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***Disintegration of Pollutants in Wastewater Using
Ultraviolet Irradiation.***

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Master of Philosophy

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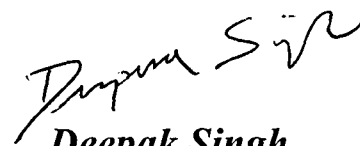
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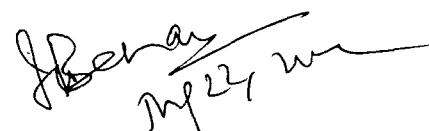
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CERTIFICATE

The research work embodied in this Dissertation entitled, "*Disintegration of Pollutants in Wastewater Using Ultraviolet Irradiation*", has been carried out in the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. The work is original and has not been submitted so far, in part or full, for any other degree or diploma in any University.


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DEDICATED TO
MY PARENTS

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CHAPTER I
INTRODUCTION

INTRODUCTION

The rapid pace of industrialization and urbanization coupled with globalization has resulted in tremendous pressure on environment in form of deterioration of air and water qualities. Now a days most of the water resources throughout the world is facing severe pollution problem. In our country, most of the rivers are in the chaotic state and it seems that they have lost their self-purification capacity itself due to continuous the addition of pollutant beyond their carrying capacity. Moreover, in some parts of the country the groundwater pollution has also been reported.

Dominant sources of water pollution are municipal sewage, industrial discharge, agricultural run-off and radioactive wastes. In the country effluents of most of the industries are discharged without any kind of treatment. Only few industries are equipped with wastewater treatment facilities. However, most of the wastewater treatment instrument of industries is not in the functional state.

Contamination of drinking water supplies and aquatic environment with Insecticides, Pesticides and chemicals, notably organic compounds is causing concern (Long, 1984 ; Helz and Kosaki-Channing, 1984; Dickson , 1983). The contamination arises in various ways: runoff from croplands,

effluents from industries, disinfections of drinking water supplies and water treatment with chlorine are major sources of contamination.

The industrial effluents mainly contain inorganic and organic pollutants. 1,4-dioxane is one of the industrial organic pollutant is discharged from industries likes tanneries, dyes, electroplating, industries etc. 1,4-dioxane which is an ether and is therefore, also of interest because it is structurally related to oxygenated fuel additives, which are groundwater contaminants in the United States (Mormile et al., 1994).

1,4 - dioxane is a synthetic organic compound with no known natural sources (Warn, 1988). Employed as numerous industrial processes and it is classified as toxic chemical and hazardous environmental pollutant by the environmental protection agency (USEPA, 1987), which has set a discharge limit of 30 microgram per liter.

1,4 - dioxane poses a serious problem both for groundwater and surface water because of its resistant towards decomposition and easily mobility through the aquifers (F. B.Dewalle et al., 1992 and S. Lesage et al., 1990.). It is resistant to both aerobic (Raj et al., 1997) and anaerobic biological processes (Adams et al., 1994.).

It is a potent health hazard for the human being. It causes liver damage and kidney failure, has being shown to be carcinogenic to animals and is

potential carcinogen for humans (U.S. Department of Health, 1994) and hence classified as hazardous waste and a priority pollutant.

It is a recalcitrant molecule to biodegradation under conventional Biotreatment Technologies (Heukelekian and Rand, 1955; Swope and Kenna, 1950), but relatively recent studies have revealed enhanced biodegradation rates under certain aerobic conditions when combined with an Advanced Oxidation Process pretreatment (Mcgrane, 1996; Adams et al., 1994). A current treatment technology for removing 1,4-dioxane from contaminated waste streams is by distillation, but this process is rather expensive (Warn, 1988). Other treatment methods, including Activated Carbon (Johns et al., 1998) and Airstripping (Warn, 1988), provide inefficient removals due to the high aqueous solubility (4.31×10^5 mg/l) and low vapour pressure (37 mm Hg at 25' C) that are properties of 1,4-dioxane (Lagrega et al., 1994). Moreover, the aforementioned treatment methods do not destroy the target compound but rather transfer it from one phase to another.

Klecka and Gonsoir (1986) studied the incomplete chemical oxidation of 1, 4-dioxane by Chlorine (as NaClO) and by using Fenton's reagent. Adam's et al., (1994) used the O₃/H₂O₂ process to remove 1,4-dioxane and enhance its biodegradability. Gamma-irradiation (Gehring and Matschner,

1998) has been explored as possible destructive treatment methods for 1,4-dioxane.

Photo induced Oxidation Methods using UV light and added H₂O₂, a branch of Advanced Oxidation Technologies (AOP), have proven to be efficient for the removal of toxic organic pollutant found in aquatic environment. Since the 1960s, UV/H₂O₂ system (Omura et al., 1968; Koubek, 1975; Mill et al., 1979) was in use for treatment of wastewater.

All the above process involves generation of OH radicals, which is a nonselective oxidant that rapidly attacks organic compounds.

Several studies have been examined the Photochemistry of 1,4-dioxane either in pure liquid (Schuchmann et al., 1979; Houser and Sibbis, 1975; Kiwi, 1977; Ausloos et al., 1984; Mazzocchi and Bowen, 1975) or in aqueous solution (Schuchmann et al., 1990; Bilski et al., 1992).

Several countries are suffering from this pollutant. The compound has been detected in surface and groundwater (Abe, 1999 and Jackson and Dwarakanath, 1999) in Japan (Yasuhara et al., 1999); Canada (Lesage et al., 1990) and the United States (Taylor et al., 1997). Structurally related compounds (1,3-dioxane) have contaminated drinking water resources in Spain (Romero et al., 1998).

India may also suffer from similar problems of this type of contamination by these pollutants. It requires more studies on this type of pollution in our country so that the long and short-term consequences can be averted in time.

Sources of 1, 4 - dioxane

1,4-dioxane is used as solvent for cellulose acetate, benzyl cellulose, resins, oils and waxes, some dyes and other organic and inorganic compounds in industry so the industry is the main source of the release of 1,4-dioxane. Occupational exposure to 1, 4-dioxane is most likely route of exposure. It has been detected in both surface and groundwater.

AIMS AND OBJECTIVE

This study aims to compare the feasibility, reliability and accuracy of two methods i.e. UV/H₂O₂ and UV/TiO₂ in the degradation of 1,4 -dioxane in aqueous solution.

Four parameters have been studied for the comparison. These are:

- (1) Degradation of 14-dioxane and formation of its by products.
- (2) pH change.
- (3) Dissolved Oxygen concentration.
- (4) Hydrogen Peroxide concentration.

Degradation of 1,4-dioxane was carried out in the deionised water so that the effect of other parameters like inorganic ions may be eliminated.

CHAPTER II
LITERATURE REVIEW

LITERATURE REVIEW

1,4-dioxane or 1,4-diethylene dioxide or $C_4H_8O_2$ is clear, volatile, colourless solutions, odour like mild ether, and is miscible with water (USEPA, 1987), alcohol, ether, most organic solvents, aromatic hydrocarbons and oils. It is flammable and may form explosive peroxides during storage.

Molecular weight of 1,4-dioxane is 88.10 g/mol (Budaran, 1989). Its Boiling point is $101^{\circ}C$ and Melting point is $11.80^{\circ}C$. Its Dielectric constant is 2.25 at $20^{\circ}C$; Dipole moment is 0.45 D at $25^{\circ}C$. Its vapour pressure is 30mm Hg at $20^{\circ}C$ (USEPA, 1987). It has faint pleasant odour, with a threshold of 24ppm in air (Budavari, 1996).

Effect of 1, 4-dioxane on Animals and Environment

Many studies have been carried out on animals. Acute inhalation exposure to high level of 1, 4-dioxane has caused vertigo and irritation of the eyes, nose, throat and lungs in humans. It may also irritate the skin (Calabrese and Kenyon, 1991).

In fatal cases of acute 1, 4-dioxane poisoning by inhalation, hepatic and renal lesions and demyelination and edema of the brain were observed in individual (USEPA, 1987).

Convulsions, collapse and effects to the kidneys and liver were observed in rabbits injected with 1, 4-dioxane (USEPA, 1987).

Acute animal test in rats, mice, rabbits and guinea pigs, have demonstrated, 1,4- dioxane to have moderate acute toxicity by inhalation or dermal exposure and low to moderate acute toxicity by ingestion (U.S. Department of health, 1994).

1,4-dioxane has some chronic effects (non-cancer) like damage to liver and kidneys have been observed in rats chronically exposed in their drinking water (USEPA, 1987).

No information is available on the reproductive and developmental effects of 1, 4-dioxane in humans.

Exposure to 1,4-dioxane may cause cancer as studied by National Cancer Institute on rats and mice exposed to 1,4-dioxane in their drinking water reported increased incidences of liver carcinomas and adenomas and nasal cavity squamous cell carcinomas. Liver carcinomas and gall bladder carcinomas were observed in mice and guinea pig respectively (USEPA, 1989).

Environmental fate of 1,4-dioxane

When released into the soil, this material is not expected to degrade, When released into the Soil, this compound may leach into groundwater. When released into the water, it is not expected to biodegrade and material may operate to moderate extent. This material is not expected to significantly bioaccumulate. When release into air, it readily degraded by reaction with photochemically produced hydroxyl radicals. Its reaction with photochemically produced hydroxyl radicals. Its half-life in air is less than one day. It is toxic to aquatic life.

Treatment technologies for pollutants in wastewater:

Technology to treat hazardous and toxic wastes is undergoing a profound transformation as a result of the new regulations and requirements on discharge limits. Conventional chemical oxidation and activated carbon, which have served the industry well for decades, cannot meet the more stringent regulation and innovative technologies such as the Advanced Oxidation Process (AOP) have emerged.

A.O.P refers to the use of the UV Light is combination with O_3 or H_2O_2 or both or TiO_2 to generate a very reactive free radical such as OH radicals formed by A.O.P increased the rate of reactions over 100 to 1000 times

higher than that observed with either oxidants or UV applied separately. As a result, many organic compounds, which are normally resistant to powerful oxidants, can be destroyed by the A.O.P in a short time and most of the inherent short comings of chemical oxidation can be over come. The oxidants commonly used in the UV/Oxidation process are ozone, H_2O_2 & TiO_2 .

The UV/Ozone processes were first used in the early 1970s. Its use was limited to water purification. In the wastewater treatment field, UV/O₃ technology was developed for cyanides in wastewater from electroplating and colour photographic process. The technology has also been applied to the destruction of mixed cyanides and organic chemical process. In 1977, it was reported that the UV/O₃ process has been used successfully at the industrial metal finishing plant. PCB's (polychlorobenzene's), which are highly resistant to ozone oxidation, also have been reported to be destroyed rapidly by UV/O₃ process. Also in 1977, AOP has been applied for the treatment of water contaminated with chlorinated hydrocarbons, organophosphorus and other compounds. Also other investigators have discovered that UV/H₂O₂ process were also effective for treatment of water contaminated with different types of organics including explosive wastes, called pink water.

In the oxidation processes OH ions can be generated by: -

1. H_2O_2 in the presence of ferrous catalyst.
2. UV irradiation of H_2O_2
3. UV irradiation of O_3
4. Combining O_3 with H_2O_2
5. UV irradiation in combination with semiconductors like TiO_2 .
6. Recently, Ultrasonic waves have been used to generate OH ions.

UV irradiation in conjunction with H_2O_2 or O_3 has gained a great deal of attention during the recent years. OH radicals, generated via UV photocatalysis of either hydrogen peroxide or ozone or by the reaction between hydrogen and ozone offers the following advantages:

1. They have higher oxidation potential than ozone alone or H_2O_2 used separately and.
2. They are less selective in carrying out the oxidation reaction. Therefore, they are not restricted to specific classes of contaminants is the case with molecular O_3 or H_2O_2 .

Three Advanced Oxidation Processes:

1. Dark based Homogeneous Advanced Oxidation Processes.
2. Light based Homogeneous Advanced Oxidation Processes.
3. Light based Heterogeneous Advanced Oxidation Processes.

(1) Dark based Homogeneous A.O.P

Dark based homogenous A.O.P do not utilize UV light in the degradation of various organic species e.g.

1. O_3 at high pH ($O_3 + \text{high pH}$)
2. O_3 in combination with peroxide ($O_3 + H_2O_2$)
3. Fenton's reaction ($Fe + H_2O_2$)

(2) Light based Heterogeneous A.O.P

Light based heterogeneous A.O.P uses UV Light with a semiconductor such as TiO_2 and CdS to generate hydroxyl radicals (OH) and hydrate ions (H).

(3) Light based Homogeneous A.O.P

Light based homogenous A.O.P combines UV with either ozone (UV/O₃) or hydrogen peroxide (UV/H₂O₂) or both UV/O₃/H₂O₂ to generate hydroxyl radicals.

One more method, which is gaining attention of the scientists in the recent years. It was the 'Sonolysis'. Sonolysis is also a potential destructive technique that has been effectively applied to other ethers (Kang and Hoffman, 1998). This process also exploits the reactivity of the hydroxyl radical (OH) a nonselective oxidant that rapidly attacks organic compounds.

Ultrasonic irradiation has been investigated in the transformation of organic pollutants such as phenols (Kotronarou et al., 1991) chlorinated organics (Catallo and Junk, 1995) and humic acids (Nagata et al., 1996). Chemical decomposition may be enhanced when an appropriate ultrasonic frequency is employed (Kang et al., 1999 and Entezari et al., 1994). A more complete discussion of aqueous sonochemistry and environmental applications is given by Hoffmann and co-worker (Hoffmann et al., 1996) and a comprehensive discussion of ultrasound and sonochemistry can be found by (Crum et al., 1999 and Suslick et al., 1993).

Mechanism for UV/TiO₂

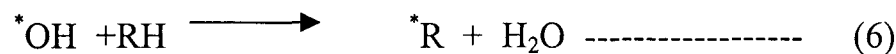
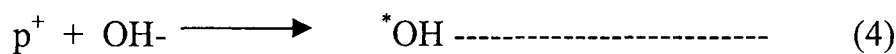
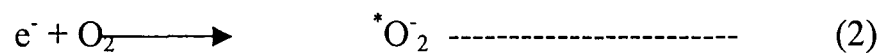
It is also called light based heterogeneous Advanced Oxidation Process.

Photocatalytic process using n-Type suspended semiconductor particles like TiO₂, CdS as catalysts under appropriate UV/Vis light, the solid surface is photoexcited because the energy state of the electrons may jump from the valence band of the solid to the conduction band (Maruska & Ghosh, 1978). Electrons and holes are formed and the holes migrate to the solid surfaces (Pelizzetti and Minero, 1993). The surface becomes so strongly oxidizing that it can initiate the oxidation of organic pollutants at the solid-liquid surface in waters by converting dissolved oxygen, water or hydroxyl ions to hydroxyl and other radicals (Minero et al., 1992). A number of experimental studies (Matthews, 1986, 1990; D'oliveira et al., 1990) have shown that the photocatalytic decomposition of many organic pollutants follows the Langmuir-Hinshelwood kinetics. The dependence of the initial decomposition rate on the concentration of the reactants can be adequately described by adsorption and surface reaction behaviors of those organic pollutants.

Illumination of TiO₂ produces photoelectrons in the conduction band and positive holes in the valence band



At the surface of the TiO₂ particle these may react with adsorbed species



It is known that the positive hole reacts rapidly with certain anions (Chandrasekaran and Thomas, 1984; Rossetti et al., 1984; Bahnemann et al., 1984). If A^- is an adsorbed hydroxyl group OH radicals are produced (reaction-4). Evidence that OH radicals are involved comes from: -

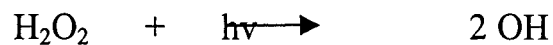
1. ESR detection of spin traps (Jaeger and Bard, 1979).
2. Competition kinetic data of salicylate formation rates in the presence of known OH radical scavengers (Matthews, 1984).
3. Comparison of hydroxybenzoic acid isomer distribution with that given by OH radicals (Matthews, 1987).
4. Absence of ring hydroxyl products when photocatalysis is in non-aqueous media (Fujihara et al., 1981).

Advantages of UV/TiO₂

The major advantages of these photocatalytic processes include the relatively mild reaction conditions required and their success in the decomposition of several toxic refractory pollutants (Matthews, 1986, 1987, 1988, 1990; Pelizzetti et al., 1989; Davis and Huang, 1988).

Mechanism of UV/H₂O₂ Oxidation

In the UV/H₂O₂ oxidation process, hydroxyl radicals are formed by the following reaction in the presence of light (ultraviolet light):



The maximum absorbance of UV light by H₂O₂ occurs at a wavelength of 200nm. UV irradiation of hydrogen peroxide, at a certain wavelength, produces two hydroxyl radical per mole of hydrogen peroxide. Photodissociation of H₂O₂ is independent of pH, however, the use of hydroxyl radical is pH dependent. Influent pH level controls the equilibrium among carbonate, bicarbonate and carbonic acid. This equilibrium is important to treatment efficiency because both carbonate and bicarbonate are hydroxyl radical scavengers.

Reaction mechanisms and pathways of 1,4-Dioxane degradation sensitised by the using UV/TiO₂ and UV/H₂O₂

The mechanism proposed by Stefan and Bolton, (1998). The initial degradation step, following the photochemical generation of reactive OH radicals (**scheme-1, reaction 1**), is the attack on the 1,4-dioxane molecules (**1**) with H-abstraction leading to the 1, 4-dioxanyl radical (**2**).

The 1, 4-dioxanyl radicals (**2**) react with oxygen by a diffusion-controlled process forming peroxy radicals (**3**). Fragmentation of **2** by B-cleavage (Zimina et al., 1986) or by reaction with H₂O₂ at a rate constant of $3 \times 10^4 \text{ M}^{-1}\text{S}^{-1}$ (Gilbert et al., 1974) is very likely in the presence of oxygen. Generally, peroxy radicals undergo head to head termination reactions with rate constant of approx $10^6 \text{ M}^{-1}\text{S}^{-1}$ in aqueous solutions (Schuchmann and Sonntag, 1982), and the resulting tetraoxide (**4**) decomposes to form molecular oxygen and alpha-oxyl radicals (**5**). Nese et al., (1995) also involving the formation of 1, 4-dioxane-2-one or 2-hydroxy-1, 4-dioxane. An electrocyclic process leading to H₂O₂ and two carbonyl compounds (Von Sonntag et al, 1991) or disproportionation leading to oxygen; a 2-hydroxy alcohol and the corresponding carbonyl compound [Russell mechanism (Russell, 1995)], seems to be unlikely in the case of tetraoxide derived from 1, 4-dioxanyl peroxy radicals considering the stereochemical hindrance.

The alpha-oxyl radical (5) derived from 1,4-dioxane appears to be the precursor of the primary major intermediates identified. This radical can undergo either an intramolecular reaction, in which the oxyl oxygen abstracts a hydrogen atom from the alpha-C position followed by fragmentation (scheme-2) or delta C-C splitting at the alpha-C position (Scheme-3). Depending on the route followed, either methoxyacetic acid (9) and formaldehyde (7) or mono and diformate esters of 1,2-ethanediol (29 and 30) and formaldehyde (7) are generated. According to the experimental concentrations determined for these organic compounds, the latter route seems to be favoured.

Reaction Pathways to and from methoxyacetic Acid:

The generation of "methyl" groups in, for example, methoxyacetic acid or acetic acid requires, the "reduction" of an RCH₂ type of radical. The reduction of 6 by HO₂ radicals is expected because HO₂ radical has both oxidising and, particularly, reducing properties (Von Sonntag et al., 1991). Due to the strong depletion of oxygen within the first few minutes of irradiation, the HO₂ radicals, which also may attain levels of approx. 0.01 mM, can compete with O₂ for RCH₂ type carbon-centered radicals. The HO₂ radicals are generated in the system not only by photolysis of H₂O₂, but also

by HO₂ elimination from peroxy radicals and by the reaction of CO₂ with O₂ in acidic media (**scheme 6**).

The carbon-centered radical (**6**) is hence either reduced by HO₂ radicals (pathways-2a) to methoxy acetaldehyde (**8**), which is further oxidised to methoxyacetic acid (**9**), or undergoes beta-scission leading to acetaldehyde (**14**) as shown in pathway-2b.

Methoxyacetic acid (**9**) reacts rapidly with OH radicals (pathways 2a, **Scheme-2**) by H-abstraction from methyl carbon followed by fragmentation leading to formaldehyde (**7**) and formylmethyl radical (**11**). The latter goes to acetic acid (**12**) by a reduction reaction involving HO₂ radicals.

Acetaldehyde hydrate (**15**) is further oxidised to acetic acid (pathway - 2b, **scheme-2**). The reaction steps are initiated 'OH by radical attack and involve peroxy radical formation and spontaneous HO₂ elimination (Schuchmann and Sonntag, 1988).

The carbon-centered radicals generated above probably also react with oxygen in parallel with the reduction reactions, but the occurrence of such oxidation reaction is less likely than reduction reactions. When the concentration of oxygen is depressed the subsequent oxidation reactions starting from the methoxyacetaldehyde radical would be expected to lead to glycolic acid, glyoxylic acid and oxalic acid as major products, which have

not been observed by a test irradiation experiments carried out on methoxyacetic acid in the presence of H₂O₂. The degradation of methoxyacetic acid using the UV/H₂O₂ system generated acetic and formic acids as the major byproduct and only a small amount of oxalic acid.

To a small extent, the reaction steps of pathway-2c involving peroxy radicals and tetraoxide formation might be considered as well. The oxyl radical (18) should undergo beta-fragmentation releasing formaldehyde (7) and the oxyl radical of acetaldehyde (19), which is a strongly H-abstrating species from any RH type of molecule (e.g. 1, 4-dioxane). The final products of this set of reactions are glycolic acid (21) and formaldehyde (7).

Formaldehyde is generated at very early time of irradiation and exists as a hydrate in aqueous solution, which is readily oxidised to formic acid (23).

Reactions Pathways to and from 1,2-Ethanediol Formate Esters

The generation of 1,2- ethanediol formate ester (**scheme-3**) involves the most oxygen consuming processes.

Delta C-C splitting of the 1,4-dioxan-x-oxyl radical (5) leads to radical (24). The radical primarily reacts with oxygen to form the corresponding peroxy radical (25) and then dimerisation to the tetraoxide(26). According to the literature reports on the peroxy radical chemistry (Von Sonntag, 1991

and Ingold, 1969 and Bothe et al., 1978), tetraoxide generated from alkyl peroxy radicals decompose either giving two oxyl radicals and molecular oxygen or through an electrocyclic process leading to H₂O₂ and two carbonyl compounds. Following these routes, the tetraoxide (26) should lead either to the alkoxy radical (27) or to 1,2-ethanediol diformate (30). The latter may also be formed as a result of disproportionation of the oxyl radical (27) in the solvent cage. This type of reaction is well known (Mendenhall et al., 1985) and leads to the same products as the Russell mechanism (49), which represents another route of decomposition of tetraoxides that does not involve free radicals as intermediates (48).

The oxyl radicals (27) can also undergo beta-fragmentation. The alkoxy radical (28) leads by H-abstraction from any RH type of compound (e.g. 1, 4-dioxane) to 1, 2-ethanediol monoformate (29).

Since there is no evidence for the presence of the alcoholic compound (31), but 1, 2-ethanediol monoformate (29) has been detected. It was considered that the disproportionation (27) plays of very minor role in the reaction mechanism compared to the beta-scission route. Moreover, if the branching ratio between the right branch (leading to 30) and the left branch (leading to 27) is approximately 3:1, as observed by Zegota et al., 1986, in the case of acetylperoxy radicals.

Radical 24 may also undergo beta-scission leading to products such as ethyl formate and ethanol by a reduction pathway or to 1,2- by-ethanediol monoformate (29), formic acid and glycolaldehyde (20) by an oxidation pathway.

1, 2-ethanediol monoformate (29) degrades slowly to glycolic (21) and formic (23) acids as major products. As the H-abstraction reaction takes place at the alpha-C, an oxidation mechanism can be assumed (scheme 4).

The alpha-hydroxyalkylperoxyl radical (33) can both dimerise to tetraoxide (34) or undergo a rapid HO₂ elimination reaction, which has been observed in the literature for peroxyl radicals derived from primary alcohol [K= 10⁷ per second (Bothe et al., 1978)].

The acid ester 35 and the aldehyde ester 38 are unstable compounds, which undergo acid catalysed hydrolysis to glycolic (21) and formic (23) acids.

The aldehyde ester (38) can react with OH radical leading by subsequent reaction to glyoxal (39), which has been identified as an intermediate in the investigated system and is a precursor of oxalic acid (41). The oxidation steps of glyoxal to oxalic acid are similar to those presented above for either formaldehyde or acetaldehyde, considering the hydrate molecules.

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The OH radical attack on the 1, 2-ethanediol monoformate (29) may also take place at the beta-C of the molecule leading to glycolic and formic acids as final products. Considering the high reactivity of primary alcohol towards OH radicals.

The degradation of 1, 2-ethanediformate (30) is also an oxygen demanding process, which is initiated by OH radical attack. The degradation products are formic acid (23), glyoxal (39) and glycolic acid (21). Probably, the mechanism goes through an oxyl radical (43) generated by H-abstraction followed by O₂ addition (**scheme-5**)

It is important to mention that 1, 2-ethanediol has not been detected as an intermediate, which suggests that the hydrolysis of its formate esters does not occur within the pH range generated under experimental conditions.

Degradation Pathways for Formic, Acetic, Glycolic and Oxalic Acids

Formic acid is a degradation product both of 1, 4-dioxane and of some intermediates generated during the UV/H₂O₂ treatment. Literature reports (Kawaguchi, 1993 and Karpel et al., 1996 and Ogata et al., 1981) have emphasised the role of oxygen on the rate and the mechanism of the photooxidation of formic acid in aqueous solution the presence of hydrogen peroxide. The formoyl radicals (47) generated in the H-abstraction reaction

formic acid are undoubtedly involved in competitive reactions as shown in scheme-6. The degradation of acetic acid goes through the glyoxylic acid and oxalic acids as intermediates. Therefore, it is assumed that the route involving the alkoxy radical (50) is followed preponderantly (scheme-7).

Glycolic acid (21) oxidation initiated OH radical attack, decays very fast with the generation of formic (23), glyoxalic (40) and oxalic (41) acids as byproducts towards a complete mineralization. Shown in scheme-8.

Glyoxylic acid (40) undergoes both thermal and light induced oxidation. The dark reaction leads to formic acid (23), whereas the light driven one leads to oxalic acid (41). The high reactivity of glyoxylic acid in the presence of hydrogen peroxide explains the concentration of this compound at trace levels.

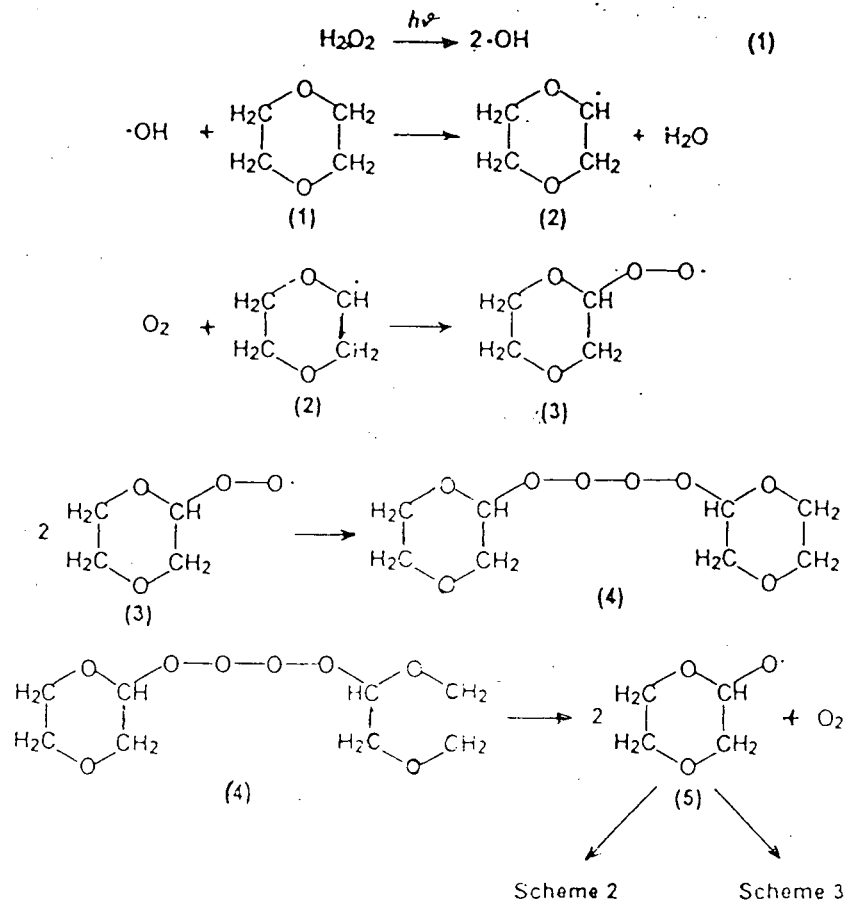
Oxalic acid is the last intermediate and is generated both through the above reactions and by the oxidation of glyoxal (39).

In the literature, it has been reported that photodegradation of several dyes which absorb visible light under the exposure to visible light in the presence of TiO₂ (Zhang et al., 1997, 1998; Qu et al., 1998; Zhao et al., 1998; Wu et al., 1998). These scientists in the degradation of dyes reported significant results.

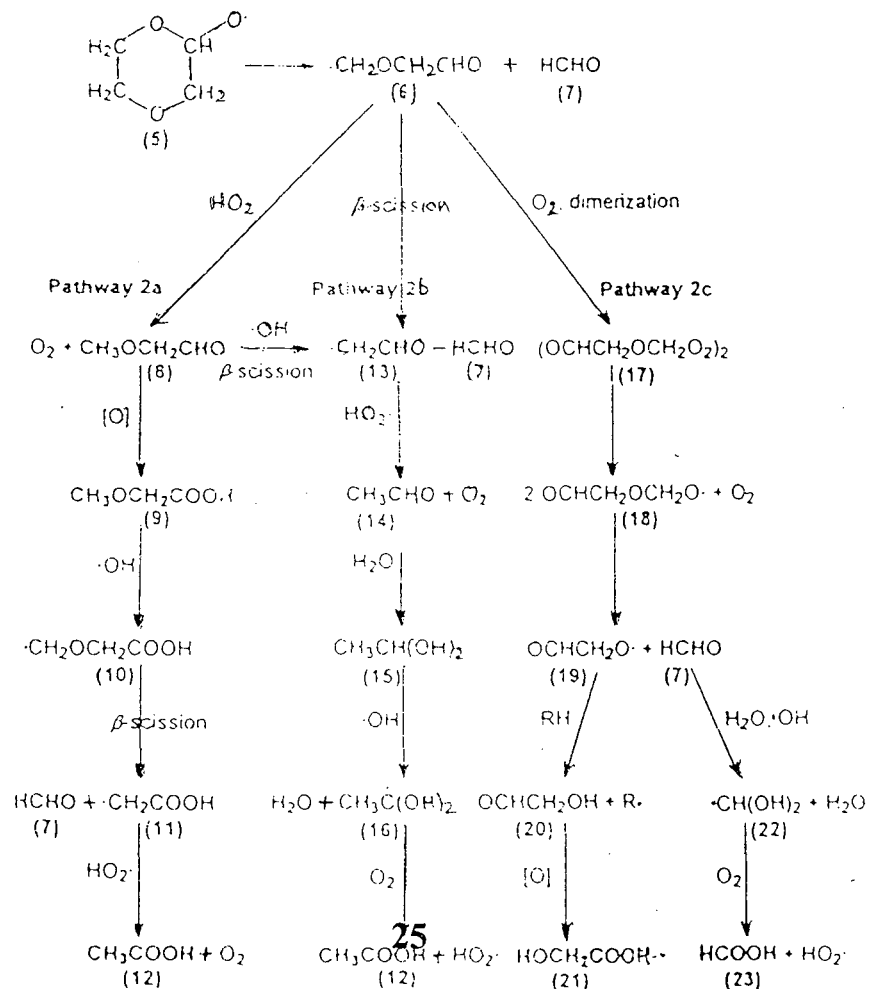
TiO₂ mediated photocatalysis which a well known advanced oxidation process for the removal of pollutants in aqueous environment (Ollis et al., 1989; Hoffmann et al., 1995; J. Adv. Oxidat. Technol, 1998).

These two methods used were not only help in destruction of organic molecules but also in destruction of microorganisms when high energy radiations is used to sterilise materials, the free radicals H[•], e⁻ aq, 'OH₂, generated in the aqueous phase are involved in this process (O'Donnell and Sangester, 1970). In a number of reports (Delincee and Radola, 1974; Watanabe et al., 1976; Adams et al., 1994; Hiller and Wilson, 1983; Billen, 1984) it has been shown that the 'OH plays a significant role in the inactivation process. It is likely that illuminated TiO₂ particles will destroys microorganisms at much greater rate that the natural UV component of spectrum alone ,this raises the possibility of disinfection of water with sunlight illuminated semiconductors (Matthews, 1986).

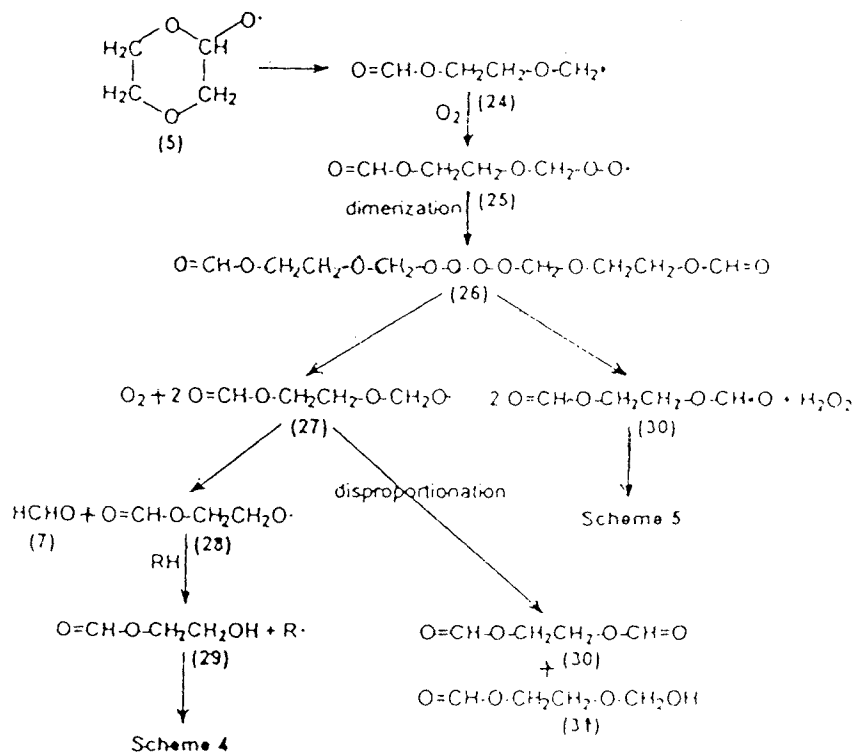
SCHEME 1. Initial Stages of the Degradation of 1,4-Dioxane



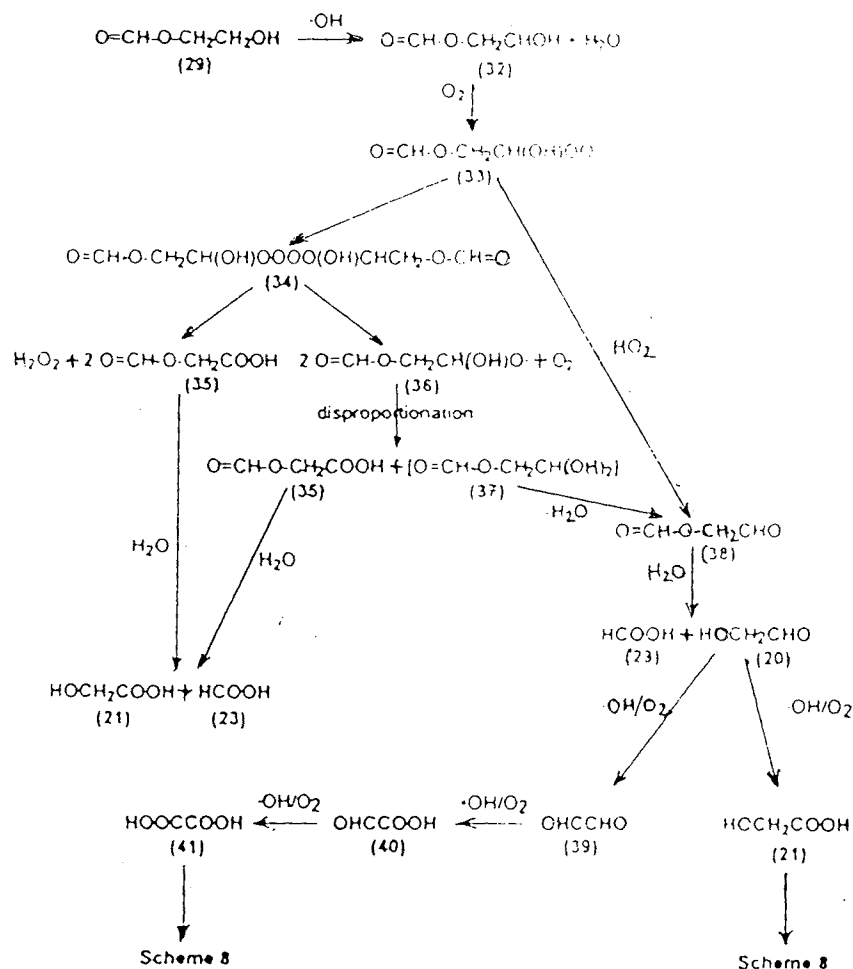
SCHEME 2. Reaction Pathways to and from Methoxyacetic Acid



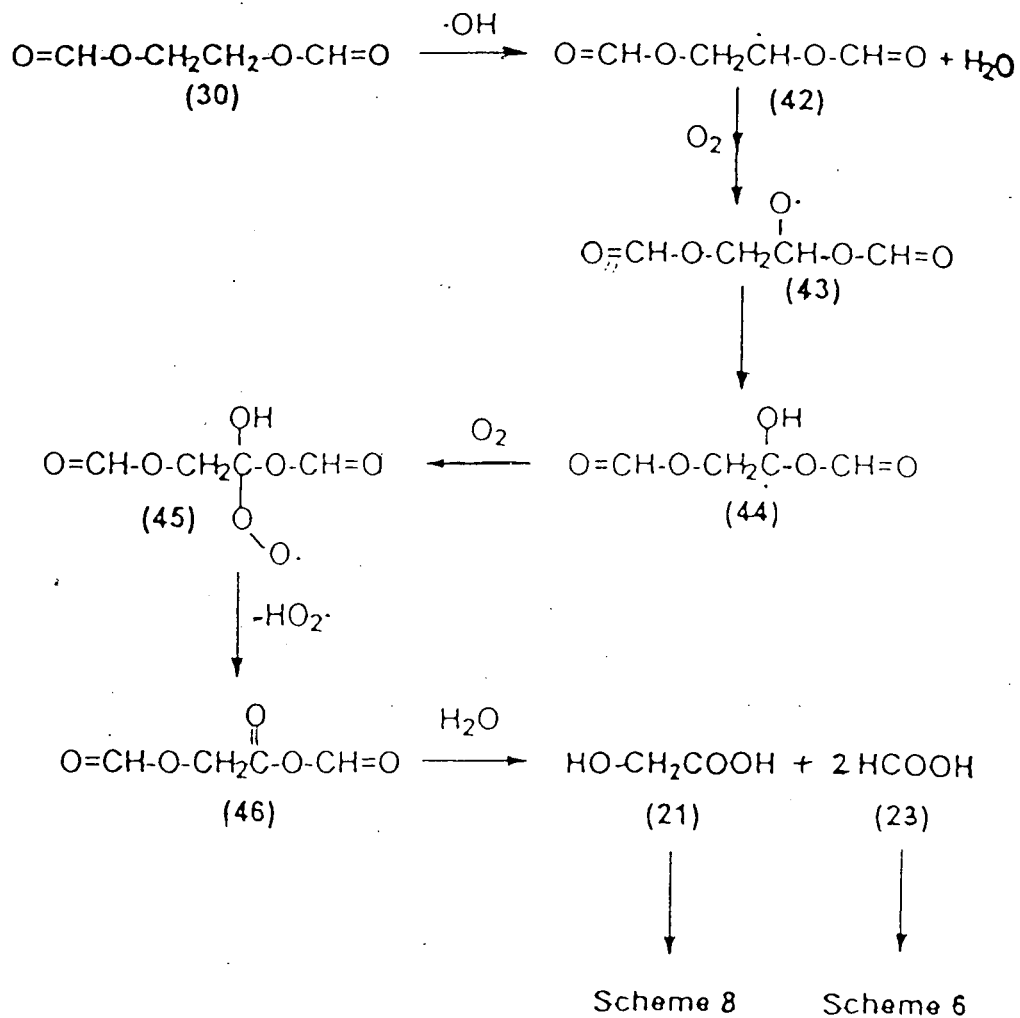
SCHEME 3. Reaction Pathways of the Generation of 1,2-Ethanediol Formate Esters



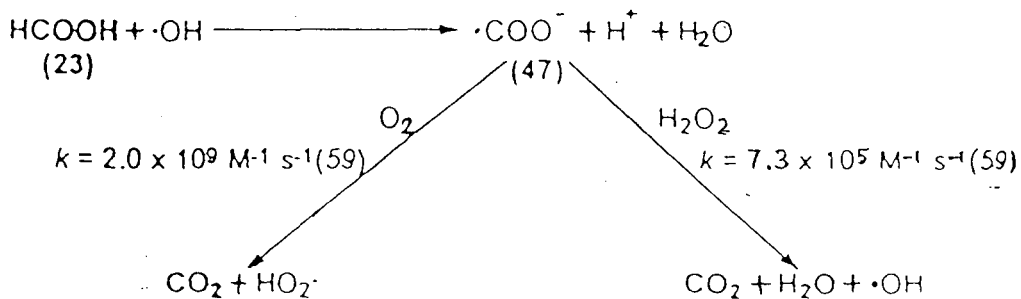
SCHEME 4. Reaction Pathways of the Degradation of 1,2-Ethanediol Monoformate



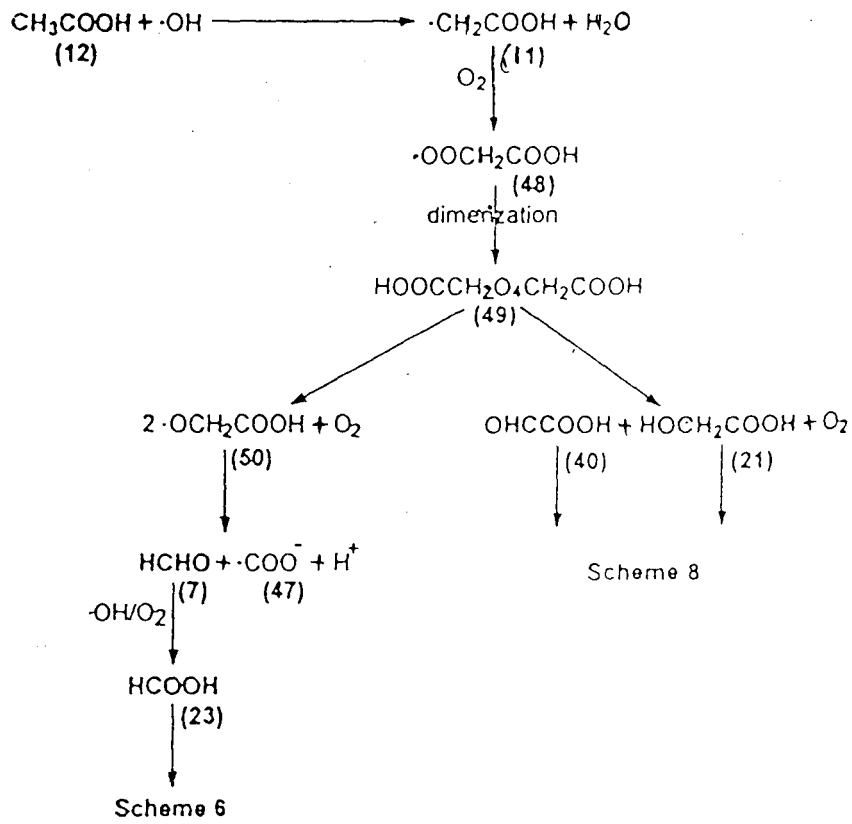
SCHEME 5. Reaction Pathways of the Degradation of 1,2-Ethanediol Diformate



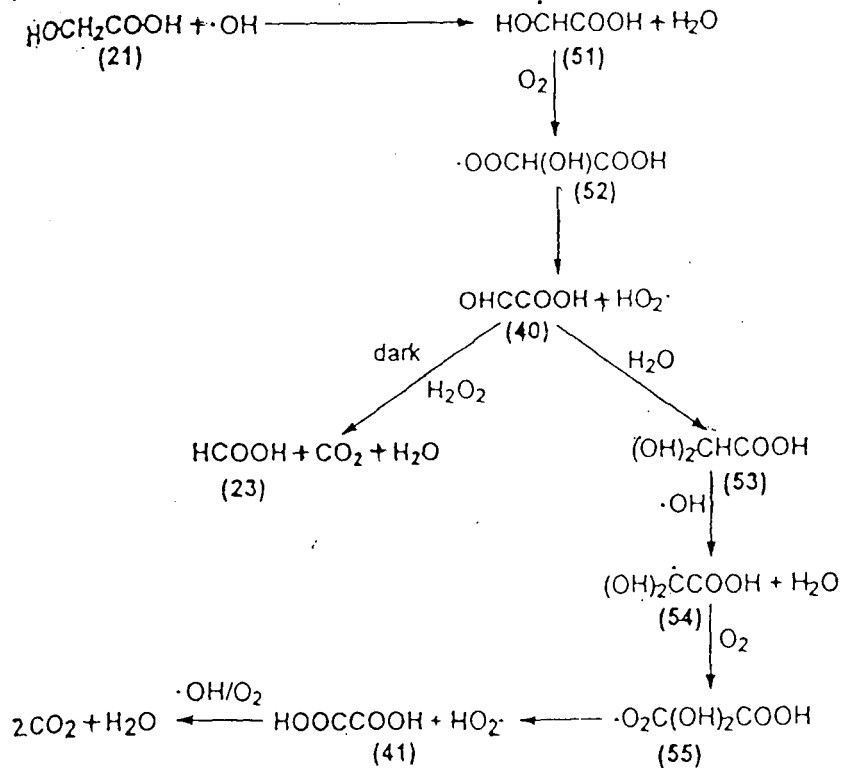
SCHEME 6. Degradation of Formic Acid



SCHEME 7. Reaction Pathways of the Degradation of Acetic Acid



SCHEME 8. Reaction Pathways of the Degradation of Glycolic, Glyoxylic, and Oxalic Acids



In the UV/H₂O₂ process it has been reported that the species like carbonate species, HCO₃⁻ and CO₃⁻ are expected to affect the photolysis of hydrogen peroxide in aqueous solution through various pathways. Both the species are known as effective OH scavengers, and hence their presence may cause a reduction in the oxidation rate of the target contaminants. Furthermore, the reaction of [•]OH with HCO₃⁻ and CO₃⁻ generates the carbonate radicals (HCO₃^{•-} and CO₃^{•-}) as oxidation transients (Buxton et al., 1988). These two forms of carbonate radicals exhibit similar reactivities toward other species (Chen and Hoffmann, 1995). It was reported that these radicals may disappear rapidly by attacking hydrogen peroxide, resulting in the formation of hydroperoxyl radicals (HO[•]O₂⁻) (Peyton and Glaze, 1988). At higher pH the radical CO₃^{•-} becomes dominant and reacts with O₂⁻ to terminate reaction (Chin et al., 1995).

Some of the factors, which interfere with the treatment process, are as follows.

(a) UV interferences:

Ions	Maximum limit
Nitrate	>10ppm
Nitrite	>10ppm
Phosphate	>1%
Chloride	>1%
Ferrous ions	>50ppm
Total suspended solids	>0.30ppm
Total dissolved solids	>400ppm

(b) Hydroxyl radical scavengers

Chlorides	>1000ppm
Nitrites	>10ppm
Carbonates	>300ppm
Sulphates	>1000ppm
Sulphides	>500ppm

CHAPTER III
MATERIALS AND METHODS

MATERIALS AND METHODS

Materials

(1) Reagents:

Following reagents were used

- (1) 1,4-dioxane
- (2) Hydrogen peroxide
- (3) Deionised-double distilled water
- (4) Ethylene glycol Diformate(EGDF)
- (5) Sulphuric acid
- (6) Ammonium molybdate.
- (7) Titanium dioxide
- (8) Potassium biphthalate
- (9) Potassium iodide
- (10) Methanol
- (11) Toluene
- (12) Ethyl acetate
- (13) Phenol
- (14) Methoxyacetic acid(MAA)
- (15) Sodium hydroxide
- (16) Ethylene Glycol Monoformate (EGMF)

(2) Apparatus:

Different instruments used in this study are as follows

- (1) Medium pressure UV/VIS lamp (300 W)
- (2) UV/VIS Spectrophotometer
- (3) pH meter
- (4) Gas Chromatograph (Nucon 5700)
- (5) 1-Microsyringe of 10 microliter
- (6) Polarographic Electrode
- (7) Thermometer
- (8) Solvent resistant 0.45 micrometer filter membrane
(millipore filter paper)
- (9) Borosil glass beakers
- (10) Petridish

(3) Experimental procedure:

- (a) Treatment methods.
- (b) Measurement techniques.

(a) Treatment methods: -

(1) UV/TiO₂ methods:

Aqueous solution was prepared by suspending 200 mg Titanium dioxide photocatalyst powder in 400ml of deionized double distilled water by sonicating for 5 min using sonicator having frequency of 25 KHz. Required amount of 1,4-dioxane was added in this aqueous solution. Aqueous solution was kept under the UV/Vis lamp (300 W). After the exposure the different parameters and concentration of 1,4-dioxane and its by products were measured using different instruments.

(2) UV/H₂O₂ methods:

Aqueous solution was prepared by suspending definite amount 1,4-dioxane in the deionised double distilled water followed by Hydrogen peroxide was added in a definite amount. Aqueous solution was kept under the UV/Vis lamp of 300 W. After the exposure the different parameters and concentration of 1,4-dioxane was measured using different instruments.

(b) Measurement methods: -

Three different parameters were measured for both methods, which were changed with the increase of time of exposure. The three-measured parameters were hydroxyl radical concentration, pH, and dissolved oxygen. These parameter were measured at every 20 min of interval up to 100 min and at the end of exposure period i.e. 200 min.

(1) Hydrogen peroxide:

Hydrogen peroxide was measured as triiodide ion by the Potassium Iodide (KI) methods of Kormann et al., (1988) and the Iodide was measured using spectrophotometer.

(2) pH change :

Irradiated samples were measured at every 20 min using pH meter electrodes.

(3) Dissolved Oxygen:

Oxygen concentration in the exposed samples were taken and dissolved oxygen was measured by taken and dissolved oxygen was measured by

Polarographic Electrode at the interval of 20 min along with other parameters.

(4) Concentration of 1,4-dioxane and its by products:

Analytical measurement (APHA, 1995) were performed on samples taken before and after every 20min of irradiation up to 100min and at the end of the exposure i.e. 200min. 1,4-dioxane and its degradation byproducts were determined by using 5700 Nucon Gas-chromatograph equipped with F.I.D (Flame Ionisation Detector) and a high performance DB 624 capillary column (30m × 0.53 mm, 3.0micrometer film thickness) under the following experimental conditions:

Injector temperature =250' C

Column temperature Isocratic at 90' C

Detector temperature = 300' C and

Carrier gas (nitrogen) pressure at the column 90 kPa.

A Computing Integrator was employed to record the Retention Times and Peak area data from the G. C Detector.

Before injecting the sample of UV/TiO₂ in the Gas Chromatograph the samples were filtered using solvent resistant 0.45-micrometer filter membrane (Millipore filter paper).

CHAPTER IV
RESULTS AND DISCUSSIONS

RESULTS AND DISCUSSION:

Degradation of 1,4-dioxane was not observed when UV or TiO₂ or H₂O₂ used alone. However, when 1,4-dioxane was treated with combination of either uv/H₂O₂ or UV/TiO₂, a substantial degradation was observed in terms of decreasing concentration.

(1) Photolysis of 1,4- dioxane using UV/H₂O₂ methods:-

(A) Concentration of 1,4-dioxane: -In this experiment, it was observed that after 20 minutes of irradiation, almost 50% of the initial concentration of 1,4-dioxane was depleted and three major primary reaction intermediates namely Ethylene Glycol Diformate(EDGF), Ethylene Glycol Monoformate (EDMF) and Methoxyacetic Acid(MAA). Retention Time is 1.48 minutes for 1,4-dioxane, 3.78 minutes for EGDF, 3.55 minutes for EGMF and 3.0 minutes for MAA were formed. The concentration of 14 dioxane and the three major primary intermediate reaction products are shown in **Table -1A** and **Graph-1A**. EGDF and EGMF were found in maximum amount after irradiation of 40 minutes and then started decreasing up to 100 minutes

of exposure and after 200 minutes these were found to degraded completely. It was observed that Methoxyacetic acid formed maximum after the interval of 20 minutes and the started decreasing.

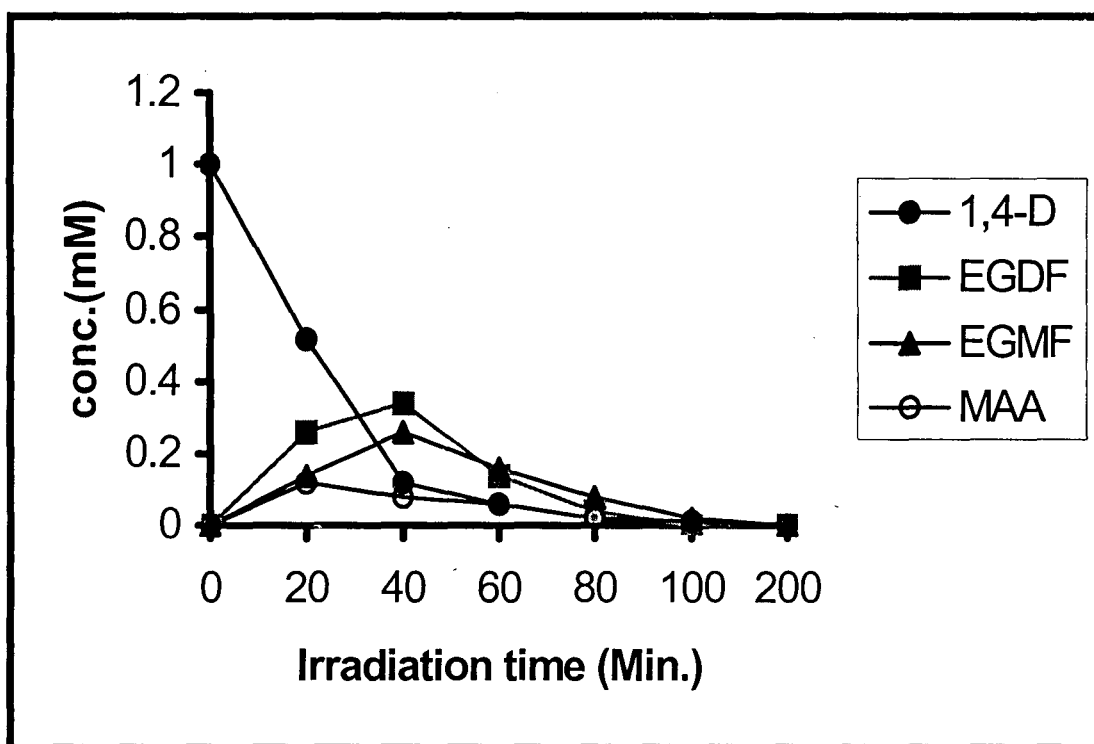
(B) Concentration of Hydrogen Peroxide: - The measured concentration of hydrogen peroxide was found to be decreasing rapidly in first 40 minutes and after that the concentration decreases steadily up to the next 100 minutes of the reaction. After 100 minutes of the irradiation, the concentration was found to decreases very slowly up to the end of the exposure (see **Table-2A** and **Graph-2A**).

(C) Change in pH value: - It was observed that there is decrease in pH during irradiation. pH dropped rapidly from 6.0 (t=0 min) to 4.2 (t=20 min) and then to 3.0 (t=40 min) after that it started increasing up to 4.5 (t=60 min) and 4.7 in 80 min and then reaches to 5.0 in 100 min and remains constant up to the end of the exposure as shown in **Table-3A** and **Graph- 3A**.

(D) Dissolved Oxygen Concentration:- It was found that the level of dissolved oxygen decreased sharply from 0.24 mM to 0.02 mM in 40 minutes and finally attained a steady state concentration and then started increasing up to the level of 0.70mM in 100minutes and again started increasing till a value of 0.72mM after 200 minutes.(see **Table-4 A** and **Graph-4A**)

Product Time(Min.)	1,4-Dioxane	Ethylene Glycol Diformate	Ethylene Glycol Monoformate	Methoxyacetic acid
0	1.00	0.00	0.00	0.00
20	0.52	0.26	0.14	0.12
40	0.12	0.34	0.26	0.08
60	0.061	0.14	0.16	0.06
80	0.020	0.04	0.08	0.02
100	0.00	0.00	0.02	0.01
200	0.00	0.00	0.00	0.00

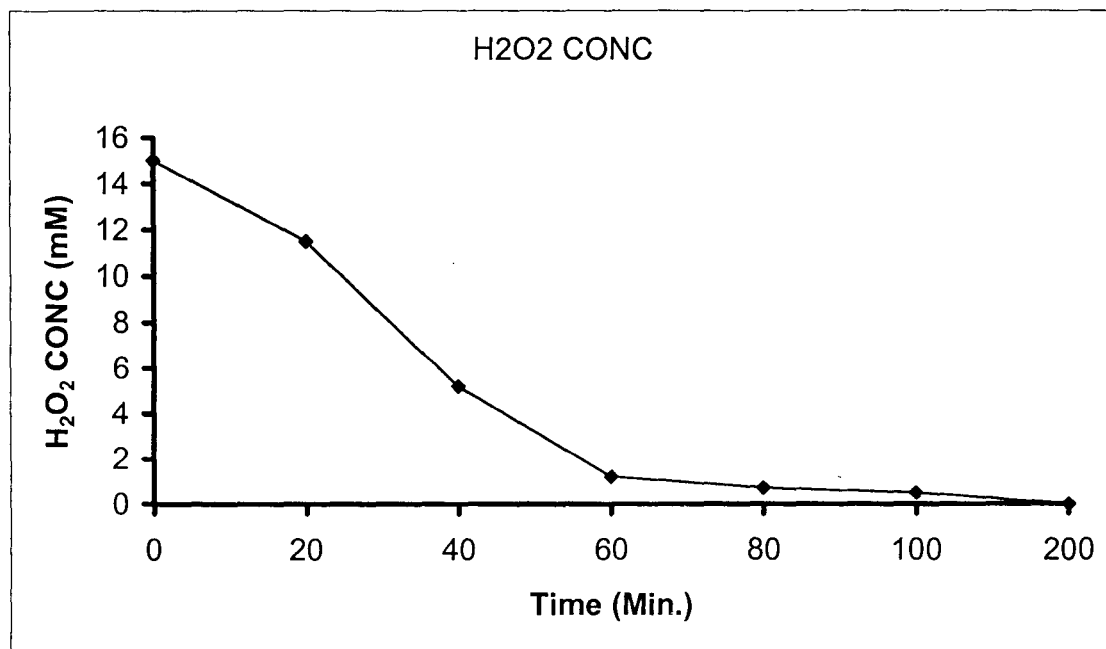
Table 1A- Change in conc. of 1,4-Dioxane and its byproducts (UV/H₂O₂).



Graph 1A- Change in conc. of 1,4-Dioxane and its byproducts (UV/H₂O₂).

Time (Min.)	0	20	40	60	80	100	200
H₂O₂ (Mm)	15.0	11.5	5.2	1.2	0.7	0.5	0.01

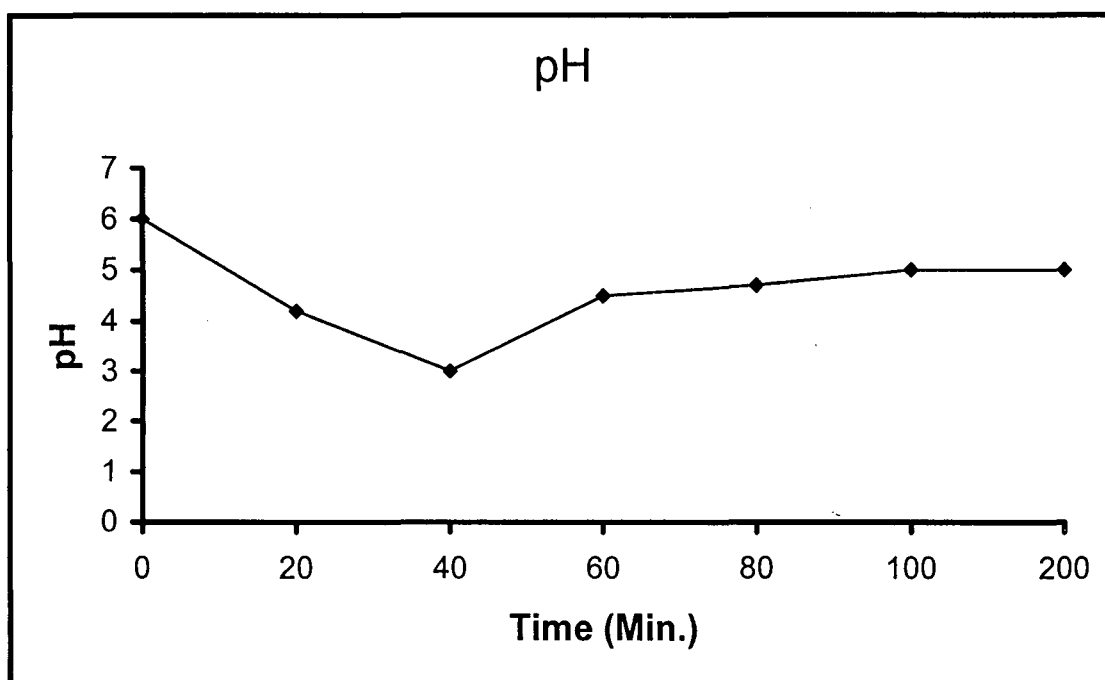
Table 2A. Change in conc. of Hydrogen peroxide (UV/ H₂O₂).



Graph 2A. Change in conc. of Hydrogen peroxide (UV/ H₂O₂).

Time (Min.)	0	20	40	60	80	100	200
pH	6.0	4.2	3.0	4.5	4.7	5.0	5.0

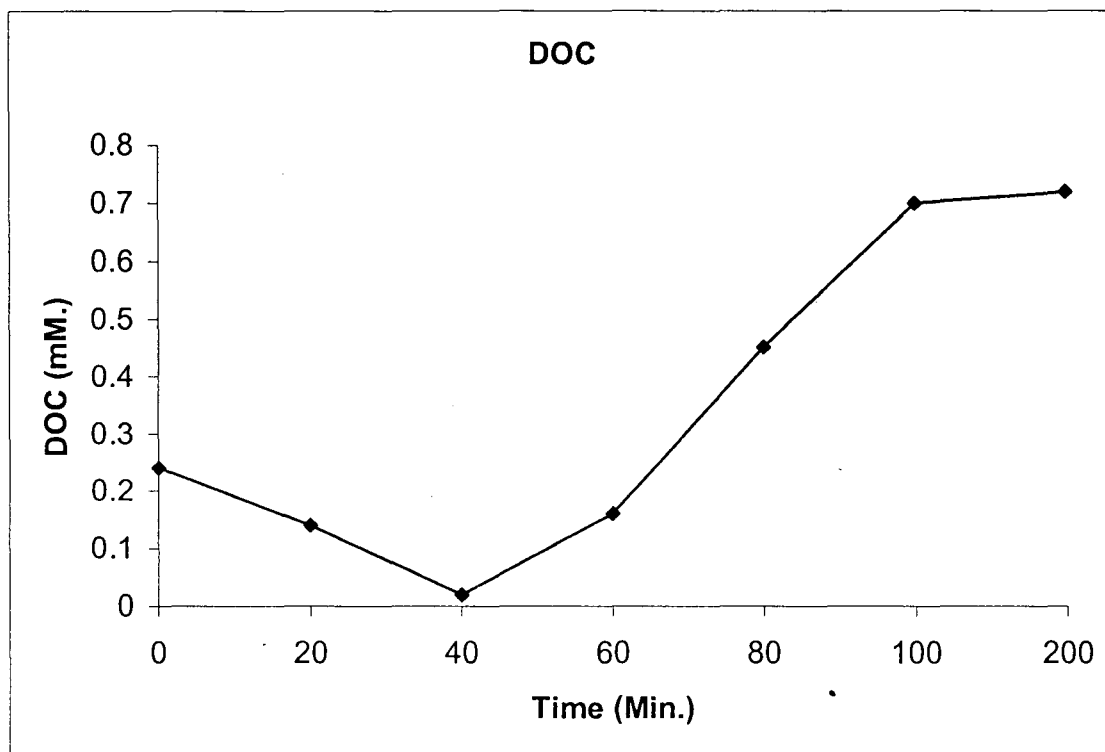
Table 3A- Change in pH value (UV/H₂O₂).



Graph 3A- Change in pH value (UV/H₂O₂).

Time (Min.)	0	20	40	60	80	100	200
DOC mM.	0.24	0.14	0.02	0.16	0.45	0.70	0.72

Table 4A- Change in conc. of Dissolved oxygen (UV/H₂O₂).



Graph 4A- Change in conc. of Dissolved oxygen (UV/H₂O₂).

Photolysis of 1,4-dioxane using UV/TiO₂ methods:-

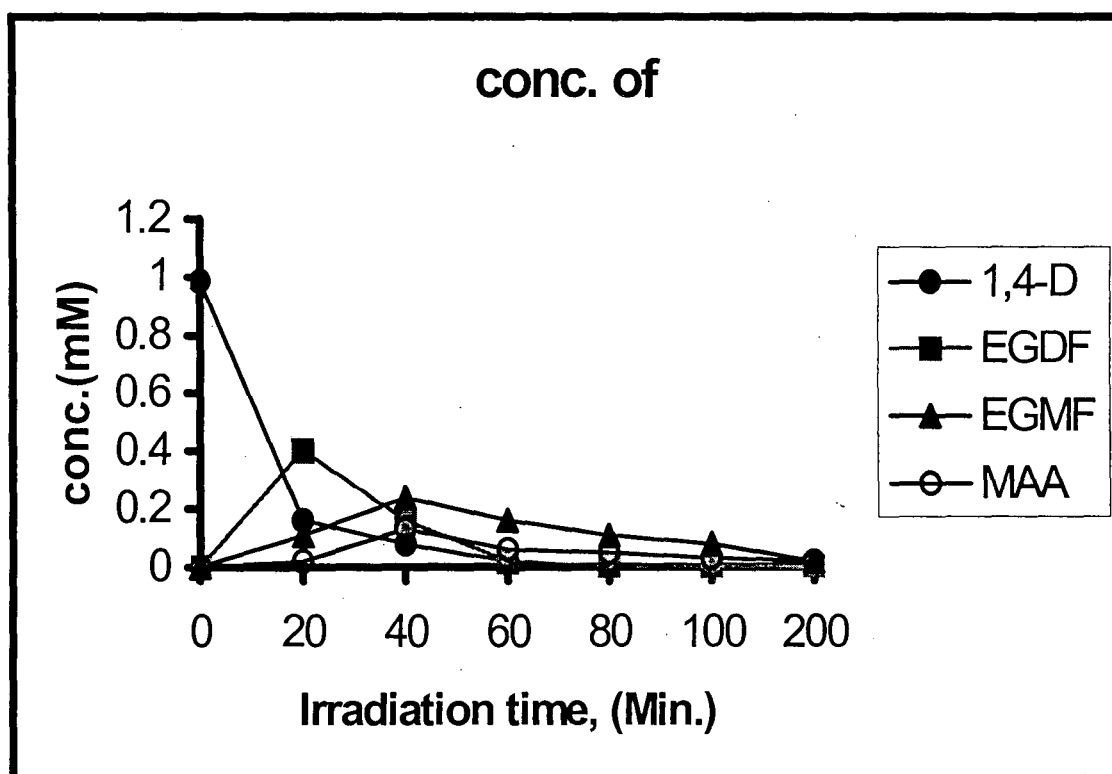
(A) Concentration of 1,4-dioxane:- In this irradiation experiment, the degradation of 1,4-dioxane was observed. Approximately, 85% of the initial concentration of 1,4-dioxane was depleted within 20 minutes of irradiation. In this experiment, three major primary by products were detected, of which 75% was EGDF and other 25% was EGMF and MAA. Retention Time were 1.48 minutes for 1,4-dioxane, 3.78 minutes for EGDF and 3.0 minutes for MAA. The concentration of 1,4-dioxane and three major primary reaction intermediates are shown in the **Table-1B** and **Graph-1B**.

(B) Change pH value:- It was observed that the pH value decreases during the irradiation during experiment. The pH rapidly dropped from 5.5 (t=0min) to 2.9(t=40min) and then started increasing up to 4.5(t=60min) 4.8 (t=80min) and 5.2 at 100min and remain constant up to 200minutes (see **Table-2B** and **Graph-2B**.)

(C) Dissolved Oxygen Concentration: - The level of dissolved oxygen rapidly decreased from 0.28 mM($t= 0\text{min}$)to 0.018mMin $t=20\text{min}$ and reaching a constant state of concentration and then increased rapidly and up to a value of 0.46mM in 100minutes and increases to the level of 0.68mM in $t=200\text{minutes}$.(see **Table-3B** and **Graph-3B**).

Product Time(Min.)	1,4-Dioxane	Ethylene Glycol Diformate	Ethylene Glycol Monoformate	Methoxyacetic acid
0	1.00	0.00	0.00	0.00
20	0.16	0.40	0.11	0.02
40	0.08	0.16	0.24	0.14
60	0.02	0.02	0.16	0.06
80	0.00	0.10	0.11	0.05
100	0.00	0.00	0.08	0.03
200	0.00	0.00	0.02	0.02

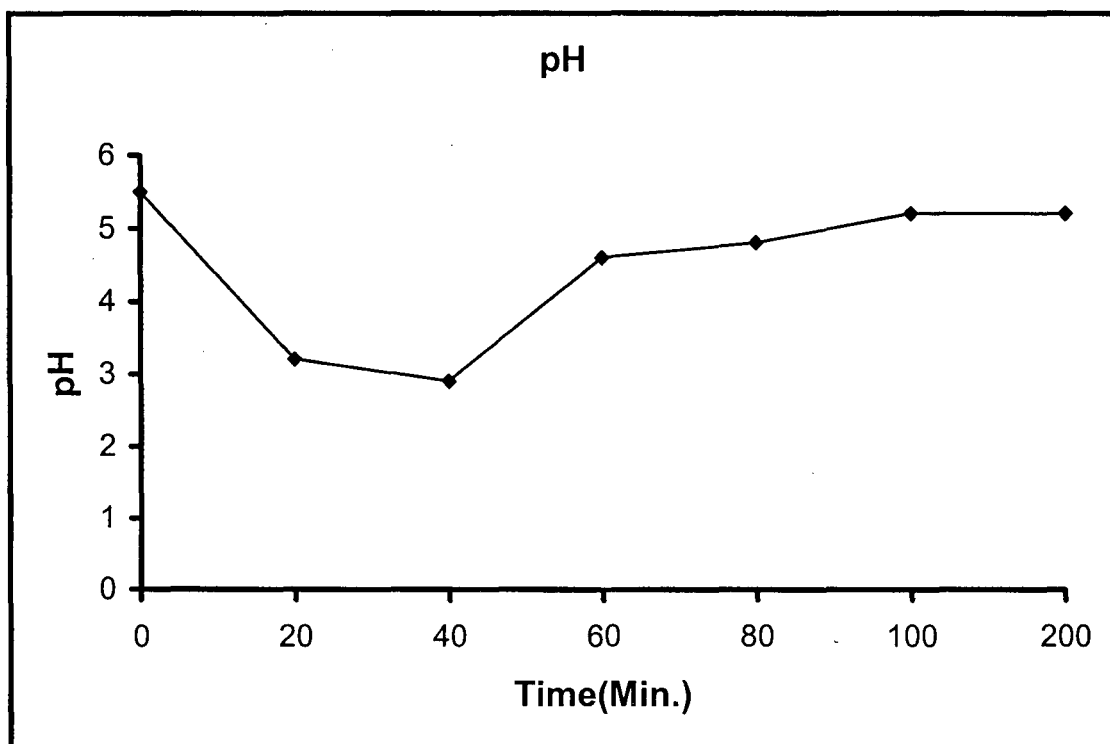
Table 1B- Change in conc. of 1,4-Dioxane and its byproducts (UV/TiO₂).



Graph 1B- Change in conc. of 1,4-Dioxane and its byproducts (UV/TiO₂).

Time (Min.)	0	20	40	60	80	100	200
pH	5.5	3.2	2.9	4.6	4.8	5.2	5.2

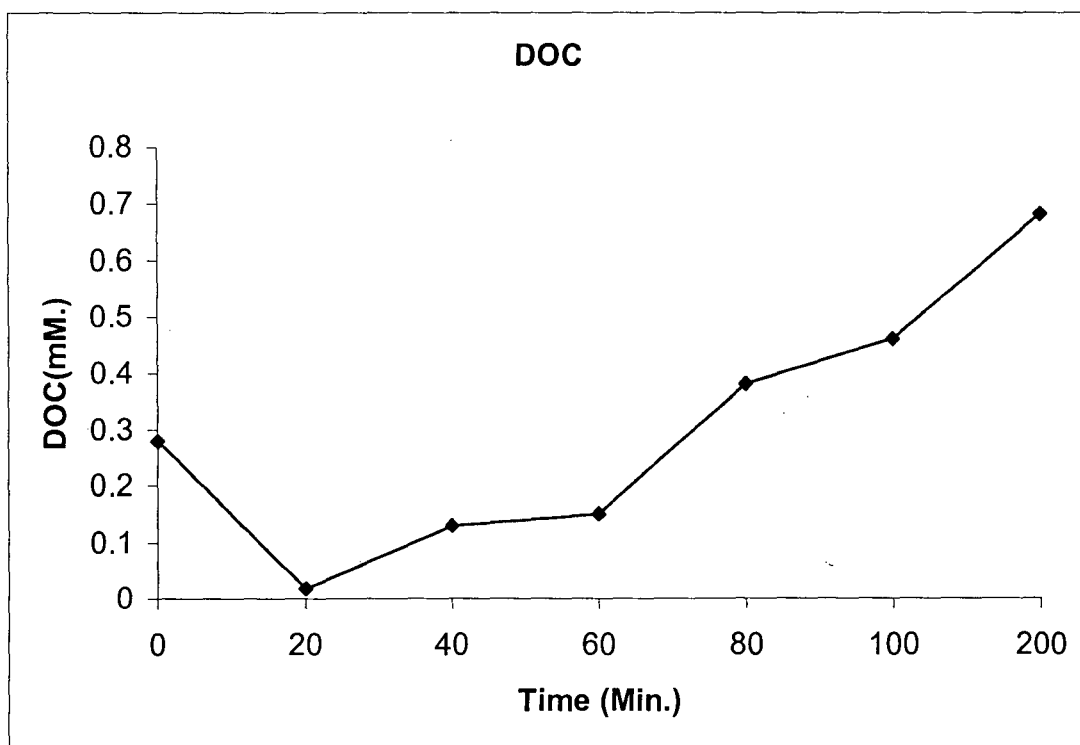
Table 2B- Change in pH value (UV/TiO₂).



Graph 2B- Change in pH value (UV/TiO₂).

Time (Min.)	0	20	40	60	80	100	200
DOC mM.	0.28	0.018	0.13	0.15	0.38	0.46	0.68

Table 3B Change in conc. of Dissolved oxygen (UV/TiO₂).



Graph 3B Change in conc. of Dissolved oxygen (UV/TiO₂).

DISCUSSIONS:

Comparative Analysis of the Data of Two Experiments (UV/TiO₂ and UV/H₂O₂ methods).

From the experiment data it can be said that the degradation of 1,4-dioxane using UV/TiO₂ is faster than UV/H₂O₂. Even though the primary reaction intermediates were similar in both cases. In the literature, it has been reported that four more secondary reaction products (Stefan and Bolton, 1998) have also been observed in the later period of exposure along with the three primary products which were measured by using Ion Chromatography (I.C), Thin Layer Chromatography(T.L.C) and High Performance Liquid Chromatography(H.P.L.C). The four secondary by product measured by the these chromatography were Formic Acid ,Glycolic Acid , Acetic Acid and Oxalic Acid which are weak acids.(see **Table-1C** and **Graph-1C**).

Initial concentration of hydrogen peroxide in UV/H₂O₂ was 15.0mM (added amount) which decreased rapidly and almost vanished at the t=200minutes, it was due to consumption of hydrogen peroxide in degradation of primary and secondary products.

A similar pH trend was observed in both the experiments. The lowest value was in case of UV/TiO₂ method is at t=20 minutes The basic reason

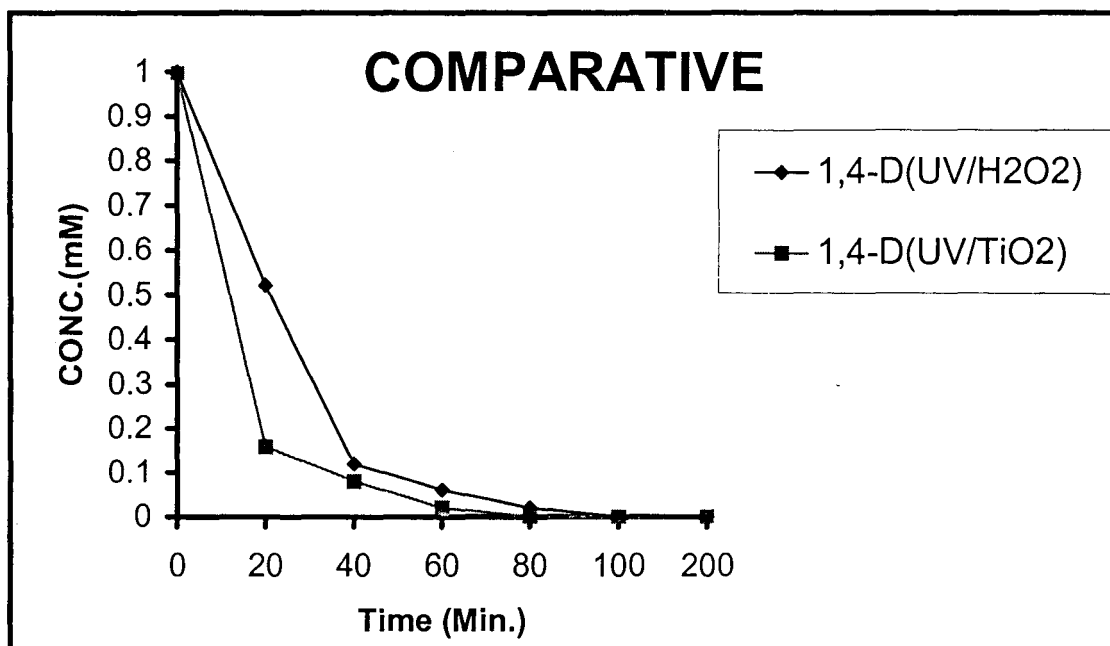
may be the early formation of organic acids which are primary products (Stefan and Bolton, 1998). However, in the case of UV/H₂O₂ method, the lowest pH was observed at t=40minutes. A consistent variation in the pH along with the formation of organic acids and their subsequent removal through oxidation reaction was observed in using both the methods. The lower pH observed at end of the experiment compared to its initial value is explained by dissolved CO₂ generated during the irradiation as shown in the **Table-2C** and **Graph-2C**.

The level of oxygen in both the methods follows the same pattern where it first decreases to a very low value then and increase .

- (1) The reason is due to rapid oxidation of parent molecules,
- (2) Formation and then the decay of highly oxygenated intermediates where as at the later stage there is a lower consumption of oxygen and
- (3) Generation of oxygen from photooxidation of H₂O₂ (Stefan and Bolton, 1998).(**Table-3C** and **Graph-3C**)

Time(Min.)	Product	
	1,4-Dioxane UV/H ₂ O ₂	1,4-Dioxane UV/TiO ₂
0	1.00	1.00
20	0.52	0.16
40	0.12	0.08
60	0.06	0.02
80	0.020	0.00
100	0.00	0.00
200	0.00	0.00

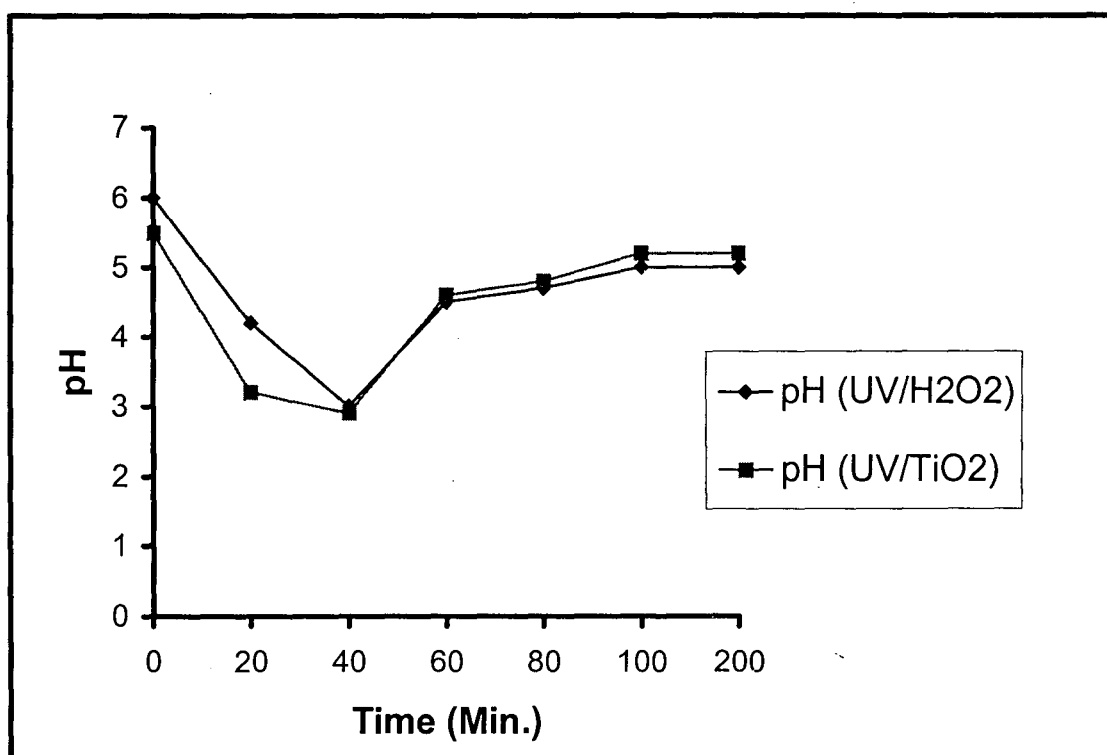
Table 1C Comparative change of 1,4- dioxane.



Graph 1C Comparative change of 1,4- dioxane.

Time (Min.)	0	20	40	60	80	100	200
pH UV/H ₂ O ₂	6.0	4.2	3.0	4.5	4.7	5.0	5.0
pH UV/TiO ₂	5.5	3.2	2.9	4.6	4.8	5.2	5.2

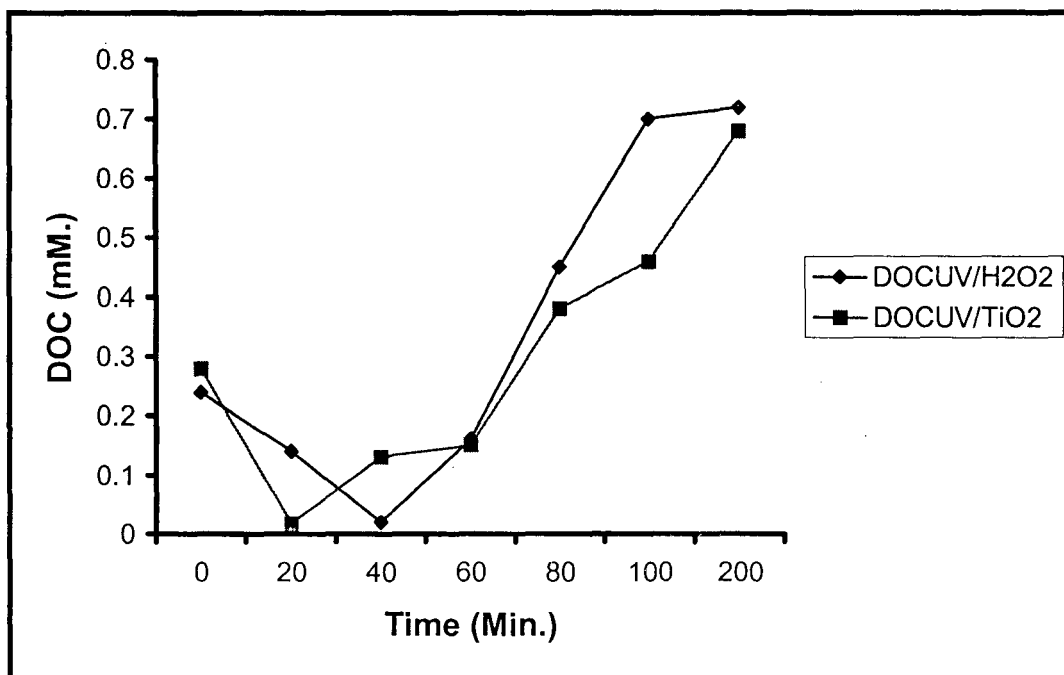
Table 2C Comparative change of pH.



Graph 2C Comparative change of pH.

Time (Min.)	0	20	40	60	80	100	200
DOC UV/H ₂ O ₂	0.24	0.14	0.02	0.16	0.45	0.70	0.72
DOC UV/TiO ₂	0.28	0.018	0.13	0.15	0.38	0.46	0.68

Table 3C Comparative change of Dissolved Oxygen.



Graph 3C Comparative change of Dissolved Oxygen.

Advantages and disadvantages of two methods: --

UV/TiO₂ method:

Advantages:

(1) This photocatalytic process requires the relatively mild reaction conditions required. (Matthews, 1986, 1987, 1988).

(2) It may decompose several toxic refractory pollutants which are not decomposed by the UV/H₂O₂ (Matthews, 1988, 1990; Pelizzetti et al., 1998; Davis and Huang, 1990)

(3) Catalyst activity does not affected and can be reused (Matthews, 1991).

(4) Activity of TiO₂ is slightly affected by the sulphates and other inorganic ions (Lows et al., 1991) because the degradation occurs at the surface where other inorganic ions are excluded because of the negatively charged surface (Kormann et al., 1991)

(5) Its use can be cost effective for treating wastewater. Matthews (1991) proposed that a lagoon of 1000m² (having the wastewater depth at 1.5 cm) would require 30 kg of TiO₂ for the treatment of 15000litre of wastewater polluted with some organic pollutants when irradiated in sun light (natural photodegradation) (Matthews, 1991).

(6) It is cost effective in treatment technology for wastewater.

Disadvantages:

- (1) Constant stirring is required in case of wastewater treatment.
- (2) Very large-scale treatment cannot be done.
- (3) It is cost effective treatment technology for wastewater.

UV/H₂O₂ method:**Advantages**

- (1) This process is suitable used for the large scale
- (2) Constant stirring is not required.
- (3) Not much labour is required to handle this type of treatment.
- (4) Recently, commercial units employing this process been developed for on-site oxidation of organic contaminants of wastewater and groundwater in some countries (Chin-Hsiang et al. 1995).
- (5) UV/H₂O₂ uses non-selective oxidants which can lead to complete oxidation of organic compounds to carbondioxide, water and inorganic ions.

Disadvantages

- (1) it is very much affected by the presence of inorganic ions like carbonates, bicarbonates and sulphates.

CONCLUSIONS

After analyzing the different parameters, advantages and disadvantages it can be said that for the degradation of 1,4-dioxane, UV/TiO₂ could be a better option.

Industries, which are using and releasing this pollutant, should have the treatment plant equipped with UV/TiO₂ or UV/H₂O₂ type of facility. Treatment of this pollutant (1,4-dioxane) at the source release should be treated with both the methods because water does not contain carbonates, bicarbonates and sulphates ions. Water bodies, which are contaminated with this pollutant, UV/TiO₂ methods can be a promising in treatment because this method is not affected by inorganic ions. These methods can be promising in wastewater treatment, which are contaminated with other organic compounds that are harmful to animal kingdom and environment.

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