SEMICONDUCTOR OXIDES MEDIATED PHOTOCATALYTIC REMOVAL OF CHEMICAL AND BACTERIAL POLLUTANTS FROM WASTEWATER

thesis submitted to cochin university of science and technology in partial fulfilment of the requirements for the award of the degree of

DOCTOR OF PHILOSOPHY
IN
ENVIRONMENTAL TECHNOLOGY
UNDER
THE FACULTY OF ENVIRONMENTAL STUDIES

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FEBRUARY 2006

Dedicated to my little kids

PRANAV AND VAISHNAV

DECLARATION

I hereby declare that the thesis entitled, "Semiconductor oxides mediated photocatalytic removal of chemical and bacterial pollutants from wastewater," is an authentic record of the research work carried out by me under the guidance and supervision of Dr. Suguna Yesodharan, Senior Lecturer, School of Environmental Studies, Cochin University of Science and Technology in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Environmental Technology and no part of this work has previously formed the basis for the award of any other degree in any University.

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Kochi-22,
February, 2006.

Certificate

This is to certify that this thesis entitled, "Semiconductor oxides mediated photocatalytic removal of chemical and bacterial pollutants from wastewater," is an authentic record of the research work carried out by Mrs. Suja .P. Devi Priya under my guidance and supervision in the School of Environmental Studies, Cochin University of Science and Technology in partial fulfilment of the requirements for the award of the degree of Doctor of Philosophy in Environmental Technology and no part of this work has previously formed the basis for the award of any other degree in any University.

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ACKNOWLEDGEMENTS

With immense pleasure, I place on record my heartfelt gratitude and great indebtedness to my supervising guide, Dr. Suguna Yesodharan, Senior Lecturer, School of Environmental Studies (SES), Cochin University of Science and Technology (CUSAT) for her inspiring guidance, motherly affection and unstinted co operation in this research work.

I gratefully acknowledge the present Director, Prof. (Dr.) Ammini Joseph, and the former Director, Prof. (Dr.) A. Mohandas, SES, CUSAT for providing me all the facilities.

I sincerely thank Prof. (Dr.) V. N. Sivasankara Pillai, former Director of the School for acting as the subject expert in the doctoral committee.

I am extremely thankful to Dr. I.S. Bright Singh, Reader, SES, for all the help I received during my research work.

My thanks are also due to the teachers Dr. M. V. Harindranathan Nair, Dr. S. Rajathy, Dr. V. Sivananandan Achari and Mr. Anand of the School for their concern.

I record my gratitude to all the non-teaching staff of the School and the Administrative Office for extending me all help.

I recall with love and gratitude the sincere cooperation and encouragement I received from my friends Peeter, Balu, Rajesh, Alex, Manu, Shiny, Rekha, Vidhya, Manju, Surekha, Jitha, Subitha, Shahanaz, Valsamma, Binu, Joseph,Ranjith, Anas, Somnath, Sunil, Jayaprakash, Shibu, Sudheer, Deepesh, Rejesh, Sreedharan, Preetha, Cini, Blessy, Surya, Sena, Manju, Rehana, Jean and Radhika of CUSAT.

I gratefully acknowledge the financial support received from CUSAT and CSIR, New Delhi as JRF and SRF.

I also take this opportunity to express my love and gratitude to my parents, parents–in-law, husband and brother for their cooperation and support.

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PREFACE

Heterogeneous photocatalysis, with primary focus on semiconductor oxides as catalysts, has been applied to a variety of environmental problems related to the decontamination and purification of air and water and the elimination of toxic and hazardous wastes from industrial effluents. It has also been shown to be useful for the destruction of micro organisms such as bacteria and viruses, for odour control, for the photo splitting of water to produce hydrogen gas, for the fixation of nitrogen and for the clean up of oil spills.

In the present study, the application of this Advanced Oxidation Process (AOP) is examined for the destruction of small amounts of chemical and microbial pollutants in water using ZnO and TiO_2 as photocatalysts. The main objectives of the investigation are:

i. To test the application of TiO_2 mediated photocatalysis and identify optimum parameters for the degradation and mineralisation of phosphamidon, one of the widely used organophosphorous insecticides, especially in developing countries. The influence of various parameters, naturally encountered in water/wastewater, such as pH, presence of anions etc. and the reaction products and intermediates such as in situ formed H_2O_2 are also to be investigated. To the best of our knowledge, this is the first investigation on the photocatalytic degradation of phosphamidon.

ii. To understand more clearly the role of two different semiconductors, ZnO and TiO_2 and their mixtures on the photocatalytic degradation of a major water pollutant from petrochemical industries; i.e. phenol. In spite of being one of the most widely investigated chemical pollutants, there is no unanimity among researchers on the mechanism of the photocatalytic degradation of phenol or the influence of various parameters on the kinetics of the reaction. This study was hence also aimed at collecting further evidence for or against the arguments forwarded by various research teams. Another aim of this investigation was to understand more about the role of dopants and inter-particular electron transfer and to exploit the observations from them to design more efficient catalysts for the photodegradation of phenol in water.

iii. To examine the possibility of using semiconductor mediated photocatalysis for the inactivation of bacteria in water. Preliminary studies by few researchers did suggest the positive contribution of catalysts such as TiO_2 in this respect. However, they do not agree on the precise role of the catalyst and there is no systematic study so far aimed at resolving the practical problem of removing suspended catalyst particles from the decontaminated water. In this context, this study also had the objective of immobilising the catalyst on commonly available supports to overcome the problem of turbidity and separation of the particles and enhance the practical applicability of the technique.

iv. To build on the findings of the investigation and to develop inexpensive, 'easy to use' immobilised catalysts for the elimination of chemical and bacterial contaminants from water. The study aims to focus on common materials such as ceramic tiles as catalyst supports and evaluate the efficacy of such supported catalysts for the photo decolourisation and degradation of dyes and the deactivation of bacteria such as *E.coli.*

The investigations were carried out in accordance with the above objectives and the results are compiled in four chapters (Chapters 2-5) in this thesis. Additionally, the thesis also has a comprehensive introduction as Chapter 1 and conclusions of the investigation as Chapter 6.

The plan of the thesis is as follows:

Chapter 1. General introduction

This chapter gives a general review of the current status of knowledge on 'Environmental applications of photocatalysis'. Primary events and reactive species in photocatalytic processes, various catalyst reactor systems and the photocatalytic degradation of different kinds of chemical and bacterial pollutants are described. The application of solar energy in photocatalysis also is briefly discussed.

An expanded version of the contents of this chapter is published as the lead review article entitled, 'Photocatalytic degradation of pesticide contaminants in water' in the journal, 'Solar Energy Materials and Solar Cells', 86 (2005) 309-348.

Chapter 2. Photocatalytic degradation of Phosphamidon on semiconductor oxides

This chapter deals with the investigations on the photocatalytic degradation of the organophosphorous insecticide, Phosphamidon in water. The kinetics of the reaction as well as the influence of various parameters on the degradation has been studied.

Some of the findings reported in this chapter are published as original research contribution entitled, 'Photocatalytic Degradation of Phosphamidon on Semiconductor Oxides' in the journal, 'J Hazard. Mater. 102 (2003) 217-229.

Chapter 3. Photocatalytic degradation of phenol on semiconductor oxides

Results of the study on the role of various semiconductor oxides on the photocatalytic degradation of phenol are presented in this chapter. The influence of various reaction parameters, additives, catalyst composition etc on the kinetics of the degradation is investigated and reported. The complexity of the reaction is emphasized by comparing the results with the findings of various authors.

Some of the results discussed here were presented as an original research paper entitled, 'Solar wastewater treatment using TiO_2 with reference to photocatalytic degradation of phenol in water,' in the National Conference on 'Titania' held at Trivandrum in 2002 and published in its proceedings (pp 167-172).

Chapter 4. Photocatalytic inactivation of bacterial pollutants using TiO_2

This chapter discusses the findings on the application of TiO_2 mediated photocatalysis for the deactivation of bacterial pollutants from water. The influence of various parameters on the killing and re-emergence of the bacteria is investigated and presented. The immobilisation of the catalyst on simple and otherwise 'thrown away' PET bottles and its application in the deactivation of bacteria in water are investigated for the first time.

Some of the results from this chapter have been published as original research paper entitled 'Inactivation of *Escherichia coli* in water using TiO_2 as photocatalyst,' in the journal, 'Poll. Research', 24 (2005) 97-101.
Another part of the findings was presented as an original research paper entitled, 'Photocatalytic Disinfection of Drinking Water using TiO_2 coated PET bottles,' in the XVII Kerala Science Congress held at Peechi, India in 2005 and published in its proceedings (pp 178-180)

Chapter 5. Photocatalytic removal of chemical and bacterial pollutants in water using TiO_2 immobilised on ceramic tiles.

The immobilisation of TiO_2 on ceramic tiles and its application as a photocatalyst for the removal of chemical pollutants such as dyes and bacterial pollutants such as *E.coli* are discussed in this Chapter. This is the first instance of using such an immobilised catalyst in these two specific applications.

Part of the findings discussed in this chapter were presented as an original research paper entitled, 'Photocatalytic Removal of Chemical and Bacterial Pollutants in Water with TiO_2 immobilised on Ceramic Tiles' at the

'International Conference on Science and Technology for Sustainable Development, held in 2005 at Changanassery, Kerala, India.

Chapter 6. Summary and Conclusions

This chapter summarises the findings and the major conclusions drawn from the current study.

The thesis is concluded with a list of publications reviewed during the course of the investigation and referred to in various chapters under the title 'References'. In the Appendix that follows is included a list of publications in journals and papers presented in various conferences based on the results of the current study.

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Chapter 1

GENERAL INTRODUCTION

Photocatalytic degradation has been proved to be a promising method for the treatment of wastewater contaminated with organic and inorganic pollutants. The process, as a means of removal of persistent water contaminants such as pesticides that exhibit chemical stability and resistance to biodegradation, has attracted the attention of many researchers in recent years [1-19]. Many of these investigations have utilized aqueous suspensions of semiconductors illuminated by UV light to photodegrade the pollutants. The method offers many advantages over traditional wastewater treatment techniques such as activated carbon adsorption, chemical oxidation, biological treatment etc. For instance, activated carbon adsorption involves phase transfer of pollutants without decomposition and thus induces another pollution problem. Chemical oxidation is unable to mineralise all organic substances and is only economically suitable for the removal of pollutants at high concentrations. For biological treatment, the main drawbacks are: slow reaction rates, disposal of sludge and the need for strict control of pH and temperature. In this context, photocatalytic processes offer many advantages for the removal of pollutants of low concentration from water. These include [18]:

- Complete oxidation of organic pollutants within few hours
- No formation of polycyclic products
- Availability of highly active and cheap catalysts capable of adapting to specially designed reactor systems
- Oxidation of pollutants in the ppb range etc.

Several catalysts have been studied as potential photocatalysts for this purpose. These include: CdS [20, 21], ZnS [22], α-Fe_2O_3, γ- Fe_2O_3, α-FeOOH, β-FeOOH, and γ-FeOOH [23,24], ZnO [22,25], TiO_2 [26-28 and most of the papers referred in this work], ZrO_2, SnO_2 and WO_3 [29-32], CN^- [33], $Cr_2O_7^{2-}$ [34], $AgCl/Al_2O_3$ [35], Niobium oxides [36], Lanthanide tantallates ($LnTaO_4$ where Ln can be La, Ce, Pr, Nd and/or Sm) [37], ZnO/TiO_2 [38], TiO_2/SiO_2 and TiO_2/Al_2O_3 [39]. Among the semiconductors used, TiO_2 is one of the most popular and promising materials, because of its stability under harsh conditions, commercial availability, existence in different allotropic forms with high photo-activity, possibility of its coating as a thin film on solid support, ease of preparation in the laboratory etc. Its absorption spectrum overlaps with the solar spectrum and hence opens up the possibility of using solar energy as the source of irradiation. Another advantage is that the photocatalytic activity of TiO_2 can be studied in the fixed bed form as well as in the suspended form. Further, TiO_2 based mixed oxide catalysts such as TiO_2/In_2O_3 [40], TiO_2-SiO_2 and TiO_2-ZrO_2 [41], supported catalysts such as Pt/TiO_2 [42], Rh/TiO_2 and Ru/TiO_2 [43,44] and titania based thin films [45,46] have also been proved to be very good photocatalysts.

Extensive investigations have been reported on the photocatalytic degradation of organic compounds such as chlorinated compounds, chloro- and nitro-phenols, dyes, pesticides and aromatic compounds. These have been summarised in a number of excellent research papers and review articles [47-59] and many books [3, 4, 14, and 19]. Despite their benefits, many of these chemicals still remain as an issue of great concern as they are often toxic to birds, mammals and other living organisms and are also more likely to contaminate surface and ground waters. This concern has led to the search for powerful methods for their complete degradation and mineralisation to environmentally compatible products. Semiconductor mediated photocatalytic oxidation is becoming one of the possible environment-friendly techniques for the removal of trace organic pollutants, including pesticides and dyes in water. Of late, the technique is being investigated extensively for the removal of bacterial pollutants as well. This chapter reviews some of the major publications in the area.

Many of the papers and reviews referred above give extensive description of the surface photo-processes on various catalysts and reaction mechanisms. Those aspects relevant in the context of the current investigation are discussed here.

1.1. Primary Events and Reactive Species in Photocatalytic Processes

Pelizzetti et al. [60] has summarised the primary events taking place in a photocatalysed reaction as follows:

$$TiO_2 + h\nu \rightarrow e^- + h^+ \qquad (1)$$

$$(O_2)ads + e^- \rightarrow (O_2^{-\cdot})\ ads \qquad (2)$$

$$\mathrm{Ti\ (IV)\text{-}OH^{-}} + \mathrm{h^{+}} \leftrightarrow \mathrm{Ti(IV)\text{-}{}^{\cdot}OH} \qquad (3a)$$

$$\mathrm{Ti\ (IV)\text{-}OH_2} + \mathrm{h^{+}} \leftrightarrow \mathrm{Ti(IV)\text{-}{}^{\cdot}OH} + \mathrm{H^{+}} \qquad (3b)$$

When a semiconductor oxide (e.g. TiO_2) is irradiated with light having energy (hυ) higher than the band gap, a pair of conduction band electron (e^-) and valence band hole (h^+) is generated (reaction 1). After this primary event, the charge carriers either recombine with the bulk of the material or migrate to the particle surface where they can also recombine or can be trapped at some defect sites, eventually as substrate bound $O^{-\cdot}$ radicals [61]. The electron-hole pair will also initiate oxidation and reduction processes of adsorbed substrates. In aqueous solutions, the holes are scavenged by surface hydroxyl groups to generate strong oxidising hydroxyl radicals ($^{\cdot}OH$), which can promote the oxidation and eventual mineralisation of organic compounds as shown in figure 1.1.

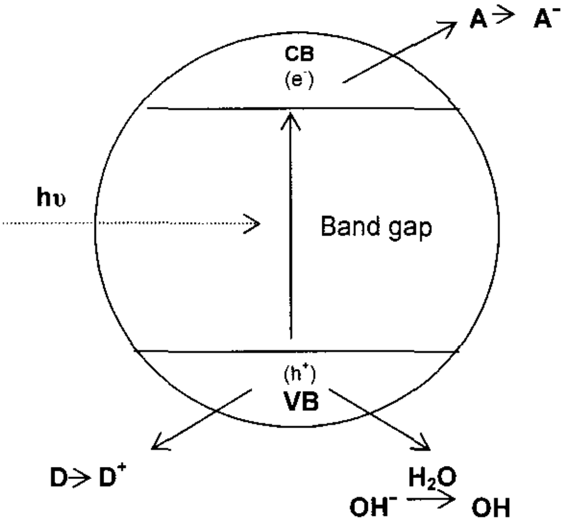


Fig 1.1. Schematic representation of the photochemical activation of a semiconductor and formation of the hydroxyl radical [49].VB: Valence band; CB: Conduction band; A: Electron acceptor compound; D: Electron donating compound.

In the case of TiO_2, the most investigated photocatalyst, the significant event that takes place at the surface is the adsorption of molecular oxygen on the Ti (III) sites which reduces O_2 to the superoxide radical anion, $O_2^{-\cdot}$ (reaction 2). The positive charge carrier, Ti(IV)-$O^{-\cdot}$-Ti(IV), can oxidise the surface hydroxyl groups or the surface bound water (reactions 3a and b) to surface-bound $^{\cdot}OH$ radicals. Pulse radiolytic studies by Lawless et al. [62] were unable to distinguish between the surface bound $^{\cdot}OH$ radicals and the Ti (IV)-$O^{\cdot-}$-Ti (IV) species.

All the studies referred here show that the presence of molecular oxygen and water is essential during the photo-mineralisation process. The trapping of charge carriers by O_2 and H_2O (equations 2 and 3) serves to suppress the electron – hole recombination (see figure 1.2), thereby increasing the competitiveness of the light-induced redox processes.

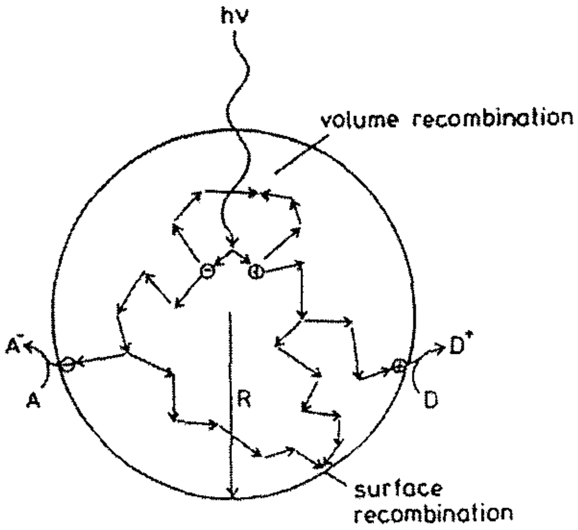


Fig 1.2. Fate of electrons and holes within a spherical particle of TiO_2 in the presence of Acceptor A and donor D [after Dr. Gerisher in ref.14]

Chemical identification of hydroxylated intermediates [63, 64] as well as the detection of $^{\cdot}OH$ radicals on irradiated TiO_2 by EPR studies [65] suggest that $^{\cdot}OH$ radicals, whether free or surface-bound, are the active oxidising species in the photocatalytic degradation of organics on TiO_2. However, the direct oxidation of the organic chemical with the hole in the valence band, indirect reaction with trapped holes and the participation of several other photogenerated reactive species also play important roles in the process [55, 66-68]. It has also been reported that in acidic media, $O_2^{\cdot-}$ gets protonated to form the hydroperoxide radical $HO_2^{\cdot}$, which is subsequently converted to H_2O_2 [69].

Where the light source has a significant UV component (250 – 300 nm), absorption of this wavelength by hydrogen peroxide and/or its interaction with the photo-formed electrons can yield $^{\bullet}OH$ radicals which can propagate the reaction. Externally added as well as in situ formed H_2O_2 was found to enhance the photocatalytic degradation of organic compounds in many cases [70, 71]. The decomposition of H_2O_2 also yields more OH radicals leading to accelerated rate of degradation of the organics. This simultaneous formation and decomposition of H_2O_2 is well illustrated by the oscillation in its concentration during the photocatalytic degradation of alcohols [70, 72]. The role of H_2O_2 in generating the reactive species is expressed in the following scheme:

$$^{\bullet}OH + {}^{\bullet}OH \longrightarrow H_2O_2 \qquad (4)$$

$$HO_2^{\bullet} + HO_2^{\bullet} \longrightarrow H_2O_2 + O_2 \qquad (5)$$

$$HO_2^{\bullet} + H^{\bullet} \longrightarrow H_2O_2 \qquad (6)$$

$$H_2O_2 + H^{\bullet} \longrightarrow H_2O + {}^{\bullet}OH \qquad (7)$$

$$H_2O_2 + {}^{\bullet}OH \longrightarrow H_2O + HO_2^{\bullet} \qquad (8)$$

$$H_2O_2 + HO_2^{\bullet} \longrightarrow H_2O + {}^{\bullet}OH + O_2 \qquad (9)$$

1.2. Catalysts and reactor systems

Many of the photocatalytic reactions, aimed at water purification, are carried out with the catalyst suspended as fine particles in the contaminated water, employing a low solid concentration and a slurry reactor. The reactor configurations tested include: fixed bed [73], fluidized bed [74], an immobilised membrane fixed on the reactor walls [75], a reactive wall reactor [76] and an immobilised film coating a bundle of optical fibres [77]. Even though not conclusively established, it had been generally accepted that the highest efficiency is obtained with the suspended solid approach. However, it has also been recognised that the cost of catalyst separation from the treated water may partially offset this advantage. In spite of this, much of the work continues to be done in slurry reactors using suspended catalysts and the highest catalytic efficiency is reported from such systems [78, 79]. The scaling up of slurry-type reactors for large-scale applications poses challenges, especially on the parameters for optimum radiation absorption. The concomitant presence of absorption and scattering of radiation in suspended solid systems makes the evaluation of light distribution difficult. A new method reported recently by Brandi et al. [80] to measure 'volume-averaged volumetric rate of photon absorption' (VRPA) is of interest in this context. Another type of reactor, tested successfully for the purpose is 'Rotating Disk Photocatalytic Reactor' (RDPR) in which pesticides such as lindane and chlorophenols are photodegraded and mineralised in a continuous flow mode [81]. The degradation rate followed a saturation type dependency with the effluent concentration.

Many studies reported that significant enhancement in photoactivity can be achieved by coupling semiconductors [82-84]. This enhancement is explained to be the result of an efficient charge separation process and a subsequent higher disposability of the reactive electron-hole pair. However, the process may be more complex and the chemistry of the substrate as well as the reaction intermediates may also have an important role in determining the ultimate photoactivity of a catalyst. For e.g. TiO_2 was reported to be far superior to ZnO in the photocatalytic degradation of nitrobenzene [62] and cellulose bleaching effluent [85] while ZnO exhibited comparatively much higher efficiency in the degradation of certain reactive dyes [49] and black liquor [86]. Clearly, further studies are needed to understand the precise role of the catalysts, especially the processes taking place at the interface.

1.3. Characteristics of TiO_2 photocatalysts

By far, the most investigated photocatalyst for the removal of organic pollutants from water is TiO_2 in various physicochemical forms [87-89]. These studies suggest that the photocatalytic activity of TiO_2 in suspension depends on the physical properties of the catalyst (e.g. crystal structure, surface area, surface hydroxyls, particle size) and operating conditions (e.g. light intensity, oxygen, initial concentration of chemicals, amount of TiO_2 and pH value). Ohtani et al. [90] investigated the effect of crystal structure of TiO_2 on its photocatalytic activity and reported that the activity of amorphous TiO_2 is negligible whereas anatase having the same particle size has appreciable photoactivity. Tanaka et al. [91] studied the effect of crystallinity of TiO_2 on its photocatalytic action for the degradation of trichloroethylene, dichloroacetic acid and phenol and reported that pure anatase has the best catalytic efficiency while pure rutile has the least. However, Lee et al. [92] report that the rutile-anatase ratio of TiO_2 is not very important in determining its photocatalytic efficiency to degrade organic pollutants. They observed that irradiation of TiO_2 with laser light resulted in the development of more rutile form of the oxide. The treatment results in the formation of more spherical shaped particles, though the average particle size remains mostly unchanged. The band gap or surface area also does not undergo much change by this irradiation. While studying the effect of particle size on the photocatalytic hydrogenation of propyne ($CH_3C{\equiv}CH$), using TiO_2 suspensions, Anpo et al. [93] noted that the activity increases with decrease in particle size, especially with particles of diameter less than 10 nm. According to them, reduction in particle size might result in some electronic modification of TiO_2 and produce an enhancement of the activities of electrons and holes and/or suppression of the radiationless transfer of absorbed photon energies. Similar results were reported by Xu et al. [56] from their study on the photocatalytic degradation of methylene blue in aqueous suspensions.

Recent studies suggest that surface modification of nanocrystalline TiO_2 with specific chelating agents such as benzene derivatives [94], aminocarboxylic acids [95] and arginine, lauryl sulfate and salicylic acid [96] increases the catalytic activity. The enhancement is explained on the basis of improved redox properties of TiO_2 and facile transfer of photogenerated electrons from the conduction band of TiO_2 to the adsorbed species. Similarly, TiO_2 modified by anchoring onto transparent plates of porous silica glass (prepared by metal ion implantation) also showed improved activity possibly due to the formation of tetrahedrally co-ordinated TiO_2 moieties [97]. It has also been reported [98] that combustion synthesised nano TiO_2 has much higher activity compared to commercial TiO_2, towards the photodegradation of organic compounds, which is attributed to crystallinity, higher surface area, more surface hydroxyl groups and optical absorption at higher wavelength. Hydrogen thermal treatment of TiO_2 at 500 – 600^0C enhances its photocatalytic activity, probably due to the formation of oxygen vacancies and trivalent titanium (Ti^{3+}) in the lattice [99]. Another study [100] showed that impregnation of polycrystalline TiO_2 with functionalised Cu(II) or metal-free porphyrine and Cu(II) phthalocyanines enhances its photocatalytic activity significantly. The mechanism indicates that the process involves co-operative roles for both TiO_2 and the sensitizer. Such observations open up the possibility of improving the photocatalytic activity of TiO_2 (as well as other catalysts) by physicochemical modification of the catalysts. The large number of research papers that continue to be published in the area suggests that researchers are investigating this possibility vigorously. However, studies on the possible ways of enhancing the catalytic activity by noble metal deposition or ion doping have not yielded consistent results so far. The effect often depends on the chemical reactions leading to the degradation of the target molecule. For example, deposition of Pt on TiO_2 is beneficial for hydrogen-evolving reactions, while it is detrimental to oxidation reactions. This was accounted for by the electron transfer to metal nano-crystallites, which is concurrent to dioxygen ionosorption [5].

$$\mathrm{Pt} + e^- \rightarrow e^-(\mathrm{Pt}) \qquad (10)$$

$$O_2(g) + e^- \rightarrow O_2^-(\mathrm{ads}) \qquad (11)$$

Further, once negatively charged, the platinum particles attract holes, which recombined with electrons, making the electrons and holes unavailable for photocatalysis. However, it has been reported recently [101] that deposition of Rhodium (Rh) on TiO_2 improved the durability of the TiO_2 in benzene photo-oxidation. The role of Rh^0 is to reduce the intermediates and by-products on the catalyst surface, which were responsible for the deactivation. XPS studies showed that the gradual deactivation of the catalyst was due to changes in the oxidation state of the surface Rh metal. The catalysts were regenerated by hydrogen reduction, indicating that Rh^0 was essential for improving the catalyst durability. Rh/ TiO_2 has been shown to be a good photocatalyst for solar splitting of water as well [44]. Similarly, the deposition of Ag on nano-particular TiO_2 enhanced the photocatalytic activity of the latter, both in the visible and UV regions, the effect being more pronounced in the visible region [102]. The enhancement is attributed to the Ag deposit acting as an effective electron trap and facilitating adsorption of the reactant molecule at the Ag- TiO_2 interface.

Ion doping is another modification aimed at extending the photosensitivity of TiO_2 into the visible region to harvest cheaper and more abundant solar photons. Either n-type (Nb^{5+}, Sb^{5+}, Mo^{6+}, Ta^{5+}) or p-type (Ga^{3+}, Cr^{3+}, Al^{3+}) ions may be used as dopants. However, ion doping was found to strongly inhibit the reaction and decrease the quantum yield [103], especially in the case of Cr^{3+}. This was explained as due to the fact that both pentavalent donor impurities and trivalent acceptor impurities behave as electron – hole recombination centres. Similarly, the presence of transition metal ions such as molybdenum, vanadium and tungsten was found to reduce the photocatalytic activity of TiO_2 [104].

Another approach, aimed at expanding the photo activity of TiO_2 towards the visible light range, which will be particularly relevant from the solar energy point of view, was reported by Omata and Matsuo [105]. In this case, composite particles composed of TiO_2 and acceptor doped perovskite involving alkaline earth elements were synthesised and tested as catalysts. Although the photocatalytic activity of perovskite type oxide $Sr(Zr_{0.90}Y_{0.10})O_{3-\delta}$, being a p-type semiconductor, is weak, it absorbs light of wavelength less than 800 nm. On the other hand, TiO_2 being an n-type semiconductor, is a good photocatalyst, though it does not absorb visible light. Under irradiation with visible light, with wavelength greater than 420 nm, the composite particles involving p-n junction exhibited several times higher photocatalytic activity in the photodegradation of organics, compared to TiO_2. Similar results were obtained for other composite powders as well. The results were explained by a model involving the flow of photogenerated holes and electrons through the p-n junction of the composite particles.

A novel method of immobilisation of the TiO_2 photocatalysts on a metallic support (SS304), using the chemically inert and photo-stable fluororesins–PTFE (Teflon) as a binder, has been reported [106]. The optimum conditions for preparing the most efficient immobilised catalyst were identified using the degradation of chlorophenol as the test reaction. Characterisation of the catalyst by SEM and XRD techniques showed that immobilised TiO_2 was mainly exposed on the top surface of the metallic support and still kept the original crystal phase (mainly anatase) of TiO_2 powder. The efficiency of the catalyst was less compared to suspended TiO_2 system. However, the method offered many advantages such as easy preparation at a relatively lower temperature (120^0C), avoiding the need to filter and providing more flexibility in catalyst configuration for photo-reactor.

Another interesting observation on modification of TiO_2 for photocatalysis has been reported recently [107]. In this case, a polyoxometalate, α-12 tungstophosphatic acid (PW_{12}^{3-}) is loaded onto the surface of TiO_2 and used as a co-catalyst in the photocatalytic degradation of organics. The PW_{12}^{3-} species enhances the charge separation in the illuminated TiO_2, thereby accelerating the hydroxylation of the substrate (2, 4-dichlorophenol), but not the mineralisation, which is surprisingly suppressed. The study infers that enhancement of charge separation in TiO_2 photocatalyst does not always result in improvement of the efficiency of mineralisation of organic substrates. The preparation of a novel paper-based material containing TiO_2 photocatalyst, reported recently [108], is also worth examining further. The method involves supporting of TiO_2 particles, on inorganic fibres by employing papermaking techniques. The catalyst has been reported to have excellent photocatalytic performance and durability. Another variation of the catalyst involves the synthesis of TiO_2 by HyCOM (Hydrothermal Crystallisation in Organic Media) which exhibit ultra high photocatalytic activity in several reaction systems [109].

1.4. Photocatalytic degradation of pesticide contaminants in water

The presence of pesticide contaminants in surface and ground water has increased many-fold in recent years due to their large-scale use in intensive agriculture. The sources of this contamination may be summarised as follows:

(i) Pesticide treatment as routine agricultural practice
(ii) Rinse water polluted with pesticides from containers and spray equipment
(iii) Waste water from agricultural industry (cleaning or post harvest treatment of fruits and vegetables) and
(iv) Plant residues contaminated with pesticides.

All these end up ultimately in polluting water bodies with pesticides. The inherent disadvantages of conventional decontamination techniques (as discussed earlier in this chapter) have prompted scientists to examine the possibility of using the Advanced Oxidation Process (AOP) based on photocatalysis. Both heterogeneous photocatalysis by semiconductors such as TiO_2 and homogeneous catalysis by Photo-Fenton have been tested in this context. Most of the photocatalytic studies, reported so far in this field, are briefly reviewed here. For convenience of reference, the pesticides are classified according to their chemistry (organo-phosphorous, organochlorine etc.) as well as their chief mode of action (insecticides, herbicides etc.).

1.4.1. Organophosphorous Insecticides

In one of the earliest studies on the photocatalytic degradation of organophosphorous (OP) insecticides, Harada et al. [59] reported that DDVP (dimethyl-2,2-dichlorovinyl phosphate) and DEP (dimethyl-2,2,2-trichloro-1-hydroxyethyl phosphonate) were degraded in the presence of suspended TiO_2 by illumination with a super-high pressure mercury lamp or sunlight. Pt loading on TiO_2 enhanced the degradation rate significantly. The addition of H_2O_2 to the suspension also enhanced the rates by 10- and 2- fold for DDVP and DEP respectively. Blank experiments in the absence of TiO_2 or H_2O_2 showed that the effect is more than the sum of the effect of illuminated H_2O_2 and that of the illuminated catalyst. The predominant intermediate was formaldehyde, with the final degradation products being Cl^-, PO_4^{3-}, H^+ and CO_2. Similar results were observed when the catalyst was supported on glass and the aqueous solution containing DDVP was continuously pumped through the photoreactor [110]. Presence of electrolytes such as Cl^-, NO_3^- and ClO_4^- inhibits the degradation rate; the degree of inhibition being in the order $Cl^- > NO_3^- \cong ClO_4^-$. The disappearance of DEP and fenitrothion by photocatalytic treatment combined with ozonation was also studied [111]. In this case, ozonation, followed by photocatalysis enhanced the rate of TOC reduction significantly. Gratzel et al. [112,113] reported the complete mineralisation of several other phosphorous containing insecticides, i.e. paraoxon (4-nitrophenyl diethylphosphate), parathion (diethyl-p-nitrophenyl thiophosphate),malathion{O,O- dimethyl-S- (1,2-dicarboxethyl) phosphorodithioate}, 4-nitrophenylethylphenyl phosphinate and 4-nitrophenylisopropylphenyl phosphinate, under photocatalytic conditions. They also reported that the disappearance rate was dramatically increased by the addition of strong inorganic oxidants such as $K_2S_2O_8$, H_2O_2, $NaIO_4$ and $KBrO_3$.

Even though the photocatalytic degradation of many organic compounds in water ultimately results in complete mineralisation, the mechanism leading to the process is not that simple. For e.g. the degradation of the OP pesticide fenitrothion results in the formation of a number of intermediates, as identified by HPLC and GCMS [15,114]. NMR (^{1}H and ^{31}P) spectroscopic measurements in combination with monitoring pH and UV spectra has also been proved to be an effective tool to follow the degradation of fenitrothion and identify the intermediates [115]. Studies on the degradation of fenitrothion on polyoxometallate ($PW_{12}O_{40}^{3-}$) photocatalysts [116] also showed complete mineralisation and the similarity of the intermediates suggested that the mechanism is same as that with TiO_2 catalysts.

Doong and Chang [58] extended the study to many other OP pesticides and reported similar results. They also observed that the rate of degradation depends on the nature of the OP compound. From a study of the photooxidation of five OP pesticides, i.e. methamidophos, phorate, malathion, diazinon and EPN in UV-TiO_2, UV- H_2O_2 and UV- TiO_2- H_2O_2 systems, they concluded that the reaction follows apparent first order kinetics and the degradation efficiencies increased in the order of phorate > methamidophos > malathion ≅ diazinon > EPN. The photooxidation of methamidophos and phorate was primarily due to direct photolysis, possibly due to the low bond energy of P-S and C-S bonds. The degradation of malathion, diazinon and EPN is primarily due to the indirect action of illuminated TiO_2. The study indicated that a combination of H_2O_2 and TiO_2 under near UV illumination shows much promise in the photodegradation of OP pesticides and their eventual detoxification in water.

They further reported that iron compounds (Fe^0, Fe^{2+}) also act as efficient photocatalysts for these degradations [117]. Similar results were obtained for another OP pesticide i.e. parathion [118]. In this case, the degradation was shown to proceed through a number of intermediates such as diethylphosphoric acid, p-nitrophenol, diethylmonothiophosphoric acid, O, O-ethyl p-nitrophenyl monothiophosphoric acid and oxalate which get oxidised further.

Several studies have indicated that the degradation rates of various organic contaminants such as OP pesticides over illuminated TiO_2 fitted the Langmuir-Hinshelwood kinetics [57, 64,119,120].

The Langmuir – Hinshelwood rate form is

$$v = dC / dt = kKC / (1 + KC) \qquad (12)$$

where v is the oxidation rate of the reactant ($mgL^{-1}\ min^{-1}$), C is the concentration of the reactant (mg/L), t is the illumination time, k is the reaction rate constant (min^{-1}) and K is the adsorption coefficient of the reactant onto the TiO_2 particles (L/mg).

Integration of equation 12 yields

$$\ln(C_0/C) + K(C_0-C) = kKt \qquad (13)$$

When the initial concentration C_0 is very small (millimolar solutions), C_0–C becomes negligible and equation 13 becomes

$$\ln(C_0/C) = kKt = k't \text{ or } C = C_0e^{-k't} \qquad (14)$$

which expresses a pseudo first order reaction where k' is the apparent photodegradation rate constant [121].

The photocatalysed degradation of a number of OP pesticides (dichlorfenthion, bromophos ethyl, bromophos methyl, parathion ethyl and parathion methyl) in aqueous TiO_2 suspensions follows this kinetics [120]. The study also showed that compounds with ethoxy groups degraded faster than those possessing methoxy groups. This observation is also explained in terms of the stability of different possible dialkyl-phosphate radicals that were formed during the reaction. Alkyl groups have an inductive effect to release electrons. The effect overlaps with the pπ-dπ contribution of lone pair electrons on the oxygen of the ester group and is increased in the order; methyl < ethyl [122]. Thus half-lives of ethoxy compounds (ethyl parathion, ethyl bromophos) were found to be 15.2 and 10.2 min, whereas the values are 20 and 35 min for the methoxy analogues, methyl parathion and methyl bromophos respectively [120].

The observation by Kerzhentsev et al. [114], that the primary products formed during the photocatalytic degradation of organophosphorous insecticides are oxon derivatives, is supported by Konstantinou et al. [120], who showed that, in the case of dichlofenthion and bromophos, the oxidant attack of the .OH on the P=S bond occurred first, resulting in the formation of bromoxon and dichlofenoxon. The continuous attack of $^{\cdot}OH$ followed by the rupture of the P-O bond results in the formation of the corresponding phenol and dialkyl phosphates [123]. Based on the spectroscopic identification of various degradation products, the authors proposed a scheme for the photocatalytic degradation pathways of dichlofenthion and bromophos methyl in aqueous solution.

Photocatalytic mineralization studies on malathion [124], in contaminated rinse water from agricultural sprayers and well-water showed that the half-life time of solar photo-mineralisation in the 100 ppb to 50 ppm concentration range was less than 1 hour in the presence of TiO_2 and the absence of added H_2O_2. Comparison of the reaction in open and polyethylene film covered vessels showed that efficient photodegradation occurred in sealed systems as well. Ku and Jung [125] studied the photocatalytic degradation of monocrotophos {dimethtyl (E)-1-methyl-2-(methylcarbamoyl)vinyl phosphate} in aqueous solution by UV/TiO_2 under various pH values, catalyst dosages, light intensities, dissolved oxygen levels and other operating conditions. The presence of oxygen inhibits the recombination of electrons and holes and enhances the decomposition of monocrotophos. Excess of oxygen had no further effect. The degradation rate was more significant in acidic conditions than in alkaline conditions. Increase in light intensity drastically increases the degradation rate, until an optimum light intensity was reached. The degradation leads to complete mineralisation forming PO_4^{3-} and NO_3^- ions, CO_2 and water.

Herrmann and Guillard [126] investigated the influence of a number of parameters on the photocatalytic degradation of OP insecticides (tetrachlorvinphos, fenitrothion, primiphos-methyl and fenamiphos) in pesticide wash-water and identified the intermediates as well as the degradation pathways. All these compounds were completely mineralised by photocatalysis. In the case of primiphos methyl, the initial intermediates were found to be more toxic than the initial pollutant. However, they were completely destroyed in subsequent steps. The study also reported that TiO_2 could be successfully used as deposits on inert supports such as glass, quartz, stainless steel and fibres, thus avoiding the need for final filtration for recovering the catalyst for reuse. It was also noted that activated carbon (AC) as an additive to titania has a synergy effect, combining the photocatalytic activity of the latter and the adsorption capacity of the former. The apparent rate constant was increased by a synergy factor of 2.5, which was ascribed to the preferential adsorption of the pollutant onto the AC, followed by a spontaneous transfer of the pollutant from AC to titania, the large concentration gradient between the two solid phases acting as a strong driving force for a mass transfer.

The use of photocatalysis as a tool for complete mineralisation of OP compounds was further illustrated by using OP simulants of chemical warfare agents [127]. The compounds studied included: dimethylmethyl phosphate (DMMP), trimethyl phosphate (TMP), triethyl phosphate (TEP) and diethylphosphoramidate (DEPA). The study also proved the Langmuir-Hinshelwood kinetics and the role of OH radicals in such degradation reactions.

1.4.2. Organo-chlorine insecticides

One of the earliest studies reported on the photocatalytic degradation of pesticides used persistent organochlorine insecticides [128] as the test reactants. These compounds, especially of the haloaromatic type are considered to be very stable and hence difficult to photodegrade. Studies on the photocatalytic oxidation of lindane (γ-isomer of 1,2,3,4,5,6- hexachlorocyclohexane) in water using TiO_2 catalyst and a high pressure Xenon arc lamp illumination showed that 99.9% of the lindane can be degraded in a reasonable time [13]. Hiskia et al. [129] reported total photodegradation of lindane to CO_2 and HCl in a homogeneous aqueous solution in the presence of polyoxometalate $PW_{12}O_{40}^{3-}$. Guillard et al. [130] identified the intermediate products formed in a photocatalytically treated aqueous solution containing 1 g/dm^3 of lindane. Several specified and unspecified isomers were found as the degradation products, which could be classified into the following categories: chlorocyclohexanes, chlorocyclohexenes, chlorobenzenes, chlorophenols, chloropropanes and chloropropanones and the pentachlorocyclohexanone isomer. The detection of heptachlorocyclohexane in the system showed that chlorine and hydrogen atoms were not only abstracted from the CHCl groups constituting lindane, but also added to them. Vidal [13] observed only 2,3,4,5,6 - pentachlorocyclohexene as the intermediate during the photocatalytic degradation of lindane and suggested that the replacement of ring chlorines and ring hydrogen by hydroxyl radicals and subsequent creation of

C=C bonds is a prelude to the aromatic ring opening. Detection and evaluation of the chloride production indicated that the intermediate is completely mineralised to CO_2 and HCl. Zaleska et al. [131] reported that the reaction products, in the case of lindane, after 150 minutes of irradiation were 1,2,3-trichlorobenzene, γ-2,3,4,5,6-pentachloro-cyclohex-1-ene and α-hexachlorocyclohexane. They also studied the photocatalytic degradation of DDT {1,1,1-trichloro-2,2- bis(4-chlorophenyl)ethane} and methoxychlor {1,1,1-trichloro-2,2-bis(4-methoxyphenyl)ethane} in water over TiO_2 catalysts. In this case, TiO_2 was used in the form of rutile, anatase and supported on glass hollow microspheres. Rutile was the least efficient while the highest efficiency was observed for supported TiO_2. Ten different degradation products were identified. Another catalyst, proved to be effective in the complete mineralisation of the persistent insecticide, hexachlorocyclohexane (HCH) is 'layered double hydroxide pillared by paratungstate A ion', whose structure is as follows:

$\{Mg_{12}Al_6(OH)_{36}(W_7O_{24}).H_2O\}$[132].

The γ - isomer of HCH is also photodegraded by TiO_2 as well as Fe_2O_3 [133]. Compared to lindane and DDT, methoxychlor exhibited greater susceptibility to photocatalytic degradation and as expected, the degradation products were similar to those in the case of DDT.

Pentachlorophenol (C_6Cl_5OH, PCP), a widely used insecticide and wood preservative, has been the subject of many photocatalytic studies. Mills et al. [134] reported that, when illuminated in presence of a TiO_2 suspension, PCP underwent complete oxidation as follows:

$$2\,C_6Cl_5OH + 7O_2 \longrightarrow 4HCOOH + 8CO_2 + 10HCl \quad (15)$$

The principal intermediates formed in the process were p-chloranil, tetrachlorohydroquinone, H_2O_2 and o-chloranil. Formate and acetate were formed in the latter stages of the photooxidation. The degradation proceeds primarily via hydroxyl radical attack on the para position of the PCP ring to form a semiquinone radical which in turn disproportionates to give p-chloranil and tetrachlorohydroquinone. The initial steps in the photocatalytic degradation of PCP, as proposed by Mills et al. are as shown in figure 1.3.

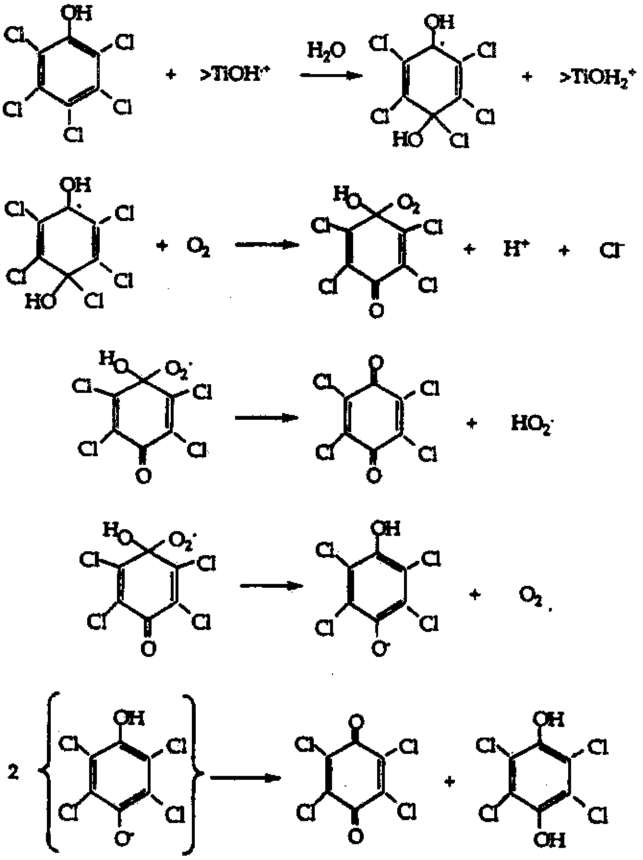


Fig 1. 3. Initial Steps in the degradation of Pentachlorophenol [134]

Under high intensity illumination, the intermediates shown in figure 1.3 are further attacked by the ·OH to yield HCO_2^-, $CH_3CO_2^-$, CO_2^-, H^+ and Cl^-, with initiation as in fig. 1.4.

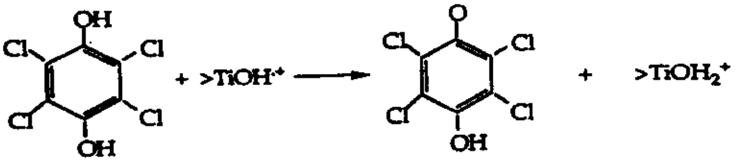


Fig 1. 4. Initiation of the OH radical attack on PCP degradation intermediates [7]

It is also possible to have direct electron–transfer reaction between a surface-trapped hole (h_{tr}^{+}) and surface bound PCP molecule yielding a phenoxy radical as in figure 1.5.

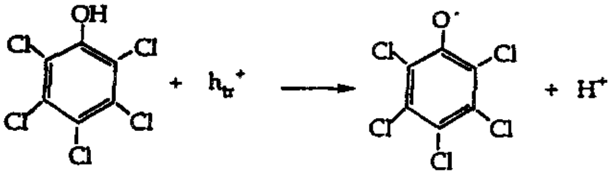


Fig 1. 5. Formation of phenoxyl radical intermediate in PCP degradation [7]

The resulting pentachlorophenoxyl radical may be reduced by electrons from the conduction band of the catalyst or by peroxide radicals to regenerate PCP, thus yielding a close loop reaction with no net degradation.

1.4.3. Carbamate insecticides

Carbamates constitute an important class of insecticides, which are widely used against pests on vast forest areas because of their rapid action and relatively low persistence in the environment. One of the most important members of this family is carbaryl (1-naphthyl N-methylcarbamate). Although it has a relatively low residual lifetime (few weeks in soil) its biological half life is much longer (e.g. 5 to 6 months in fish [135]. Some of its toxic metabolites are rather persistent (1-4 months) in the environment [136] and this has prompted researchers to examine the photocatalytic degradation possibility of carbaryl in polluted waters. Peris et al. [137] investigated the degradation of carbaryl under UV light using a continuos flow of TiO_2 slurry and proposed that the degradation proceeds through a multi-step process involving the attack of the substrate by $^{\cdot}OH$ radicals. Detailed studies on the degradation pathways of carbaryl in aqueous TiO_2 dispersions, under illumination by simulated solar light showed that the reaction follows pseudo first-order kinetics and the complete mineralisation to CO_2 is achieved in less than 30 minutes [138]. Nitrate and ammonium ions are the nitrogen containing end-products. Based on the identification of various intermediates, the authors have also proposed a mechanism for the degradation.

Tanaka et al. [139] studied the photocatalytic degradation of MCC (methyl 3, 4-dichlorocarbanilate), MIPC {2-(1-methylethyl)phenyl methylcarbamate}, MPMC

(3,4-dimethylphenyl methylcarbamate), MTMC (m-tolyl methylcarbamate) and XMC (3,5-xylyl methylcarbamate) in water using TiO_2 and irradiating with a super high pressure mercury arc lamp. The rate of degradation was found to be governed by the adsorbability of the pesticide to TiO_2. The authors also proposed a degradation mechanism involving successive hydroxylation of the aromatic ring, leading to opening of the aromatic ring and the formation of oxygenated aliphatic intermediates. The reaction rate was shown to be dependent on the acidity of the medium.

In an interesting study on the photodegradation of propoxur {2-(1-methylethoxy) phenyl methyl carbamate} in water using 266 mm laser flash photolysis, 2,4,6-triphenyl pyrilium encapsulated inside supercages of zeolite Y was used as the catalyst [140]. The process could be initiated by single electron transfer between the excited 2,4,6-triphenylpyrylium cation and propoxur to form the corresponding 2,4,6-triphenylpyrylium radical and propoxur radical cation.

Another widely used insecticide which belongs to the family of carbamates, oxamyl {N,N-dimethyl-2-methylcarbamoyloxyimino-2-(methylthio) acetamide}, also was found to undergo complete mineralisation in water by TiO_2 mediated photocatalysis. The use of additional oxidants such as peroxydisulphate enhanced the degradation rate by a factor of 7 compared to TiO_2 alone [141]. In the case of EPTC (S-ethyl-N,N-dipropyl thiocarbamate), a widely used thiocarbamate insecticide, laboratory-scale as well as field study showed that TiO_2 photocatalysis leads to complete mineralisation, through the formation of persistent intermediate species [13,142]. At least 16 intermediates were found in the early part of the process through diode array detection.

Pesticides are never applied as such in the field and are always used as formulations. Non-ionic and anionic surfactants constitute an important ingredient of these formulations and can influence the degradation of the pesticide. This was investigated [143] by studying the effect of ionic and non-ionic surfactants on the TiO_2 photocatalysed degradation of carbaryl. Depending on the nature of the surfactant and acidity of the medium, an inhibition of the degradation rate was observed. The kinetics of the degradation followed a pseudo-first order kinetic law below the critical micellar concentration and a complex pattern above it. Carbaryl was completely mineralised to CO_2, NO_3^- and NH_4^+. TiO_2 photocatalytic treatment has also been demonstrated to be useful for the detoxification of commercial formulated carbamate pesticides such as formetanate (3-dimethylaminomethyleneaminophenyl methylcarbamate) [144] and propamocarb {propyl 3-(dimethylamino) propyl carbamate} [144,145]. However, the complete mineralisation is not achieved often as is the case with vapam (monoalkyl dithiocarbamate), possibly due to the inactivation of TiO_2 by the sulphur formed during the degradation [146].

Inhibition of photocatalytic degradation of pesticides by surfactants present in the formulated products has been observed for a number of organochlorine and OP insecticides, possibly due to the competitive adsorption of the surfactants at the surface sites [147].

1.4.4. Herbicides

The photocatalytic degradation of some of the widely used herbicides such as 2,4-D (2,4-dichlorophenoxyacetic acid) [148-150], 2,4,5-T (2,4,5 trichlorophenoxyacetic acid) [148], bentazon {3-isopropyl-1H-2,1,3-benzothiadiazin-4(3H)-one 2,2-dioxide}[151], S-triazines [152-154], carbetamide {(R)-1-(ethylcarbamoyl)ethyl carbanilate}[155] and monuron {3-(4-chlorophenyl)-1-methoxy-1-methylurea}[29] in water have been studied in order to evaluate the process as a waste treatment technique for this kind of compounds. In all cases, the degradation is complete leading to mineralisation, even though the rate of degradation depends on the chemistry. Tanaka and Reddy [156] investigated the photocatalytic degradation of 2,4-D, 2,4,5-T and 4-chloro-2-methylphenoxyacetic acid (MCP) on TiO_2 and reported nearly complete mineralisation within 2 hr. The order of the mineralisation was 2,4,5-T > 2, 4-D ≈ MCP. The degradation of MCP proceeds through the formation of aromatic intermediates (4-chloro-o-cresol, methylhydroquinone and 4-chloro-catechol) and subsequent polyhydroxylation of the aromatic ring, resulting in ring opening and formation of oxygen containing aliphatic intermediates. Four organic acids, i.e. acetic, formic, glyoxylic and glycolic acids were identified and the ultimate mineralisation proceeds via formic acid.

TiO_2 doped with lanthanide oxide has been reported to be an excellent photocatalyst for the degradation of the herbicide p-chlorophenoxyacetic acid [157]. The authors also observed that europium, praseodymium and ytterbium oxide doped TiO_2

exhibited significantly higher activity compared to the non-modified TiO_2 catalyst. The enhanced degradation is attributed to the formation of lewis acid-base complex between lanthanide ion and the substrate. Topalov et al. [158] reported that another herbicide of the same family, i.e. MCPA (4-chloro-2-methylphenoxy acetic acid) is completely mineralised after 15 hr irradiation over TiO_2.

Recently, Konstantinou et al. [120] examined the photocatalytic degradation of a series of S-triazine herbicides; atrazine, propazine, cyanazine, prometryne and irgarol. It was observed that the degradation rate depends on the structure of the herbicide in the early part of the irradiation experiments, upto 20 minutes. But for prometryne, atrazine and propazine similar degrees of degradation were reached finally. This has confirmed earlier findings on ZnO catalysts that the initial rates often cannot be used as a measure of the photocatalytic efficiency [70].

Hiskia et al. [54] studied the photocatalytic degradation of aqueous solutions of atrazine on polyoxometalate catalysts ($PW_{12}O_{40}^{3-}$ or $SiW_{12}O_{40}^{4-}$) with $\lambda > 300$ nm and compared the results with those under sonolysis. Both methods led to the same intermediates and end products. The final products in both methods is cyanuric acid (2,4,6-trihydroxy-S-triazine), NO_3^-, Cl^-, CO_2 and H_2O. The cyanuric acid is resistant to further degradation under both conditions. However, it decomposes upon photolysis with $\lambda > 200$ nm.

Studies on the photodegradation of prometryn {N^2,N^4-di-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine} and prometon {N^2,N^4-di-isopropyl-6-methoxy-1,3,5-triazine-2,4-diamine} in aqueous solution, using membranes immobilising TiO_2, with H_2O_2 as added oxygen supplier, showed the reaction to be of first order kinetics [158]. The quantum yield for the degradation were 40% for prometryn and 66% for prometon. Cyanuric acid was found to be the photo stable product of the reaction. Another triazine herbicide, metamitron {4-amino-6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one} was investigated [159] on a plate photoreactor with immobilised TiO_2 or as Q-TiO_2 particles. The main photoproducts reported were deaminometamitron {6-phenyl-3-methyl-1,2,4-triazin-5(4H)-one}, deaminohydroxymetamitron {6-(2'-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4H)-one} and hydroxymetamitron {4-amino-6-(2'-hydroxyphenyl)-3-methyl-1,2,4-triazin-5(4H)-one}. The mechanism proposed, involves two pathways: heterogeneous catalysis and homogeneous photolysis. Surface mediated photocatalysis is the major route when the plate photoreactor is used while the contribution from the homogeneous process is significant in colloidal solutions of TiO_2 particles.

Another herbicide, investigated for its photocatalysed degradation, is asulam (sodium N-methoxycarbonyl sulfanilamide), which is active in both pre-emergence and post-emergence treatment against many broad leaf and grass weeds. When the aqueous suspension of asulam containing TiO_2 catalyst is irradiated by UV light, the herbicide is completely decomposed and mineralised [111]. Ozone treatment prior to the photocatalytic reaction enhances the rate of decomposition.

Photocatalysis has also been proved to be effective in the degradation of relatively persistent herbicides such as triclopyr (3,5,6-trichloro-2-pyridinyloxyacetic acid) [160], alachlor (2-chloro-2',6'-diethyl-N-methoxymethyl acetanilide) [161], dicamba (3,6-dichloro-o- anisidic acid) [162], mecoprop {(RS)-2-(4-chloro-o- tolyloxy) propionic acid)}[163] as well as thiocarbamate group of herbicides [164] such as molinate (S-ethyl azepane-1-carbothioate), eptam (S-ethyl dipropylcarbamothioate), thiocarbazil (S-benzyl di-sec-butylthiocarbamate) and thiobencarb (S-4-chlorobenzyl diethylthiocarbamate). Studies on the photocatalytic degradation of the herbicides, propanil (3',4'-dichloropropionanilide) and molinate (S-ethyl azepane-1-carbothioate) [165] as well as 3,4-dichloropropionamide [88] also showed complete mineralisation on TiO_2 catalysts. TiO_2 in colloidal suspension form is also a good photocatalyst for the degradation of urea based herbicide diuron {3-(3,4-dichlorophenyl)-1,1-dimethylurea}[166]. The degradation mechanism involves consecutive oxidative demethylation on the aliphatic side chain of the molecule. Imazaquin {(RS)-2-(4-isopropyl-4-methyl-5-oxo-2-imidazolin-2-yl)quinoline-3-carboxylic acid}, a herbicide belonging to the imidazolinone class also is reported to undergo complete photo mineralisation on TiO_2 resulting in the formation of nitrate ions [167]. In this case, solar irradiation was more efficient than artificial light. In the case of herbicides terbacil (3-tert-butyl-5-chloro-6-methyluracil) and 2,4,5-tribromoimidazole, the TiO_2 mediated photodegradation is enhanced by additives such as $KBrO_3$, H_2O_2 and $(NH_4)_2S_2O_8$ [168].

1.4.5. Fungicides

The photocatalytic decomposition of an aqueous suspension of metalaxyl {N-(2,6-dimethylphenyl)-N-(methoxy-acetyl)-D,L-alanine methyl ester, $C_{15}H_{21}NO_4$}, an extensively used fungicide, on TiO_2 was found to result in complete mineralisation of the chemical [57]. The intermediates formed during the photomineralisation and the reaction pathways were analysed by recording proton NMR spectra. Experiments using various concentrations of metalaxyl showed that the more diluted the initial solution, the faster are the degradation. On the basis of the measurements of total organic carbon, the authors have explained the decomposition in terms of Langmuir-Hinshelwood kinetic model.

Pyrimethanil {N-(4,6-dimethylpyrimidin-2-yl)aniline}, an effective fungicide used against a variety of fungi in vineyards and other crops is also found to undergo complete photodegradation in presence of TiO_2 catalysts [169]. However, under sunlight, total mineralisation is not observed, as confirmed by the measurements of TOC values at the end of the experiments (907 minutes). GC-MS studies detected upto 22 intermediates during the degradation. Structure identification of the degradation products indicate two main routes in the degradation process; one route involving the attack of hydroxyl radicals on the pyrimidine and benzene rings with further ring opening and the other one corresponding to the photoinduced hydrolysis of the molecule by the amine group bonds. Another fungicide, fenarimol {(±)-2,4'-dichloro-α-(pyrimidin-5-yl)benzhydryl alcohol}, also was reported to decompose slowly under photocatalytic conditions, resulting in the cleavage of the bond between the quaternary carbon and either the chloroaromatic or the pyrimidine ring [170].

Two other fungicides, chlorothalonil (tetrachloroisophthalonitrile) and dichlofluanid (N-dichlorofluoromethylthio-N',N'-dimethyl-N-phenylsulfamide), were studied by Sakkas and Albanis [171] for the photocatalytic degradation in aqueous TiO_2 suspensions under simulated solar irradiation. The total disappearance of chlorothalonil and dichlofluanid was achieved in 90 and 20 minutes respectively. The complete mineralisation of organic carbon to carbon dioxide took 240 minutes in the case of chlorothalonil while during the same time period, the mineralisation was only 78% in the case of dichlofluanid. Evolution of heteroatoms (Cl, N, S, F) was followed by ion chromatography which showed mineralisation into chloride, ammonium, nitrate, sulphate and fluoride ions. The intermediates detected during the degradation were identified by GC-MS techniques and accordingly, the reactions leading to the mineralisation were proposed as dechlorination, hydroxylation, dealkylation and decarboxylation.

Two seed-treatment fungicides, i.e. carboxin (5,6-dihydro-2-methyl-1,4-oxathi-ine-3-carboxanilide) and oxycarboxin (5,6-dihydro-2-methyl-1,4-oxathi-ine-3-carboxanilide 4,4'-dioxide) are being investigated in our laboratories at present, using ZnO and TiO_2 as catalysts. Preliminary results [147] show that the fungicides slowly disappear on irradiation under UV light and simulated sunlight. Complete mineralisation is slow, but is taking place as seen from the slow formation of CO_2. Many organic intermediates are detected and these are being identified at present.

1.4.6. Other Pesticides

Acrinathrin {(S)-α-cyano-3-phenoxybenzyl (Z)-(1R,3S)-2,2-dimethyl-3-[2-(2,2,2-trifluoro-1-trifluoromethylethoxycarbonyl)vin-yl]cyclopropanecarboxylate}, a new contact systemic insecticide of the pyrethroid family, introduced recently for insect control on a variety of fruits and vegetables, has been reported to undergo photocatalysed degradation over TiO_2 [142]. Peroxydisulphate has a very significant synergic effect on the degradation rate. In the case of imidacloprid {1-(6-chloro-3-pyridylmethyl)-N-nitroimidazolidin-2-ylidineamine}, a chloronicotinoid insecticide, investigations using its formulated product confidor [172] showed that the reaction follows first order kinetics and the presence of TiO_2 significantly reduced the half-life. However, comparison of the degradation achieved by photo-fenton and TiO_2 photocatalysis in a solar pilot plant showed that the former is at least 2.4 times faster than the latter [53,172].

1.5. Photocatalytic degradation of phenolic contaminants

Aqueous effluents from industries such as pharmaceutical, chemical, petrochemical etc. contain refractory organics such as phenols, in concentrations far below the limits that would permit recovery processes, but high enough to severely curtail the effectiveness of conventional waste treatment processes. Phenol is the basic structural unit for a variety of synthetic organic compounds and therefore the wastewater originating from many chemical plants and pesticide and dye manufacturing industries contain phenols. Besides this, wastewater originating from other industries such as paper and pulp, resin manufacturing, gas and coke manufacturing, tanning, textile, plastic, rubber and petroleum also contain different types of phenols. In addition to phenols generated as a result of these industrial activities, wastewaters also contain phenols formed as a result of decay of vegetation. Because of their toxicity and the frequency of their presence in wastewaters, phenols and phenolics have gained increased attention in the last two decades.

Phenol is considered to be an intermediate in the oxidation route of high molecular weight aromatics and is taken as a model compound for research studies dealing with advanced wastewater treatments. Some of the techniques used for the removal of phenols from water include: oxidation with ozone/hydrogen peroxide [173], biological methods [174], ion exchange [175], electrochemical oxidation [176], reverse osmosis [177], adsorption [178,179] and photocatalytic degradation [180]. Of these, heterogeneous photocatalysis using semiconductor photocatalysts has been considered as one of the most effective technologies, mainly due to the advantages of low cost and the potential to use sunlight as the source of energy.

A number of studies have been published on the photocatalytic degradation of phenols [181-189] on semiconductor oxides. They show that the catalytic activities were strongly influenced by the crystal structure and chemical composition of the catalysts. In the case of TiO_2, the anatase form is found to be the most efficient for phenol degradation [189]. The active sites responsible for the high photocatalytic activity are the TiO_2 crystallites, with particle sizes and bonding structures, similar to those of bulk anatase. TiO_2 crystallites, impregnated on silica gel were also equally active. Rutile, layered and pillared titanates, as well as pillared clays, showed relatively low activities mainly due to coke formation on their surfaces and this was explained to be the result of strong interaction between the charged surfaces and phenolic intermediates. TiO_2 immobilised on glass fibres was also found to be efficient for the complete degradation of phenol [190]. From a study on the photocatalytic degradation of phenols under UV and Vacuum UV, Han et al. [191] suggested that the rate of degradation was dependent on the structure of the substrates. The degradation was shown to follow pseudo first order kinetics [192]. Recent studies have also reported that the addition of small quantities of Pt and Ag enhances the efficiency of TiO_2 catalysts. Ag/ TiO_2 catalyst, prepared by deposition of small amounts of metallic silver by in situ metal photoreduction, has been found to be very efficient for the mineralisation of trace amounts of phenol in water [193]. Another key factor that determines the efficiency of degradation is the availability of dissolved oxygen [194].

Different types of reactors have been designed and tested in recent years, in the search for more efficient photocatalytic systems, using phenol as the test pollutant. Thus it has been shown that a reactor named 'TiO_2 coated rotating drum reactor' is very efficient, with the entire phenol decomposing in a relatively shorter time, not only under artificial ultraviolet light but also under solar light [195]. The enhanced activity is attributed to the fact that the whole surface of the drum itself is the reaction site and the catalyst has very effective contact with the reactants. Another reactor, named as 'Thin film cascade reactor' consisting of an array of UV lamps, illuminating a cascade of three inclined stainless steel plates, on which TiO_2 was immobilised by electrophoretic deposition, was found to be more efficient than a single plate reactor [196]. Another innovation reported in the context of designing new photocatalytic reactors is the 'Rotating Disc Photocatalytic Reactor (RDPR)', referred earlier in this chapter.

All these studies point to the fact that there is immense potential to enhance the rate of degradation and eventual mineralisation of phenol and other organic water pollutants by developing better catalyst-reactor systems and illumination techniques. The structure, texture and composition of the catalysts and the reaction conditions are equally important. Phenol remains as one of the best and simplest organic substrates which can be used as the test reactant to optimise the reaction parameters. In the process, technology for the removal of one of the most common types of refractory industrial pollutants also can be developed.

1.6. Photocatalytic degradation of dyes in water

Another class of pollutants subjected to photocatalytic investigations is dyes, especially those used in the textile industry. A number of these compounds are recalcitrant and have shown carcinogenic and mutagenic character. They are also resistant to microbial degradation [197]. There are no universally accepted methods available for treatment of dye wastes, probably because of the complex and varied chemical structures of these compounds. Some of the normal treatment methods such as chemical coagulation, flocculation, activated carbon adsorption and ultra-filtration merely transfer the pollutants from wastewater to other media and hence do not offer an ultimate solution. In this context, photocatalysis, which has been proved to be successful in the complete mineralisation of many organic pollutants, is receiving attention in recent years [198-200]. In this case also, semiconductor oxides such as TiO_2 [49, 201-203, 56] and ZnO [200, 204-206] are the most widely investigated catalysts. Some of the dyes reported in these studies include methylene blue, acid-red 3B, remazol brilliant blue R, reactive blue 221, scarlet 4BS, acid brown 14, alizarin red, acid blue 25 and scarlet 4BS. Doping with Ag is found to enhance the photocatalytic activity of ZnO [49] and TiO_2 [207, 208]. Similarly supportimg TiO_2 on Na-Y and 4A zeolites enhances its activity for the degradation of azo dyes [201], while silica supported catalyst was found better for the degradation of acid orange 7 [209]. In suspended catalyst systems, particle size is an important parameter that determines the efficiency. In the case of methylene blue, adsorption rate and adsorbability on suspended TiO_2 particles increase as the particle size of TiO_2 is decreased [56]. Correspondingly, the photocatalytic activity also increased. Comparison of fixed bed and suspended models showed that the initial degradation rate is high in a suspended system.

Wu and Zhang [210] reported that thin films of anatase TiO_2 prepared by direct oxidation of metallic titanium using H_2O_2 by a novel method is highly efficient for the photodegradation of rhodamine B in water. The dye decayed directly to colourless end products of water and mineral acids. Another interesting catalyst that enhanced the photodegradation of rhodamine B is $ZnFe_2O_4$ doped TiO_2 [211].

These and other studies have clearly established that photocatalysis is an effective tool for the removal of dyes from wastewater even though many aspects related to the mechanism of the process are yet to be understood. Many parameters relevant to the commercial viability of the technology also are to be developed and/or optimised.

1.7. Photocatalytic inactivation of bacterial pollutants in water

One of the major disadvantages of using chlorine to disinfect wastewater effluents and to inactivate bacteria and most viruses is the formation of potentially toxic by-products. Consequently, a number of physicochemical disinfection processes have been studied as alternatives to chlorine. These include the use of UV radiation, ozonisation, water soluble photochemical sensitisers that can generate transient oxygen species and photocatalysis.

Heterogeneous photocatalysis, in spite of its proved efficiency for the removal of organic chemical pollutants, has not received due attention from researchers for its potential to remove bacterial pollutants from water. One of the earliest studies in this context is of Matsunaga et al. [212]. These workers showed that TiO_2 particles are effective in sensitizing the photo-killing of bacteria such as *Lactobacillus acidophilus, Saccharomyces cerevisiae* and *Escherichia coli.* The authors used TiO_2 particles immobilized on acetyl cellulose and Pt/TiO_2 as photocatalysts. Other studies include the use of catalysts in various forms such as sleeve of fibre glass mesh coated with TiO_2 (for the destruction of *Escherichia coli),* TiO_2 suspended in $FeSO_4$ solution in which the latter acted as a promoter (for the deactivation of viruses), TiO_2 suspension in a flow system with diffuse light emitting optical fibres as light source (for the destruction of *Escherichia coli)* [51] and TiO_2 as a stationary phase on the inner wall of a commercial UV sterilizer [213].

The killing mechanism underlying the photocatalytic deactivation is not fully understood yet. Matsunaga et al. [212] reported a decrease in intracellular coenzyme A (CoA) for various micro organisms. The authors proposed the direct oxidation of CoA that inhibited cell respiration and subsequently caused cell death as the first killing mode. This mode emphasized a direct contact between TiO_2 and target cells to ensure the direct oxidation of cell components. Photocatalytic studies using TiO_2 revealed that that the sensitivity of micro organisms to photocatalysis is likely to be in the order virus > bacterial cells > bacterial spores [214, 215]. This suggests that different micro organisms respond differently to TiO_2 photocatalyst, due to their structural differences, particularly in the complexity and thickness of the cell envelope. Based on Transmission Electron Microscopy (TEM) findings, Saito and co-workers reported [216] that the cell wall of *Streptococcus sobrinus* AHT was partially broken after cells had undergone TiO_2 photocatalytic treatment for 60 minutes and they recorded cell disruption after 120 minutes. They further demonstrated that TiO_2 photocatalytic reaction induced rapid leakage of potassium ions and the slow leakage of RNA and proteins. Thus they argue that the bacterial death was caused by significant disorder in cell permeability and decomposition of the cell wall. Sunada et al. [217] demonstrated the inactivation of *E.coli* endotoxin, which is an integral constituent of the outer membrane of gram negative bacteria, in TiO_2 photocatalysis. These findings suggest that cell wall damage takes place, prior to cytoplasmic membrane damage. Some other investigators report that there was no significant difference in the time required for the killing of Gram positive and Gram negative bacteria, even though the former has a thicker cell wall [218]. Recently, Huang et al. [219] proposed that cell wall damage, followed by cytoplasmic membrane damage leading to a direct intracellular attack may be the sequence of events when micro organisms undergo photocatalytic attack. In another study, the antibacterial efficiency of long wave UV-irradiated thin films as well as ultra-structural damage on bacterial cells was evaluated using *Pseudomonas aeruginosa* as a model [220].

The effect of irradiation of thin films of TiO_2 on the ultra-structure of the bacterial cell was studied using TEM. After 40 minutes of irradiation, an abnormal cellular division was observed: instead of normal septum, an 'elongated bridge' was formed. At a long irradiation time, wavy structures all around the outer cell membrane were observed, which expelled the inner material. The mechanism of irreversible bacterial cell damage caused by the photocatalytic effect of TiO_2 could be related to abnormal cell division, in addition to the physicochemical alteration of the cell membrane. Some clues on the mechanism of destruction of the bacteria were also reported based on the results using *E. coli, Pseudomonas aeruginos* and *Salmonella typhimurium* as the test bacteria [221].

In spite of the uncertainty regarding the exact mechanism of destruction, research papers continue to be published on the application of photocatalysis on the removal of bacterial pollutants from water, with newer and more efficient systems being reported periodically [222-226]. New research tools also are being employed, of late, to understand the mechanism of the whole process. Some of these techniques include Attenuated Total Reflection Fourier Transform Infrared Spectroscopy (ATR-FTIR), Atomic Force Microscopy [227] and Acoustic Wave Impedance Analysis [228]. These studies showed that changes in the cell wall membranes of the bacteria are the initial effects of photocatalysis, which eventually lead to bacterial lysis.

1.8. Solar photocatalysis in the degradation of pesticides

Heterogeneous photocatalysis is now approaching the pre-industrial level. Several pilots and prototypes have been built in various countries. Different types of photo-reactors have been built, with the catalysts used in various forms/shapes: fixed bed, magnetically or mechanically agitated slurries, catalyst particles anchored on the walls of the photo-reactor or on membranes or on glass beads or on glass wool sleeves, small spherical pellets etc. [14, 229]. The main criterion is to have easy separation of the catalyst from the fluid medium and this is achieved using supported TiO_2.

Various devices have been developed and tested. These include TiO_2 coated tubular reactors, annular and spiral photo-reactors, falling-film photo-reactors etc. Of these, two systems are in commercial use at present for the treatment of wastewater [15]. One uses TiO_2 powder while the other uses TiO_2 supported on fibreglass mesh cloth. Comparison of the heterogeneous photocatalysis using TiO_2/UV with other UV oxidation systems such as O_3/UV, H_2O_2 + additive/UV for the removal of 2,4,6-trinitrotoluene from groundwater showed that the former can compete economically with the other UV oxidation processes for water treatment.

The solar photocatalytic treatment for the decontamination of pesticide pollutants in water, reported from PSA (Plataforma Solar de Almeria, Spain) is an excellent example of solar water detoxification using photocatalysis [15]. The treatment system employs the compound parabolic collector technology (CPC) in which the static collectors capture diffuse as well as direct sunlight [230-233]. The CPC system is intrinsically simple, cost-effective, easy to use and requires low capital investment. Design and configuration details on the CPCs have been illustrated by Malato et al. [234, 235]. The technique has been successfully applied to a number of pollutants such as benzofuran [15] and oxamyl [141].

In an encouraging development in the field, an industrial consortium of nine public and private institutions has initiated a project entitled 'SOLARDETOX' for developing and marketing the best available solar photocatalytic systems in the detoxification of water contaminants [235]. The project employs the CPC technology and a full size pilot plant has been installed to identify pre and post processing requirements, potential operating problems and cost evaluation. An isometric drawing of the solar detoxification demonstration plant is given in figure 1.6.

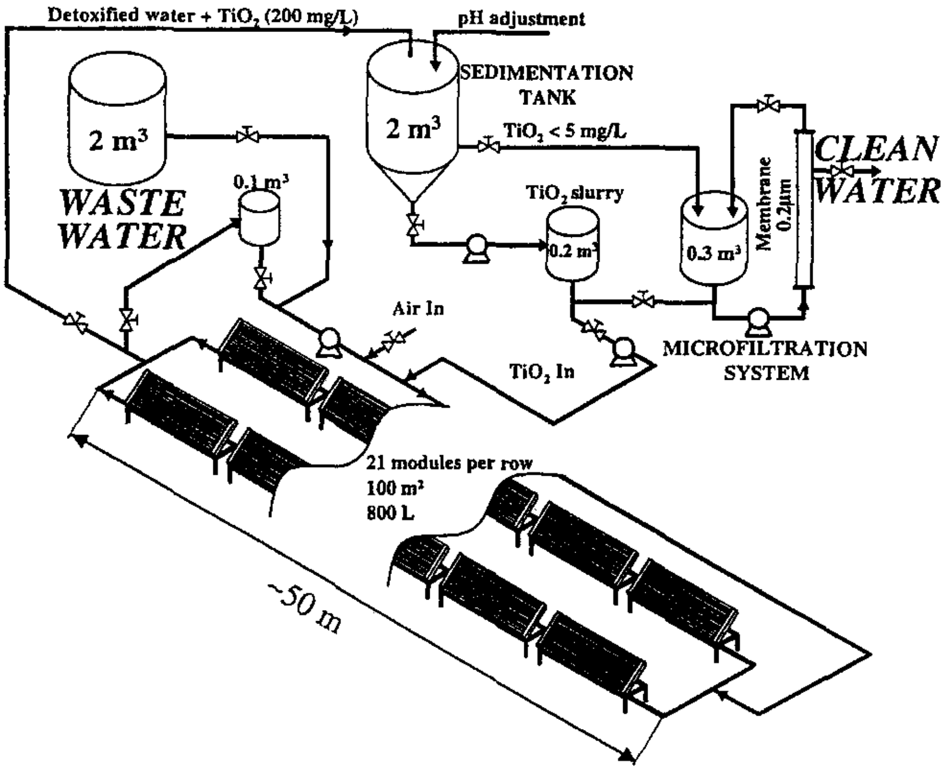


Fig 1. 6. Isometric drawing of solar detoxification demonstration plant [236]

Wastewater enters the system from a 2-m^3 wastewater storage tank while detoxified water from a previous run is discharged into the catalyst sedimentation tank. When the system is completely full (0.8 m^3), a pump recirculates the water through the collectors and a small tank (0.1 m^3). The concentrated TiO_2 slurry and the air necessary for the reaction are injected in the circuit. Once the water is detoxified, the entire volume leaves the sedimentation tank and the system is filled with more wastewater for another batch. Meanwhile, the detoxified water and the TiO_2 in the sedimentation tank undergo pH adjustment to provoke fast sedimentation of the catalyst. The concentrated catalyst slurry is transferred from the bottom of the tank to another smaller tank from which the catalyst enters the photoreactor. The supernatant is removed through an outlet in the side almost at the bottom of the sedimentation tank and enters another tank (0.3 m^3) where the small fraction of the initial catalyst contained in the supernatant is removed by micro membrane filtration before the water is disposed. The membrane has two outlets; one for clean water and another for concentrated slurry. The concentrated slurry is recirculated through the membrane until there are several grams of catalyst per litre. Then this is added to the TiO_2 injection tank and also reused.

Some of the pesticides detoxified in solar pilot plants include PCP [236], atrazine [230], 2, 4-D [237], imidacloprid [53], acrinathrin [142], lindane, butiphos and EPTC [13], methamidophos [237], oxamyl [141] and pyrimethanil [169].

The use of additional oxidants is recommended when the organic content of the water is relatively high and/or the mineralisation rate is low. These additives should be capable of dissociating into harmless by-products and leading to the formation of $^{\cdot}OH$ or other oxidising agents. Peroxydisulphate is one such additive which has been successfully used to enhance the photocatalytic degradation of oxamyl in water [141]. The effect is being explained both in terms of the scavenging action of $S_2O_8^{2-}$ and of the participation of $SO_4^{\cdot-}$ in the oxidation reactions, directly or through the formation of $^{\cdot}OH$ radicals [238] i.e.

$$S_2O_8^{2-} + e^-_{(CB)} \rightarrow SO_4^{2-} + SO_4^{\bullet-} \quad (19)$$

$$SO_4^{\cdot-} + H_2O \rightarrow SO_4^{2-} + {^{\cdot}OH} \quad (20)$$

1.9. Current status

A large volume of literature has been published in the last 10-15 years on the photocatalytic degradation of chemical and bacterial pollutants. In most cases of chemical pollutants, the degradation products have been identified. However, mechanistic studies leading to the formation of such products are relatively few. This may be, in part, due to the very short life time of most intermediates and the absence of ultrafast kinetic techniques such as laser flash photolysis or pulse radiolysis in the nano- or picosecond regime in many laboratories. The effect of many parameters such as the presence of salts and other natural organic matter in the water also is not clearly understood. Similarly, the mechanism of destruction of bacterial pollutants also is not quite clear. Nevertheless, studies aimed at developing better water disinfection systems employing new catalysts, existing catalysts in new practical forms and new reactor designs are yielding encouraging results in the search for commercially viable water purification systems. Studies on the use of sunlight as the source of energy for the degradation process have yielded encouraging results and the solar photocatalytic treatment of pesticides is already at the pilot plant and pre-industrial level.

Chapter 2

PHOTOCATALYTIC DEGRADATION OF PHOSPHAMIDON ON SEMICONDUCTOR OXIDES

2.1. Introduction

The possibility of using photocatalysis for the removal of persistent organic pollutants, such as pesticides in water, started receiving the attention of researchers only recently [239-243]. Of these, organophosphorous (OP) pesticides [59, 244, 114, 118] such as monocrotophos, fenitrothion and parathion, carbamate pesticides [138] and triazine herbicides [120] have received most of the attention. Another OP pesticide phosphamidon (IUPAC name: 2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate), which has been used extensively as a rice insecticide in India and around the world and still remaining popular in many developing countries does not seem to have received any attention in this respect. As part of our current studies on the application of semiconductor photocatalysis for the degradation of organic pollutants in water, an attempt has been made to fill this gap, by choosing phosphamidon as the principal substrate for detailed investigations. The results are presented in this chapter.

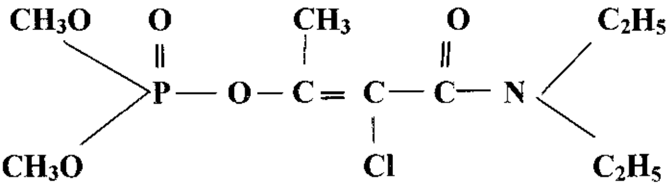
Phosphamidon is a systemic organophosphorous insecticide, with a broad - spectrum activity. It is a cholinesterase inhibitor with rapid contact and stomach action. The technical product is very highly toxic to mammals and is listed in WHO hazard class A. Some of the pests controlled by phosphamidon include: sap-feeding insects, sugar cane and rice stem borers and rice leaf beetles.

Phosphamidon is a pale yellow to colourless oily liquid with a faint odour. It exists as a mixture of 70% cis-isomer and 30% trans-isomer. It is miscible with water and aromatic hydrocarbons.

Some relevant general information on phosphamidon is as follows:

Common Name: Phosphamidon
IUPAC Name: 2-chloro-2-diethylcarbamoyl-1-methylvinyl dimethyl phosphate
CAS Reg No. 297-99-4 (trans-isomer), 23783-98-4 (cis-isomer), 13171-21-6 (mixture)
Molecular formula: $C_{10}H_{19}ClNO_5P$
Molecular weight: 299.7

Structural formula:



Synonyms: Phosphamidone, Famfos, Dimecron, Dixon.

Toxicity:
Oral LD_{50} (Rat): 17 mg/kg body weight
Dermal LD_{50} (Rat): 374 mg/kg body weight
Inhalation LC_{50} (Rat): 102 $mg/m^3/4h$

As explained in Chapter 1, when a semiconductor oxide is excited by radiation energy at least equal to its bandwidth in the presence of air or oxygen and water, oxidising species such as hydroxyl radicals and, to a lesser extent, superoxide anions are created. These species can very effectively degrade and even mineralise organic micro pollutants. TiO_2 is considered particularly efficient in this context due to its (i) high production capacity of hydroxyl radicals; (ii) spectral characteristics which allow excitation in a broad spectral range including solar spectrum; (iii) stability under harsh conditions;(iv) commercial availability at low price and (v) ease of preparation in the laboratory.

This chapter presents the results of our studies on the possibility of using two semiconductor oxides, i.e. ZnO and TiO_2 as photocatalysts for the degradation of trace amounts of phosphamidon in water.

2.2. Experimental

2.2.1. Chemicals:

Phosphamidon technical grade (97.5% purity) was provided by the Hindustan Insecticides Limited., India. The water used for all experiments was purified by double distillation. Other chemicals used were of reagent grade and used as such without further purification. The photocatalysts TiO_2 and ZnO were supplied by

Merck India limited. In both cases, the particles were approximately spherical and non-porous, with a purity of over 99%. XRD analysis showed that the TiO_2 contains approximately 75% anatase and 25% rutile. The surface areas of TiO_2 and ZnO, as determined by the BET technique, were approximately 25 m^2/g and 22 m^2/g respectively. The average particle size in both cases was approximately 35 nm. A phosphamidon solution in water was prepared by stirring weighed amount of phosphamidon in water at room temperature. Appropriate dilute solutions were prepared from this stock solution by mixing with the required quantity of doubly distilled water.

2.2.2. Photocatalysis Experiments and Analytical Methods

In a typical experiment, required amount of the catalyst is suspended in an aqueous solution (250 mL) of the insecticide in a Pyrex round bottomed flask. The reaction system was continuously stirred to achieve a homogeneous suspension and thermostated by circulating water to keep the temperature at 27 $\pm 1^0$C. The water also served as a filter to remove IR light. The suspension was illuminated by a 500 W super high-pressure mercury lamp, mounted axially. See figure 2.1.

The intensity of the light was approximately 8 mW/cm^2 in the wavelength range 330-390 nm (based on manufacturer's data). For solar experiments, 250 ml suspension was exposed to sunlight for a fixed time daily between 0930 and 1600 hr, for 12 consecutive days in summer months. After illumination for the specified period, the suspension was centrifuged and the supernatant solution was extracted [245] with methylene chloride, dried with anhydrous Na_2SO_4, concentrated by evaporation and analysed for phosphamidon by gas chromatography [246] using flame ionization detector and 180 x 0.6 cm glass column packed with 3% SE 30 (100-150 mesh size). The detector temperature was 240^0C and the column was maintained at 230^0C

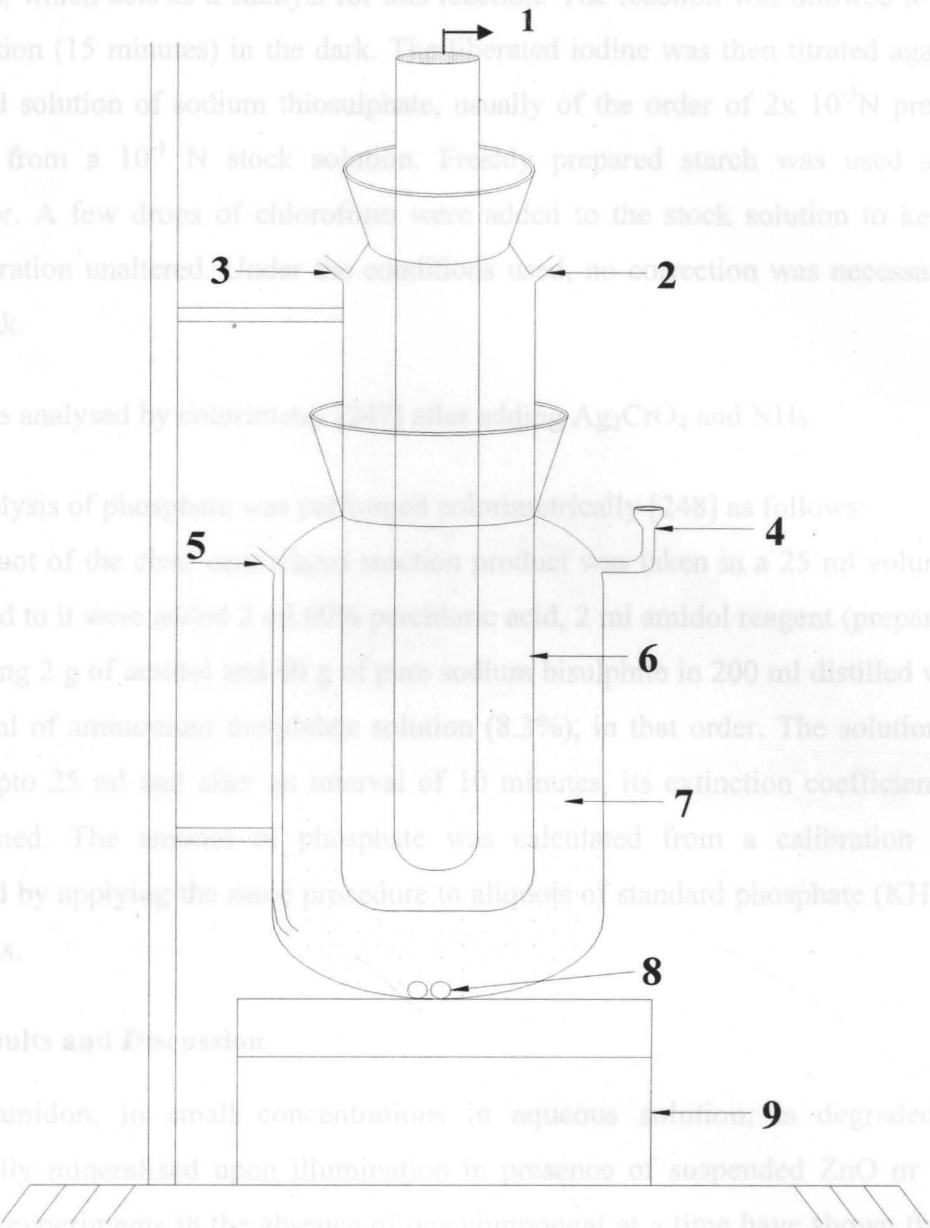


Fig 2.1. Experimental Setup for the photocatalytic degradation of Phosphamidon
1.UV lamp 2. Inlet for water 3. Outlet for water 4. Sample inlet 5. Gas purging tube 6. Water 7. Sample 8. Magnetic pellets 9. Magnetic Stirrer

CO_2 formed after long illumination of a higher concentration of the insecticide was analysed by bubbling the gas through a saturated $Ba(OH)_2$ solution and estimating the amount of $BaCO_3$ formed.

H_2O_2 was analysed by iodometry. The oxidation of iodide ions was carried out in ~ 1N sulphuric acid in presence of a few drops of saturated ammonium molybdate solution, which acts as a catalyst for this reaction. The reaction was allowed to go to completion (15 minutes) in the dark. The liberated iodine was then titrated against a standard solution of sodium thiosulphate, usually of the order of 2x 10^{-3}N prepared freshly from a 10^{-1} N stock solution. Freshly prepared starch was used as the indicator. A few drops of chloroform were added to the stock solution to keep its concentration unaltered. Under the conditions used, no correction was necessary for the blank.

Cl^- was analysed by colorimetry [247] after adding Ag_2CrO_4 and NH_3.

The analysis of phosphate was performed colorimetrically [248] as follows:
An aliquot of the clear centrifuged reaction product was taken in a 25 ml volumetric flask and to it were added 2 ml 60% perchloric acid, 2 ml amidol reagent (prepared by dissolving 2 g of amidol and 40 g of pure sodium bisulphite in 200 ml distilled water) and 1 ml of ammonium molybdate solution (8.3%), in that order. The solution was made upto 25 ml and after an interval of 10 minutes, its extinction coefficient was determined. The amount of phosphate was calculated from a calibration curve obtained by applying the same procedure to aliquots of standard phosphate (KH_2PO_4) solutions.

2.3. Results and Discussion.

Phosphamidon, in small concentrations in aqueous solution, is degraded and eventually mineralised upon illumination in presence of suspended ZnO or TiO_2. Control experiments in the absence of one component at a time have shown that the simultaneous presence of catalyst, light and oxygen is essential to effect the decomposition. The role of dissolved oxygen was confirmed by conducting the experiment using a reaction system, continuously deaerated with N_2 gas. The rate of disappearance of phosphamidon at same initial concentration and under identical reaction conditions, in presence of ZnO or TiO_2 at the same loading, is given in figure 2.2.

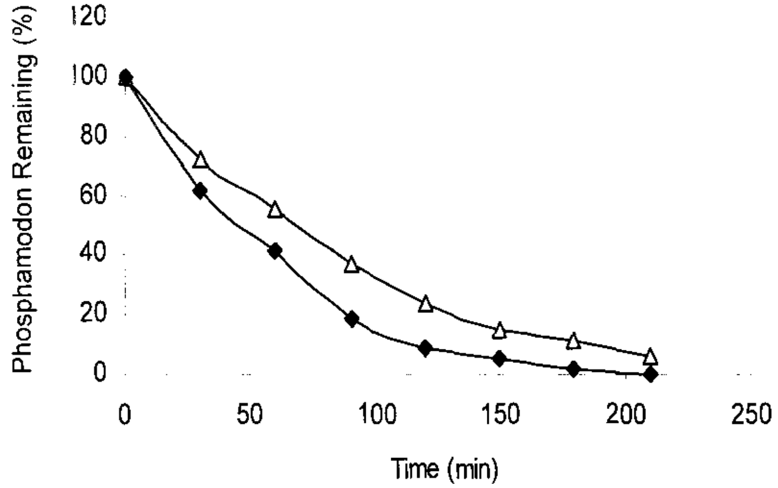


Fig.2.2. Photocatalytic degradation of phosphamidon in presence of ZnO and TiO_2 catalysts. ♦- TiO_2, Δ- ZnO Catalyst : 1g/L. Phosphamidon concentration: 1.0 $\times 10^{-4}$M

As seen from the figure, TiO_2 is a superior catalyst, even though ZnO also is highly efficient for the photodegradation of phosphamidon. Since the main objective of the current study was the identification of a suitable catalyst – reactor system for achieving optimum efficiency for the degradation of organic pollutants, all further studies were carried out using TiO_2 catalysts, even though the relative efficiency of ZnO vis á vis TiO_2 also merits further investigation.

2.3.1 Effect of catalyst loading

The effect of catalyst loading on the degradation of phosphamidon was investigated using TiO_2 at different loading, keeping all other parameters identical. The results of the study are shown in figure 2.3.

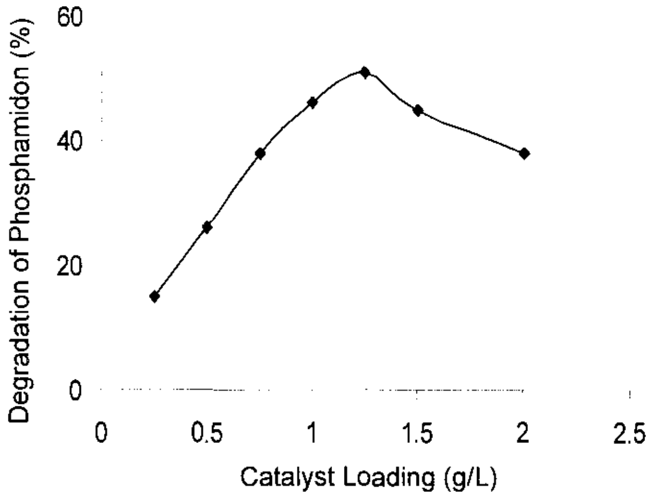


Fig.2.3. Effect of catalyst loading on the photodegradation of phosphamidon.Conc. of phosphamidon: 1 x 10^{-4}M, Irradiation time: 30 min.

A steady increase in the degradation of phosphamidon is observed upto 1.25 g/L of catalyst loading followed by a slow decrease at higher loadings. The higher degradation with increase in catalyst loading can be attributed to the increase in catalyst surface area, increase of light absorption and consequently, the creation of higher number of active species. However, at higher loadings, beyond the optimum, part of the catalyst will be in the dark and there will be a decrease in the light penetration. Further, it was difficult to maintain the suspension homogeneous and the catalyst had a tendency to settle at the bottom of the reactor. Variation in the degree of settling influences the consistency of the sampling process, total amount of light absorption and scattering of the incident light by the catalyst. These factors together contribute to a decrease in the efficiency of the catalyst at loadings above the optimum level. Similar observations were reported by other authors as well [249, 250]. All further studies were made using a TiO_2 loading of 1.25 g/L.

2.3.2. Effect of concentration of phosphamidon

The effect of initial concentration of phosphamidon on the overall rate of degradation was studied by varying the concentration over a wide range. The results are shown in figure 2.4.

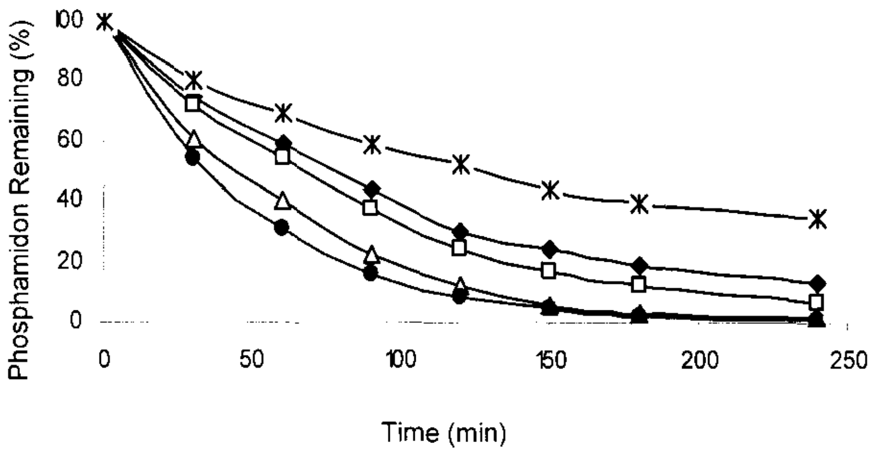


Fig.2.4. Effect of initial concentration on the photocatalytic degradation of phosphamidon in water. (Ж) 6.0 x 10^{-4} M; (♦) 4.5 x 10^{-4} M; (□) 3.0 x 10^{-4} M; (Δ) 1.5 x 10^{-4} M; (●) 1.0 x 10^{-4} M

It is obvious that the rate of degradation increases with increase in phosphamidon concentration. However, at very high concentrations, the rate slows down as reflected in the rate of degradation at 6.0 x 10^{-4}M. See table 2.1.

Table 2.1. Effect of initial concentration on the rate of degradation of phosphamidon

Initial Concentration x 10^{4}M	Rate x 10^{6} moles min^{-1}
1.0	0.9
1.5	1.5
3.0	2.8
4.5	3.4
6.0	3.0

Many authors [249, 110] have reported that the TiO_2 photocatalysed degradation of OP compounds follows first order kinetics. By applying the following simple first order rate law [251]

$$\ln([C]_i/[C]_t) = kt$$

to the results of the current study, it has been observed that there is a linear relationship between ln ($[C]_i/[C]_t$) and time (t), which is consistent with first order kinetics. The results of this application are presented in figure 2.5. The slope k of the best-fit line through the data points represents the first order rate constants for corresponding initial concentration.

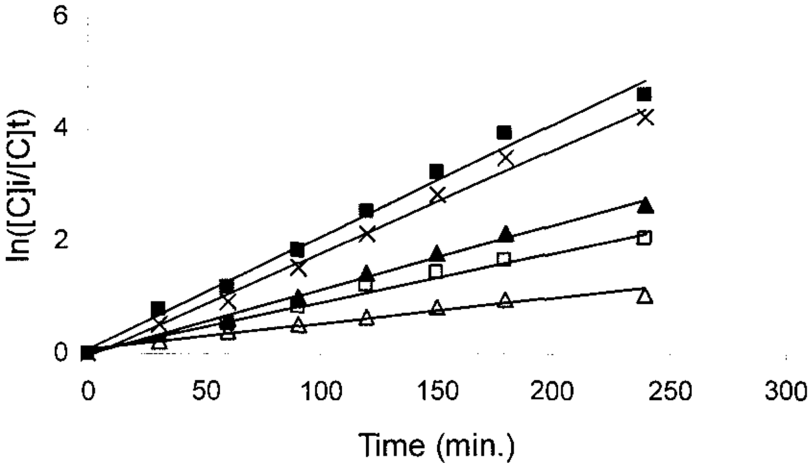


Fig. 2.5. Pseudo-first order kinetics for the photocatalytic degradation of phosphamidon in water. (■) 1.0 x 10^{-4} M ; (x) 1.5 x 10^{-4} M, (▲) 3.0 x 10^{-4} M,(□)4.5 x 10^{-4} M; (Δ)6.0 x 10^{-4} M

The apparent kinetic parameters determined for the degradation of phosphamidon are summarised in Table 2.2.

Table 2.2. Apparent First order rate constants and half-lives for the Photodegradation of phosphamidon at different initial Concentrations

Concentration (x 10^4M)	Rate constant, $k_{app.}$ (x 10^3 min^{-1})	Half-life ($t_{1/2}$) (Min.)
1.0	20.1	31
1.5	16.5	49
3.0	9.09	65
4.5	6.61	85
6.0	5.60	147

The decrease in the rate of degradation (at higher concentrations) and thus the order of reaction with increase in initial concentration of the reactant in TiO_2 photocatalysis has been reported by many other authors [249, 252, and 253]. At high substrate concentration, the adsorbed reactant molecules may occupy all the catalytic sites on the TiO_2 surface and this leads to zero order kinetics. At low concentrations, the number of catalytic sites will not be a limiting factor and the rate of degradation is proportional to the substrate concentration, in accordance with apparent first order kinetics. Reaction orders smaller than unity are reported in the TiO_2 photocatalysis of phosphonic acids, as a result of slow diffusion of the product from the surface of the catalyst [253]. Major products such as low molecular weight organic acids and phosphates, formed during the photocatalysed degradation of OP compounds, remain strongly adsorbed onto the surface of the catalyst through hydrogen bonding with the hydroxylated surface of the catalyst [249]. This also leads to reduction in the number of catalytic sites and consequent reduction in the rate of degradation observed at higher substrate concentration.

2.3.3. *Effect of pH*

It has been reported by many workers [110, 59, 254 - 256] that pH of the solution is an important parameter in the photocatalysed degradation of organic wastes. This is due to the fact that pH influences the surface charge of the semiconductor, thereby affecting the interfacial electron transfer and the photoredox process [110]. In the present case, the experiments were carried out at an initial pH of 6-6.5. As the photodegradation progressed, there was a slow decrease in the pH and the solution was becoming more acidic. This indicated the release of H^+ during the reaction. Preliminary studies showed that the rate of degradation decreased with decrease in pH and it proceeded faster under alkaline pH. A summary of the results of the study is presented in Table 2.3

Table 2.3. Effect of initial pH on the degradation of Phosphamidon.
Catalyst: TiO_2 1g/L ; Phosphamidon Concentration: 1.0×10^{-4}M

Initial pH	% Removal of Phosphamidon after 60 minutes of irradiation
4.0	49
5.5	53
6.5	57
8.5	63
10.0	67
11.0	64

The results show that the influence of pH is not quite marked at values above 10 and it shows even a slight decrease in the removal rate of phosphamidon. The enhancement in the rate of degradation under neutral or mild alkaline conditions is consistent with the findings of other researchers [257-259], even though many reports on decreasing the photocatalytic degradation of organics under increasing pH values also exist [17, 260, and 261]. A simple explanation for the enhancement in the degradation rate at higher pH is the increase in the rate of formation of OH radicals by the reaction of hydroxyl ions and the holes as follows:

$$TiO_2 + h\nu \rightarrow TiO_2(h^+ + e^-) \qquad (1)$$

$$OH^- + h^+ \rightarrow OH^{\cdot} \qquad (2)$$

The slightly lower degradation observed at pH 11 may be due to the dissolution of carbon dioxide, formed by the total mineralisation of phosphamidon, and consequent formation of carbonates, which inhibit the formation of $OH^{\cdot}$ [105].

However, it is too premature to draw any conclusion on the effect of pH from these preliminary results. As mentioned earlier, there is no consistent conclusion, or agreement among established research workers, on the effect of pH on the photocatalytic decomposition of organic pollutants in aqueous solution, even though it has been accepted by all that the pH of the aqueous solution is one of the important environmental parameters which significantly influences the physicochemical properties of semiconductors, including the charge on the particle, the aggregation numbers of particles and the position of the conduction and valence bands. Schmelling et al. [258] depicted that a change in pH causes a shift in the Fermi level of the semiconductor such that the photocatalyst becomes a better oxidant with decreasing pH. However, the surface of titanium dioxide carries a net negative charge under alkaline conditions and increases the degradation rate of some pollutants [259]. Mills et al. [262] showed that the rate of photocatalysis is not usually found to be strongly dependent upon pH value [47]. Higher reaction rates for various TiO_2 sensitized photomineralisations have been reported at both low and high pH values [42]. Therefore, any meaningful conclusion on the effect of pH can be drawn only from an extensive study, which is being planned as an extension of the current investigation.

2.3.4. Products of Degradation

The final products of degradation of phosphamidon (mixture of approx. 70% Z-isomer and 30% E- isomer) were examined by irradiating a higher concentration of the substrate in presence of TiO_2. As expected from reported studies on similar OP pesticides [110, 59, 254, 255] the degradation leads to complete mineralisation and the products are found to be Cl^- and phosphate ions. With reference to the fate of nitrogen, the attack by hydroxyl radicals can induce cleavage of the C-N bond and the organic nitrogen can be transformed into NH_4^+, NO_2^- and NO_3^-. In the current experiments, the presence of NH_4^+, NO_2^- or NO_3^- was not detected. This may be due to their extremely low concentration and the possibility of their remaining adsorbed onto the surface at the experimental conditions. The inability to account for all the nitrogen liberated during photocatalytic degradation of nitrogenous compounds has been reported earlier also [263-265]. However, based on the results of the studies reported earlier [60, 263-265] under similar conditions, it is reasonable to assume that NH_4^+ (which gets eventually transformed [264] to NO_3^- and H^+) and NO_3^- are also formed as the mineralisation products, though the possibility of formation of small quantities of NO_2^- by the direct photolysis of aqueous NO_3^- cannot be ruled out [266].

The fate of nitrogen atoms in the photocatalytic degradation of nitrogenous organic compounds depends on the structure of the compound, especially the position and the number of N atoms. For example, the photocatalytic mineralisation of nitrogen containing compounds with one N atom such as alkyl and alkanolamines [264], amides [141] etc. was reported to yield only NH_4^+, NO_3^- and/or NO_2^- and no gaseous nitrogen. However, the photocatalytic oxidation of hydrazine derivatives [263] with N-N bonds, at TiO_2-H_2O interfaces, generates gaseous N_2 in addition to the formation of NH_4^+ and NO_3^-. Azo dyes such as congo red and alimentary (amaranth) with N=N (azo group) also yield gaseous dinitrogen under photocatalytic conditions [265]. In this case, the authors measured the evolution of nitrogen gas quantitatively and showed that it corresponds stoichiometrically to the mineralisation of the central N=N (azo group). Based on such findings by other investigators under similar conditions, it is reasonable to assume that the possibility of formation of N_2 in the case of phosphamidon, with only one N atom at the tertiary amide moiety, is remote. The overall mineralisation reaction may hence be empirically represented as in figure 2.6.

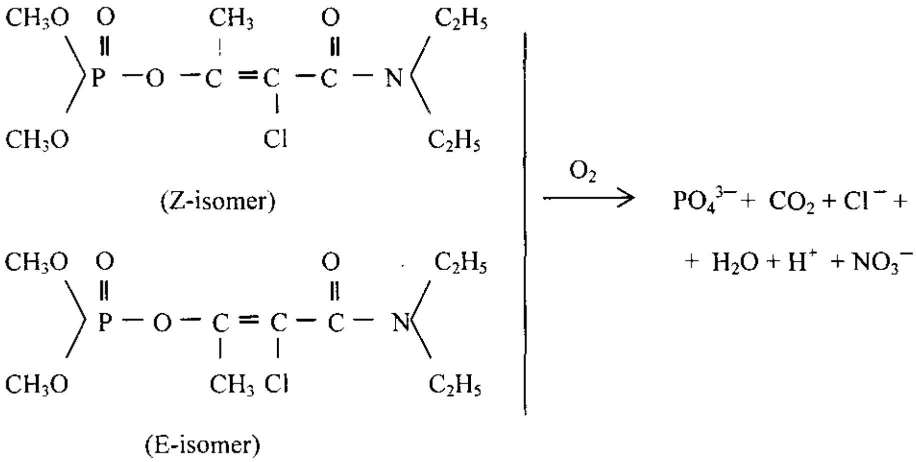


Fig.2.6. Empirical reaction scheme for the photocatalytic mineralisation of Phosphamidon

2.3.5. Effect of Anions

The effect of Cl^-, PO_4^{3-} and NO_3^- ions on the rate of degradation of phosphamidon was examined individually, by adding NaCl, Na_3PO_4 and $NaNO_3$ to the system such that the resultant solution contains 1.5×10^{-4} M of Cl^-, PO_4^{3-} and NO_3^- ions, before the irradiation begins. In view of the inconsistent results reported on pH effects and the possibility of the effect being further complicated by the presence of added ions, the study is conducted only at the pH of 6.0-6.5. The results showed that under the reaction conditions, these ions have no significant effect on the rate of degradation of phosphamidon. However, at higher concentrations (10^{-1} M), all these ions inhibit the degradation considerably. (see figure 2.7.) This might be due to the competition of these ions for adsorption sites on the catalyst, thereby reducing the number of sites available for the organic substrate and O_2. The possibility of these anions penetrating into the inner co-ordination sphere of TiO_2 at concentrations exceeding 0.1 M and pH close to the point–of-zero-charge (PZC, between 6 and 6.5), thereby reducing the rate of disappearance of various pollutants has been reported earlier also [267]. The inhibition efficiency of the three anions is in the order

$$PO_4^{3-} > Cl^- > NO_3^-$$

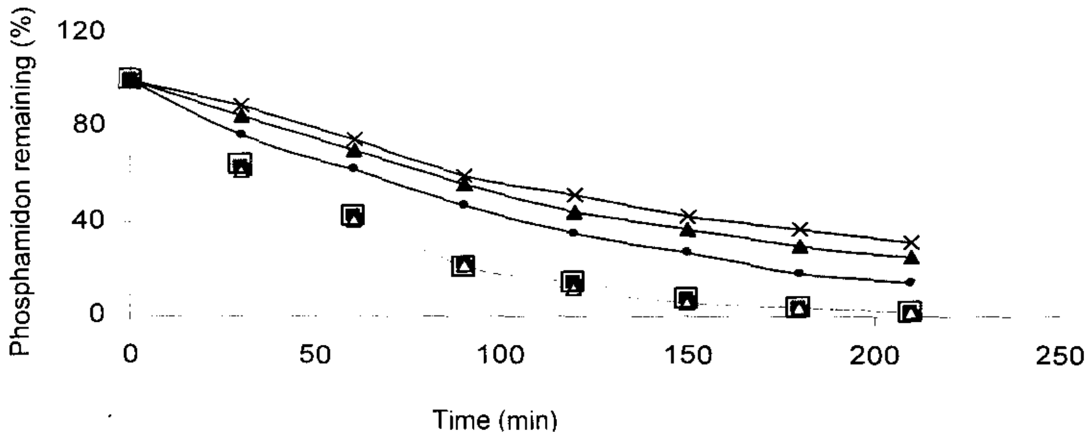


Fig.2.7. Effect of anions on the photocatalytic degradation of phosphamidon in water (---)1×10^{-4} M phosphamidon (A), (Δ) A with 1×10^{-4} M NO_3^-, (□) A with 1×10^{-4} M Cl^- and (■) A with 1×10^{-4} M PO_4^{3-}. (●)A with 1×10^{-1} M NO_3^- (▲) A with 1×10^{-1} M Cl^-, and (x) A with 1×10^{-1} M PO_4^{3-}

Wang et al. [47] have demonstrated that the effect of anions on the photocatalytic degradation of dichlorvos (an organophosphorous insecticide) on TiO_2 depends on a variety of factors such as pH and origin of the catalyst. Other authors [110, 268 and 149] also reported similar observations. For example, at alkaline pH, the surface charge σ of TiO_2 is negative according to

$$TiOH + OH^- \rightarrow TiO^- + H_2O \qquad (3)$$

and hence the anions will be expelled from the surface. Under such conditions, the anions are not expected to have much effect on the degradation of an organic pollutant. Under acidic pH, σ is positive as a result of

$$TiOH + H_3O^+ \rightarrow TiOH_2^+ + H_2O \qquad (4)$$

and therefore anions are attracted to the surface, resulting in their inhibition of the photocatalytic degradation.

The inhibition observed by the addition of higher concentrations of phosphate, chloride and nitrate ions in the current study, can be attributed to their adsorption on the surface, considering the fact that the reactions are carried out at pH 6-6.5 when σ is positive. The strong inhibition by Cl^- can also be attributed to its competition with O_2 for electrons [269], while the blocking of large number of surface sites by the PO_4^{3-} due to steric factors may be the reason for its strong inhibiting tendency. Other authors also reported the relatively poor inhibiting effect by NO_3^- ions, possibly due to its weak adsorption on the catalyst surface [270].

2.3.6. Effect of H_2O_2

It has been observed that the reaction system also contained H_2O_2, formed during the photocatalytic reaction. However, the concentration of H_2O_2 does not show a steadily increasing trend, even though the degradation of phosphamidon continued unhindered. It reaches a maximum at around 50-100 minutes of irradiation (the time varies and the concentration at the maximum level also varies with experiments) and levels off or drops slightly and picks up again, though inconsistently. This possibly indicates the simultaneous formation and decomposition of H_2O_2 under the reaction conditions. This is further confirmed by the observation that in repeat experiments under identical conditions, the rate of disappearance of phosphamidon was quite reproducible, while the amount of H_2O_2 measured at identical intervals varied significantly. Since H_2O_2 is known to produce hydroxyl radicals [271] upon reduction by the electrons in the conduction band of TiO_2, addition of H_2O_2 to the current reaction system was expected to increase the amount of hydroxyl radicals. Experiments with added H_2O_2 show that the rate of TiO_2 catalysed photodegradation of Phosphamidon is enhanced and the combined efficiency of the catalyst and H_2O_2 is slightly more than the sum of the effect of H_2O_2 and the catalyst. See table 2.4.

Table 2.4. Effect of H_2O_2 on the photocatalysed degradation of phosphamidon. Phosphamidon conc. 1.5×10^{-4} M

Reaction system	% Degradation of Phosphamidon*	
	30 min. irradiation	60 min irradiation
No catalyst, no H_2O_2	0.5%	1.0%
Catalyst only	39.0%	58.6%
H_2O_2 only (20 mg/L)	5.5%	8.3%
Catalyst + H_2O_2	49.5%	69.2%

*Approximate. Average of 3 experiments

This synergy, though modest, may be due to the partial inhibition of electron – hole recombination on TiO_2 surface, by H_2O_2, which scavenges some of the electrons. This is also consistent with the observations reported by many workers for the degradation of various OP compounds [58, 249, 258].

The effect of H_2O_2 on the TiO_2 photocatalysed degradation of organic pollutants in water was examined by Almaric et al. [272] while studying the effect of antioxidant enzymes catalase and superoxide dismutase on the rate of TiO_2 and ZnO photocatalysed degradation of 1, 2-dimethoxybenzene (DMB) in water. The authors demonstrated that the effect of H_2O_2 might be favourable or unfavourable, depending on the initial ratio $[H_2O_2]/[DMB]$. This was attributed to the competition between H_2O_2 and DMB for the adsorption sites and/or photo-produced holes, the formation of additional $OH^{\bullet}$ radicals and the detrimental modification of TiO_2 surface.

The reaction between the hydroxyl radicals and the substrate is expected to occur at or near the surface of the semiconductor, as no $OH^{\bullet}$ radicals are produced by direct photolysis, without the catalyst, under our experimental conditions. However, once the surface initiated reaction has begun, the $OH^{\bullet}$ radicals generated can propagate the decomposition of H_2O_2 in both the liquid phase as well as on the surface. Decomposition of H_2O_2 will result in the formation of more $OH^{\bullet}$ radicals, which can enhance the rate of degradation of phosphamidon. Thus, there is simultaneous formation and decomposition of H_2O_2 and depending on the predominance of one or the other at any particular time, there is oscillation in its concentration. This has been observed in the semiconductor mediated photo-oxidation of alcohols as well [70]. However, addition of H_2O_2 need not necessarily result in enhanced photocatalytic degradation of all organophosphorous pesticides, as has been demonstrated by Doong and Chang [58] in the case of methamidophos and phorate. For another organophosphorous insecticide, i.e. EPN, addition of H_2O_2 significantly enhanced the degradation efficiency, comparable to our results. The concentration of hydroxyl radicals generated from H_2O_2 is negligible when compared to that from holes [181]. Hence if OH radicals are the prime initiators and propagators for the reaction, the enhancement should have been at best cumulative. Hence the synergy observed in our study may be due to the direct participation of H_2O_2 in the degradation process, in presence of the catalyst. Current results are not adequate to draw any specific conclusion on this observation, which is of significant importance in the environmental application of the technology.

The photocatalytic degradation of a series of alcohols on ZnO was reported [70] to be initially autocatalytic and this was attributed to the in situ formed H_2O_2 that could act as a reserve of $OH^{\bullet}$ radicals. However, no such phenomenon was observed in the current study. Our results show that H_2O_2, added at concentration comparable to the in situ formation, has no effect on the rate of ZnO catalysed degradation of phosphamidon. This is consistent with the findings of Almaric et al. [272] that H_2O_2, formed in situ, does not decompose on ZnO and consequently, does not generate $OH^{\bullet}$ radicals capable of enhancing the degradation of the organic pollutant. On the other hand, the stability of H_2O_2 leads to unfavourable effects due to its competition for adsorption sites at higher concentrations. The effect of H_2O_2, on the photocatalysed degradation of various organics and the difference in the effect in presence of different semiconductors is a subject that warrants detailed investigation.

2.3.7. General Mechanism of the process

When a semiconductor oxide is irradiated with light having energy higher than the band gap (in the case of TiO_2 it is ca.3.2 eV), a pair of conduction band electron (e^-) and valence band hole (h^+) is generated. The charge carriers can subsequently recombine within the bulk of the material or migrate to the particle surface where they can also recombine or can be trapped at some defect site, eventually as surface bound O^- radicals [8, 61, 21]. In the case of TiO_2, this will be followed by adsorption of molecular oxygen on the Ti (III) sites, which reduce O_2 to the superoxide radical anion $O_2^{\cdot -}$, while the positive charge carrier, Ti(IV)–$O^{-\cdot}$ –Ti(IV) can oxidise the surface hydroxyl groups or the surface bound water to surface bound $OH^{\cdot}$ radicals [27, 240]. Radiolytic studies by Lawless et al. [62] showed that it is not possible to distinguish between the surface bound $OH^{\cdot}$ radicals and the Ti(IV)–$O^{-\cdot}$ –Ti(IV) species.

The overall catalytic process can hence be presented as

$$TiO_2 + h\nu \rightarrow TiO_2\ (h^+_{vb} + e^-_{cb}) \tag{5}$$

$$O_2 + e^- \rightarrow O_2^{\cdot -} \tag{6}$$

$$h^+ + H_2O \rightarrow OH^{\cdot} + H^+ \tag{7}$$

$$h^+ + OH^- \rightarrow OH^{\cdot} \tag{8}$$

$$h^+ + RH \rightarrow R^{\cdot} + H^+ \tag{9}$$

$$O_2^{\cdot -} + H^+ \leftrightarrow HO_2^{\cdot} \tag{10}$$

$$HO_2^{\cdot} + HO_2^{\cdot} \rightarrow H_2O_2 + O_2 \tag{11}$$

$$O_2^{\cdot -} + HO_2^{\cdot} \rightarrow HO_2^- + O_2 \tag{12}$$

$$HO_2^- + H^+ \leftrightarrow H_2O_2 \tag{13}$$

Hydroxyl radicals are powerful oxidants of organics in aqueous solutions [273]. As seen from the above scheme, oxygen can act as an effective electron scavenger, thus preventing the electron-hole recombination, resulting in the formation of H_2O_2. However, only about 15% of the oxygen is normally converted to H_2O_2 in UV-TiO_2 system [58], thus illustrating that electron-hole recombination is a major process in the reaction system. H_2O_2, though to a limited extent, also contributes to a reduction on this recombination, by acting as an electron scavenger, as shown in the reaction scheme below.

The mechanism of the formation of $OH^{\bullet}$ radicals from H_2O_2 on TiO_2 surface is established to be as follows [47, 183, 274].

$$H_2O_2 + O_2^- \rightarrow OH^{\cdot} + O_2 + OH^- \tag{14}$$

$$H_2O_2 + h\nu \rightarrow 2\ OH^{\cdot} \tag{15}$$

$$H_2O_2 + e^-(TiO_2) \rightarrow OH^{\cdot} + OH^- \tag{16}$$

$$2\ OH^- + h^+ \rightarrow OH^{\cdot} + OH^- \tag{17}$$

$$OH^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot} \tag{18}$$

$$HO_2^{\cdot} + H_2O_2 \rightarrow O_2 + H_2O + OH^{\cdot} \tag{19}$$

Almost all the studies reported so far indicate that, $OH^{\bullet}$ radicals, irrespective of whether they are free or surface bound, are the active oxidising species in photocatalytic degradations over TiO_2. EPR studies on irradiated TiO_2 have also identified the OH radicals by spin trap techniques [275]. No other radical species were detected under ambient conditions in aqueous dispersions. Studies on the photooxidation of aliphatic alcohols on ZnO [25 and 276] and TiO2 [277] also suggested that the rate-determining step in these reactions is the formation of $OH^{\bullet}$ radicals.

A simplified representation of the degradation pathways of Phosphamidon under UV/TiO_2 is given in figure 2.8.

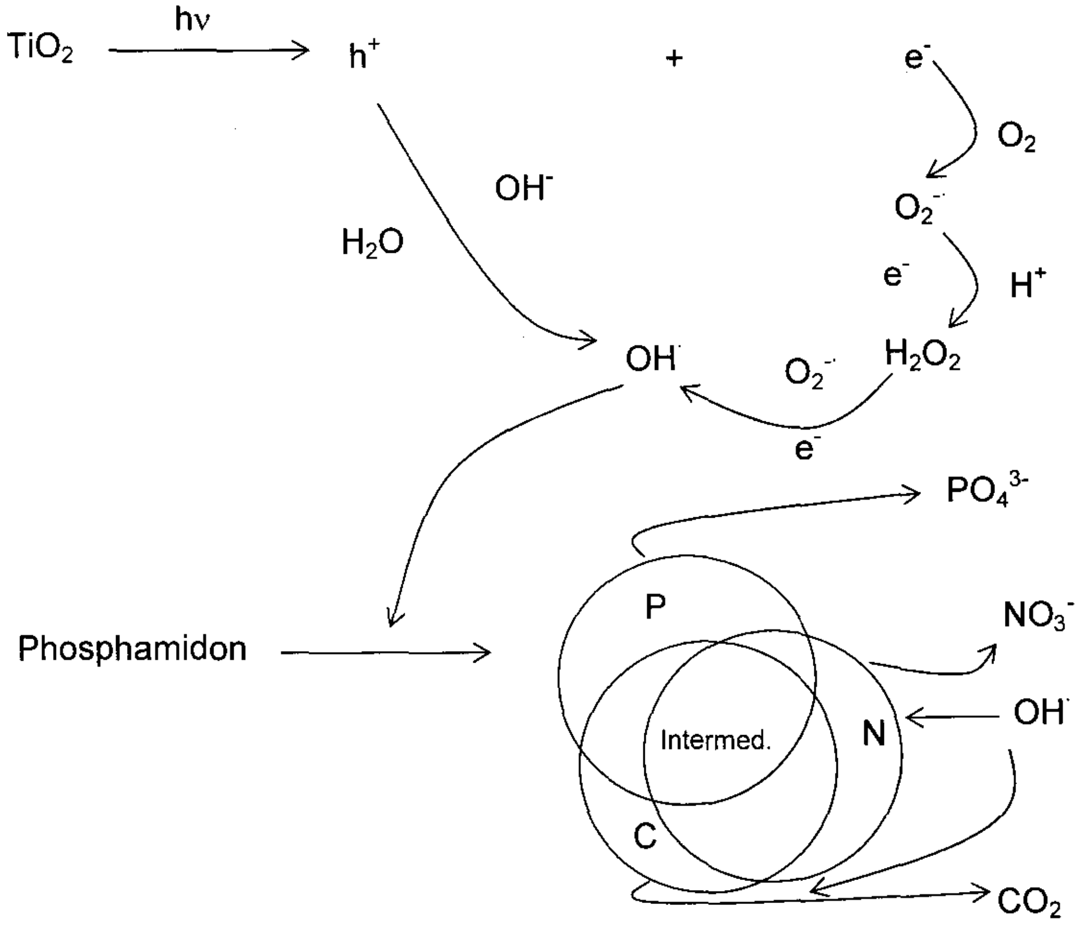


Fig. 2.8. Simplified photocatalytic degradation pathways of Phosphamidon under UV/TiO_2

2.3.8. Photocatalytic decomposition under solar radiation

The possibility of using TiO_2 as a photocatalyst for the degradation of phosphamidon in wastewater under natural sunlight was examined by conducting similar experiments, as described above, using solar radiation. Control experiments with solar irradiated phosphamidon solution in the absence of TiO_2 showed practically no degradation. In the presence of TiO_2, phosphamidon disappeared slowly but steadily. The rate was not significantly different with the position of the sun. However, with the onset of darkness, the decomposition slowed down and stopped fully within 10-15 minutes. The degradation picked up again when exposed to sunlight next day morning. The rate of degradation over a six-day period is shown in figure 2.9.

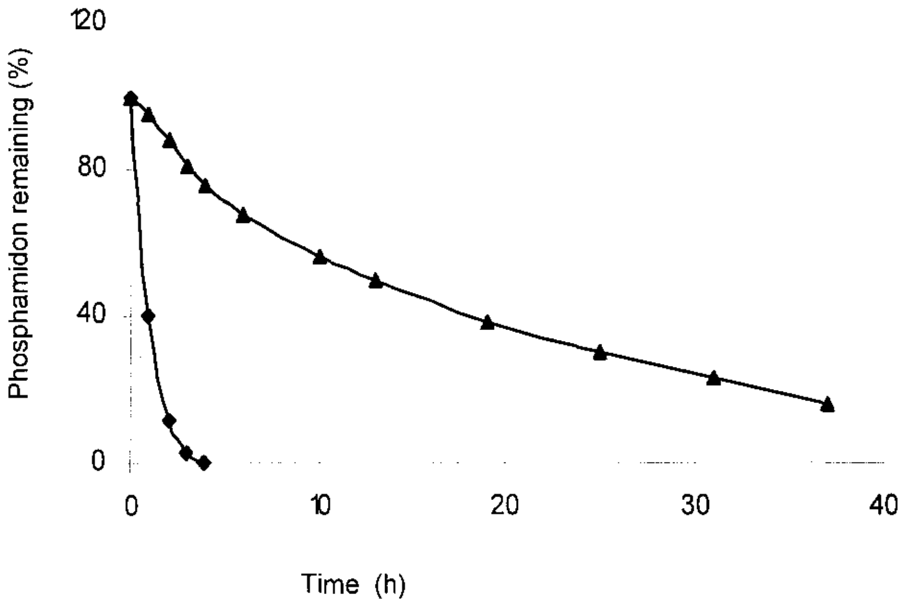


Fig.2.9. Degradation of phosphamidon under UV and solar irradiation. Conc.1.5x10^{-4} M
(♦) UV irradiation; (▲) Solar irradiation

The complete disappearance of phosphamidon, at the experimental concentration of 1.5 x 10^{-4} M was achieved in over 75 hr (in 12 days) of irradiation, even though the rate of degradation was becoming slower and slower with decrease in concentration of the substrate. It is worthwhile to observe that the degradation continued under solar radiation without aeration of the system or mixing. As mentioned earlier, oxygen in the solution serves as an electron scavenger to form the superoxide ion O_2^{-} and prevents the recombination of holes and electrons [183]. Laboratory experiments have shown that purging of the solution with N_2 reduced the degradation efficiency drastically. At the same time, saturating the system with pure oxygen did not enhance the reaction rate. From these observations, it is inferred that while dissolved oxygen is essential for the degradation, its quantity, normally present in water is relatively excessive to the low concentration of the organics in solution and the slow natural replenishment of oxygen in open aqueous system is adequate to ensure the continuation of the degradation. This will be an important consideration in the solar treatment of industrial wastewater.

2.4. Conclusions

The present study clearly shows that semiconductor oxides can be used as effective photocatalysts for the degradation of phosphamidon contaminated wastewater. Although a direct comparison of the efficiency of the two catalysts tested here, ZnO and TiO_2, may not be precise due to the difference in their surface characteristics as well as the absence of adequate data, it appears that TiO_2 is by far superior in its efficiency to degrade phosphamidon. The difference in the activity may arise from a number of factors including the lifetime of the active species, surface area, concentration of hydroxyl groups, absorption and adsorption efficiency etc. The rate of degradation is influenced by pH of the system, even though the results are not always consistent. The H_2O_2 formed in the system undergoes simultaneous decomposition, leading to periodic increase and decrease in its concentration. This decomposition may be taking place on the surface as well as in the solution, depending on the concentration. Anions formed during the degradation have little influence on the rate of the reaction at low concentrations. However, at higher concentrations, they inhibit the degradation of phosphamidon. These observations, together with the finding that rate of degradation of phosphamidon is higher in presence of TiO_2, compared to ZnO, supports the view that the surface mediated process is more prominent in the degradation reaction.

Chapter 3

PHOTOCATALYTIC DEGRADATION OF PHENOL ON SEMICONDUCTOR OXIDES

3.1. Introduction

Phenols and phenolic compounds are major contaminants of wastewater from many industries. They are released into the environment from effluents discharged by industries such as petroleum refining, coal tar, steel, dyestuff, synthetic resins, coal gasification and liquefaction, surface runoff from coal mines, byproducts of agricultural chemicals, paper and pulp mills, tanning, fiberboard production and paint stripping operations. According to environment protection rules of Central Pollution Control Board, India (1992) the discharge limit of phenols in inland water is 1 mg/L. Among the list of priority organic pollutants identified by the U.S. Environmental Protection Agency, phenols represent a group of organics frequently found in various industrial effluents and reported in hazardous waste sites.

Phenols are widely recognized among the most important pollutants in water and wastewater. More specifically, monochlorophenols constitute an important category of water pollutants [278]. Their presence in water stems principally from industries, which produce chemical intermediates or generate them during the chlorination of effluents containing phenolic compounds. They can also be formed by the degradation of phenoxy herbicides. They have been found in the river water, usually at levels of few ppb. Use of chlorine in the disinfection treatment of drinking water can also result in the formation of monochlorophenols. In recent years, Advanced Oxidation Processes (AOPs) involving hydrogen peroxide, ozone and /or Fenton reagents, with or without a source of UV light have been reported to be useful for the photo-oxidation of organic pollutants in waste waters [279, 280, 281]. It removes substantial amount of Chemical Oxygen Demand (COD) and Total Organic Carbon (TOC) from industrial effluents. However, these oxidation methods result in partial oxidation of organics and more often lead to the generation of potentially harmful chemicals. Total oxidation of organics by these technologies is both cost and energy intensive. Among the various AOPs, semiconductor mediated photocatalysis has been accorded great importance over the last few years due to its potential to destroy a wide range of organic and inorganic pollutants at ambient temperatures and pressures, without the production of harmful by-products [64, 282,283].

Over the years, a large number of semiconductors have been reported as efficient photocatalysts. The most widely studied among them are TiO_2, ZnO and CdS. In fact, TiO_2 has been one of the most active photocatalysts reported so far and has become the bench mark against which photocatalytic activity of other semiconductors is measured. ZnO is a suitable alternative to TiO_2 and is in fact proved to be more efficient than TiO_2 in several applications. Many researchers have shown that addition of heavy metals such as platinum (Pt), palladium (Pd) and gold (Au) can enhance the degradation efficiency of semiconductor photocatalysts [262, 279, 284-286] which is attributed to the rapid transfer of photogenerated electrons from the semiconductors to the metal particles resulting in the effective separation of electrons and holes. Similarly, coupled semiconductor systems such as CdS/TiO_2, ZnO/Fe_2O_3 and ZnO/TiO_2 have also been shown to enhance the photocatalytic activity of their constituents, probably by the inter-particle electron transfer and more efficient charge separation [51, 259, 287]. Some of these and other studies are briefly discussed in Chapter 1.

In this chapter, the photocatalytic activity of ZnO, TiO_2, mixed oxides and doped TiO_2 is evaluated under various reaction conditions and in presence of various additives for the complete degradation of traces of phenol in water.

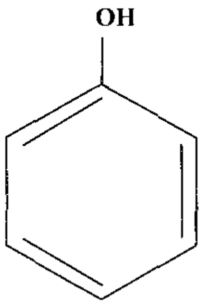
Some of the relevant physicochemical properties of phenol are as follows:
It is a clear, colourless, mobile liquid under normal temperature and pressure. It is readily soluble in most organic solvents and forms an azeotropic mixture with water.

Other names: Hydroxybenzene, Carbolic acid

Molecular formula: C_6H_5OH

CAS Registry Number: 108-95-2

Structural Formula:



Toxicity:

LD$_{50}$ (Mouse): 500 mg/kg

Though phenol was used as a germicide in earlier years, its use in pharmaceuticals is limited today, because of its toxicity. The limiting value of phenol in the air laid down for worker protection is 19 mg/m^3. Its major commercial applications include production of formaldehyde resins, caprolactum, polycarbonates and epoxy resins.

3.2. Experimental details

3.2.1 Materials

Phenol Analar grade (99.5% purity) from Qualigens (India) was used without further purification. The photocatalysts TiO_2 and ZnO were same as described in Chapter 2. Fe_2O_3 and Al_2O_3 (SQ grade) from Qualigens, India were used in the preparation of mixed oxide catalysts. Other chemicals used were of reagent grade and used as such without further purification. The water used in all the experiments was purified by double distillation. A stock phenol solution was prepared by dissolving 1 gm of phenol in water and diluting to 1000mL at room temperature. Appropriate dilute solutions were prepared from this stock solution by mixing with the required quantity of double distilled water.

3.2.2. Preparation of mechanically added oxides

Mixed catalysts with TiO_2 were prepared by adding the respective oxides such as Fe_2O_3, Al_2O_3 and ZnO to TiO_2 in the required ratio by weight and mixing them thoroughly using a cyclo-mixer.

3.2.3. Preparation of doped catalysts

The metal ions used for doping are Cu^{2+}, $Co^{2+}$and Fe^{3+}. The doping is done as follows:

To 10g of TiO_2, added a minimum volume of salt solution of the metal containing the required amount of metal and mixed well. The salts used were: $CuSO_4.5H_2O$, $Co(NO_3)_2.6\ H_2O$ and $Fe(NO_3)_3.9\ H_2O$ (Merck India Ltd.).The resulting paste is dried at 110^0C for 6 hours to remove the excess water. Then it was powdered and calcined at 450^0 C for 6 hours. TiO_2 mixed with same volume of water and treated the same way as above served as control.

3.2.4. Experimental set up

The experimental set up is same as that used in the case of Phosphamidon described in Chapter 2. For solar experiments, 250 ml solution was exposed to sunlight for a fixed time daily between 0930 and 1600 hr. Experiments were conducted on the roof top of our laboratory in Kochi, India ($9^0 57' 51''$N, $76^0 16' 59''$E) during summer. After illumination for the specified period, the suspension was centrifuged and the supernatant was analysed for its phenol content by spectrophotometry [288], using Varian UV-VIS spectrophotometer. The analysis is based on the reaction of phenolic compounds with 4-amino antipyrine at pH 7.9 ± 0.1 in the presence of potassium ferricyanide to form a coloured antipyrine dye. The absorbance of this dye solution is measured at 500 nm.

H_2O_2 and CO_2 formed were analysed by methods as outlined in chapter 2.
Light intensity measurements were made using Spectrosense, Skye instruments, Wales, U.K.

3.3. Results and discussion

3.3.1 Photocatalytic degradation of phenol under UV irradiation

A series of experiments were carried out in presence of TiO_2 and ZnO, without UV illumination as well as with UV illumination in the absence of catalysts. Similarly, experiments were conducted in presence of light and catalyst, using catalyst-reactant suspension, deaerated with N_2. The concentration of phenol remained virtually the same thereby confirming our earlier findings with phosphamidon that the simultaneous presence of catalyst, dissolved oxygen and light is essential for the photodegradation of organics in water. The results presented in figure 3.1 show that both ZnO and TiO_2 are effective for the removal of phenol from water and the latter is superior in its activity. The degradation is very facile in the early stages and more than 85% of phenol disappears after 90 minutes of irradiation. The degradation is complete in approximately 150 minutes.

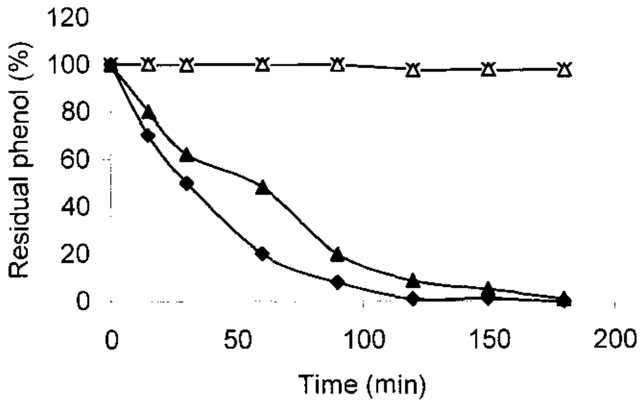


Fig 3.1. Photodegradation of phenol in presence of ZnO and TiO_2 catalysts. [Phenol]: $4x10^{-4}M$; Catalyst loading: 1 gL^{-1}. (x) No irradiation; (Δ) No catalyst; (▲) ZnO; (♦) TiO_2

3.3.2. Effect of catalyst loading

The effect of catalyst loading on the degradation efficiency was investigated using both ZnO and TiO_2 at different loadings, keeping all other parameters identical. The results of the study are shown in Figure 3.2. A steady increase in the degradation of phenol is observed up to 1.00 g/L of catalyst loading followed by a slow decrease at higher loadings. The higher degradation with increase in catalyst loading can be attributed to the increase in catalyst surface area, increase in light absorption and consequently, the creation of higher number of active species. However, at higher loadings beyond the optimum, part of the catalyst will be in the dark and there will be decrease in the light penetration. Further, it was difficult to maintain the suspension homogeneous and the catalyst had a tendency to settle at the bottom of the reactor. Variation in the degree of settling influences the consistency of the sampling process, total amount of light absorption and scattering of the incident light by the catalyst. These factors together contribute to a decrease in the efficiency of the catalyst at loadings above the optimum level. The result is similar to that observed in the case of phosphamidon as the organic pollutant (Chapter 2), indicating that under identical conditions of reaction and reactor geometry, the optimum loading of the catalyst will be more or less the same. Similar observations were reported by other authors as well [110, 249, 250]. All further studies were made using a catalyst loading of 1.00 g/L.

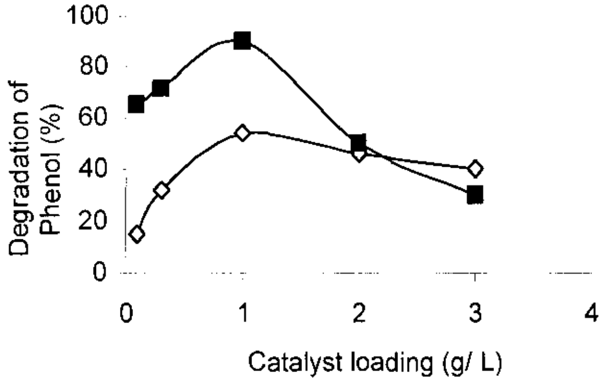


Fig 3.2. Effect of catalyst loading on the photodegradation of phenol.
[Phenol]: 4x 10^{-4}M; Time of irradiation: 60 min.(◊) ZnO; (■) TiO_2

3.3.3. Effect of Concentration

The effect of initial concentration of phenol on the rate of degradation in presence of both ZnO and TiO_2 catalysts was studied, by varying the concentration over a wide range. The initial rate was calculated from the degradation pattern in the first 30 minutes of irradiation. The results are presented in Figure 3.3. It is obvious that, in the case of both catalysts, the rate increases with increase in initial concentration of the substrate at lower concentration range (0.5 to 2 x 10^{-4} M for ZnO and 0.5 to 4x10^{-4}M for TiO_2), and the results are consistent with first order kinetics. However at higher concentrations, the increase in rate slows down, suggesting a reduction in the order of the reaction, as the substrate concentration increases. Interestingly, while the rate of degradation almost levels off in the case of TiO_2, it picks up slowly again in the case of ZnO.

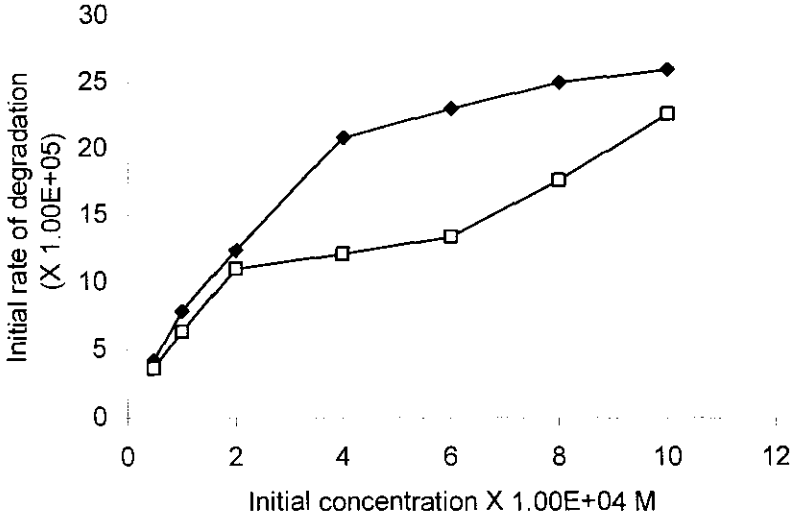


Fig 3.3. Rate of degradation of phenol in water at different initial concentrations on ZnO and TiO_2 catalysts. Catalyst Loading: 1gL^{-1}. (♦) TiO_2; (□) ZnO.

Reduction in the reaction order at higher substrate concentrations in TiO_2 photocatalysis has been reported by many authors [192, 249, 253] and was observed in our studies on phosphamidon degradation as well (Chapter 2 of this thesis). One of the causes for this, as suggested by earlier workers, is that at high substrate concentrations, all the catalytic sites of the semiconductor surface are occupied and concentration is not a constraint for the reaction to proceed. Any further increase in substrate concentration does not affect the actual catalyst surface concentration and this may result in a decrease of observed first order rate constant at higher initial concentration. However, at low concentrations, the number of catalytic sites is not the limiting factor of the degradation rate, which is now proportional to the substrate concentration, in accordance with apparent first order kinetics [252]. Gerischer and Heller [289] and Wang [290] proposed another reason for the kinetics. According to these authors, the generation and migration of photogenerated electron-hole pair in the semiconductor oxide catalysts and the reaction between photogenerated hole (or hydroxyl radical) and organic compounds are the two processes that occur in series. Therefore, each step may become rate determining for the overall process. At lower concentrations, the latter process dominates and therefore the degradation rate increases linearly with the concentration. On the contrary, at higher concentrations the former will become the governing step and the degradation rate increases slowly with concentration and even a constant degradation rate may be observed at higher concentration for a given illumination intensity. Gerischer and Heller [289] proposed that the interfacial electron transfer process involving the reduction of O_2 was the rate determining step in the TiO_2 sensitised photodegradation of organics. Another reason for this kinetic behaviour may be the nature of the intermediates generated in the process. In the case of phenol, these intermediates are shown to include a number of compounds such as hydroquinone, pyrocatechol, 1, 2, 4-benzene triol, pyrogallol, 2-hydroxy-1, 4-benzoquinone and 1, 4-benzoquinone which eventually get completely mineralised into CO_2 [183]. The intermediates are expected to remain strongly adsorbed onto the surface of the catalyst through hydrogen bonding with the hydroxylated surface of the catalyst. The effective number of active sites available for phenol adsorption is thus drastically reduced and this also contributes to the reduction in rate of degradation at higher substrate concentrations. In order to verify this, small quantities of two of the degradation intermediates, i.e. hydroquinone and catechol were added to the reaction system at the beginning and the disappearance of phenol was followed, in presence of both ZnO and TiO_2 as catalysts. The results of the study are presented in figures 3.4 and 3.5 which show that the degradation rate slows down in presence of the initially added intermediates, with both catalysts.

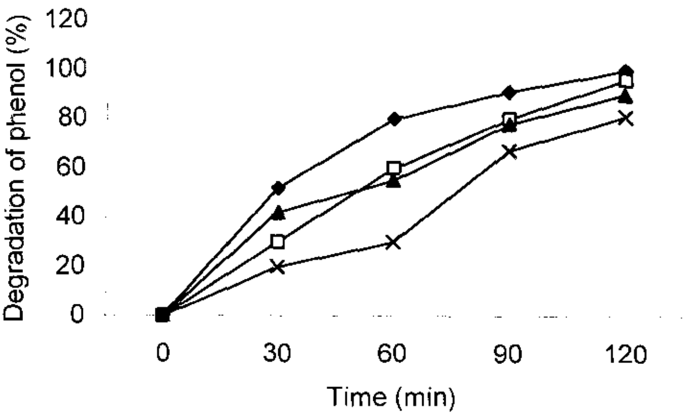


Fig 3.4. Effect of added hydroquinone on the degradation of phenol.
[Phenol]: 4×10^{-4}M; HQ: 4 ppm; Catalyst loading $1gL^{-1}$.
(♦) TiO_2; (□) TiO_2 + HQ; (▲) ZnO; (x) ZnO+ HQ

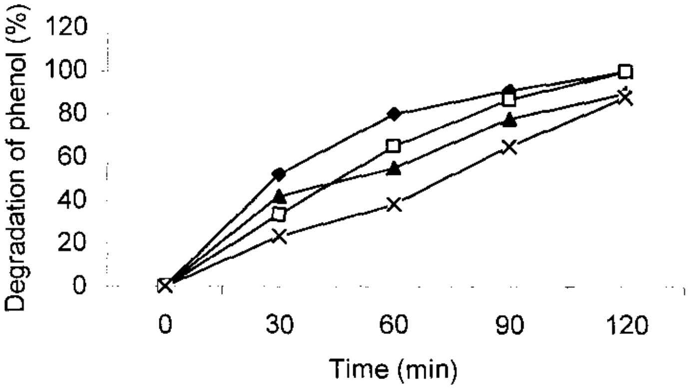


Fig 3.5. Effect of added catechol on the degradation of phenol.
[Phenol]: 4×10^{-4}M; Catechol: 4 ppm; Catalyst loading $1gL^{-1}$
(♦) TiO_2; (□) TiO_2 + Catechol; (▲) ZnO; (x) ZnO+ Catechol

The kinetics of the degradation of phenol on TiO_2 appears to be different from that on ZnO, in the later phase of the reaction. In the case of the former, the rate of degradation decreases and eventually levels off at higher concentration of phenol, while the rate levels off early in the case of ZnO, only to increase again at a later stage. This suggests that the reaction kinetics is more complex in the case of ZnO catalyst, which may be one of the reasons for the contradicting reports on the comparative efficiency of TiO_2 and ZnO as photocatalysts. For e.g. in the photocatalytic degradation of reactive and azo dyes, ZnO exhibits better efficiency, compared to TiO_2 [49 and 200]. However, Zamora et al. [204] reported that the comparative efficiency of ZnO and TiO_2 depends on the pH of the reaction system.

Their results show that TiO_2 is a better photocatalyst than ZnO for acidic or slightly basic effluents (pH = 2.5-7.4) while ZnO shows a significantly superior activity for strongly basic samples like textile effluents (pH = 11.5). From a study of the phototransformations of nitrogen containing organic compounds, it was shown that TiO_2 is far superior to ZnO in terms of the disappearance of the initial compound as well as the formation of the final product [60]. Our studies with phosphamidon (Chapter 2) also showed that TiO_2 is superior to ZnO for the photocatalytic mineralization of this pesticide. Similar results were reported in the case of the herbicide 2, 4-D as well [291].

The increase in the rate of degradation of phenol and hence the order of the reaction after a brief zero order phase in the case of ZnO is perplexing. This also shows that the saturation of the surface by the phenol molecules alone may not be the reason for the zero order kinetics at higher concentration. Had it been so, the kinetics should have been similar on both ZnO and TiO_2. The possibility of the many intermediates formed before the complete mineralization of phenol having different adsorption and reaction profiles on ZnO and TiO_2 catalysts may be one of the factors leading to the difference in kinetics on the two catalysts. Comparison of the results in figures 3.4 and 3.5 shows that even though both hydroquinone and catechol inhibit the degradation of phenol on both ZnO and TiO_2, the effect is slightly more pronounced on the former. This suggests that phenol and the intermediates have different degrees of adsorption on TiO_2 and ZnO. In the case of TiO_2, phenol is adsorbed better competitively while in the case of ZnO, the reaction intermediates formed also remain strongly adsorbed. Hence, the degradation of the intermediate is relatively faster (though its formation is slower) on ZnO, leading to the early availability of surface sites. Once the adsorbed intermediate is mineralised more sites are available for phenol to be adsorbed and the rate picks up again.

Another reason for the acceleration of the reaction rate after the slow phase in the case of ZnO may be the contribution from the homogeneous reaction, which sets in at a later stage. The role of OH radicals-initiated homogeneous process in ZnO catalysed photocatalysis has been well illustrated by earlier researchers [70 and 292]. The OH radicals participating in the process originate mainly from the decomposition of H_2O_2 (see steps 2 and 4 later). The OH radicals produced from the hydroxyl anions by trapping of the holes ($OH^- + h^+ \rightarrow OH^\cdot$) will remain adsorbed on the ZnO surface and will be oxidized further by reaction with holes [293].

The complex and often inconsistent behaviour of ZnO as well as the stability and consistently superior activity of TiO_2 as photocatalysts has been reported earlier also by many authors [25, 272 and 294]. A direct comparison of the efficiency of these two photocatalysts may not be complete unless the influence of a number of parameters such as pH of the medium, size, shape and distribution of catalyst particles, adsorption- desorption characteristics of the initial reactants as well as the intermediates and final products, possible corrosion/destruction of ZnO catalysts under UV irradiation, formation and decomposition of H_2O_2 in the presence of these two catalysts etc. has been delineated.

As in the case of the degradation of phosphamidon, described in Chapter 2, the degradation of phenol also results in the formation of H_2O_2 in the case of both ZnO and TiO_2. Again, the concentration of H_2O_2 did not have a steadily increasing trend, even though the degradation of phenol continued unhindered. Quantitative estimation of H_2O_2 at different intervals of irradiation gave inconsistent and irreproducible results and hence not reported here, even though the presence of H_2O_2 was confirmed in all cases. This result is in agreement with other researchers [74] and indicates the simultaneous formation and decomposition of H_2O_2 under the reaction conditions. In the case of ZnO, H_2O_2 is known to be fairly stable [272]. However, the inconsistency observed here in the amount of H_2O_2 at various intervals during the irradiation shows that it undergoes decomposition under our reaction conditions. It is also possible that the relatively stable H_2O_2 will be adsorbed onto the surface of the catalyst, thereby reducing its concentration in the solution. Participation of the H_2O_2 in the homogeneous process may also contribute to the irreproducibility of the result. The inconsistency was more prominent in the case of TiO_2, compared to ZnO, showing the more aggressive role of the former in the simultaneous production and destruction of H_2O_2.

3.3.4. Effect of Added H_2O_2

Based on the above, it was expected that initially added H_2O_2 would have a positive influence on the photocatalysed degradation of phenol, at least on TiO_2, by virtue of its contribution to the generation of reactive OH radicals. This possibility was tested by carrying out experiments with initially added H_2O_2. The results of the study in presence of both catalysts are summarised in Table 3.1

Table 3. 1. Effect of added H_2O_2 on the photocatalysed degradation of phenol
Catalyst loading: $1 gL^{-1}$. [Phenol]: $4x10^{-4}M$

Reaction System	% Degradation of Phenol after 60 min irradiation	
	ZnO	TiO2
No catalyst, No H_2O_2	Nil	Nil
Catalyst only	38	50
H_2O_2 only (4 mg/L)	Nil	2-3%
Catalyst + H_2O_2	51	57

As expected, externally added H_2O_2 enhances the degradation of phenol, in presence of both ZnO and TiO_2. The effect is slightly more in the presence of TiO_2. The synergy observed in the case of phosphamidon is not quite obvious here. The fate of added and in situ formed H_2O_2 may be summarized as follows:

$$\text{Catalyst (Semiconductor Oxide)} \xrightarrow{hv} h^+ + e^- \tag{1}$$

$$H_2O_2 + e^- \rightarrow OH^{\cdot} + OH^- \tag{2}$$

The superoxide ions $(O_2^{-\cdot})$ formed as in step 3 can also lead to the generation of OH radicals from H_2O_2 as in step 4.

$$O_2\,(ads) + e^- \rightarrow O_2^{-\cdot} \tag{3}$$

$$H_2O_2 + O_2^{-\cdot} \rightarrow OH^{\cdot} + OH^- + O_2 \tag{4}$$

$$H_2O_2 + OH^{\cdot} \rightarrow H_2O + HO_2^{\cdot} \tag{5}$$

$$HO_2^{\cdot} + OH^{\cdot} \rightarrow H_2O + O_2 \tag{6}$$

All the H_2O_2 that decomposes in the system need not necessarily result in the formation of OH radicals, as seen in steps 7 and 8.

$H_2O_2 + 2h^+ \rightarrow 2H^+ + O_2$ (7)

$H_2O_2 + h^+ \rightarrow H^+ + HO_2^{\cdot}$ (8)

The mechanism of photocatalysed degradation of organic molecules on semiconductor oxide catalysts is well established [7]. When the semiconductor particles absorb a photon of energy equivalent to or greater than its band gap, the electrons are excited from the valence band to the conduction band forming an electron-hole pair, capable of initiating oxidation and reduction processes of adsorbed substrates. In aqueous solutions, the holes are scavenged by surface hydroxyl groups to generate strongly oxidising hydroxyl radicals ($OH^{\cdot}$). Insertion of the OH radicals into C-H bonds leads ultimately to the complete degradation of the organic substrate. Oxygen plays a crucial role in these reactions. Adsorbed oxygen traps the conduction band electrons as shown in step 3 and forms superoxide ion, thus delaying the electron – hole recombination process. The $O_2^{-\cdot}$ can also generate highly reactive $HO_2^{\cdot}$ radicals by interaction with H^+ ions formed in the system [289] , which can also lead to the complete oxidation of organics such as phenol.

$h^+ + H_2O \rightarrow OH^{\cdot} + H^+$ (9)

$H^+ + O_2^{-\cdot} \rightarrow HO_2^{\cdot}$ (10)

3.3.5. Effect of pH

It has been reported by many workers [12,183 and 290] that pH of the solution is an important parameter in the photo-catalysed degradation of organic wastes. This is due to the fact that the pH influences the surface charge of the semiconductor thereby affecting the interfacial electron transfer and the photoredox process [110]. However, the results published by various authors on this aspect are not consistent showing that the effect of pH on the decomposition of organic compounds in photocatalytic systems is not that simple. The results of our study on the degradation of phosphamidon, described in Chapter 2, also illustrate the complexity of the effect of pH. In this context, the effect of pH on the photodegradation of phenol in presence of both ZnO and TiO_2 is investigated in the current study. The results are presented in figure 3. 6.

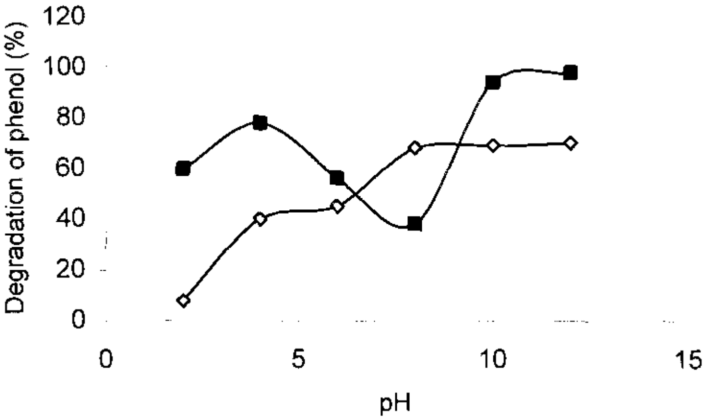


Fig 3.6 Effect of pH on the photocatalytic degradation of phenol in water. [Phenol]: 4x 10^{-4}M; Catalyst loading: 1gL^{-1}. (◊) ZnO; (■) TiO_2.

As expected, the results present a complex picture. In the case of TiO_2, the degradation increases with increase in pH in the acidic range, reaching a maximum at pH 4, followed by a decrease around the neutral region, to pick up again, reaching another maximum at pH 10. This is in agreement with the results of Wang et al. [47] as well as Ku and Hsieh [295]. In the case of ZnO, the degradation reaches an initial maximum at pH 4. However, unlike in the case of TiO_2, it does not decrease in the neutral range. Instead it remains fairly steady in the range 4-7, and picks up again to reach a maximum at pH 8 and it levels off thereafter. In the case of both catalysts, the maximum is observed in the alkaline pH range.

The surface functional groups of TiO_2 in water may be $TiOH_2^+$, >TiOH (surface titanol groups) and TiO^-. The isoelectric point for TiO_2 in water is about pH = 6 and the positive surface charge is expected at lower pH and negative surface charge is predicted at higher pH values [9]. Thus, under weak alkaline conditions, TiO^- is the predominant species of TiO_2 and phenol remains primarily in its molecular state [47]. Both of them may combine by hydrogen bonding leading to increase in the adsorption of phenol. Hence the observed maximum degradation under alkaline conditions may be resulting from the better adsorption of phenol. In the case of chlorophenols also, on TiO_2, higher degradation efficiency is reported under alkaline conditions [258, 259 and 287], which is consistent with our results.

Higher degradation of phenol under acidic conditions, according to Wang et al. [47], is attributed to the role played by the OH radicals. According to these authors, the rate-limiting step under acidic conditions might be the free radical formation and not the surface adsorption. Hence the higher amounts of OH radicals generated by reactions (11) and (12) may lead to enhanced degradation.

$$TiO_2 + h\upsilon \rightarrow TiO_2\,(h^+ + e^-) \qquad (11)$$

$$OH^- + h^+ \rightarrow OH^{\cdot} \qquad (12)$$

The higher degradation of phenol under acidic conditions, observed in the presence TiO_2 is not so prominent as in the case of ZnO. This may be due to the low concentration of reactive OH radicals in presence of ZnO. As noted earlier, the decomposition of H_2O_2 leading to the formation of reactive OH radicals also is not quite facile on ZnO, compared to TiO_2. The low reactivity on ZnO can also be due to the photo-corrosion of the catalyst in aqueous suspensions. Okamoto et al. [183] detected significant amounts of Zn^{2+} in ZnO suspensions irradiated for 1 hr. Peral et al. [292], also demonstrated that the photo corrosion takes place via the valence band holes as follows:

$$ZnO + 2h^+ \rightarrow Zn^{2+} + \tfrac{1}{2}\,O_2 \qquad (13)$$

Consequently, the availability of holes for the phenol oxidation and the catalyst availability for the adsorption and reaction is reduced leading to a decrease in the degradation. On the other hand, TiO_2 was found to be extremely stable with no Ti^{4+} ions detected in solution, even after prolonged irradiation and the phenol has been completed degraded.

Despite the clear evidence on the importance of surface charge for substrate adsorptivity, the precise role and effect of pH in photocatalytic conversions still remain inconclusive. This complexity has been well illustrated from studies on a number of different phenols. Terzian et al. [296], studied the effect of pH on photocatalytic reaction of m-cresol with UV-light and TiO_2. The decomposition rates at different pH followed the order pH 12>6.5>3, i.e. the reaction was faster under alkaline conditions. However, no explanation was provided by the authors.

D'Oliveira et al. [64], observed that, for m-chlorophenol, the reaction rate increased as the pH value increased at the pH > pKa (of m-chlorophenol) and there was no significant change of reaction rate in the range of pH 3.5 – 9. Auguliaro et al [297], investigated the effect of pH on the photocatalytic degradation of phenol. They observed that the reaction rate increased with increase of pH in pH>10. In the range of pH 3-10, the highest degradation rate was noticed at pH 3. In the case of o-chlorophenol on TiO_2, the degradation rate decreased with increase in pH [110]. The rate followed the order of pH 3>5>7>9>11. Auguliaro [298] reported that the photocatalytic degradation rate of nitrophenol decreased as pH value is increased. However the study of Palmisano et al. [299] demonstrated that the reaction rate of nitrophenol increased in the alkaline range. Obviously, all these results illustrate the complex nature of the influence of pH on photocatalysed reactions. Our studies, reported in this Chapter as well as in Chapter 2 also point to the complicated and often inconsistent nature of pH effect.

3.3.6. Mechanism of the Photocatalytic Degradation of Phenol

We have observed that the degradation leads to complete mineralization and the final product is CO_2. The intermediates formed in the reaction have already been identified by earlier workers [183 and 300]. These intermediates such as hydroquinone (HQ), pyrocatechol (CC), 1, 2, 4-benzene triol (HHQ), pyrogallol (PG), 2-hydroxy-1,4-benzoquinone (HBQ) and 1,4-benzoquinone (BQ), which are primary or secondary hydroxylated products of phenol confirm the role of hydroxyl radicals as the reactive species. They undergo further oxidation to yield polar intermediate products like aldehydes and carboxylic acids, before being finally mineralised to CO_2 and water.

The general mechanism of the reactions, leading to the mineralisation of organic pollutants, in line with the proposal made by Mills and Le Hunte [51] may hence be represented as in figure 3.7.

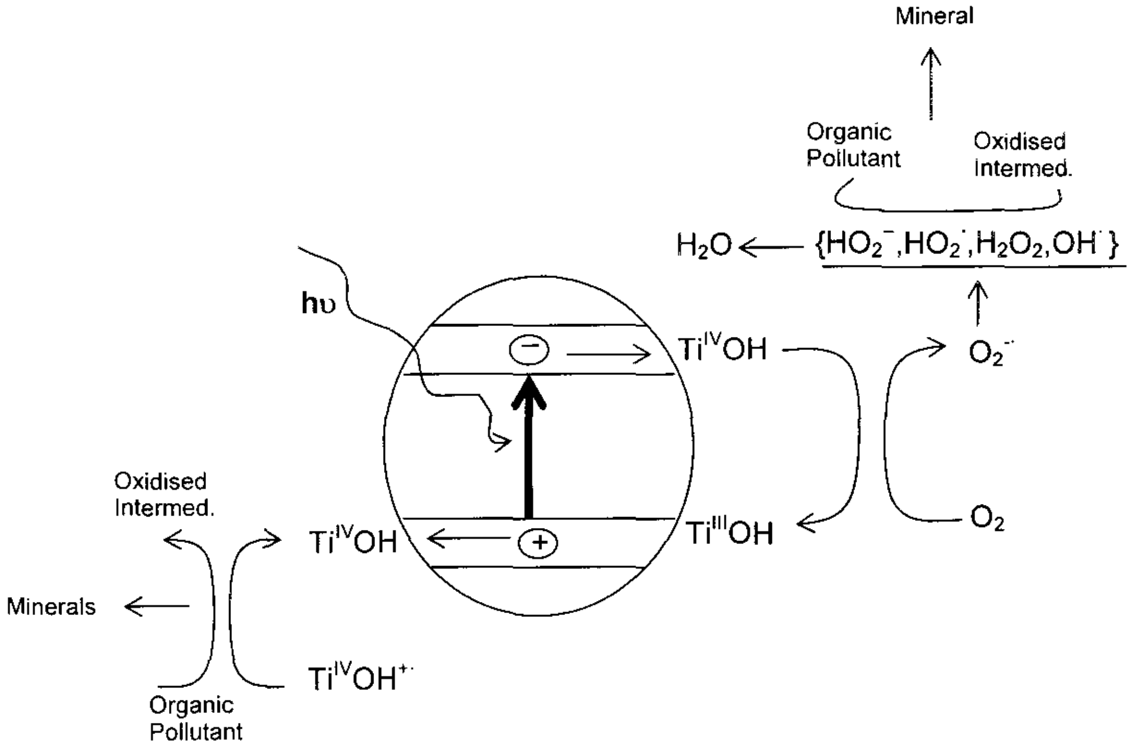


Fig 3.7. Energetics and major processes for the semiconductor mediated photo-oxidative mineralisation of organic pollutants in aqueous solution

The kinetics of the reaction, the effect of various parameters on the rate and the eventual mineralisation of phenol, observed in our investigations, is in agreement with the findings of other authors, as indicated above. Accordingly, the reaction scheme in figure 3.8 can be considered as relevant in the present context as well, considering the important role of hydroxyl radicals in the degradation reaction.

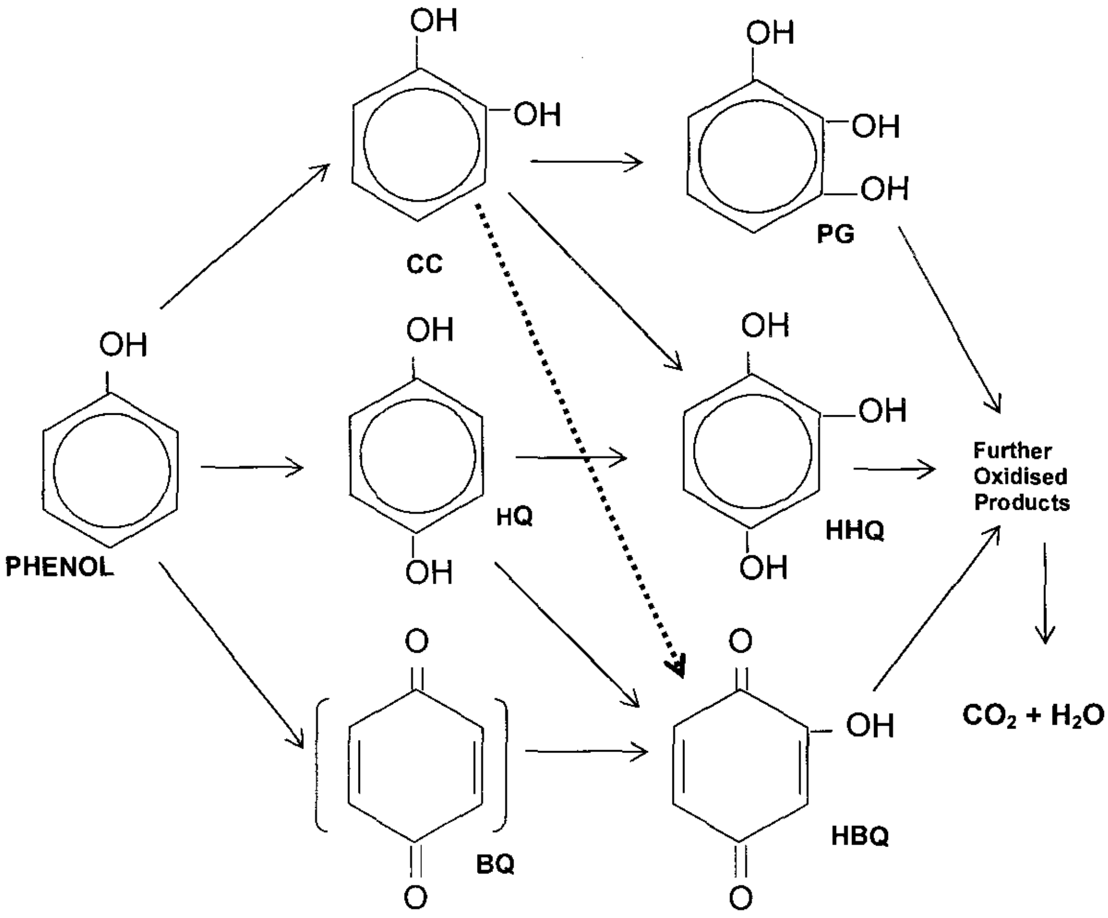
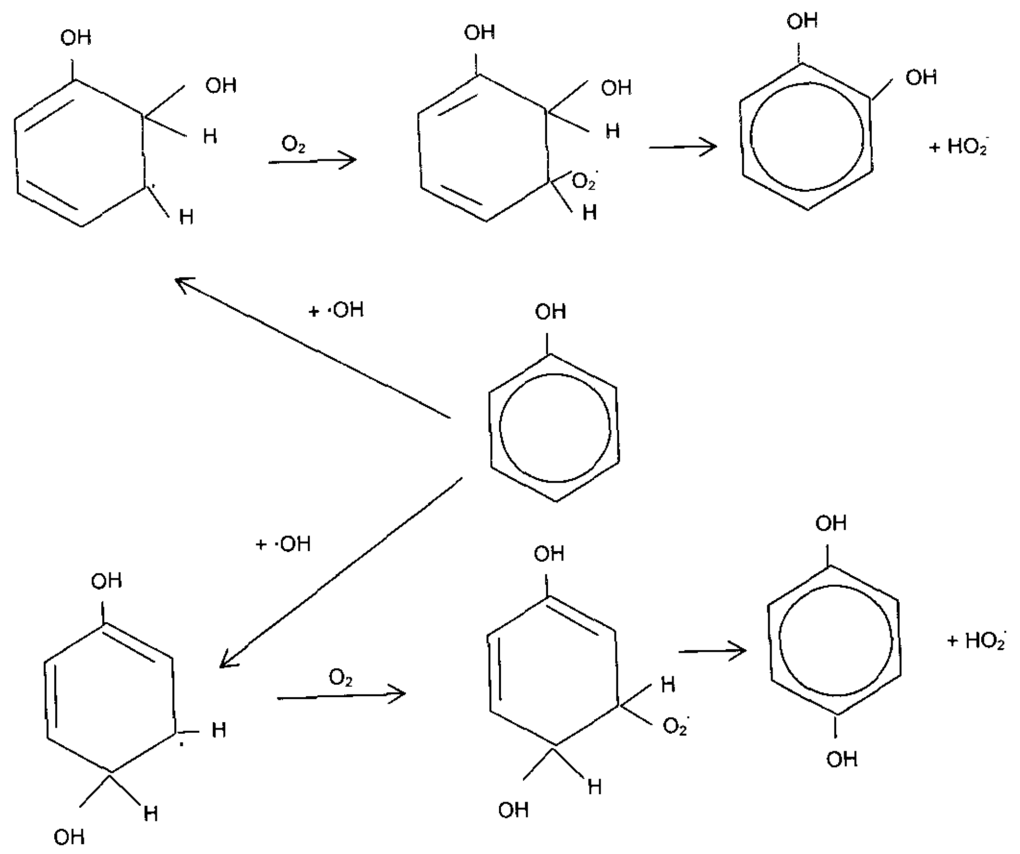


Fig 3.8. Reaction Scheme for the photocatalytic degradation of phenol

Hydroxyl radicals are known to react with phenol readily to give dihydroxycyclohexadienyl radicals [301]. These radicals react with O_2 according to equations 14 and 15. Some of the molecules undergo unimolecular elimination of water to yield phenoxy radicals which react with O_2 to yield HBQ via BQ according to equation 16.

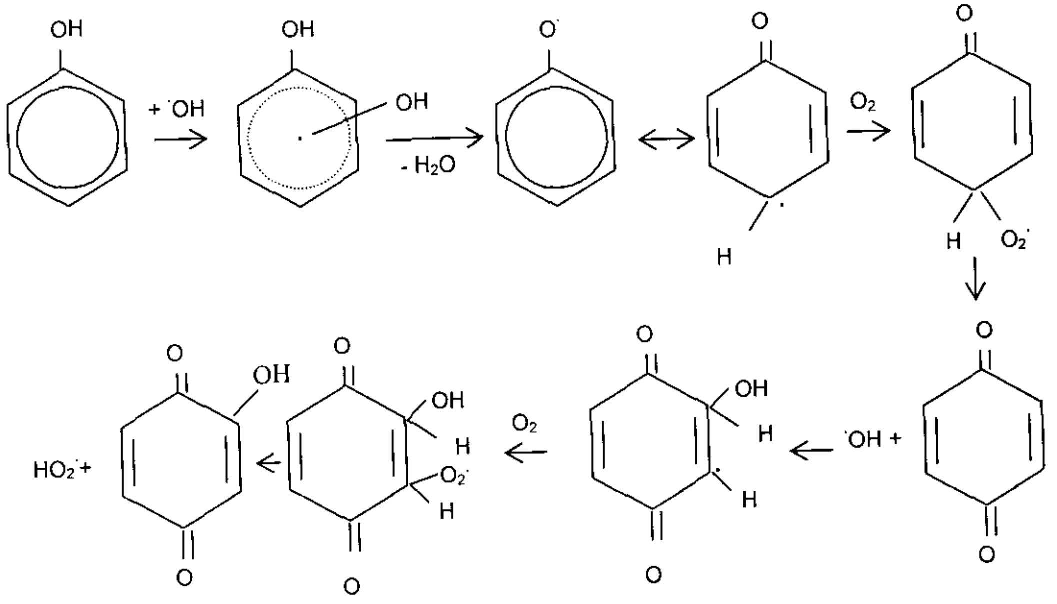
Similar reactions occur for HQ and CC, resulting in the formation of PG and HBQ, which get mineralised eventually to CO_2 and water. See equations 17 and 18.

The HO_2 radicals generated as in equations 14 -17 can regenerate OH radicals as explained earlier.

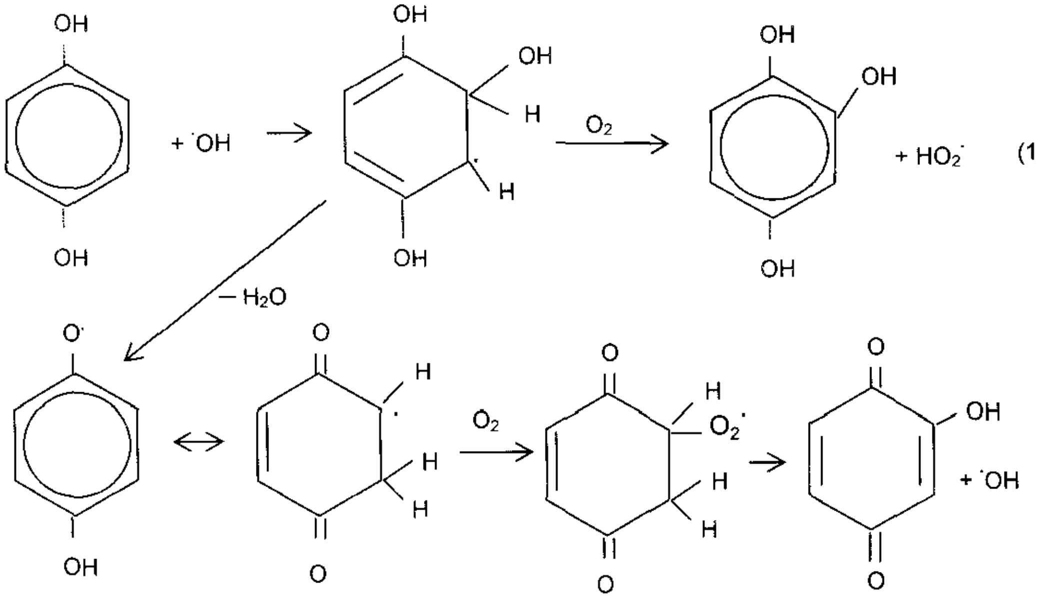

OH
H
O_2
$O_2^{\cdot}$
+ $HO_2^{\cdot}$
+ ·OH
+ ·OH
O_2
+ $HO_2^{\cdot}$

(14)

(15)


OH
+ ·OH
- H_2O
O
O_2
H
$O_2^{\cdot}$
·OH +
O_2
$HO_2^{\cdot}$+

(16)



(17)

(18)

The overall reaction leading to the mineralization of phenol may be presented in its simplest form as

$$C_6H_5OH + 7\,O_2 \longrightarrow 6\,CO_2 + 3\,H_2O \qquad (19)$$

3.3.7. Mixed Oxide Catalysts

It has been reported by many researchers that coupled semiconductor systems, in which illumination of one of the semiconductors produces a response in the other, is an effective method for promoting the degradation of organic pollutants [51, 83, 259, 287, 302]. The increased efficiency is attributed to inter-particle electron transfer [289]. In view of this, we examined the effect of mixing three oxides i.e. ZnO, Fe_2O_3 and Al_2O_3 individually with TiO_2 on the photocatalytic activity towards the degradation of phenol. The experiments were carried out under conditions identical with those in presence of TiO_2 only. The results with ZnO- TiO_2 mixtures are presented in figure 3.9, which shows that the activity of the mixture is an average of the activities of the individual oxides. They do not exhibit any inhibitive or synergic effect. In a standard experiment in which half of the TiO_2 is replaced by ZnO, the photodegradation is reduced by approximately 20% after 60 minutes of irradiation.

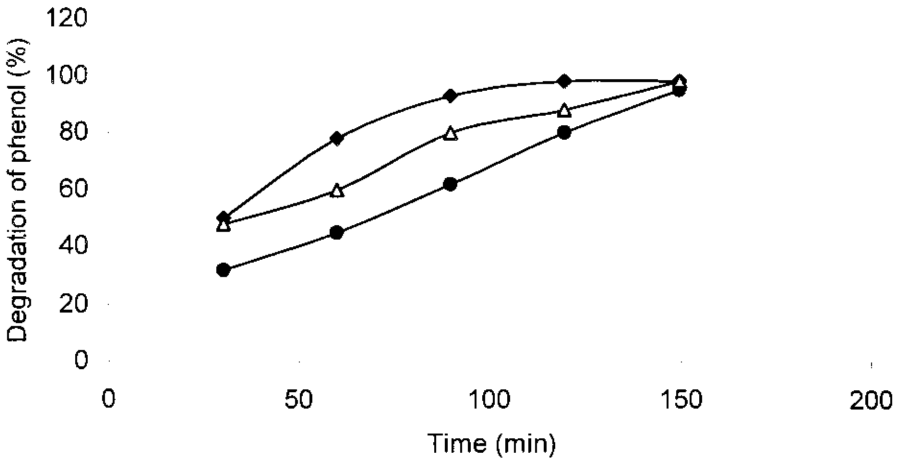


Fig.3.9. Relative efficiencies of the catalyst systems for the photocatalytic degradation of phenol. Phenol: 4x10^{-4}M; Catalyst loading: 1gL^{-1}.(♦) TiO_2; (●) ZnO; (Δ) TiO_2/ZnO.

In the case of Al_2O_3, addition to TiO_2 (up to 1 atom %) does not affect the rate of degradation at the optimum loading (1 g/L) used in our experiments. Any further addition of Al_2O_3, which in effect reduces the amount of active TiO_2 in the system, reduces the degradation. This is expected as Al_2O_3 itself does not contribute to any increase in the activity, except in cases where it acts as a support to provide maximum dispersion and enhanced availability of catalytic sites for TiO_2 mediated reactions [303].

Of the various combinations of mixed oxides, Fe_2O_3/TiO_2 has been subjected to numerous investigations for photocatalytic activity. Since iron compounds are relatively inexpensive and non-toxic, it will be more prudent to couple them with TiO_2 for the treatment of contaminated wastewater by photocatalysis. It is expected that the production of hydroxyl radicals, responsible for the photocatalytic degradation of most organic compounds will be enhanced by the inter-particle electron transfer (IPET) between the two semiconductors.

The results of the study on the photocatalytic degradation of phenol on TiO_2-Fe_2O_3 mixtures are summarized in Table 3.2. In view of the complexity and inconsistency of the effect of pH on the reaction, all the studies were conducted at the near neutral to slightly acidic pH of 6.7.

Table 3.2 Effect of Fe_2O_3 on the TiO_2 mediated photodegradation of Phenol

Concentration of phenol : 4×10^{-4} M
Amount of catalyst : 1 gL^{-1}
Time of irradiation : 30 min.

% of Fe_2O_3 as atom % of Fe	% Degradation
0	50
0.2	63
0.5	65
1	76
2	76

The results show that addition of Fe_2O_3 enhances the photocatalytic activity of TiO_2 towards the degradation of phenol. The increase in the efficiency continues until the concentration of Fe_2O_3 is approx. 1% and remains fairly steady thereafter until 2%. However, this optimum may be different at different pH, as illustrated in the case of the decomposition of dichloroacetic acid [7].

One of the limiting factors that control the efficiency of photocatalysis is the rapid recombination of photogenerated electrons and holes in semiconductor particulates. Addition of dopants, electrons/hole scavengers adsorbed on the surface and coupling of semiconductors are some of the techniques employed to retard such recombination. Serpone et al. [287 and 304] showed that coupling of two semiconductors possessing different redox energy levels for their corresponding conduction and valence bands provides an attractive approach to achieve more efficient charge separation, increase the lifetime of the charge carriers and enhance the efficiency of interfacial charge transfer to adsorbed substrates. In the case of Fe_2O_3 and TiO_2, a photoelectron generated on TiO_2 can be injected into the Fe_2O_3 carriers, as the conduction band of the latter is lower than that of the former. See figure 3.10.

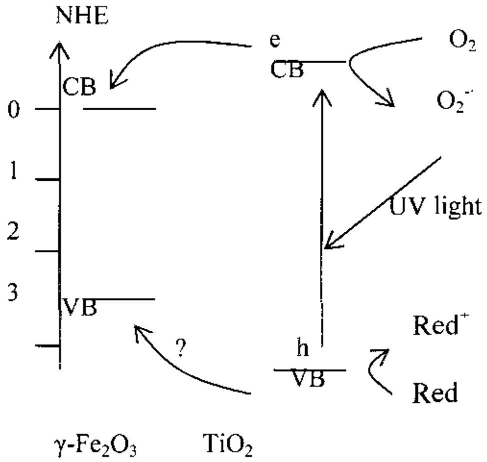


Fig. 3. 10. Possible mechanism for the photocatalytic activity of Fe_2O_3/TiO_2

Thus the photoholes remain trapped on TiO_2 without the possibility of recombination. The possibility of VB holes transfer from the VB of TiO_2 to the VB of Fe_2O_3 (which is higher than that of TiO_2) has been suggested by some authors [175]. However, there is no universal agreement on this. Our results also do not support this line, because, had it been so, the photocatalytic activity of TiO_2 should have been reduced drastically by the mixed oxide as Fe_2O_3 will be seizing most of the electrons and holes generated on TiO_2. Enhancement in the lifetimes of photogenerated electrons and holes on TiO_2 due to electron or hole trapping by Fe(III) centres has been reported earlier also [305]. Enhanced reaction shows that this inter-particular electron transfer results in transfer of charge and enhances the photooxidation of the adsorbed organic substrate.

Under UV irradiation, the Fe_2O_3 in the coupled system is not light activated. However it gets sensitised by IPET from the irradiated TiO_2 particulate by transfer of electrons from the CB of TiO_2 to that of Fe_2O_3, thereby leaving an excess of surface trapped holes on TiO_2 (equation 20). This transfer of charge should enhance the photooxidation of the sorbed organic substrate as in equation 21.

The photogenerated hole can react with OH^- or H_2O as shown earlier to form OH radicals which can oxidise phenol as follows:

TiO_2 (e- + h+) + Fe_2O_3 → TiO_2 (h+) + Fe_2O_3 (e-) (20)

TiO_2 (h+ or OH radical) + phenol (ads) → intermediates → products (21)

At the same time, the electrons that remain in the conduction band of TiO_2 as well as that of Fe_2O_3 get scavenged by adsorbed oxygen resulting in the formation of the superoxide radical anion $O_2^{\cdot-}$ which also leads to the degradation of phenol as described earlier. Enhanced rate in the presence of Fe_2O_3 also highlights the importance of hole initiated reaction, according to the reaction mechanism outlined earlier.

3.3.8. Effect of Doping TiO_2 on its photocatalytic activity

Selective doping of the crystalline matrix has been tested as a means of enhancing interfacial charge-transfer reactions of TiO_2 bulk phase and colloidal particles. Fe(III) doping of TiO_2 has been shown to inhibit electron – hole pair recombination [306]. However, the doping had little effect on the efficiency of phenol degradation [307]. Similar inconsistent results were reported for Cr^{3+} doping as well. Borgarello et al. [308] reported enhanced photo reactivity for water cleavage with Cr (III) doped TiO_2 while others found opposite effects with the doping [309]. Negative effects for doping have been noted for Mo and V on TiO_2 [310] while Gratzel and Howe [311] reported an inhibition in electron-hole recombination with the same dopants. Karakitsou and Verykios [312] reported that doping of TiO_2 with cations of higher valency than that of Ti(IV) resulted in enhanced photo reactivity. Again Mu et al. [309] had results contradicting this finding.

The above series of contradicting results on the effect of doping of TiO_2 from established research workers and our own observations, in disagreement with many authors, on the effect of mixed oxide catalysts on the photodegradation of phenol prompted us to make a preliminary examination of the effect of doping TiO_2 with various ions. The ions used for doping are Fe^{3+}, Co^{2+} and Cu^{2+}. The results are shown in table- 3.3

Table 3.3. Effect of Doping of TiO_2 on the photocatalytic degradation of Phenol

Concentration of phenol : 40 ppm
Amount of catalyst : 1 gL^{-1}
Time of irradiation : 30 min
pH : 6.7

Catalyst with	No dopant	Fe^{3+} 0.1 At %	Co^{2+} 0.1 At %	Cu^{2+} 0.1 At %
% Degradation	52	88	84	83

As seen from the table, doping by Fe^{3+}, Co^{2+} and Cu^{2+} leads to enhanced photocatalytic activity by TiO_2. This increased reaction rate in the case of Fe^{3+} is similar to the result with mixed oxide catalysts and may be due to the inhibition of the recombination of charge carriers by the Fe^{3+} ions within the TiO_2 matrix. Fe^{3+} doping has been proved to enhance the carrier life time in TiO_2 [305]. In the case of Co^{2+}, the enhanced photo reactivity may be partially attributed to the extension of the light absorption of the doped catalyst to the visible range ($\lambda > 400$ nm). Improvement of photocatalytic efficiency of Co^{2+} doped TiO_2 for the degradation of organics in the UV region also has been reported, though the mechanistic details are still not established [313]. Since the light source used in our study was predominantly UV, the improved activity of Co^{2+} - TiO_2 may be due to a combination of both these factors. From the practical application point of view of utilizing solar energy for water purification, this is an important finding, which needs to be pursued. In the case of Cu^{2+} doping of TiO_2 also, enhancement in photocatalytic activity can be attributed to the inhibition of the recombination of photogenerated electrons and holes. Di Paola et al. [314] measured the rate constants of recombination of photogenerated charges in a number of doped TiO_2 samples using femtosecond pump-probe diffuse reflectance spectroscopy (PP-DRS) and showed that Cu doping does reduce the rate of recombination.

In this study, we have chosen only those dopants which have been reported to increase the photocatalytic activity of TiO_2 for the degradation of organics, though there is no consistency in the results reported by various workers. Our objective was to identify suitable catalyst systems for the purification of contaminated water and detailed mechanistic studies of the catalysts, reactants and the interfaces, essential for the understanding of the processes is beyond the scope of the current study and not attempted here. For example, it is generally believed that an increase in the concentration of long- lived charge carriers results in corresponding increase in photo reactivity. However, if an electron is trapped in a deep trapping site, it will have a longer life time but it may also have a lower redox potential that could result in a decrease in photo reactivity. Reactivity of doped TiO_2 appears to be a complex function of the dopant concentration, the energy level of the dopant within the TiO_2 lattice, their d-electronic configuration, the distribution of dopants, the electron donor concentration and the light intensity. Some other questions that need to be answered include: i) Are the dopant ions located primarily on the surface or in the lattice? ii) Do these ions influence the charge pair recombination? iii) Is the adsorption and superficial binding of the substrates affected by doping? Extensive investigations will be required to answer these questions. In the meantime, the results reported here as well as those of other workers prove beyond doubt that doping by suitable ions enhances the photocatalytic activity of TiO_2 for the removal of organic pollutants from water.

3.3.9. Effect of common inorganic anions:

Common inorganic anions present in natural waters are HCO_3^-, Cl^-, SO_4^{2-} and NO_3^-. Therefore, these ions are expected to be present in wastewaters too. Studies reported in Chapter 2, on the degradation of phosphamidon showed that the anions such as Cl^-, NO_3^- and PO_4^{3-} inhibit the reaction. In view of this, the effect of some of the anions on the photocatalytic degradation of phenol is studied under standard conditions of catalyst weight, substrate concentration, pH etc. The results are tabulated in Table 3.4

Table-3.4. Effect of added anions on the photocatalytic degradation of phenol

Concentration of phenol : 4×10^{-4} M.
Amount of catalyst : 1 gL^{-1}
Time of irradiation : 30 min
pH : 6.7

Ions	Percentage degradation of phenol at different anion concentrations				
	0.00M	0.01M	0.05M	0.1M	0.5M
Cl^-	52	55	46	40	29
CO_3^{2-}	52	38	38	29	27
SO_4^{2-}	52	43	17	14	14
NO_3^-	52	53	49	52	43

As in the case of phosphamidon, inhibition by NO_3^- ions is the least while Cl^- and CO_3^{2-} inhibit the reaction significantly. Negligible effect by weakly adsorbed ions like NO_3^- suggests that the inhibition may be caused mainly by surface occupation by the anion which is competitive with the adsorption of the organic molecules. However, it has been established by Calza and Pellizzetti [315] that in the case of halides, in addition to this adsorption, the inhibition is also caused by interference with the processes leading to the photocatalytic degradation of organics. This interference may be explained based on the general mechanism of photocatalytic degradation of organics as follows:

Charge Separation $TiO_2 + h\upsilon \rightarrow e^-_{CB} + h^+_{VB}$ (22)
Surface trapping $h^+_{VB} + \equiv TiOH \rightarrow \equiv TiO^{\cdot} + H^+$ (23)
Recombination $e^-_{CB} + h^+_{VB} \rightarrow$ heat (24)
$e^-_{CB} + \equiv TiO^{\cdot} + H^+ \rightarrow \equiv TiOH$ (25)

If electron acceptors (Ox_1) or electron donors (Red_1, H_2O) are present at the surface, interfacial electron transfer may occur according to the following reactions:

Interfacial charge transfer $h^+_{VB} + Red_1 \rightarrow Ox$ (26)
$\equiv TiO^{\cdot} + Red_1 \rightarrow Ox'$ (27)
$h^+_{VB} + H_2O \rightarrow H_2O^{\cdot +}$ (28)
$H_2O^{\cdot +} \rightarrow H^+ + OH^{\cdot}$ (29)
$OH^{\cdot} + \equiv TiOH \rightarrow \equiv TiO^{\cdot} + H_2O$ (30)
$OH^{\cdot} + Red_1 \rightarrow Ox''$ (31)
$e^-_{CB} + Ox_1 \rightarrow Red_2$ (32)

Back reactions $\mathrm{Red_2}(\text{or} \equiv \mathrm{TiO^{\cdot}}) + h^{+}_{VB} \rightarrow \mathrm{Ox_1}$ (33)
$\mathrm{Ox}\ (\text{or } \mathrm{Ox'}, \mathrm{Ox''}) + e^{-}_{CB} \rightarrow \mathrm{Red_1}$ (34)

As explained earlier, oxygen acts as the electron scavenger in reaction 32.

Oxygen reaction $\mathrm{O_2(ads)} + e^{-}_{CB} \rightarrow \mathrm{O_2^{\cdot -}(ads)}$ (35)

When halides (X^-) are present, more reactions can occur. The primary events taking place at the catalyst surface in the presence of an anion X^- may be summarised as follows:

Surface complex $\equiv \mathrm{TiOH} + X^- \rightarrow\ \equiv \mathrm{TiX} + \mathrm{OH^-}$ (36)
Surface trapping $h^{+}_{VB} + \equiv \mathrm{TiX} \rightarrow\ \equiv \mathrm{TiX^{\cdot +}}$ (37)
Interfacial charge transfer $\equiv \mathrm{TiX^{\cdot +}} + \mathrm{Red_1} \rightarrow \mathrm{Ox_1''}$ (38)
Halide oxidation $h^{+}_{VB} + X^- \rightarrow X^{\cdot}$ (39)
Recombination $e^{-}_{CB} + \equiv \mathrm{TiX^{\cdot +}} \rightarrow\ \equiv \mathrm{TiX}$ (40)
$e^{-}_{CB} + X^{\cdot} \rightarrow X^-$ (41)
Back reaction $\equiv \mathrm{TiX^{\cdot +}} + \mathrm{Red_2} \rightarrow\ \equiv \mathrm{TiX}$ (42)

The halides can be thermodynamically oxidized by the valence band holes thus acting as hole scavengers. The TiO_2 valence band hole is able to oxidize chloride ions to chlorine radical according to reaction 39. However, the formed radical could back react with conduction band electrons according to reaction 41. This gives a null process, which lowers the concentration of available holes and electrons, leading to a decrease in the rate of degradation of the organics.

In the case of carbonates, which do not partake in a reaction as above, the high inhibition may be explained by its own reactivity under the reaction conditions. Studies by Guillard et al. [316] showed that carbonate ions get completely eliminated as CO_2 under photocatalytic conditions. At higher concentrations of the carbonate, phenol is left behind in the competitive adsorption and reaction, leading to greater inhibition of the degradation of the latter.

The higher inhibition by SO_4^{2-} ions also is not unexpected. D'Oliveira et al. [150] have shown that SO_4^{2-} ions get more strongly adsorbed compared to even Cl^- ions and may even penetrate into the TiO_2 inner co-ordination sphere. That also explains why at higher concentrations, when the surface is occupied by more and more SO_4^{2-} ions, the inhibition is quite severe.

3.3.10. Photocatalytic decomposition of phenol under solar radiation

The possibility of using TiO_2 as a photocatalyst for the degradation of phenol in wastewater under natural sunlight was examined by conducting similar experiments, as described above, using solar radiation. Control experiments with solar irradiated phenol solution in the absence of TiO_2 showed practically no degradation. In presence of TiO_2, phenol disappeared slowly but steadily. The rate of degradation over a six-hour period is shown in Figure 3.11. The complete disappearance of phenol, at the experimental concentration of 4×10^{-4} M was achieved in over 6 h of irradiation, even though the rate of degradation was becoming slower and slower with decrease in concentration of the substrate. It is worthwhile to observe that the degradation continued under solar radiation without aeration of the system or mixing. This will be an important consideration in the solar treatment of industrial wastewater. The study is to be followed up by conducting detailed investigations on optimizing the catalyst composition and exploiting the positive influence of mixed oxides and doped catalysts.

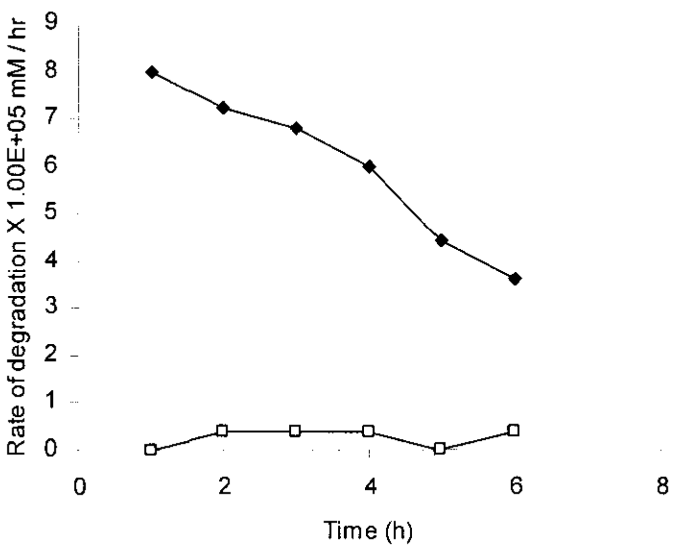


Fig 3.11. Rate of photocatalytic degradation of phenol under sunlight.
[Phenol]: 4×10^{-4}M; Catalyst loading: $1 gL^{-1}$.
(♦) TiO_2; (□) No TiO_2.

3.4. Conclusions

Semiconductors such as TiO_2 and ZnO are found to be efficient photocatalysts for the degradation of phenol in water. The degradation rate depends on a number of reaction parameters which include catalyst composition and loading, pH of the medium, concentration of the substrate and presence of added ions. TiO_2 is more active than ZnO and the kinetics of the reaction follows different patterns on these two otherwise similar catalysts. Mixing ZnO and TiO_2 does not produce any synergic or inhibitive effect on the catalyst, though physical mixing with Fe_2O_3 and doping with Fe^{3+} have a positive influence on the rate of degradation. The catalyst system is active under solar radiation as well. Based on the data generated from the current study, a general mechanism applicable for the photocatalytic degradation of phenol in water is proposed.

Chapter-4

PHOTOCATALYTIC INACTIVATION OF BACTERIAL POLLUTANTS USING TiO_2

4.1. Introduction

The current practice of using chlorine for the disinfection and treatment of water, especially when it contains high 'total organic carbon' is likely to be severely restricted in future, due to the possible formation of unacceptable levels of trihalomethanes and other carcinogenic by-products. Alternative technologies to chlorination include ozonation, UV irradiation and advanced filtration process.

Our studies reported in Chapters 2 and 3 of this thesis as well as numerous other research reports have proved the advantages of using photocatalysis for the removal of chemical pollutants from water. Semiconductor oxides in various forms, and TiO_2 in particular, are the most investigated catalysts in this context. However, in recent years, the use of TiO_2 mediated photocatalysis for the treatment of wastewaters, removal of noxious organics in potable water and disinfection has received considerable attention [317, 318]. Matsunaga et al. [212] have shown that TiO_2 particles are effective in sensitizing the photo-killing of bacteria such as *Lactobacillus acidophilus, Saccharomyces cerevisiae* and *Escherichia coli.* TiO_2 photocatalysis has also been shown to be an effective germicidal method [319 - 322].

The advantages of photocatalytic disinfection are: i) There is no consumption of expensive chemicals; the oxidant is atmospheric oxygen and the catalyst is non-hazardous and inexpensive. ii) The catalyst activation and subsequent disinfection of water can be achieved using sunlight. Thus there is no need for power source or system maintenance. iii) The process results in complete elimination of most types of microorganisms and mineralization of majority of organic pollutants. iv) The technology will be particularly suitable for developing and underdeveloped regions where electricity and other infrastructure requirements make competing technologies unviable.

In this chapter, the results of our studies on the application of TiO_2 photocatalysis for the removal of bacterial pollutants in water, with special focus on *Escherichia coli,* are presented. The effects of various parameters such as pH, catalyst loading, light intensity, periodicity of irradiation etc. on the efficiency of disinfection have been investigated. Experiments were also conducted to test the efficiency of the catalyst on deactivation of *Bacillus subtilis* and *Vibrio harveyi.* The practical feasibility of the method is demonstrated by performing outdoor experiments in direct sunlight and also by using a simple, otherwise disposed off, PET bottle, coated inside with TiO_2, as the reactor. The application of this method for the treatment of actual domestic wastewater is also presented.

Escherichia coli (usually abbreviated as *E. coli*) is one of the main species of bacteria that live in the lower intestines of warm-blooded animals (including birds and mammals) and are necessary for the proper digestion of food. *E. coli* is usually harmless, but can cause four clinical syndromes which are i) diarrhea or gastroenteritis ii) urinary tract infection iii) pyrogenic infection and iv) septicemia. Its presence in groundwater is a common indicator of fecal contamination. Voided in feces it remains viable in the environment only for some days. Detection of *E.coli* in drinking water therefore is taken as evidence of recent pollution with human or animal feces. The main reasons for using *E. coli* are that there are a lot more coliforms in human feces than there are pathogens (such as *Salmonella typhi*, which causes typhoid), and *E. coli* is usually harmless to handle in the lab. It belongs to the family Enterobacteriaceae, and is commonly used as a model organism for bacteria in general. *E. coli* is a non spore forming gram negative straight rods arranged singly or in pairs.

Bacillus subtilis is a spore forming, gram - positive rod widely adopted as a model organism. It is not considered a human pathogen, but it can contaminate food and rarely causes food poisoning and it is responsible for causing ropiness in spoiled bread. It forms tough, protective endospore which allows it to tolerate extreme environmental conditions. It belongs to the family Bacillaceae.

Vibrio harveyi is a marine bioluminescent gram- negative bacterium. It is a potential pathogen, a more common cause of luminous vibriosis in commercially farmed marine invertebrates. It belongs to family Vibrionaceae.

4.2. Experimental

4.2.1. Materials

The water used for all experiments was purified by double distillation. The photocatalyst TiO_2 was supplied by Merck India limited (Details are given in Chapter 2). Some experiments were conducted under the same experimental conditions using tap water.

4.2.2. Microorganisms and culture conditions

Microorganisms *E. coli* ATCC 11775, *Bacillus subtilis* MTCC 2274 and *Vibrio harveyi* were obtained from Centre for Fish Disease Diagnosis and Management, Cochin University of Science and Technology.

The culture medium for stock cultures of *E. coli* and *B. subtilis* was nutrient broth containing 5 g L^{-1} yeast extract, 5 g L^{-1} peptone, 5 g L^{-1} NaCl in distilled water at pH 7.5. The culture medium of *Vibrio harveyi* consists of 1 g L^{-1} yeast extract, 5 g L^{-1} peptone, 0.1 g L^{-1} ferric phosphate in sea water at pH 7.5. The bacterial strains were inoculated and grown overnight at 37^0C by constant agitation under aerobic conditions. At an exponential growth phase, bacterial cells were collected by centrifugation at 8000 x g for 15 minutes at 4^0C and the bacterial pellet obtained was washed with sterile distilled water. Then the bacterial pellet was resuspended in sterile distilled water and its absorbance was measured at 600 nm using Shimadzu UV-1601 UV-visible spectrophotometer. Finally, the cell suspensions were diluted with sterile distilled water in Pyrex glass beakers to the required cell density corresponding to 10^5- 10^7 colony forming units per milliliter (CFU/ml). TiO_2 was added to this at a concentration of 0.25- 1 g L^{-1} and irradiated under natural sunlight. Sampling of the solutions were done at requisite time intervals and serial dilutions were prepared if necessary in sterile saline. After mixing 0.1mL aliquot of each dilution / sample was spread plated onto Mac conkey agar (Himedia) plates in the case of *E.coli,* Nurtient agar (Himedia) plates for *B. subtilis* and TCBS agar (Himedia) plates for *V. harveyi*. Since *V. harveyi* is a marine bacterium, sterile seawater was used in place of distilled water. The plates were incubated at 37^0C for 24h before counting. All experiments were repeated thrice and the average taken.

4.2.3. Photocatalytic Experiments

Pyrex glass beakers of 250 ml capacity were used as batch reactors. In a typical experiment, requisite amount of TiO_2 was added to 100 ml distilled water (sea water for V. harveyi) containing bacterial suspensions corresponding to 10^5-10^7 CFU/ml. The reactors were exposed to direct sunlight and the catalytic inactivation was monitored by counting the CFUs at different time intervals. The experiments were conducted under day sun during summer months (March-May) on the roof top of our laboratory in Kochi, India. ($9^0$57'51" N, $76^0$16'59" E). The light intensity was measured using Spectrosense, Skye instruments, Wales U.K. The temperature during the experiment was maintained at 27±2^0C by circulating water from a thermostat to eliminate the possibility of thermal disinfection.

4.2.4. Estimation of Total coliforms

Total coliforms are a group of closely related, mostly harmless bacteria that live in soil and water as well as the gut of animals. The total coliform count of the source water can indicate its general quality and the likelihood that it is contaminated with feces. Some of the health risks associated with fecal-contamination of water are gastroenteritis, ear infections, typhoid fever, dysentery, and hepatitis. Fecal bacteria can make the water cloudy and bad-smelling, and also increase oxygen demand due to the decomposition of the fecal matter.

The coliform group comprises of all aerobic and facultative anaerobic gram negative non-spore forming rod-shaped bacteria that ferment lactose with gas and acid formation within 48 h at 35^0C. The standard test for the coliform group was carried out by multiple tube fermentation technique. The most probable number per 100ml was calculated using three tubes each inoculated with 10, 1.0 and 0.1 ml of sample as per standard methods. [288].

The chemical oxygen demand (COD) of the sample was measured by open reflux method [288].

4.2.5. Immobilization of TiO_2 on PET bottles

The inner surface of PET bottles were roughened, washed with dilute alcohol and rinsed with sterile distilled water several times and dried. TiO_2 suspension of definite composition (3g/mL) was heated and the hot suspension was poured in to the PET bottles and rotated (half the diameter full length/ full) so that it gets coated on the rough inner surface. The bottles were left to dry in the sun for 4 days (total intensity ≈ $1000Wm^{-2}$). Then the bottles were rinsed with sterile distilled water to remove the loosely bound particles and again sun-dried. The resulting coated bottles have their inner surface coated with TiO_2 which will not peel off on rinsing or shaking. X-ray diffraction patterns were recorded with Rigaku X-ray diffractometer using CuKα radiation.

4.2.6. Photocatalytic experiments in PET bottles

In a typical experiment, 500 ml distilled water containing *E. coli* suspension (culture conditions same as in 4.2.1.) corresponding to 10^5-10^7 CFU/ml was poured into TiO_2 coated/uncoated PET bottles. Uncoated PET bottles served as control. Then the bottles were exposed to direct sunlight and the catalytic inactivation was monitored by counting the CFUs at different time intervals. Sampling of the solutions was done at requisite time intervals and serial dilutions were prepared if necessary in sterile saline. After mixing, 0.1mL aliquot of each dilution / sample was spread plated onto Mac conkey agar plates, incubated at 37^0C for 24 hours and counted. The experiments were conducted under day sun (August to December 2003) on the roof top of our laboratory in Kochi, India. ($9^0$57'51" N, $76^0$16'59" E). All experiments were done in triplicate. The temperature during the experiment was maintained at 27±2^0C.

4.3. Results and Discussion

4.3.1. Photocatalytic inactivation of bacteria in TiO_2 suspension.

Figure 4.1 shows the effect of light and TiO_2 on the survivability of *E. coli*. The time required for the total inactivation of *E. coli* was about 40 minutes in the presence of both light and the catalyst. The inactivation proceeded very slowly under illumination in the absence of the catalyst and was completed in 150 minutes. An induction period of approx. 40 minutes was noticed, when illuminated in the absence of the catalyst during which no appreciable reduction in the number of *E. coli* was detected. This might be the reason why some of the earlier researchers [320] could not observe any inactivation of *E. coli* in their studies, which were in fact performed for time periods of 60 minutes. It has to be emphasized that contrary to the inference by Wei et al. [320], the inactivation in the current study is not due to any temperature rise of water samples as these studies have been conducted under a constant temperature of 27 ± 2^0C by thermostating the samples. However, in the absence of light, but in presence of the catalyst, no inactivation could be observed. This clearly showed that TiO_2, under illumination, played a significant role in the inactivation of *E. coli* in water.

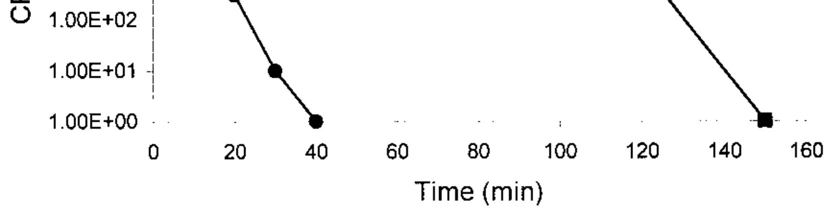


Fig. 4.1. Inactivation of E.coli (●) in presence of catalyst + sunlight (540W/m^2), (■) in presence of sunlight but no catalyst, (▲) in presence of catalyst but no light.

The effect of catalyst loading on the bactericidal activity was examined by varying the TiO_2 concentration from 0.25 gL^{-1} to 1 gL^{-1} and measuring the *E. coli* concentration after 20 minutes of irradiation in each case. The number of surviving bacteria after 20 minutes is shown in figure 4.2. The results showed that the inactivation of the bacteria was enhanced significantly with increase in catalyst loading, with the inactivation completed in 20 minutes using 1 gL^{-1} of the catalyst. This also proved the role of TiO_2 in the inactivation, thereby discounting the findings of Melian et al. [322] that it was only the light and not the catalyst responsible for the inactivation of *E. coli.*

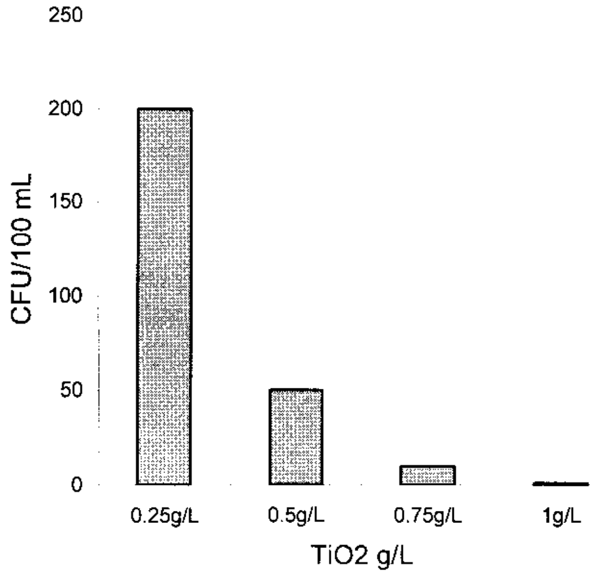


Fig.4.2. Effect of catalyst loading on inactivation of *E. coli* by sunlight.
Time of irradiation: 20 minutes.

The effect of light intensity on the inactivation of *E. coli* was investigated using light at two different intensities; i.e. ~ 400 W/m^2 and ~ 940 W/m^2. The rate of cell death increased with increase in light intensity, both in the absence and in presence of TiO_2. The results are presented in figures 4.3 and 4.4 which show that the intensity of light has a positive effect on the efficiency of bacterial deactivation. The increase in bacteria kill at higher light intensity may be due to the direct attack on the bacteria by the high flow of photons. In the system with catalysts, the concurrent generation of more oxidative species on the TiO_2 surface, which can attack the bacteria, enhances the efficiency further.

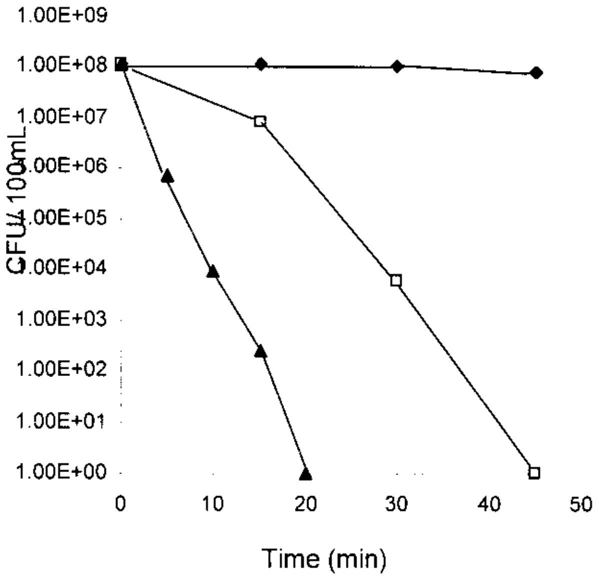


Fig.4.3. Inactivation of *E.coli* with TiO_2 at different light intensities.
(♦) Dark; (□) ~ 400 W/m^2; (▲) ~ 940 W/m^2.

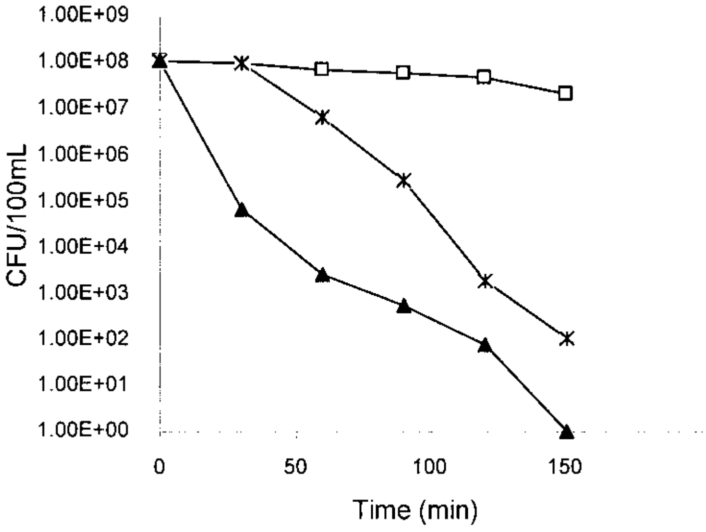


Fig.4.4. Inactivation of *E.coli* without TiO_2 at different intensities.
(□) Dark; (x) ~ 400 W/m^2; (▲) ~ 940 W/m^2.

Our studies reported in earlier chapters showed that pH of the reaction system has significant influence on the degradation of chemical contaminants in water. Normal wastewaters (urban or industrial) also have different pH ranges, depending on the source. In view of these, we investigated the influence of pH on the rate of disinfection of water in presence of TiO_2 and light. The results are presented in figure 4.5, which show that, at least in the range (pH 5-8) of our study, pH does not affect the disinfection rate. This is in agreement with the findings of other authors as well [322, 323]. Since highly acidic and alkaline conditions are known to be detrimental to these bacteria, delineation of the effects of photocatalytic and extreme pH conditions may be difficult. For this reason, studies outside the pH range of 5-8 are not attempted here.

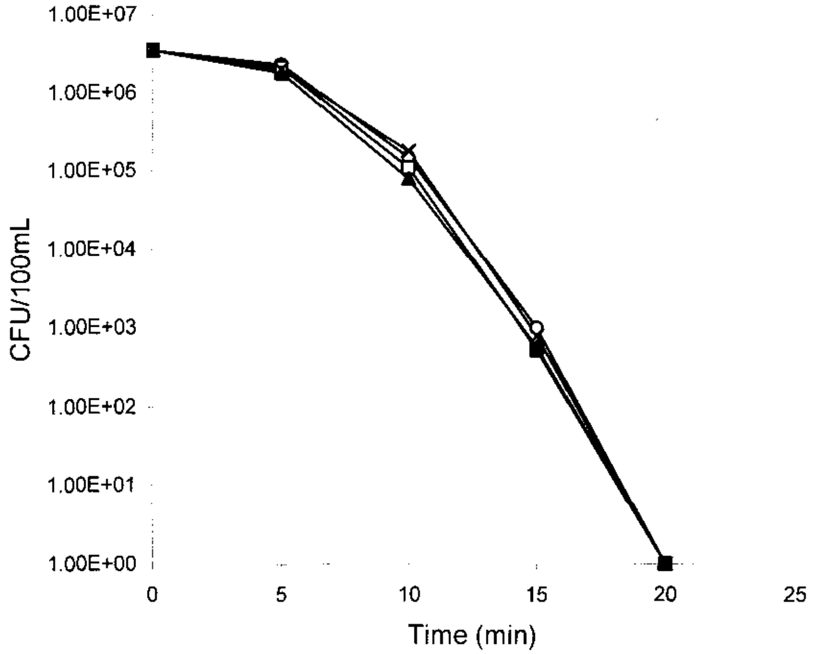


Fig.4.5. Effect of pH on TiO_2 catalysed solar inactivation of *E. coli*.
(○) pH 5; (□) pH 6; (▲) pH 7; (x) pH 8.

One of the major advantages of chemical disinfection is that it ensures complete destruction of the bacteria and inhibits its re-emergence. This is an important consideration in the commercial application of any disinfection process. Thus the viability of photocatalysis as an effective substitute for chlorination depends on the ability of the method to prevent the reappearance of bacteria in treated waters. In this context, we have examined the possible reappearance of *E. coli* in photolytic (no catalyst, only light) and photocatalytic systems as follows.

After irradiation and the complete inactivation of the bacteria (after 3 hours at ~940W/m^2), the light source was turned off and the medium enriched. The reappearance of the bacteria was tested after 24 h and 48 h (see Figure 4.6). Bacterial reappearance was observed after 24 and 48 h and there was significant difference in the bacterial count in the two systems (with and without catalysts). The system without catalyst had shown higher number of re-emerged bacteria. This clearly indicated that the photochemical inactivation of *E.coli* as a substitute for chemical inactivation must involve the use of a catalyst, which could reduce the rate of reemergence of the bacteria in the dark. The higher reappearance rate in the absence of the catalyst also indicated that the destruction might not be total and the bacteria can reactivate and grow. The destruction is more severe in the presence of the catalyst and hence the reappearance and growth are slower.

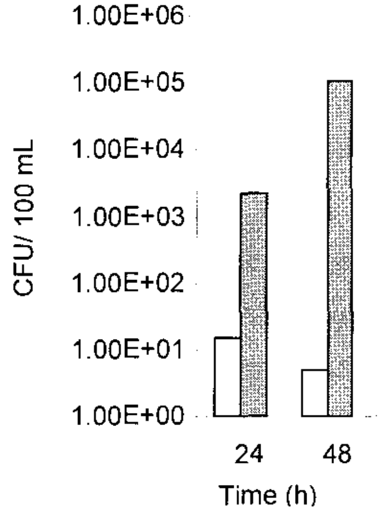


Fig.4.6. Reappearence of *E.coli* after treatment with and without TiO_2.
(□) With TiO_2; (▨) Without TiO_2.

The present study builds on some of the earlier findings on the inactivation of *E .coli* by TiO_2 photocatalysis. While our result supports many of the earlier findings [320] on the photo-inactivation of the bacteria, it disproves the conclusion by some authors [322] that TiO_2 does not play a role in the inactivation. We observed that, TiO_2 not only enhanced the photo-inactivation of *E. coli*, but it also inhibited the reappearance of bacteria, to a greater extent after the illumination was discontinued even under favorable nutrient conditions.

The mechanism of action of TiO_2 may be explained on the basis of the conjugate reactions triggered by the photo activation of TiO_2 [320]. When TiO_2 is irradiated by light of energy higher than its band gap, electron-hole pairs are generated. The photo-generated holes lead to the formation of OH radicals at the catalyst-water interface [9]. The electrons are scavenged by oxygen, forming O_2^- thereby preventing the electron–hole recombination. Details of the mechanism are discussed in Chapters 2 and 3.

Photocatalytic methods are unique in having several modes of action that can be brought to bear on disinfection. Each target organism presents a challenge in terms of the structure and defense mechanism that must be overcome.

Organisms have evolved defense and repair mechanisms to overcome photochemical and oxidative damage that allow them to live in an aerobic environment and to deal with low levels of UV radiation found in sunlight.

It is well documented that an increased pressure of oxygen is toxic to all forms of life, and the production of oxygen radicals is the root cause of oxygen toxicity. During respiration, the stepwise reduction of oxygen leading to H_2O generates the reactive intermediates superoxide radical (O_2^-) and H_2O_2, both of which are reactive toward biological macromolecules and can be precursors for hydroxyl radical. Therefore, all organisms prevailing in the aerobic atmosphere have evolved a protective mechanism to scavenge both O_2^- and H_2O_2 to a very low steady –state concentration.

Indeed, all aerobic life forms are reported to have a superoxide dismutase (SOD) enzyme to dismutate O_2^- to H_2O_2 and O_2, and a catalase enzyme to convert H_2O_2 to H_2O and additional O_2 as innocuous end products. Several prokaryotes including *E. coli*, have evolved to produce different forms of SOD strategically distributed within a cell to shield the cells from any oxidative damage resulting from their normal metabolism. In *E.coli*, an Fe-SOD is distributed along the periphery of the cytoplasm close to the inner membrane to dissipate any radicals produced from aerobic respiratory pathways.

When a bacterium comes in contact with the TiO_2 surface, there may also be direct electron or hole transfer to the organism or one of its components. If TiO_2 particles are of small size, they can penetrate into the cell and these processes could occur in the interior. Since light is an essential component of the photocatalytic system, there can be direct photochemistry as there would be from any UV source. There is also the possibility of enhanced or unique photochemistry resulting from irradiation of the microbe while it is adsorbed on an oxide surface, as has been observed for molecules. Orientation and distance effects are likely to be more pronounced in the case of microbes which are comparable in size to aggregates of the titanium dioxide particles.

The exact mechanism of deactivation of *E. coli* is not yet known clearly. Some authors suggested that free radicals have an adverse influence on cell DNA replication and the modification of cellular membranes, while others proposed an alternative mechanism involving the direct oxidation of intracellular coenzyme [320]. The possibility of inactivation of *E. coli* by the H_2O_2 formed in the reaction system also cannot be ruled out. The bactericidal properties of H_2O_2 are well known and evidence of its formation in irradiated semiconductor oxide suspensions has been presented by many authors [7, 51 and 70]. The formation of H_2O_2 in semiconductor mediated photo catalytic systems, as explained in detail in earlier chapters, takes place as follows:

$$O_2^- + H^+ \rightarrow HO_2^\cdot \qquad (3)$$

$$HO_2^\cdot + e^- \rightarrow HO_2^- \qquad (4)$$

$$HO_2^- + H^+ \rightarrow H_2O_2 \qquad (5)$$

The H_2O_2 can in turn generate more $OH^\cdot$ radicals as follows:

$$H_2O_2 \xrightarrow{h\upsilon} 2\,OH^\cdot \qquad (6)$$

$$H_2O_2 + O_2^{-\cdot} \rightarrow OH^\cdot + OH^- + O_2 \qquad (7)$$

$$H_2O_2 + e^- \rightarrow OH^\cdot + OH^- \qquad (8)$$

Enhancement in the formation of $OH^{\cdot}$ radicals may be one of the reasons for the increased deactivation of the bacteria at higher intensity of light and higher catalyst concentrations.

Blake et al. [319] suggest that hydroxyl radicals are highly reactive and therefore short-lived. Superoxide ions are longer-lived; due to the negative charge they cannot penetrate the cell membrane. Upon their production on the TiO_2 surface, both hydroxyl radicals and superoxide would have to interact immediately with the outer surface of an organism unless the TiO_2 particle has penetrated into the cell. Compared to hydroxyl radicals and superoxide ions, hydrogen peroxide is less detrimental. However, H_2O_2 can enter the cell and be activated by ferrous ion via the Fenton reaction.

$$Fe^{+2} + H_2O_2 \rightarrow OH^{\cdot} + OH^{-1} + Fe^{+3}$$

The ability of bacteria, such as *E.coli*, to sequester iron is well documented. Iron levels on the cell surface, in the periplasmic space or inside the cell, either as iron clusters or in iron storage proteins (such as ferritin) are significant and can serve as a source of ferrous ion. Therefore, while the TiO_2 is being illuminated to produce H_2O_2, the Fenton reaction may take place in vivo and produce the more damaging hydroxyl radicals. When the light is turned off, any residual H_2O_2 would continue to interact with the iron species and generate additional hydroxyl radicals through Fenton reaction. When both H_2O_2 and superoxide ion are present, the iron- catalysed Haber-Weiss reaction can provide a second pathway to form additional hydroxyl radicals.

$$Fe^{+3} + O_2^{\cdot} \rightarrow Fe^{+2} + O_2$$
$$Fe^{+2} + H_2O_2 \rightarrow Fe^{+3} + OH^{-} + OH^{\cdot}$$

Since the initial actions of these reactive oxygen species (ROS) target the outer surface of a cell, the rigidity and chemical arrangements of their surface structure will determine how effectively the TiO_2 photocatalytic disinfection process functions.

Preliminary studies on the deactivation of *Bacillus subtilis* and *Vibrio harvae* also show that photocatalysis mediated by TiO_2 is efficient for the removal of these two microorganisms from water. The results of these studies, carried out under conditions identical to those for the *E.coli* experiments are presented in table 4.1 and figure 4.7.

Table 4.1. Inactivation of *Bacillus subtilis* in water irradiated with sunlight (≈750 W/m^2) in presence of TiO_2 as a photocatalyst.

Sample Description	Cell density (Cell/mL)				
	Dilutions				
	X 1	X 10	X 100	X 1000	X 10000
Blank: No TiO_2 added No irradiation	TNTC*	TNTC	TNTC	198(±9)	19(±6)
Control 1: TiO_2 added No Irradiation	TNTC	TNTC	TNTC	189(±10)	7(±3)
Control: 2 Without TiO_2 Irradiated 1 (h)	TNTC	TNTC	TNTC	172(±8)	9(±3)
TiO_2 added (1g/L) Irradiated 1 (h)	9(±6)	9(±3)	0	0	0
TiO_2 added (1g/L) Irradiated 4 (h)	3(±3)	0	0	0	0

* Too numerous to count

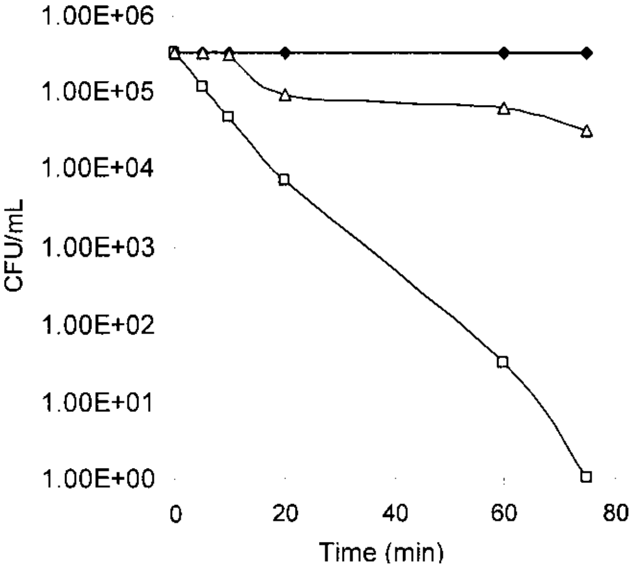


Fig. 4.7. Inactivation of *Vibrio harvae* (♦) Dark; (Δ) SL; (□) SL+ TiO_2.

Under severe environmental conditions bacillus can produce spores within their cells (endospores). The bacterial spore contains a uniqie Ca^{+2}–dipicolinic acid-peptidoglycan complex, quite different from its parent vegetative cell. It is believed that the nature of this complex, along with its dehydrated protoplast, and the extent of mineralization account for the spore's extreme resistance to many adverse physical and chemical agents. Sporulation represents a dormant stage during the development of a cell's life cycle. Their durability allows them to survive for a long time while being carried by dust in air-only to germinate when nutrients become available.

The thick wall of spores is impermeable to most damaging agents. However, H_2O_2 and organic peroxides are reported to penetrate freely [319]. Most spores contain high levels of transition metal, therefore, a Fenton–type reaction is likely to take place under this condition. The degradation of the outer coat by these radicals is not lethal to the subsequent germination of the de-coated spores. Nevertheless, once the protective coat is removed, the protoplast and its membrane become the target of direct radical attack, a lethal event. Therefore, destruction of spores by oxidative damage using the photocatalytic process is a viable concept.

In order to overcome the disadvantage of using catalysts in the suspended form, supported catalysts have been used in recent years. Immobilisation of TiO_2 on a solid carrier has been a successful technique employed in this context [324, 325]. In addition to avoiding turbidity, it eliminates the recovery steps such as filtration and decantation. In the current study we have extrapolated and simplified the technique by using commonly used (and thrown away) PET bottles as the supporting medium. The methodology essentially involves coating the inner surface of the bottle with TiO_2 by a simple technique, filling it with water to be decontaminated and effecting disinfection by exposure to sunlight.

4.3.2. Disinfection of water using TiO_2 immobilized on the inner walls of a PET bottle

The immobilisation of TiO_2 was carried out as described in the experimental section. Its presence on the inner surface of the PET bottles was confirmed by the XRD pattern obtained as shown in figure 4.8. All experiments were carried out in the open using solar energy as the source of irradiation.

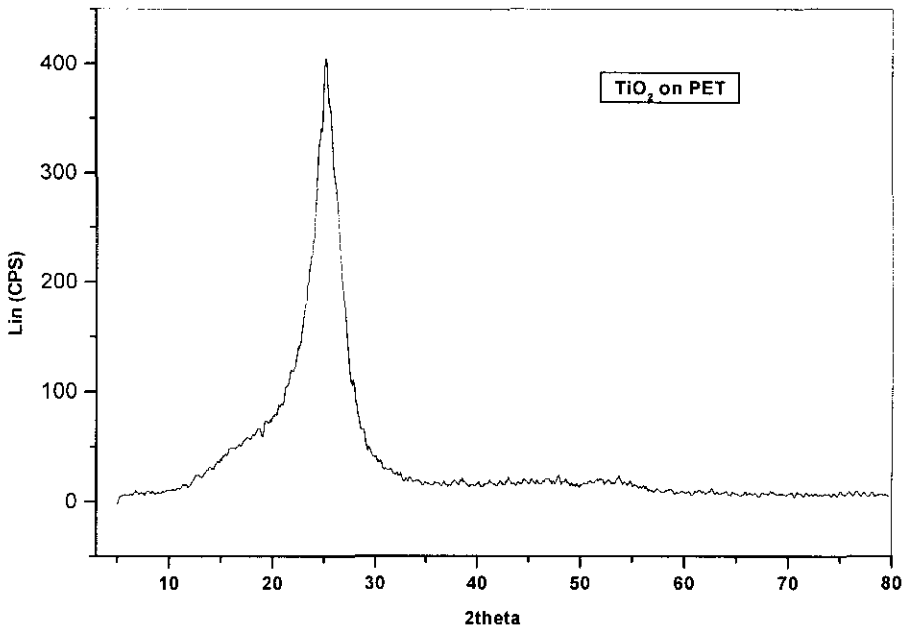


Fig.4.8. XRD patten of the inner surface of the PET bottle

Three types of one liter PET bottles were used in the initial exploratory experiments. Type 1 was uncoated PET bottles. In type 2, the entire bottle interior was coated with TiO_2. In type 3, the interior of the bottle was coated to full length but only to half width so that the bottle surface exposed to light is transparent as shown in figure 4.9.

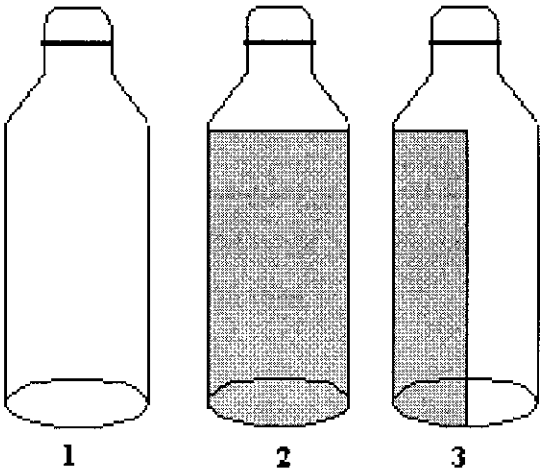


Fig 4.9. Different types of Pet bottles used for solar irradiation.
1- Uncoated; 2-Full coated; 3- Half coated

The bottles were filled with approx. 500 ml of water and irradiated. Control samples in both types of bottles were kept in the dark under identical conditions. The results of the experiment are given in figure 4.10.

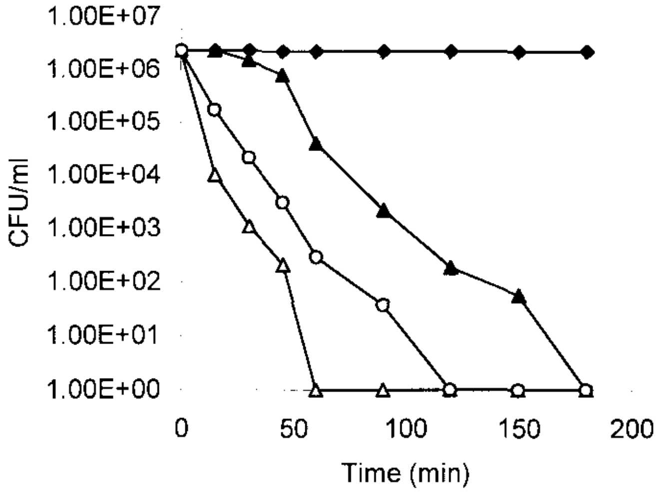


Fig.4.10. Inactivation of E.coli in TiO_2 coated PET bottles.
(♦) Dark; (▲) Uncoated; (○) Full coated; (Δ) Half coated

The results reconfirm the finding from the study of suspensions that the deactivation of *E.coli* happens in presence of light and the process is significantly enhanced by the presence of TiO_2 catalyst. Control experiments in presence of TiO_2 but in the dark showed that even after 180 minutes, all the bacteria remain alive thereby confirming that simple contact with the catalyst is not enough for deactivation. The bottle half-coated with TiO_2 is more effective than the fully coated one. This shows that the penetration of light through the transparent surface and activation of the catalyst is more important than the surface area of the catalyst bed in contact with the water. When the bottle is fully coated, there is obstruction to the full intensity of the light reaching the catalyst surface in contact with water. All further experiments were hence carried out using the half-coated bottles.

In another experiment, the half coated bottles were kept horizontally and vertically and the deactivation of *E coli* is evaluated under identical conditions. The results are shown in figure 4.11. As expected, the deactivation was more in horizontally placed bottles, due to more effective penetration of light and consequent exposure and activation of the catalyst.

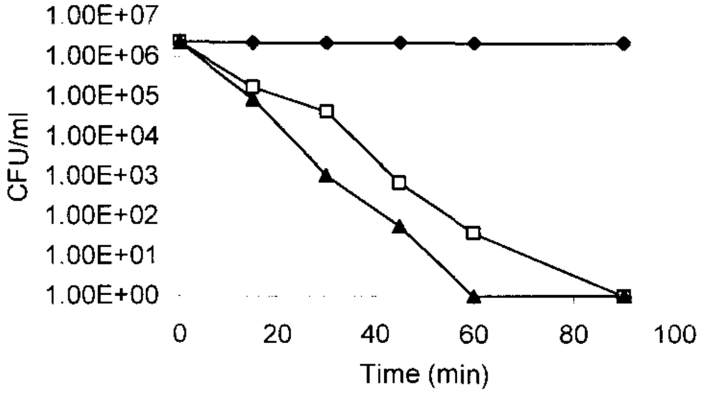


Fig.4.11. Inactivation of E.coli in TiO_2 coated PET bottles placed horizontally and vertically under sunlight. (♦) Dark; (□) Vertical; (▲) Horizontal.

The effect of intensity of light on the photocatalytic deactivation of the bacteria was tested at three different intensities of sunlight. The results are plotted in figure 4.12. As expected from the results using the suspension of TiO_2, increase in light intensity enhances the kill. Comparison of the two systems show that at lower light intensities, the suspended catalyst system is more efficient for the kill while at higher intensities (approx. 1000 Wm^{-2}) the efficiency is comparable. The superior efficiency of suspended systems for the photocatalytic degradation of chemical pollutants has already been reported and the trend remains the same for bacterial pollutants as well. However, at higher light intensities, when both self-defense and auto-repair mechanisms of bacteria are insufficient to protect the cells, both systems have similar efficiency. In this case, the number of reactive OH radicals formed by the immobilized TiO_2, though less compared to the suspended system, is more than sufficient to achieve the required kill.

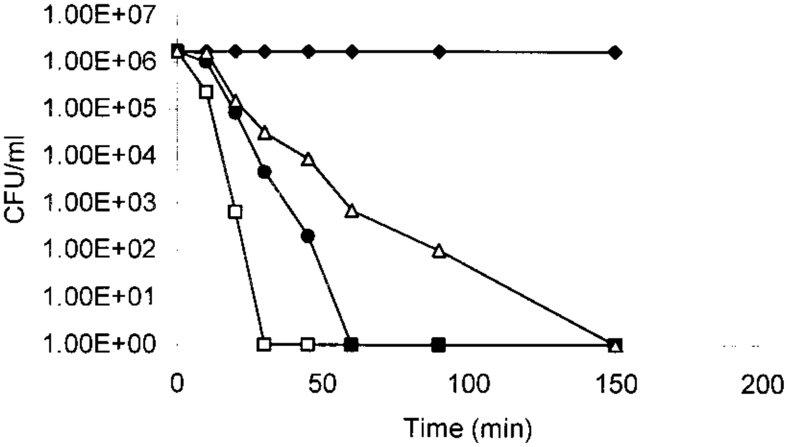


Fig.4.12. Inactivation of E.coli at different intensities of solar irradiation (♦) Dark; (□) ~1000W/m^2; (●) ~750 W/m^2; (Δ) ~ 400 W/m^2.

The reemergence of E.coli after the irradiation has been interrupted, was investigated in the case of the immobilized catalyst using 'half-coated' PET bottles. The results are presented in figure 4.13. This reemergence of the bacteria after the illumination has been discontinued implied that intermittent irradiation in place of continuous irradiation will be less effective and will take more time. This was verified by conducting experiments under continuous illumination and intermittent illumination, under otherwise identical conditions. During intermittent irradiation, the samples were exposed to sunlight for three minutes and kept in dark by covering the sample with black box for three minutes repeatedly. The results show that in the case of discontinued illumination, the complete elimination of the bacteria takes much longer total irradiation time, possibly due to the reemergence of the bacteria in the dark.

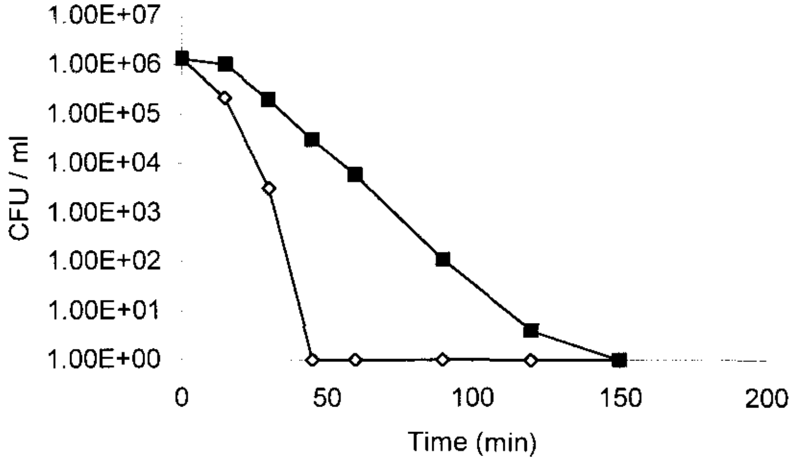


Fig.4.13. Effect of continuous and intermittent solar irradiation on the inactivation of E.coli. (◊) Continuous; (■) intermittent.

During the interruption of illumination, the bacteria have time to recover by a self defense mechanism. The synthesis of the superoxide dismutase (SOD) enzyme constitutes one of the major defense mechanism of cells against oxidation stress by catalyzing the disproportionation of superoxide anions $O_2^{\cdot-}$ (precursors of $^{\cdot}OH$) into hydrogen peroxide and molecular oxygen;

$$2O_2^{\cdot-} + 2H^+ \xrightarrow{SOD} O_2 + H_2O_2 \quad (1)$$

Such a response to oxidative stress has been well demonstrated for Gram negative bacteria such as *E.coli* [326]. These bacteria produce also catalase, in response to oxidative stress. This enzyme reduces the intracellular concentration of hydrogen peroxide by causing its decomposition to water and oxygen;

$$H_2O_2 + H_2O_2 \xrightarrow{Catalase} O_2 + 2\,H_2O \quad (2)$$

Thus the SOD enzyme prevents the formation of most OH radicals and catalase eliminates photogenerated H_2O_2. However, the $^{\cdot}OH$ concentration in solution increases with illumination time due to its massive production by photooxidation of adsorbed water on the surface of TiO_2. Thus it may be presumed that the relative duration of irradiation and dark exposure periods determines the concentration of OH radicals and the efficiency of bacterial kill/recovery.

The initial induction period in the deactivation of *E coli*, observed in the absence of the catalyst, can also be explained by the self-defense mechanism induced by the UV in the stressed cell. This resistance, effective in the initial stage, diminishes with time. In the presence of TiO_2, the massive generation of OH radicals lead to facile destruction of the bacteria and the self-defense mechanism is overpowered. The relatively slow inactivation of the bacteria towards the later stages is possibly due to the competition for the active OH radicals by the remaining active bacteria with both the inactivated bacteria and their metabolites released during the photoprocess.

4.3.3. Photocatalytic treatment of actual waste water, sewage

The application of the method has been tested for the treatment of domestic wastewater, collected from the neighborhood. The water was allowed to settle to remove larger particles. The decanted water was tested for various physicochemical properties and the results are shown in Table-4.2. Total coliforms present in the wastewater were estimated by MPN method and were found to be $1.1x10^5$ per 100ml. The water was irradiated by sunlight in the presence and absence of suspended TiO_2. The results are presented in figure 4.14 and it shows the complete inactivation of the bacteria in 5 h. The treatment was found to reduce the COD of domestic wastewater also by 94.8% in 5 h as shown in figure 4.15.

Table-4.2: Physicochemical Characteristics of domestic wastewater.

Characteristic	Value
pH	7.5
Conductivity	0.05 mS/cm
Alkalinity	323 mg/L
Hardness	103 mg/L
COD	115 mg/L
Iron	0.084 mg/L
Phosphate	0.053 mg/L
Chloride	96 mg/L
Total coliforms	1.1×10^5 CFU/100mL

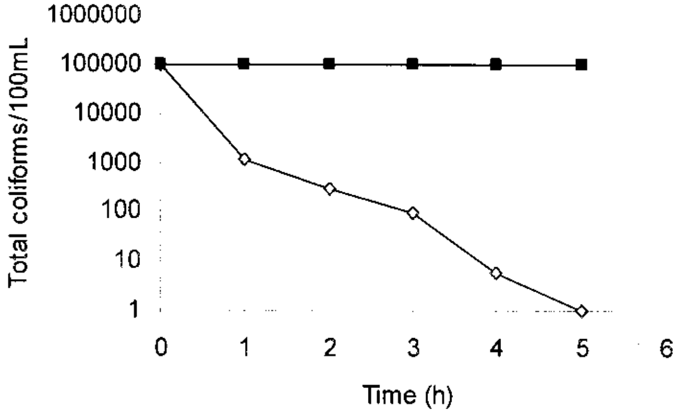


Fig.4.14. Disinfection of total coliforms by photocatalysis
(■) Without TiO_2; (◊) With TiO_2

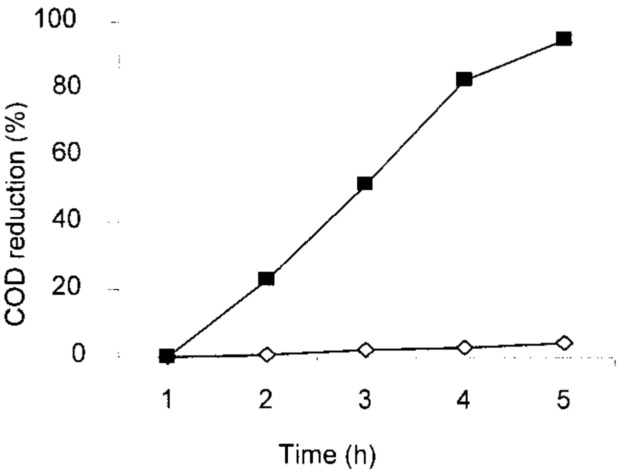


Fig.4.15. Reduction of COD of wastewater in sunlight.
(◊)In the absence of TiO_2; (■) in presence of suspended TiO_2

4.4. Conclusions

Results presented in this chapter clearly demonstrate the potential of TiO_2 photocatalysis to inactivate the micro organisms in water. The technique can be used for the disinfection of water and wastewater even in areas which lack electricity or other infrastructure. The study also proves the use of sunlight as the energy source for the activation of the catalyst and is particularly relevant for tropical countries like India. Concurrent removal of organic, inorganic and bacterial pollutants from water is an added advantage of TiO_2 photocatalysis.

Chapter 5

PHOTOCATALYTIC REMOVAL OF CHEMICAL AND BACTERIAL POLLUTANTS IN WATER USING TiO_2 IMMOBILISED ON CERAMIC TILES

5.1 Introduction

Studies reported in earlier chapters show that the use of slurry type reaction system is efficient for the photocatalytic removal of chemical and bacterial pollutants from water. However, the use of suspensions suffers from the disadvantage that the catalyst has to be separated and the ultra fine catalyst has to be recycled. This is time consuming, expensive and inconvenient and is a major handicap in the commercialisation of the process. This has led to a number of attempts to immobilise the catalysts on supports such as ceramics [327], fibre glass [328], glass, quartz and stainless steel [329], activated carbon [201] etc. The immobilisation of TiO_2 on the inner walls of a PET bottle, and its application in the decontamination of water from bacterial pollutants is discussed in the previous chapter. In this chapter, we report an extension of the study using TiO_2 immobilised on ceramic tiles, commonly used for a variety of purposes around the world.

Among the TiO_2 based suspension systems which were proved to be efficient for the photocatalytic degradation of a variety of pollutants, we have chosen the well established reaction of decolourisation of dyes [198, 199, 330] for testing the efficacy of the immobilised catalyst. Since we have already tested a highly toxic organophosphorous pesticide (i.e. phosphamidon) and a major water pollutant from petrochemical industry (i.e. phenol), a different class of pollutant, i.e. dyes, is examined here, as it would prove the applicability of the technique for the removal of a wide variety of water contaminants.

Several studies have been published on the application of photocatalysis for the degradation of dyes. Matthews [198] investigated the photocatalytic oxidation of Methylene Blue (MB), Rhodamine B (RB) and Methyl Orange (MO) using TiO_2 supported on sand as the catalyst and showed the complete mineralisation of these dyes. David and Grainer [331] reported that the colour of municipal sewage water is removed and the COD can be reduced by TiO_2/UV treatment. Many research papers continue to be published in this area, which report improved catalysts and reactor designs [56, 205, 209].

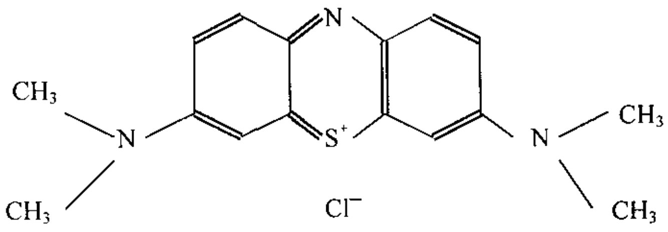
For the current study, we have chosen MB and RB as the substrates. Many reports are available on the photocatalytic studies of these dyes in slurry systems [50, 332]. This chapter presents our results on the investigation of the decolourisation of these dyes using TiO_2 immobilised on ceramic tile as the photocatalyst. Since, TiO_2 immobilised on the interior of PET bottles has been found to be very effective for the removal of bacterial pollutants, the tile coated with catalyst is also examined for the photo-deactivation of *E. coli.*

5.2 Experimental

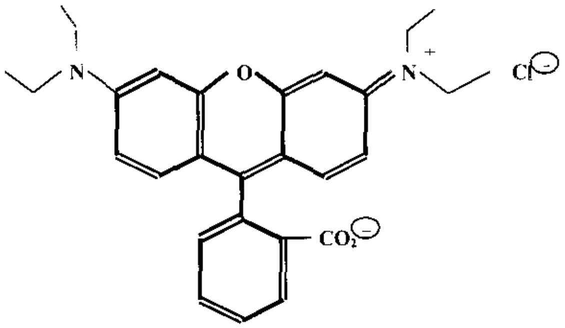
5.2.1. Materials

Methylene blue powder (Qualigens, India) and Rhodamine B powder (Merck, Germany) were used as such without further purification. The catalyst TiO_2 was supplied by Merck India Limited and its characteristics have been described earlier. All other chemicals were of reagent grade and used as such, unless otherwise mentioned.

MB is a dye, widely used as a stain in biological applications. Its molecular formula is $C_{16}H_{18}ClN_3S$ and its IUPAC name is 3,7-bis(dimethylamino)phenothiazin-5-ium chloride. Its structural formula is given below.



Rhodamine B is an amphoteric dye used for dyeing fibres, cotton etc. and also in the preparation of carbon paper, ball-pen, stamp pad ink etc. Its molecular formula is $C_{28}H_{31}ClN_2O_3$ and its IUPAC name is [9-(o-carboxyphenyl)-6-(diethylamino)-3Hxanthen-3-ylidene] diethylammonium chloride. It has the following structural formula,



5.2.2. Coating of the Tiles

Glazed tile readily available in the market was used for the study. The tile was initially etched by standard procedure as follows:

A boundary of wax was created on the surface of the tile by pouring molten wax using a glass dropper and allowing it to set. Dilute HF was poured over the tile such that it flooded the area inside the boundary and was allowed to stay for 3 minutes. The wax coating was removed with a sharp knife, followed by washing with hot water and liquid detergent to remove the last traces of wax and HF.

3 g of polymethylmethacrylate (plexi glass) was dissolved in 25ml chloroform by leaving them together overnight. To this solution, appropriate quantity of TiO_2 was added and mixed well to get a paste. The paste was coated on the surface of the etched tile evenly. The tile was allowed to dry in an oven at 110^0 C for two hours. Then the tile was placed in a muffle furnace and heated at 350^0C for 3 hours. The methylmethacrylate and chloroform were completely evaporated off leaving TiO_2 bound to the surface of the tile. The tile, after cooling, was washed thoroughly. A thin film of TiO_2 remained on the surface of the tile. For control experiments, the tile was prepared exactly as above excluding TiO_2.

X Ray Diffraction (XRD) analysis of the surface of the coated tile showed the peaks characteristic of TiO_2 used, indicating that it is coated with TiO_2. XRD features of the surface are shown in figure 5.1

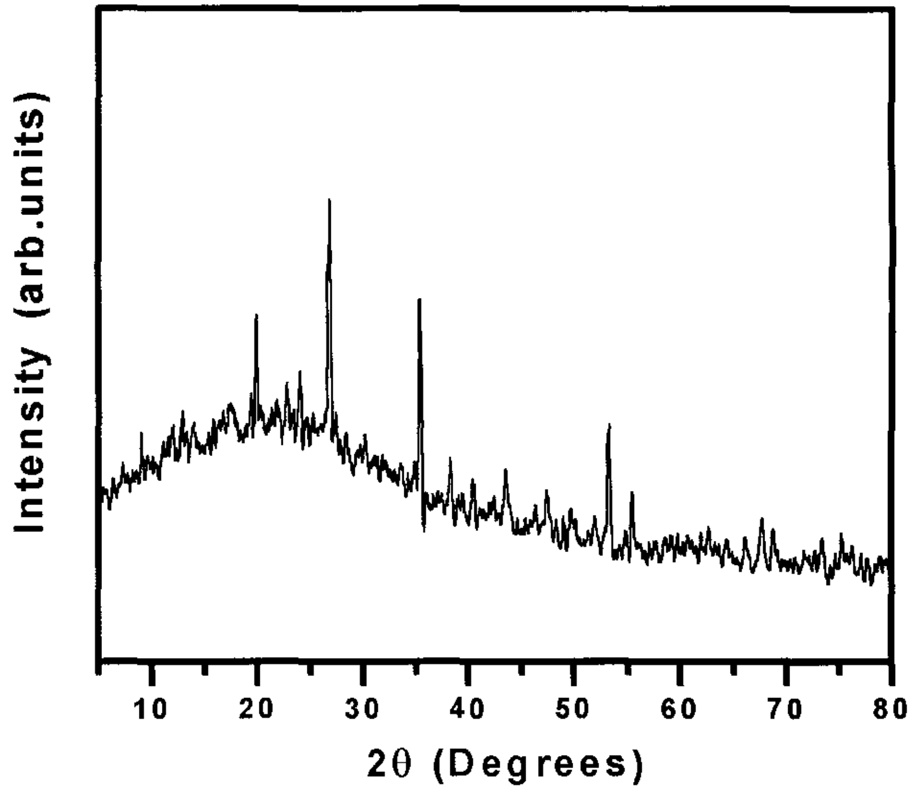


Fig. 5.1. XRD Pattern of TiO_2 coated surface of the ceramic tile.

5.2.3. Photocatalytic experiments with dye Solution

Dye solutions of appropriate concentrations were prepared from a standard stock solution of concentration 1000 ppm by dilution. 50 ml of this solution was flooded on the TiO_2 coated part of the tile, with a thick boundary of wax to serve as the border. The tile was then kept in a Pyrex jar which was kept horizontally inside a thermostat, with water circulating, to maintain constant temperature of the reaction mixture as in figure 5.2. The solution was irradiated with a 400W medium pressure mercury vapour lamp (for UV radiation). Solar irradiation was carried out in the same set up, with the system placed on the roof top of our laboratory at Kochi, during sunny days in April-May. Samples were drawn periodically and analysed for the dye concentration by spectrophotometry (λmax of MB and RB are 664nm and 555nm respectively). Unless otherwise stated, all studies were conducted at a pH of 7±0.2.

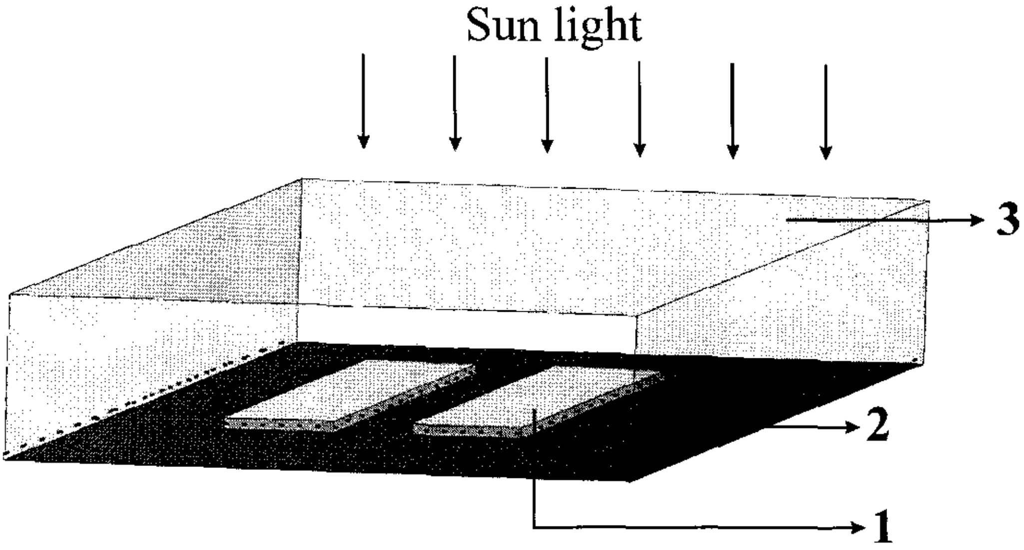


Fig. 5.2 Photocatalytic Experiments with TiO_2 Coated Tiles- Experimenatal setup
1. Tile holding dye solution 2. Water 3. Pyrex plate holding water

5.2.4. E.coli disinfection experiments

Cells of *Escherichia coli* (ATCC 11775) used as the test organism in these studies were prepared as described in Chapter 4. The inactivation experiments were done with the coated tiles placed in aquarium jars of 25 L capacity. Sterile distilled water (10 L) was taken in the aquarium jars. Bacterial cultures (10^6 CFU/ml) were added to it and exposed to radiation. The jar was kept in a thermostat to maintain the temperature at 27±2^{0}C. Sampling was done at periodic intervals by pipetting out 1ml from the tank into 9 ml of sterile saline which was then serially diluted and the cell inactivation monitored as described in Chapter 4.

5.3 Results and Discussion

5.3.1. Photodecolourisation of dyes on TiO_2 coated tiles.

TiO_2 catalyses the photo-decolourisation of Methylene blue under UV as well as natural sunlight. Figure 5.3 shows the effect of concentration of the dye on the efficiency of decolourisation in presence of UV light. The decolourisation proceeds very fast in the early stages of irradiation and very slowly thereafter. The decolourisation takes place in the absence of the catalyst also, but very slowly. The experiments were carried out under identical conditions in presence of natural sunlight and the results are presented in figure 5.4. Similar studies were conducted using RB solution and the results are presented in figures 5.5 and 5.6.

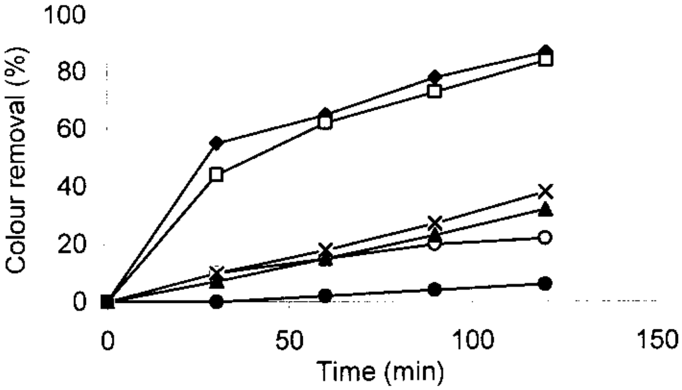


Fig. 5.3. Effect of concentration of methylene blue on the efficiency of decolorisation in UV light. (♦)TiO_2 /UV 5 ppm; (□) TiO_2 / UV 10 ppm; (○) TiO_2 / UV 50 ppm; (x) UV 5 ppm; (▲) UV 10 ppm; (●) UV 50 ppm

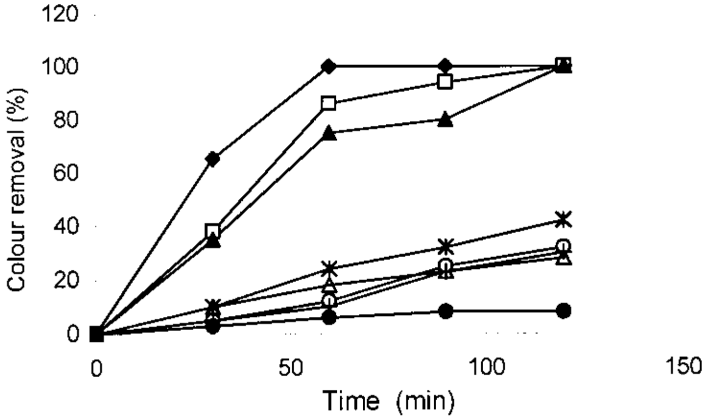


Fig. 5.4. Effect of concentration of methylene blue on the efficiency of decolorisation sunlight. (♦)TiO_2 /SL5 ppm; (□) TiO_2 / SL 10 ppm; (▲) TiO_2 / SL 15 ppm; (Δ) TiO_2 /SL 50 ppm (Ж) SL 5 ppm; (○) SL 10 ppm; (+) SL/15 ppm (●) SL 50 ppm

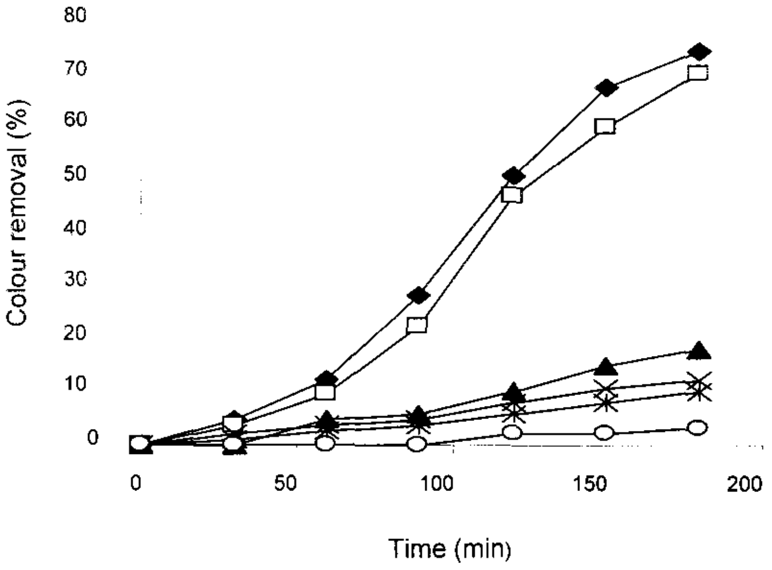


Fig. 5.5. Effect of concentration of Rhodamine B on the efficiency of decolorisation in UV light. (♦)TiO_2 /UV 5 ppm; (□) TiO_2 / UV 10 ppm; (▲) TiO_2 /UV 50 ppm; (x)UV 5 ppm; (Ж) UV 10 ppm; (○) UV 50 ppm.

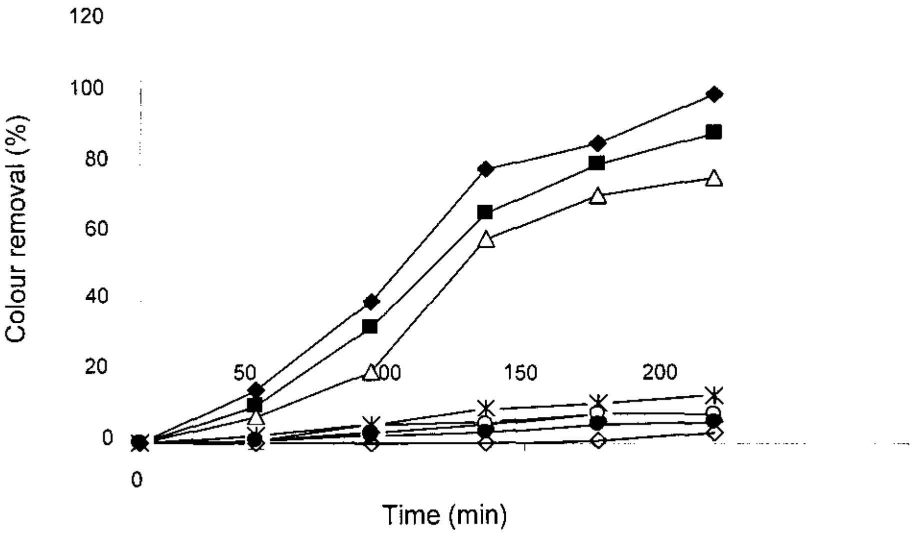


Fig. 5.6. Effect of concentration of Rhodamine B on the efficiency of decolorisation in sunlight. (♦)TiO_2 /SL5 ppm; (■) TiO_2 / SL 10 ppm; (Δ) TiO_2 / SL 15 ppm; (▲) TiO_2 /SL 50 ppm (ж) SL 5 ppm; (○) SL 10 ppm; (●) SL/15 ppm (◊) SL 50 ppm

It is seen that in the case of both dyes, under sunlight and UV irradiation, the colour removal efficiency in terms of percentage of the initial dye concentration decreased with increase in the initial concentration of the dye, both in the presence and absence of the catalyst. This is consistent with the observations of Sakthivel et al. [200] and Kuo and Ho [50], who used the catalyst in suspension for the decolourisation of MB.

At higher concentration of the dye, the path length of photons entering the solution decreases and at low concentration the reverse effect is observed [331]. Higher concentrations lead to a reduction in the light penetration and thus reduction in the exposure of catalyst surface. Major part of the decolourisation occurs at or near the irradiated surface, termed as reaction zone and higher concentration of the dye leads to a decrease in the irradiated surface. Consequently, the reactive OH radicals formed by the illuminated catalyst surface also will be less. The result is lower percentage of decolourisation and degradation.

Another reason for this inverse relation between the concentration of the dye and the rate of decolourisation may be related to the role of OH radical, which is the critical species in the degradation process. The equilibrium adsorption of reactants on the catalyst surface and the rate of reaction of OH radicals with other chemicals, formed in the system, are also significant in the rate of degradation of the dye [200]. Accordingly, the overall rate constant k is expressed as

$$k = k_0 \, P_{\bullet OH} \, P_{dye} \qquad (1)$$

where k_0 is the reaction rate constant, $P_{\bullet OH}$ is the probability of generation of the OH radicals on the catalyst surface and P_{dye} is the probability of OH radicals reacting with the dye molecules. While k_0 is independent of the initial dye concentration, $P_{\bullet OH}$ and P_{dye} will depend on the dye concentration implicitly [333]. It has been suggested by many authors that the rate determining step in these reactions is the formation of OH radicals as they react very rapidly with aromatic ring compounds [183, 334]. The OH radicals are formed by the reaction of holes with adsorbed OH^- and H_2O. Assuming that the adsorbed OH^- ions are replaced by dye ions (dye^-), the generation of OH radicals will be reduced, because only fewer sites are available for their formation. Thus $P^{\cdot}_{OH}$ is adversely affected by the higher concentration of the dye, which now occupies more of the catalyst surface along with probable reaction intermediates.

Except for the very high concentration of 50 ppm, at concentrations in the range of 5-15 ppm, the adverse effect of increasing the initial concentration is not that severe for systems with and without TiO_2. In any case, in terms of absolute quantities, the amount of dye degraded is more at higher concentrations and the decolourisation takes place very efficiently at all the concentrations tested here.

Comparison of the effect of UV and sunlight on the decolourisation efficiency using 5 ppm solution of the dyes is shown in figures 5.7 (for MB) and 5.8 (for RB), which illustrate that in the absence as well as in the presence of the catalyst, sunlight is more efficient for the decolourisation compared to UV light.

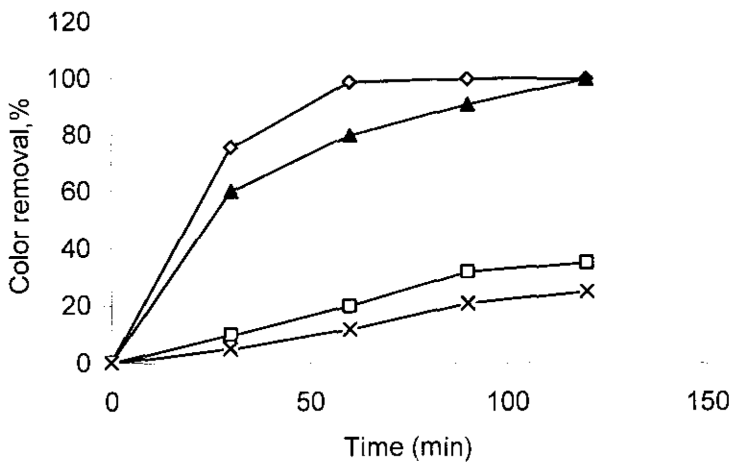


Fig.5.7. Comparison of the effect of UV and Sunlight on the decolorisation efficiency using 5 ppm Methylene Blue (◊) SL/TiO_2; (□) SL; (▲) UV/TiO_2; (x) UV

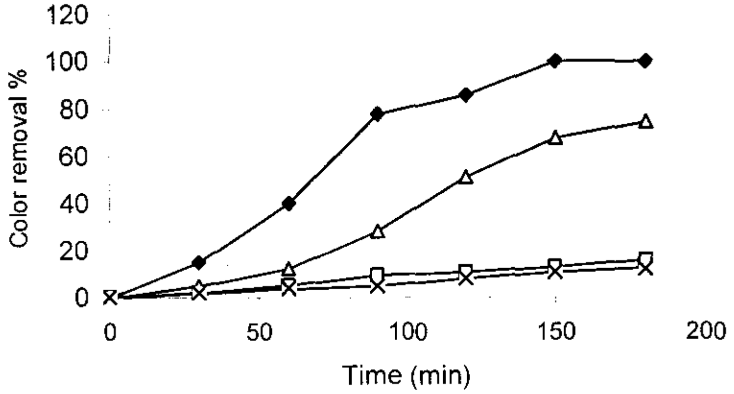


Fig 5.8. Comparison of the effect of UV and Sunlight on the decolorisation efficiency using 5 ppm Rhodamine (♦) SL/TiO_2; (□) SL; (Δ) UV/TiO_2; (x) UV

Kuo and Ho [50] also made similar observations with MB, even though the degree of enhancement by the sunlight was significantly higher, compared to current results. These authors attributed the higher decolourisation efficiency in sunlight, partially to a high temperature of the dye solution under solar irradiation. Based on the activation energy calculated by Lee et al. [332] and the application of Arrhenius's equation for the photocatalysed decolourisation of MB, Kuo and Ho argued that the colour removal rate could be increased by 20% when the operation temperature is raised from 25 to 35^{0}C. However, in the present studies, both UV and sunlight experiments were conducted at similar temperatures (27±2^{0}C). Even assuming a marginal difference in temperature, due to the inadequacy of the thermostat, such large enhancement as observed in the present case cannot be explained based on temperature difference alone. Also, unlike in the case of the results of Kuo and Ho [50], the enhancement in the decolourisation efficiency in presence of sunlight, as compared to UV light, was much less in the absence of the catalyst. Hence it is clear that TiO_2 has a major role in the enhanced decolourisation of the dye, more so in presence of sunlight. Accordingly, a mechanism involving the catalyst and the dye, which itself can act as a photosensitizer will be more appropriate to explain the higher efficiency of sunlight as follows:

The intensity of solar light at 254nm (~0.1 mW/cm^2) is much lower than that of artificial light at 254 nm (~3.0 mW/cm^2) [50]. However, the normal intensity of solar light at 365 nm has a mean value of 1.4 mW/cm^2 which is sufficient to allow the dye molecules adsorbed on TiO_2 to undergo photosensitisation (equations 2-5) resulting in the formation of reactive OH radicals or forming electronically excited oxygen atoms, i.e. the singlet oxygen atom (2O(^{1}D) (equation 6), which promote decolourisation.

$$\text{Dye (MB or RB)}_{(ads)} \xrightarrow{\text{Sunlight}} \text{Dye*}_{(ads)} \qquad (2)$$

$$\text{Dye*}_{(ads)} + TiO_2 \longrightarrow \text{Dye}_{(ads)} + h^+ + e^- \qquad (3)$$

$$e^- + O_2 \longrightarrow .O_2^{\cdot -} \qquad (4)$$

$$h^+ + OH^- \longrightarrow {}^{\cdot}OH \qquad (5)$$

$$\text{Dye*}_{(ads)} + O_2 \longrightarrow \text{Dye}_{(ads)} + 2O(^1D) \qquad (6)$$

In situ generated $^{\cdot}OH$ radicals have already been proven to be efficient oxidising species in photocatalytic degradation of organics. Further, the superoxide radical anion, $O_2^{\cdot -}$, on protonation produces $HOO^{\cdot}$ radical in acidic media, which also acts as predominant oxidant in the initial photodegradation stages; it accepts another proton and electron to yield H_2O_2. In the current study also we detected H_2O_2 in the system. As already proved by Yesodharan et al. [250], H_2O_2 in photocatalytic systems decomposes to form $^{\cdot}OH$ radicals. Attack by $^{\cdot}OH$ and $HOO^{\cdot}$ radicals on the dye molecules produces organoperoxides and/or hydroxylated intermediates [74]. The hydroxylated species decomposes further to smaller mineralised products, thus eventually resulting in the complete decolourisation and degradation of the dye.

Comparison of the colour removal efficiency for the two dyes under identical conditions shows that for RB there is an initial induction period before the rate picks up in presence of both sunlight and UV light. This induction period is not quite distinct in the absence of the catalyst thereby indicating that it may be related to a surface phenomenon. From a study of the adsorption of dyes on TiO_2 powders, Xu et al. [56] showed that it is very important to remove the effects of adsorption intervals at the beginning of the reaction in order to achieve faster degradation and decolourisation. They showed that in the case of MB, the surface gets saturated in approximately 10 minutes and the photocatalytic reaction picks up after the completion of the adsorption process. However, in the current study, the photocatalytic decolourisation of MB is so facile on TiO_2 that it takes place from the beginning itself and the induction period is not quite distinct. The efficiency of adsorption will also depend on the chemistry of the adsorbent and in the case of a larger and more complex molecule such as RB, the saturation of the surface may be reached very slowly. It may also be possible that the surface may not get saturated due to the stereochemistry of RB as well. This explains the initial induction period and the relatively longer time required for the decolourisation of RB compared to MB. Under identical conditions of catalyst loading, irradiation source, concentration and pH, RB takes approx. 150 minutes for complete decolourisation while it takes only 60 minutes for MB. In the case of both dyes, the decolourisation slows down at the later stages of reaction, even though this retardation is more significant in the case of RB. This may be due to the formation of relatively more stable intermediates and their competition with the parent dye molecules for surface sites. The slow kinetics of degradation of the dye after the initial accelerated pace may also be due to the difficulty in converting the N-atoms of the dye into oxidised nitrogen compounds [335]. However, it is possible that the phenomenon is even more complex and hence warrants further studies including the mechanism of photo-adsorption of complex dye molecules on semiconductor oxides, which is beyond the scope of the current investigation. In any case, the formation of OH radicals and singlet oxygen continues with the illumination and the dye is completely decolourised and degraded in the course of time.

The effect of intensity of the irradiation on the decolourisation efficiency was investigated by conducting the experiments at two different intensities (~ 400W/m^2 and ~ 750Wm^2). The results of the study are presented in figure 5.9 which show that increase in light intensity by almost double enhances the decolourisation only slightly in presence of the catalyst. However in the absence of the catalyst, the increase in decolourisation is significant and almost directly proportional to the intensity of light.

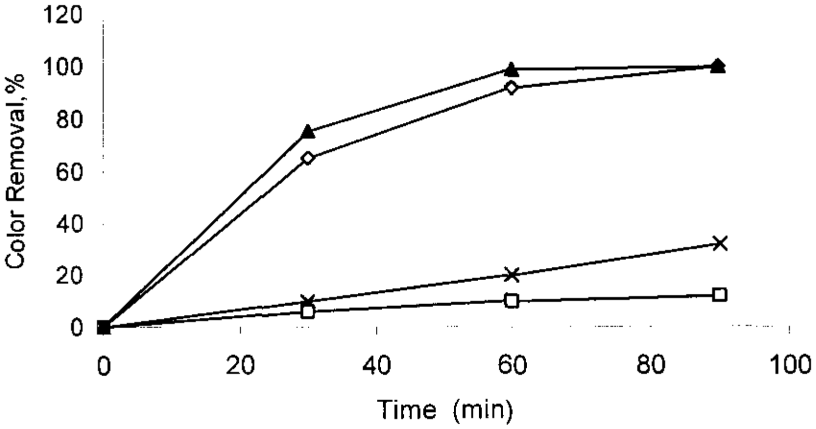


Fig.5.9. Effect of solar light intensity on the decolourisation of methylene blue
(◊) SL/TiO_2, ~ 400 W/m^2; (▲) SL/TiO_2, ~ 750 W/m^2
(□) SL, ~ 400 W/m^2; (x) SL, ~ 750 W/m^2

The limited data based on just two different intensities of light is not sufficient to draw any conclusions on the effect. However, certain observations can be made in the light of published literature on this. The effect of intensity of light on the kinetics of photocatalysis was reviewed in detail by Ollis [336], according to which, at low light intensities, the rate would increase linearly with increase in light intensity. At intermediate light intensities, the rate would depend on the square root of the light intensity and at high light intensities the rate is independent of it. In the current study, the intensity of the light from the artificial lamps may be considered to be in the range of 'intermediate' to 'high'. As expected from Olli's observation, the decolourisation in this case follows either a linear relation with the square root of the light intensity in the early stages of reaction or almost independent of the intensity. However, in the absence of the catalyst, the decolourisation follows almost a linear relation with light intensity, thereby reconfirming the definite role of catalyst in these reactions.

This square root dependence is given further credence based on our observation that H_2O_2 is formed in the system. Memming [337] has shown that the square root dependence on light intensity occurs in processes involving consecutive absorption of two photons by the same semiconductor particle. Kormann et al. [338] also observed the square root dependence between the reaction rate and light intensity and explained the same based on the competition between the oxidation of the pollutant molecule and the combination of charge carriers generated by the subsequent absorption of two photons by a single semiconductor particle. In the present case, as described in earlier chapters, OH radicals are the reactive oxidising species and the competing reaction is the formation of H_2O_2 as in equation 7

$$2\,^{\cdot}OH \rightarrow H_2O_2 \qquad (7)$$

At intermediate and high intensities, this competing reaction is quite prominent, leading to 'square root' or negligible dependence of the degradation reaction on the light intensity.

Our studies reported in earlier chapters using various substrates and catalyst systems show that pH of the reaction system plays an important role in the photocatalytic degradation of chemicals, with the catalyst either in suspension or immobilised form. In order to examine this for the dyes tested here in the current form of immobilisation of the catalyst, the reaction was studied at varying pH with MB and RB as the substrates, in presence of sunlight. Two different concentrations, 5ppm and 10ppm of the dye were used in each case. The results are presented in figures 5.10 -5.13. In the absence as well as in the presence of the catalyst, the maximum decolourisation was observed at pH 4, with the rate decreasing with increase in pH, at both concentrations, for both dyes. This is qualitatively consistent with the findings of Lee et al. [332] and Kuo and Ho. The enhanced rate at acidic pH may be attributed to the adsorption of more (dye¯) ionson the surface of the electrically positive TiO_2 and increased interaction with the oxidising radicals. Also, in acidic media (pH ≈ 3.8), the superoxide radical anion $O_2^{\cdot-}$, formed as described earlier, gets protonated and produces $HO_2^{\cdot}$ radicals, which are predominant oxidants in the initial photodegradation stage [74]. The effect of pH is less significant in systems without the catalyst, thereby proving the importance of catalyst in the photodegradation of the dye. Since it is observed that considerable photocatalytic reaction occurred in the alkaline range as well, it is inferred that the reaction occurs not only on the surface but also in its close vicinity. Heterogeneously initiated homogeneous reactions have been observed in earlier studies also [43]. Further, alkaline pH favours the formation of more OH radicals due to the presence of large quantity of OH^- ions in the alkaline medium, which can enhance the photocatalytic degradation.

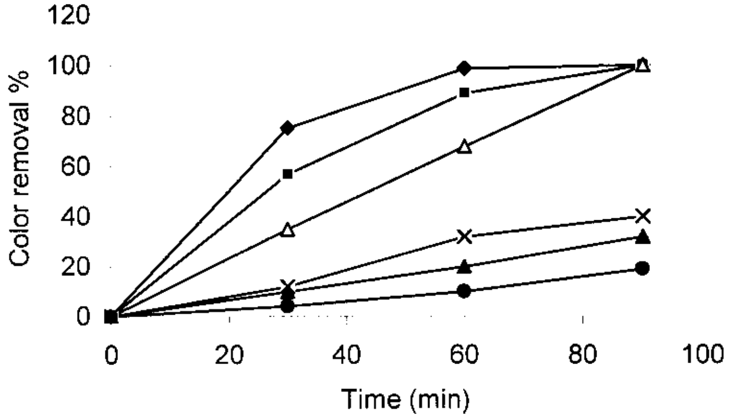


Fig. 5.10. Effect of pH on the decolourisation of Methylene Blue (5 μM) on TiO_2 coated and uncoated tiles under sunlight. (♦) SL/TiO_2, pH 4; (■) SL/TiO_2, pH 7; (Δ) SL/TiO_2, pH 10; (x) SL, pH 4; (▲)SL, pH 7; (●) SL, pH 10

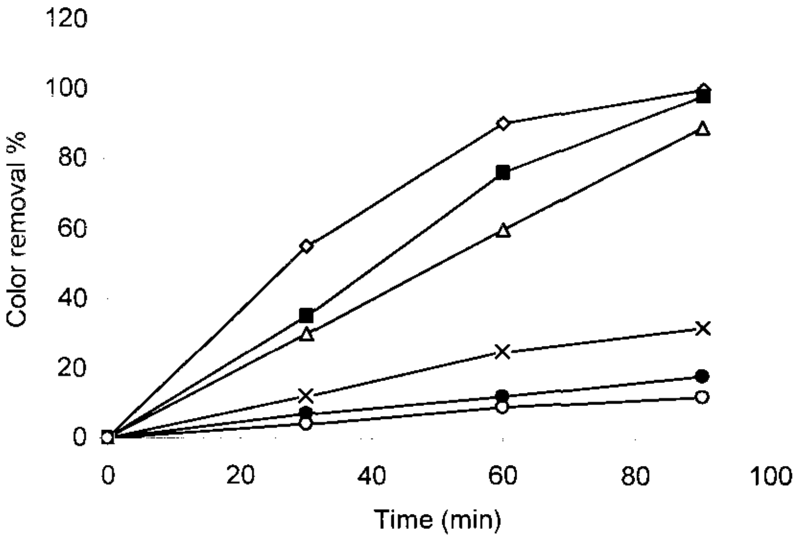


Fig.5. 11. Effect of pH on the decolourisation of Methylene blue (10 μM) on TiO_2 coated and uncoated tiles under sunlight. (◊) SL/TiO_2, pH 4; (■) SL/TiO_2, pH 7; (Δ) SL/TiO_2, pH 10; (x) SL, pH 4; (●) SL, pH 7; (○)SL, pH 10

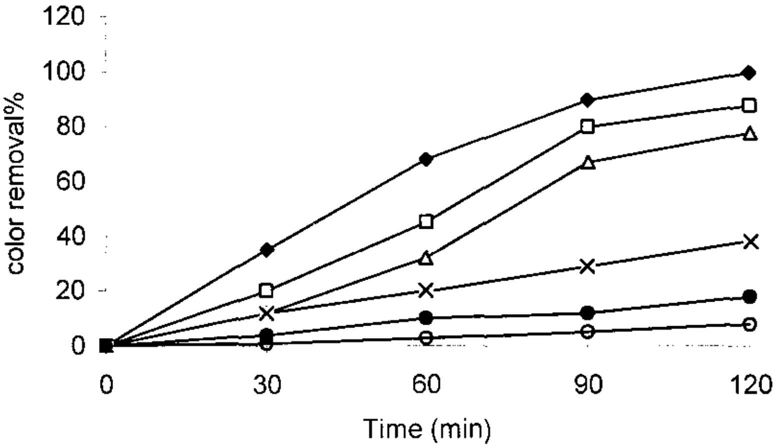


Fig 5.12. Effect of pH on the decolourisation of Rhodamine B (5 μM) on TiO_2 coated and uncoated tiles under sunlight. (♦) SL/TiO_2, pH 4; (□) SL/TiO_2, pH 7; (Δ) SL/TiO_2, pH 10; (x) SL, pH 4; (●) SL, pH 7; (○)SL, pH 10

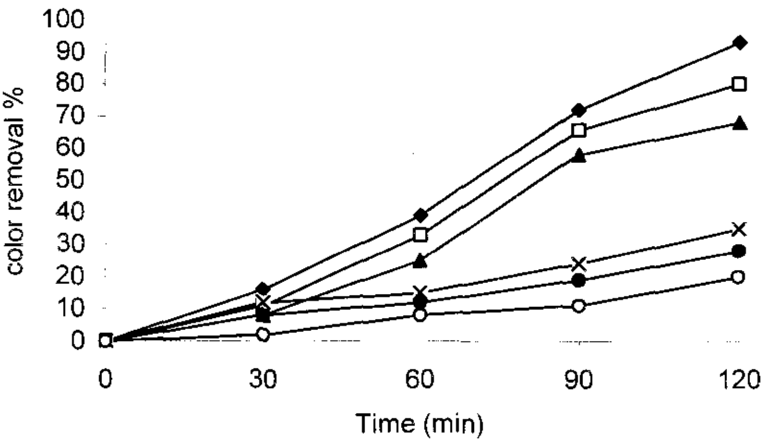


Fig 5.13. Effect of pH on the decolourisation of Rhodamine B (10 μM) on TiO_2 coated and uncoated tiles under sunlight.(♦) SL/TiO_2, pH 4; (□) SL/TiO_2, pH 7; (▲) SL/TiO_2, pH10; (x)SL, pH 4; (●) SL, pH 7; (○) SL, pH 10

5.3.2. Photocatalytic deactivation of E. coli on TiO_2 coated tiles.

The encouraging results for the removal of *E. coli* from water using TiO_2 immobilised on the interior of common PET bottles prompted us to examine the application of TiO_2 coated tile for the purpose. Figure 5.14 shows the results in the dark as well as in the light on uncoated and TiO_2 coated tiles. As seen in our earlier study, with TiO_2 suspensions, the inactivation proceeds in the absence of the catalyst also, in presence of light. As expected, the presence of the catalyst enhances the deactivation significantly. In the case of coated tiles, complete deactivation is achieved in less than 50 minutes while it takes almost twice that time in the case of uncoated ones. (See figure 5.14).

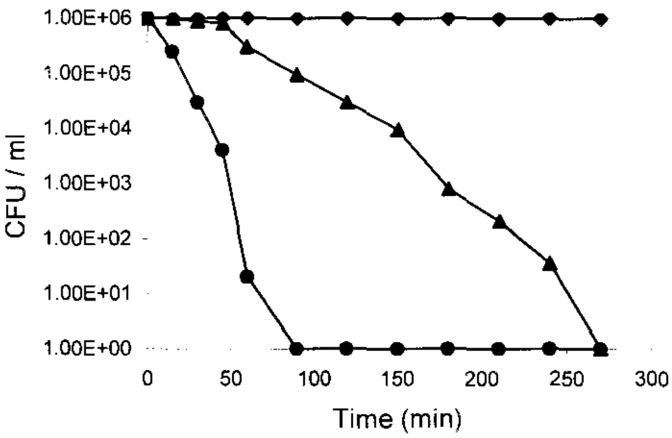


Fig.5.14. Solar inactivation of *E.coli* under different conditions. Volume of sample: 10 L; Initial concentration of E.coli: 10^6 CFU/ml. (♦) in dark; (•) on TiO_2 coated tiles; (▲) on uncoated tiles.

The killing mechanism(s) underlying the photocatalytic reaction is not yet fully understood. Most of researchers are of the view that the initial step is the cell wall damage which takes place in the first 10-15 minutes of irradiation followed by progressive damage of cytoplasmic membrane and intracellular components. This leads to direct intracellular attack. Some of the suggestions advanced by various researchers for the photocatalytic kill of *E.coli* are discussed in Chapter 4. However, much research needs to be done and more evidences gathered before conclusively establishing a mechanism for the process.

5.4. Conclusions

TiO_2 immobilised on tiles is an efficient tool for the removal of chemical and bacterial pollutants from water, without the inconvenience of filtration as in the case of suspensions. While artificial UV light is more efficient for the removal of most organic pollutants, natural sunlight is found to be more efficient for the decolourisation of dyes such as Methylene blue and Rhodamine B. Concentration of the dye and pH of the system have significant effect on the decolourisation while the intensity of light has only limited influence when medium or high intensity irradiation source is used. Thus TiO_2 coated ceramic tiles are found to be very effective against organic materials as well as bacteria. TiO_2 coated tiles can find great applications in swimming pools and water theme parks where chances of contamination is higher.

They can also be used in hospitals. health care facilities, in public and commercial facilities, schools, kitchens, baths, and floors to promote family hygiene and in food processing, pharmaceutics, microbiological laboratories and where ever there is a strong requirement for clean surfaces.

Design of better reactor systems, combined with immobilization of the catalyst will also be a viable practical approach for the large scale purification of water and wastewater from chemical and bacterial pollutants.

Chapter 6

SUMMARY AND CONCLUSIONS

The main objective of the current investigation was to identify suitable semiconductor oxide catalysts for the photocatalytic removal of chemical and bacterial pollutants from water using sunlight as the energy source. Three representative organic chemical pollutants, i.e. an insecticide (Phosphamidon), a petrochemical (Phenol) and two dyes (Methylene blue and Rhodamine B) and a typical bacterial pollutant, i.e. *Escherichia coli* were chosen for the study. The catalyst used was primarily TiO_2 in suspension or immobilised form. Some observations were also made using ZnO as the catalyst.

Salient findings of the study and the conclusions are as follows:

i) TiO_2 is a very efficient photocatalyst for the degradation and complete mineralisation of phosphamidon. ZnO also is efficient, though less compared to TiO_2. The rate of degradation is dependent on a number of factors including the concentration, catalyst loading, pH, presence of anions etc. H_2O_2 is formed in the reaction system and it undergoes simultaneous decomposition, leading to periodic increase and decrease in its concentration (oscillation). At the concentration in which they are formed in situ, intermediate anions do not have any influence on the rate of degradation. Based on the findings, it was concluded that surface mediated process is more important in photocatalytic degradation of chemical contaminants and accordingly a mechanism has been proposed.

ii) The study confirms that TiO_2 is very efficient for the photocatalytic degradation of phenol as well. The kinetics of the degradation follows different patterns on ZnO and TiO_2. The complex nature of the kinetics and the effect of pH on the reaction have been demonstrated and these might be the main reasons for the inconsistencies in the results reported by various researchers. Fe_2O_3 enhances the photocatalytic activity of TiO_2, possibly by the inter-particular electron transfer, though no such positive effect is shown by ZnO. Doping with Fe^{3+}, Co^{2+} and Cu^{2+} also enhances the photocatalytic activity of TiO_2. Based on the observations, which support the findings of some researchers while disagreeing with others, a mechanism is proposed for the mineralisation of phenol.

iii) TiO_2, in suspension as well as in immobilised form, is demonstrated to be an effective catalyst for the removal of bacterial pollutants such as *Escherichia coli* in water. The positive contribution of TiO_2 for the rapid photo-deactivation of the bacteria and inhibition of its re-emergence in the dark is demonstrated. Immobilisation of the catalyst on a common PET bottle, its successful application for the decontamination of water from bacterial pollutants and the use of sunlight as the source of illumination, as illustrated in this study, will be an important step towards the practical application of the technology in rural areas of developing countries.

iv) The immobilisation of TiO_2 is successfully tested on common ceramic tiles also and its efficiency for the photocatalytic decolourisation of dyes and deactivation of *Escherichia coli* is investigated. Natural sunlight, compared to artificial UV light, is more efficient for the decolourisation of dyes. Concentration of the dye and pH of the system have significant effect on the decolourisation while the intensity of light has only limited influence when medium or high intensity irradiation source is used.

v) In short, the study concludes that TiO_2, in suspension as well as in immobilised form, is effective for the photocatalytic removal of chemical and bacterial pollutants from water. The study also throws more light into the inconsistencies of the findings by various researchers and the possible reasons for the same. While proving the advantages of immobilisation of the catalyst, this investigation also points to the need for further innovations in reactor design and the technique of immobilisation itself, in order to enhance the possibility of practical application of the technology.

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APPENDIX

List of Publications and Papers Presented in Conferences, Based on the Results from the Current Study

1. Solar wastewater treatment using TiO_2 with reference to photocatalytic degradation of phenol in water, **Proc. of the National Conference on Titania** held at Trivandrum, Kerala, India (2002) pp. 167-172.

2. Photocatalytic Degradation of Phosphamidon on Semiconductor Oxides, **J Hazard. Mater.** 102 (2003) 217-229.

3. Disinfection of domestic wastewater using TiO2 photocatalyst, **Proc. Indian Environment Congress**, Trivandrum, India (2004) 196-200.

4. Photocatalytic degradation of pesticide contaminants in water, **Solar Energy Materials and Solar Cells**, 86 (2005) 309-348.

5. Inactivation of *Escherichia coli* in water using TiO_2 as photocatalyst, **Pollution Research,** 24 (2005) 97-101.

6. Photocatalytic Disinfection of Drinking Water using TiO_2 coated PET bottles **Proc. of the XVII Kerala Science Congress** held at Peechi, Kerala, India (2005) pp. 178-180.

7. Photocatalytic Removal of Chemical and Bacterial Pollutants in Water with TiO_2 immobilised on Ceramic Tiles, Paper presented at the **'International Conference on Science and Technology for Sustainable Development'** held at Changanassery, Kerala, India (2005).