CHAPTER 5
PHOTOSTABILITY EFFECT OF MESOPOROUS TiO$_2$ ON THE
PHOTODEGRADATION OF PYRETHROID INSECTICIDES

5.1 Introduction
Deltamethrin and fenvalerate are pyrethroid insecticides that kill insects on ingestion and dermal contact. They are used to control apple and pear suckers, plum fruit moth, caterpillars on brassicas, pea moth, aphids (apples, plums, hops), winter moth (apples and plums), codling and tortrix moths (apples). They also control numerous insect pests of field crops. Formulations include emulsifiable concentrates, wettable powders and flow-able formulations and granules. There are no known incompatibilities with other common insecticides and fungicides. Both fenvalerate and deltamethrin are synthetic insecticides based structurally on natural pyrethrins, which rapidly paralyze the insect nervous system giving a quick knockdown effect. These insecticides were reported to show the highest selectivity towards tsetse fly but degraded relatively quickly with a half-life of 3-4 weeks. Torr [1] found that both fenvalerate and deltamethrin were susceptible to photolysis and suggested the use of photo stabilizers in the formulations. Although the synthetic pyrethroids are much more photo stable than the natural pyrethrins, they are still sensitive to sunlight. Ultra-violet light absorbers such as 2, 4 dihydroxybenzophenone have been added to some formulations in an attempt to prevent this breakdown and prolong insecticide persistence on the traps or targets. Some early work on deltamethrin carried out in Zimbabwe by Holloway [2] compared different 0.1% formulations on targets. Results did not indicate a very big advantage of the suspension concentrate (S.C.) formulation with UV absorbers over the standard S.C., or even over emulcifiable concentrates used in agriculture or the S.C. used in dipping.

However trials undertaken in the Agrochemicals Unit of the International Atomic Energy Agency (IAEA), Vienna, indicated decreased photolytic decomposition of pyrethroid insecticide on cloth screens depending on the type and amount of UV absorber used. There is some suggestion that the UV absorber added to the pesticide formulation in recent commercial use such as 2, 4 dihydroxybenzophenone may not be
as suitable in the rainy season, as it is water soluble and can be washed out. These UV absorbers may also be very expensive and it was not clear whether the extra cost involved is justified over the extra persistence achieved in the field. Beside this, there is increasing interest in using photo stabilizers like 2, 4 dihydroxybenzophenone, zinc oxide etc. which can enhance the life time of pyrethroid insecticides. As a result, while farmers are looking for effective long life insecticides, the producers are now looking forward for cost effective photostabilizers which can enhance the life of insecticides.

Titanium dioxide (TiO$_2$) is a versatile semiconductor oxide from the view point of its potential applications such as photocatalyst [3, 4], solar cell [5-6], gas sensor [7], non linear optics material [8] etc. It is expected to provide solution to many environmental issues like waste water treatment, air pollution and decomposition of toxic organic pollutants. Among the currently available semiconductor oxides, TiO$_2$ nanoparticles have been proved to be excellent photocatalyst, and identified as an effective, photo stable, reusable, inexpensive, non-toxic and easily available material [9,10]. The photoactivity of titania has been influenced by several structural parameters like phase composition, crystalline quality, morphology, particle size, size distribution, porosity and band gap. In addition to these, the presence of high surface area of the nanoparticles is a vital parameter for effective photo-absorption activity. Hence, an in-depth understanding of the morphology and crystallization of nano sized TiO$_2$ powders which are prepared by different techniques and processed under varying conditions is helpful to establish an effective control on the processes of nucleation and growth of the nanoparticle. With the reduced particle size it is possible to achieve enhancement in the structural, optical and surface properties of the material. There are eight polymorph of titania [11]. Among these, only anatase and rutile are employed for practical applications, because they can be easily synthesized. Again it has been reported that anatase phase has more photocatalytic activity than rutile. Therefore, it is still a challenge to synthesize mesoporous TiO$_2$ containing the anatase phase [12]. In this study, we report the direct synthesis of mesoporous TiO$_2$ [13-21] with anatase phase and its preventive effect on the photolytic decomposition of pyrethroid insecticides deltamethrin and fenvalerate by UV light. The rutile phase of commercial titania was found surprisingly less effective in stabilizing the pesticides compared to anatase phase of titania synthesized.
5.2. Experimental:

5.2.1 Preparation of photocatalyst TiO$_2$:

7.2 gm of K$_2$TiF$_6$ was dissolved in 10 ml distilled water. The solution was then added into cetyltrimethylammoniumbromide solution under stirring. The molar ratio of K$_2$TiF$_6$: CTAB: H$_2$O was 1:0.12:100. After stirring for 30min, the resulting mixture was aged at 300 K for 21 hrs and then transferred into teflonlined stainless steel autoclave at 373K for hydrothermal treatment for 75 hrs. The autoclave was cooled, and the product was separated by centrifugation, washed with water and ethanol, and then dried at 393K overnight. To remove organic materials, ion-exchanged treatment was performed on the as-synthesized powders by stirring the solids in a NaCl solution of water and ethanol (1:1) at 300 K for 5 hrs. The resulting solid were washed with water and ethanol and then dried at 393K overnight. The as-synthesized sample was divided into two parts. One part was calcined in air at 873 K for 6 hrs with a heating rate of 275K per minute and the other part is labeled as-synthesized sample. It was found that no anatase to rutile conversion took place at that calcination temperature.

5.2.2 Photolysis:

For experiments under UV light, the desired deltamethrin concentrations were prepared in double distilled water. An immersion well photochemical reactor (HEBER) made of Pyrex glass was used in this study. For irradiation experiment 1000ml of the desired solution was filled into the reactor and required amount of TiO$_2$ was added. The suspension was stirred for at least 15 minute in the dark to allow equilibration of the system. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with air throughout each experiment. Irradiations were carried out using a 25W, 254nm medium pressure mercury lamp. IR radiation and short wavelength UV radiation were eliminated by a water circulating Pyrex glass jacket. Samples (10ml) were collected before and at regular intervals during the irradiation for analysis. The degradation of deltamethrin and fenvalerate were monitored by measuring the absorbance on a Shimadzu Spectrophotometer at 210 nm and at 265 nm respectively.
5.3 Results and discussion

The X-ray diffractogram (figure 5.1) shows characteristic peak for anatase at 25.14° (101) 38.02° (004), 48.20° (200) 2θ values. The increase of intensity of the calcined TiO\textsubscript{2} in comparison to as-synthesized TiO\textsubscript{2} suggests increase of crystalinity on calcinations. The d-values for the 1st order peak of all samples were calculated from the 2θ values of X-ray diffractogram.

\[ \text{The values were } 3.39 \text{ Å (as-synthesized) and } 3.54 \text{ Å (calcined).}\]

\[ \text{The particle size of TiO}_2 \text{ as calculated from width of X-ray peak was16 nm. The SEM image (figure 5.2) shows the morphology of the TiO}_2 \text{ with needle like crystals.}\]
Figure 5.2- SEM images of mesoporous TiO$_2$.

Figure 5.3- TGA of titania synthesized.
The thermal behavior of titania synthesized was investigated with TG at temperatures ranging from room temperature to 973K (figure 5.3). The first weight loss at 373-623 K for P1 is the dehydration and loss of residual solvent from the surfaces of the powdered materials. As thermal treatment increases, the remaining water, strongly bonded inside the pores of the particles, can be eliminated thus giving the second weight loss effect at 423K for P1. In fact, according to findings by Bickley et. al. [23] the loss of adsorbed molecular water in the range 373-573 K appears to be related to the development of porosity. The pore size distributions and N\textsubscript{2} adsorption-desorption isotherms of calcined titania is shown in figure 5.4. The isotherm is type IV, which is characteristic of mesoporous materials. The BET surface area of titania synthesized is 56 m\textsuperscript{2}/gm.

![Figure 5.4- Surface area of mesoporous titania synthesized.](image)

The infrared spectrum of undoped TiO\textsubscript{2} calcined at 873K is shown in figure 5.5 and it shows a broad band in the region from 3600-2600 cm\textsuperscript{-1} (OH stretching mode vibration). For titania synthesized the peak at 3424 cm\textsuperscript{-1} is assigned to stretching vibration mode of the OH group. This was accompanied by a small band at 1625-1629 cm\textsuperscript{-1} (H-O-H bending mode vibration), indicating that this sample contains heterogeneously distributed loosely adsorbed water molecules.
Figure 5.5- FTIR of titania synthesized.

DRS spectra of titania synthesized shows that the fundamental absorption edge of TiO$_2$ appeared in the UV region at 389 nm. The band gap calculated is 3.19 eV (figure 5.6).

Figure 5.6 DRS of titania.
5.4 Photolysis of deltamethrin in the presence of TiO$_2$:

Figure 5.7 shows the change in concentration of an aqueous solution of deltamethrin ($10^{-5}$M) in the absence and presence of mesoporous TiO$_2$ (0.213 g) under air flow, irradiated by a 25 W medium pressure mercury lamp.

![Graph showing the variation of absorption intensity as a function of irradiation time for an aqueous solution of deltamethrin.](image)

**Figure 5.7- Variation of absorption intensity as a function of irradiation time for an aqueous solution of deltamethrin.**

It has been observed that in the absence of TiO$_2$ 98% of the pesticide degrade on 10 minute of irradiation, whereas no degradation takes place, when the irradiation was carried out in presence of mesoporous TiO$_2$. Figure 5.8 shows the change in absorbance of deltamethrin in presence of titania.
Figure 5.8 Change of concentration of deltamethrin with irradiation time.

5.5 Photolysis of fenvalerate in the presence of TiO$_2$:

Figure 5.9 shows the change in concentration of an aqueous solution of fenvalerate (10$^{-5}$ M) in absence and presence of the mesoporous TiO$_2$, (0.213 g) under air flow, irradiated by a 25 W medium pressure mercury UV lamp. It has been observed that 98% degradation of pesticide takes place after 10 minute of irradiation in absence of TiO$_2$, whereas no degradation takes place, when the irradiation was carried out in presence of mesoporous TiO$_2$. 
5.6 Comparison of different photocatalyst:

It has been demonstrated that degradation by photocatalyst can be more efficient than by other wet oxidation method. To determine that, degradation of deltamethrin and fenvalerate were carried out with the catalyst we prepared and with that obtained from
market. Figure 5.10 shows that for deltamethrin, mesoporous titania synthesized was more efficient than commercial titania.

5.7 Effect of catalyst concentration:
The influence of catalyst concentration on the degradation of deltamethrin and fenvalerate were investigated by varying catalyst from 0.1 to 0.213 gm L\(^{-1}\). Figure 5.11 shows the variation of the degradation rate of fenvalerate as a function of catalyst concentration.

5.8 Conclusion:
Deltamethrin and fenvalerate applied to insect control, degrades rapidly under UV light. Compounds like TiO\(_2\) which absorb UV light when used in combination with these pesticides extended the life of these pyrethroid pesticides. The degree of protection increases with the decrease of particle size and increase of amount of the UV absorber up to an optimum concentration. Electron and holes which are created when uv light falls on titania does lead to decomposition of these two pesticides, rather hinders uv light to decompose them by utilizing the energy. Thus by incorporation of mesoporous TiO\(_2\) in formulations containing synthetic pyrethroid insecticide, the residual activity of these insecticides can be considerably extended.

![Graph showing the effect of catalyst concentration on stability of pesticide.](image-url)
References:

SUMMARY

S-doped TiO$_2$, P- doped TiO$_2$, N- doped TiO$_2$, Zr- doped, Fe-doped and Co-doped TiO$_2$ were synthesized by sol-gel and hydrothermal techniques. The nanomaterials were characterized by using electron microscopy, FTIR, TG, XRD, N$_2$ physisorption, UV-Vis, XPS etc. The XRD, SEM, TEM, XPS, IR, TGA, DRS and BET Surface area of the samples reveal formation of the desired framework and the d-values in XRD are in good agreement with those reported for the same framework. The main conclusions of the present study are given in the following sections

(i) A new approach was developed to prepare sulfur doped titania by treating the TiO$_2$ precursor with thiophene and oxalic acid under very simple condition. The systematic investigation on the operating variables of S-doped samples revealed that the most important variable in the synthesis of S-doped titania is the oxalic acid/metal salt ratio. The S-doped TiO$_2$ nanostructure materials have a high surface area, smaller crystallite size, and greater thermal stability, which are highly desirable properties as catalysts, support materials, semiconductors, and electrodes in dye-sensitized solar cells (DSSC). During photodegradation of 2,7-dichlorofluoresceine under UV light irradiation, such a catalyst exhibited higher activity and enhanced quantum efficiency than the corresponding undoped titania or commercial titania. The activity is depended on both the structural and textural characteristics of titania, evolved as a result of doping.

(ii) A nanocrystalline phosphate doped TiO$_2$ has been synthesized by a simple hydrothermal method involving titanium isopropoxide, phosphoric acid and block polymer. The incorporation of phosphate ions stabilized the titania in the anatase phase and Lewis acid sites were developed. Phosphate modification caused a mark change in the TiO$_2$ particle size as well as surface area thereby increasing photocatalytic activity. Phosphate is not adsorbed simply in the surface of titania but exist as TiPO$_4$ and surrounds anatase crystallites in such a way so that no crystal growth occurs at high temperatures due to quantum growth effect. Since no XRD peak of TiPO$_4$ is observed, hence we conclude that it is amorphous in nature. Photocatalytic activity of phosphated titania is much more than that of undoped titania due to higher surface area.
(iii) Triethanolamine, diisopropylamine and triethylamine were separately used as dopant to prepare N-doped samples by base catalysed sol-gel process. The photocatalytic activity of all the synthesized nanomaterials was compared by monitoring the photodegradation of fluorescein dye under UV-light. It was found that triethanolamine doped TiO$_2$ (TOL) possessed highest photocatalytic activity. N-doped titania played a role in separating photogenerated $e^-h^+$, contributing to high photocatalytic activity. Photocatalytic activity of N-doped TiO$_2$ samples were attributed to the formation of SETOV. This might account for the different photocatalytic performance of “TOL, ET and DIS”, N-doped TiO$_2$ samples. In view of the exclusive characteristics of triethanolamine, it should be pronounced that triethanolamine is one of the most promising precursors for designing N-doped photocatalyst.

(iv) A series of Zr-doped titania photocatalysts have been prepared by using acid catalysed sol-gel process. The zirconium doping showed significant effect on the texture structure, band gap and thermal stability. The photoactivity of the undoped and doped titania obtained by the degradation experiments of quinalphos solution established that 0.5% Zr doped TiO$_2$ annealed at 773 K is the better catalyst. The activity was found to be superior to that of commercial TiO$_2$ sample. The activity is depended on both the structural and textural characteristics of titania, evolved as a result of doping. It was determined that the optimum amount of Zr-doping has number of advantages over undoped as well as commercial titania but excess dopant reduces the efficiencies of catalysts. The formed modified TiO$_2$ nanostructured materials had smaller band gap, smaller crystallite size, adequate surface area and greater thermal stability, which are all desirable features for catalysts, support materials, semiconductors, and electrodes in dye-sensitized solar cells (DSSC).

(v) Successful synthesis of Fe doped TiO$_2$ nanomaterials by the simple sol-gel process with K$_2$TiF$_6$ demonstrated that this is a promising technique for synthesizing cation doped TiO$_2$ nanostructures. Fe doping was favorable for organizing a mesoporous structure and maintaining the pore structure at higher temperatures. It suggests that proper Fe doping to the framework may become an effective way to improve the properties of mesoporous TiO$_2$ materials. A small amount of Fe
doping showed better performance; hence, these materials may be used as a photocatalyst for the degradation of organic compounds under solar irradiation to prevent environmental pollution.

(vi) An aqueous sol–gel method was used for the preparation of Cobalt doped nano-
TiO$_2$. The prepared materials were analyzed using various physico-chemical characterization techniques. XRD analyses revealed the presence of mixed anatase and brookite phase of titania without any evidence for the rutile phase. Doping of cobalt in nano-TiO$_2$ lead to a decrease in particle size, an increase in surface area and low band gap value. The average particle size of the prepared samples ranged from 8–14 nm. TEM analyses revealed the spherical morphology of the particles without any aggregation of metal species. The calcined cobalt doped titania was found to be room temperature ferromagnetic while the as synthesized cobalt doped titania was diamagnetic. The photoactivity of the undoped and doped titania obtained by the degradation experiments of Sunset Yellow solution established that as synthesized cobalt doped TiO$_2$ was the better catalyst. The activity was found to be superior to that of commercial TiO$_2$ sample. The activity was depended on both the structural and textural characteristics of titania, evolved as a result of doping.

(vii) Deltamethrin and fenvalerate applied to insect control, degrades rapidly under UV light. Compounds like TiO$_2$ which absorb UV light when used in combination with these pesticides extended the life of these pyrethroid pesticides. The degree of protection increased with the decrease of particle size and increase of amount of the UV absorber up to an optimum concentration. Electron and holes which are created when uv light falls on titania does lead to decomposition of these two pesticides, rather hinders uv light to decompose them by utilizing the energy. Thus by incorporation of mesoporous TiO$_2$ in formulations containing synthetic pyrethroid insecticide, the residual activity of these insecticides can be considerably extended.
FUTURE WORK:

- Preparation of Metal Oxide and Chalcogenite/TiO$_2$ nanocomposite and its characterization.
- To check the catalytic activity of the prepared photocatalyst in the decomposition of pesticides under visible light.
PAPER PRESENTED IN SEMINAR


PAPER PUBLISHED

1. Goswami, P.; Ganguli, J. N.; Evaluating the potential of a new titania precursor, Materials Research Bulletin, accepted for publication. [dx.doi.org/10.1016/j.materresbul.2012.03.037].


PAPERS TO BE COMMUNICATED

1. Goswami, P.; Ganguli, J. N.; Tuning the band gap of Zr-doped titania for effective degradation of pesticide quinalphos,

2. Goswami, P.; Ganguli, J. N.; Synthesis, Characterization and photocatalytic reactions of Sulfated Titania

3. Goswami, P.; Ganguli, J. N.; Effect of Nitrogen Precursor on Microstructures and UV Light Photo activity of N-Doped TiO\textsubscript{2} Powders

4. Goswami, P.; Ganguli, J. N.; Photophysical Properties of Nanosized Cobalt-Doped TiO\textsubscript{2} Photocatalyst Working under UV Light

5. Goswami, P.; Ganguli, J. N.; Photostability Effect of Mesoporous TiO\textsubscript{2} on the Photodegradation of Pyrethroid Insecticides