^{-1} min^{-1}$) × 10^5	K ($L mol^{-1}$)
ZnO	1.28	1.19 x 10^3
TiO_2	1.01	0.32 x 10^5

Table- 6.3 Comparative studies of the effects of the various amout of TiO_2 and ZnO on the degradation of BGY

pH : 6.20

[BGY] : 11.06 x 10^{-5}M

Oxides x 10^3g		% Degradation			
TiO_2	ZnO	10 min.	20 min.	30 min.	40 min.
1.00	—	34.32	47.32	56.07	64.12
2.50		37.86	49.15	56.63	65.68
3.50		39.41	50.99	59.04	67.10
4.50		41.95	58.33	68.50	74.44
—	2.50	52.90	72.06	84.36	94.30
	5.00	54.07	72.65	85.00	94.94
	7.50	55.42	73.51	85.53	95.48
	10.00	56.78	74.14	86.80	95.03

CHAPTER 7

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নং ৯৫৬৯৫
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