

II. Nanocrystalline photocatalytic treatment for degradation of dichlorvos by using nano TiO₂

2.1 Introduction

The demand of organophosphate pesticides is increased in industrialized countries. Organophosphorous pesticides are derived from phosphoric, phosphonic, phosphorothioic or phosphorothioic acid. They exert their acute effect by inhibiting the acetylcholinesterase (AChE) enzyme in insect, fish, birds and mammals, but sometimes also have a direct toxic effect [1]. Dichlorvos is a commonly used pesticide in India. Dichlorvos (2, 2-dichlorovinyl dimethyl phosphate) (figure 2.1) is a chlorinated organophosphate compound commonly known as DDVP, was discovered in the 1950s and first marketed in 1960 [2]. Dichlorvos is an organophosphorous insecticide. DDVP is used to control insects in food storage areas, green houses, workplaces and homes and also being used to control parasites on pets [3, 4]. Compare to other pesticides, dichlorvos is preferred because of its low cost and high range of bioactivity [5].

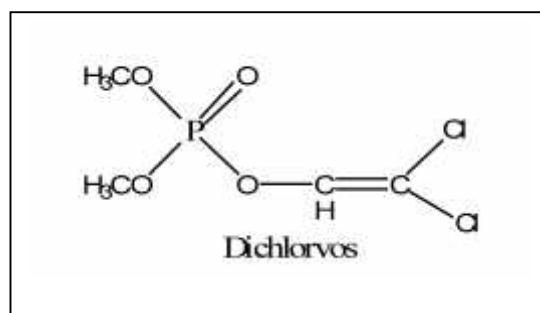


Figure 2.1 Structure of Dichlorvos

Dichlorvos shows adverse effect on human being if inhaled, swallowed or absorbed through skin and eyes. DDVP is a good inhibitor of acetyl cholinesterase enzyme, which results in headache, nausea, vomiting, excessive sweating, and blurred vision, tightness in chest and muscle tremors at high levels on prolong exposure or large doses of dichlorvos. Environmental exposures to dichlorvos in early age may lead to increased breast cancer risk in adulthood. Laboratory research has proved increased rates of mammary tumors in rodents [2]. So it is classified in Heterogeneous catalysis for Degradation of Pesticide and Organic Transformations

the list of Group B 2 by United State Environment Protection Agencies (USEPA), as probable human carcinogen [5, 6]. Binukumar et al. have examined the effect of chronic exposure of dichlorvos on rats. Dichlorvos exposed animals showed nigrostriatal neurodegeneration and significant behavioral impairments [7]. Catalepsy was also observed in such animals whose symptoms are the same as those of Parkinson's disease in humans. The US EPA had first considered a ban on dichlorvos in 1981 but later granted supplemental registration in 2009. Due to all these adverse effects it becomes imperative to develop efficient treatment schemes for possible complete removal of dichlorvos.

Chen Shifu et.al. reported photocatalytic degradation of DDVP using TiO_2 thin films. The final degraded product is PO_4^{3-} which formed within a short time under illumination with a medium pressure mercury lamp of 375 W. The various parameters such as the amount of TiO_2 , initial concentration of organophosphorous DDVP, initial pH, amount of air flow, concentrations of H_2O_2 and Fe^{3+} on the photocatalytic degradation are studied [8]. N. Balkaya reported that DDVP can be efficiently removed from the water within 60 min. 1000 mg of TiO_2 requires for 35 mg per liter pesticide solution. Solar photocatalytic degradation also gives good results [9].

Inez Hua et. al. reported the sonochemical degradation of dichlorvos in a batch reactor. Dichlorvos was irradiated with 500 kHz ultrasound at input powers ranging from 86 to 161 W. Acoustic power and purge gas are two factors which greatly affect sonochemical degradation efficiency. The major degradation products are determined and quantified by total organic carbon and ion chromatographic analyses. A pathway for dichlorvos decomposition is proposed which is based on formation rates of the various intermediates and products and the rate of decrease of the total organic carbon in the system [10]. S.A. Naman et. al. reported the study of photodegradation of DDVP by using different photocatalyst such as TiO_2 , ZnO , and $\text{V}_x\text{S}_y/\text{TiO}_2$. The effect of various parameters such as sensitizers, concentration, temperature, different light sources and semiconductors on this photo-oxidation

reaction was investigated. Better photodegradation of DDVP was observed in TiO_2 /sensitizer system under solar exposure [11].

K. Fytianos and co-workers studied the photocatalytic degradation of dichlorvos by using two different photocatalysts such as TiO_2 and ZnO . Disappearance of DDVP was achieved in 20 min when illuminated with TiO_2 and in 120 min when illuminated with ZnO . The degradation follows first-order kinetics according to the Langmuir–Hinshelwood model. The effect of temperature and pH on initial rate of the reaction was also investigated. The addition of an oxidant H_2O_2 or $\text{K}_2\text{S}_2\text{O}_8$ with TiO_2 suspensions leads to an increase in the rate of photooxidation. On the contrary, the addition of hydrogen peroxide in ZnO suspensions caused a decrease in the reaction rate. TiO_2 was proved to be effective in mineralizing dichlorvos [12]. M. Muneer et. al. reported the photocatalysed degradation of dichlorvos and phosphamidon in aqueous suspensions of titanium dioxide. Degussa P 25 was used for the degradation process. The photocatalyst Degussa P25 was found to be more efficient as compared with other TiO_2 powders [13].

I. Konstantinou and co-workers had studied the identification of the intermediates that are formed during photocatalytic treatment of DDVP. Intermediate products were identified by means of solid-phase extraction (SPE) coupled to gas chromatography–mass spectroscopy techniques (GC–MS). Three possible by-products were identified for dichlorvos. A proposed degradation pathway for each insecticide was presented, involving mainly oxidation and dealkylation reactions [14]. Petruta Oancea and co-worker reported the photocatalytic degradation of the DDVP in suspended TiO_2 under solar irradiation. The photocatalytic reaction followed pseudo-first-order kinetic with a characteristic half-life time [15].

Mohamad Sleiman et. al. reported degradation of DDVP in gas phase by using TiO_2 . The analysis of reaction products was done by means of various analytical techniques such as Fourier transform infrared spectroscopy, automated

thermal desorption technique coupled to gas chromatography–mass spectrometry instrument, gas chromatography equipped with a pulse discharge helium photoionization detector, and ion chromatography [16]. Ligy Philip and co-worker used nitrogen doped TiO₂ for degradation of dichlorvos under visible and solar radiation. Nitrogen doped TiO₂ showed higher photocatalytic activity under solar radiation compared to UV and visible light irradiation [17].

T. Siva Rao and co-worker used the Mg doped TiO₂ for degradation of DDVP. Different concentration of Mg was doped on the TiO₂. The doped and undoped samples were synthesized by sol-gel method. The effect of dopant concentration, pH of solution, dosage of catalysts, and initial pesticide concentration has been studied. [18] Parag R. Gogate and co-worker reported the degradation of DDVP in aqueous solution, using hydrodynamic cavitation reactor. The effect of important operating parameters such as inlet pressure, temperature and pH on the extent of degradation had been investigated [19].

Table 2.1 gives the summary of the reported methods for the degradation of DDVP by using various photocatalyst under given conditions.

Table 2.1 Degradation of DDVP under various conditions

Sr. No.	Catalyst	Treatment	Reference
1	TiO ₂ thin film	UV Irradiation + Air purging 375 W medium pressure mercury lamp	8
2	TiO ₂ and Mixed photocatalyst	UV Irradiation + Oxygen purging 150 W medium pressure mercury lamp	11

3	TiO ₂	UV Irradiation + initial pH 6.5 125 W High pressure mercury lamp	12
4	ZnO	UV Irradiation + initial pH 7.2 125 W High pressure mercury lamp	12
5	TiO ₂	UV Irradiation + Oxygen purging 125 W medium pressure mercury lamp	13
6	Degussa P 25	UV Irradiation 125 W High pressure mercury lamp	14
7	TiO ₂	UV Irradiation 228 W medium pressure mercury lamp	15
8	TiO ₂	Solar Irradiation	15

All the above reported methods were carried out with air purging or oxygen purging along with the photocatalyst and UV irradiation. The UV source are used in above said process were 125 – 375 W medium or high pressure mercury lamps.

In this work, we have prepared TiO₂ nanoparticles and explored the photocatalytic activity of TiO₂ for degradation of DDVP by using 16 W low pressure mercury lamp (max = 254 nm) without any air or oxygen purging. We had studied the photo-catalytic degradation of DDVP, different operational parameters such as effect of catalyst, effect of initial concentration of DDVP, effect of H₂O₂ concentration and effect of pH on degradation.

2.2 Experimental

2.2.1 Materials

DDVP was purchased from Sabero organics (98% technical), Gujarat, India. Titanium butoxide was purchased from M/S S.D. Fine Chemical, Mumbai, India. All other reagents used were of analytical grade and were used without any further purification.

2.2.2 Methods

2.2.2.1 Synthesis of nano TiO₂

10 mL of titanium butoxide was dissolved in 100 mL of ethanol. The mixture of titanium butoxide and ethanol was dropwise added in 1000 mL of water under ultrasonication with constant stirring. The white turbid solution of Ti(OH)₄ is obtained which was passed through the spray drier. The inlet and outlet temperature of spray drier was set at 120 °C and 80 °C respectively. The prepared dry powder was calcined at 500 °C for 3 hrs to get TiO₂ powder.

2.2.2.2 Preparation of DDVP solution

Stock solutions of DDVP were prepared by dissolving 500 mg of DDVP in 1000 mL of distilled water. It gives 500 ppm solution of DDVP. Various concentrations for degradation study were prepared from the stock solutions.

2.2.2.3 Photodegradation experiment

Photodegradation experiments were carried out in a cylindrical reactor (**Figure 2.2**). The reactor was a simple cylindrical tube like a measuring cylinder with outlet provided at the top to withdraw samples at specific time intervals without disturbing the reaction system. The cylinder was surrounded by a cooling jacket to maintain the reaction temperature constant during reaction, as the heat is generated because of irradiation. Reaction mixture was stirred magnetically using a Teflon coated stirrer magnet. The radiation sources used were a low pressure mercury vapor lamp (Philips, UV-C, 16 W) emitting ultra violet radiation. After

specific time interval samples were with the help of suction bulb from the sample outlet and further analyzed.

Experiments were carried out with 300 mL of the pesticide solution of desired concentration ($C_0 = 20 \text{ mg/L}$) prepared in the double distilled water. A known amount of nano TiO_2 particles was added in solution. Irradiation was carried out by using a 16 W low pressure mercury lamp (Philips UV-C). 1 mL of sample solution was collected before and at regular intervals for analysis during irradiation. Catalyst was removed by centrifugation.

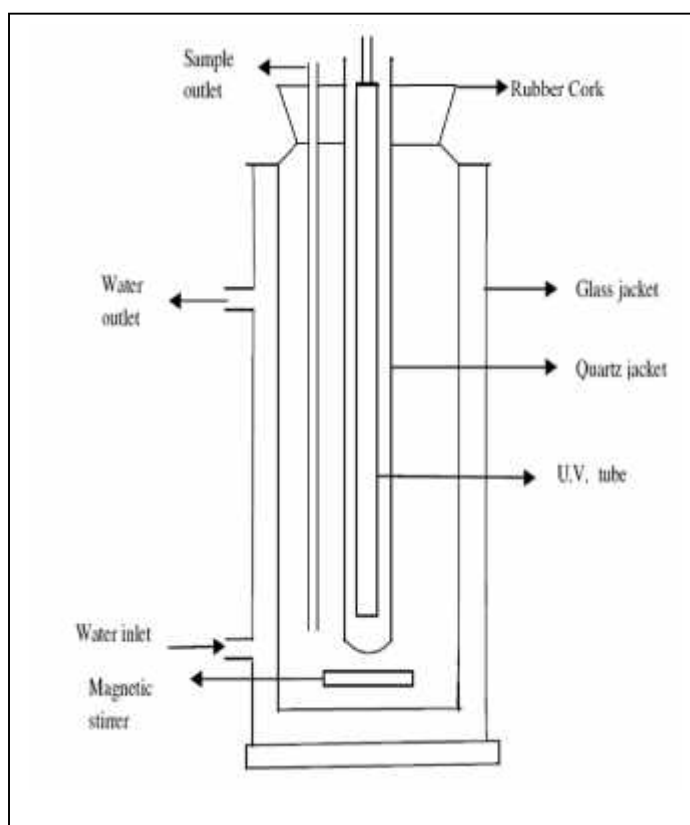


Figure 2.2 Photoreactor

2.2.2.4 Analysis

The degradation of pesticide derivative was monitored by measuring the absorbance on a Jasco UV-VIS spectrophotometer V 530 model. PO_4^{3-} is the stable degraded product of the DDVP. The rate of formation of PO_4^{3-} indicates the rate of degradation of DDVP. The concentration of PO_4^{3-} was determined by calorimetrically using molybdenum blue method [20]. The formed phosphomolybdic acid solution showed maximum absorbance at 820-830 nm. The % degradation of DDVP was calculated from

$$\% \text{ degradation} = P_t/P_o \times 100$$

Where P_t is the amount of phosphate ion in solution after irradiation time t and P_o is the total amount of organophosphate ion in solution before irradiation.

2.2.2.5 Kinetic Measurement

In photodegradation kinetic measurements, 300 mL of the pesticide solution of various concentrations were prepared in the double distilled water. A known amount of nano TiO_2 particles was added in solution. Irradiation was carried out by using a 16 W low pressure mercury lamp. 1 mL of sample solution was collected before and at regular intervals for analysis during irradiation. Catalyst was separated by centrifugation. The concentration of PO_4^{3-} was determined by calorimetrically using molybdenum blue method. The degradation of DDVP was measured by increase in concentration of PO_4^{3-} . The plot of $\ln (C_o/C_t)$ Vs t was plotted to determine initial rate of the reaction.

2.2.3 Characterization of Nano TiO₂

2.2.3.1 X-Ray Diffraction

The X-ray diffractograms were obtained (XRD, MINI FLEX RIGAKU MODEL) with Cu K- radiation (1.5418 Å) with scanning rate of 2° per min from 2° to 80°. XRD patterns of TiO₂ were shown in fig. 2.3 which shows anatase phase formation after heat treatment at 500°C for 3 hrs. The TiO₂ nanoparticles show peak at 2θ value about 24.56 which is the characteristic of anatase TiO₂ (JCPDS no. 84-1286). The average crystalline size of TiO₂ was determined according to Scherrer equation using full width at half maximum (FWHM). The crystalline size calculated from XRD pattern from equation was 23 nm.

$$D = 0.9 \lambda / \cos$$

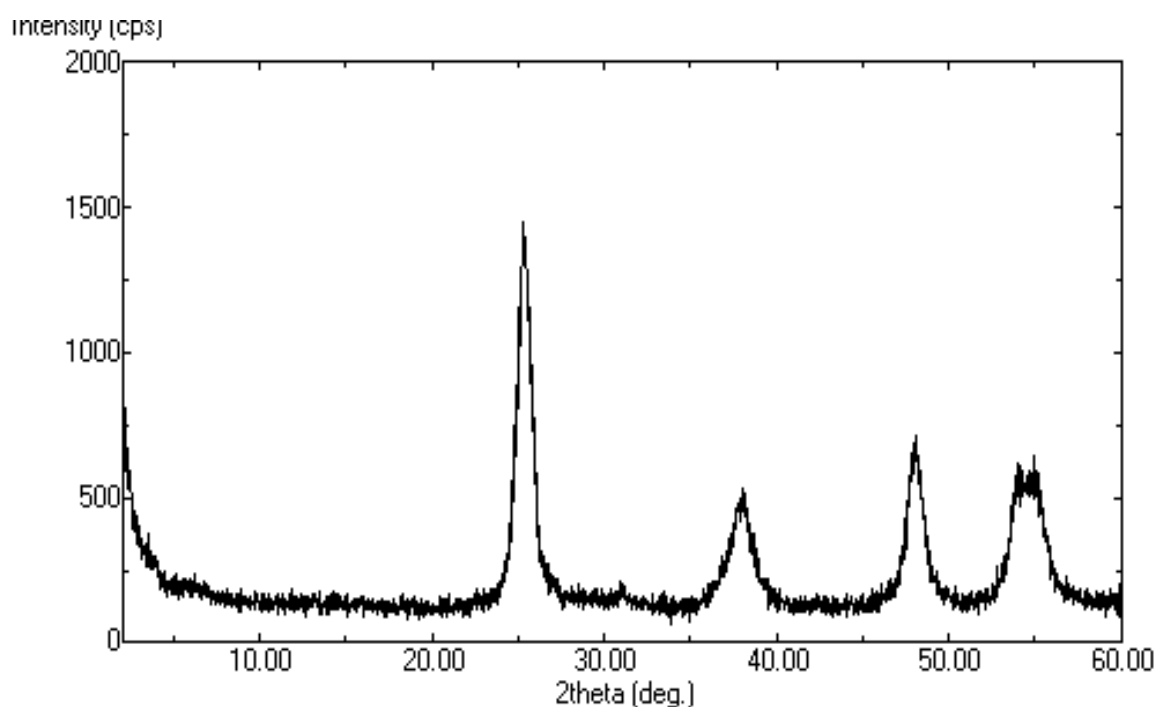


Figure 2.3 XRD of Nano TiO₂

2.2.3.2 Transmission Electron Microscope

Particle size and external morphology of the prepared particles were observed on a Transmission Electron Microscope (TEM) (Philips CM 200, operating at 20 – 200 kV accelerating voltage and having resolution upto 2.4 Å). TEM images of the nano TiO₂ particles are shown in fig.2.4 Spherical shaped uniform sized particles were observed. In addition, the crystalline size observed is 10-20 nm, which is in good agreement with the XRD data.

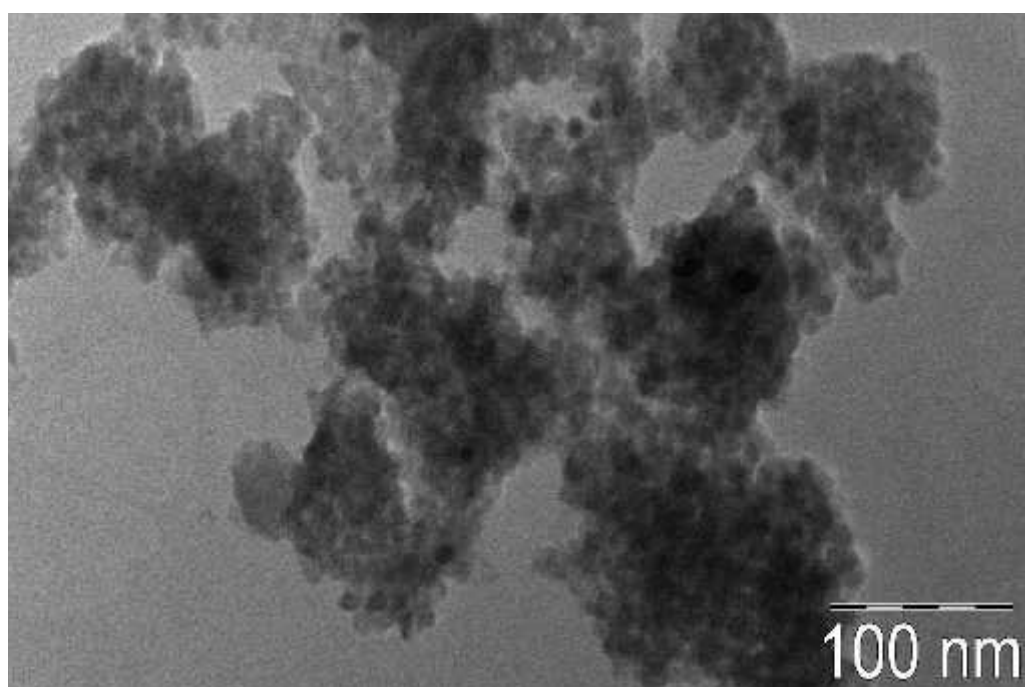


Figure 2.4 TEM image of Nano TiO₂

2. 2.3.3 Scanning Electron Microscope and EDAX

Surface morphology of the nano TiO_2 was done by SEM and elemental analysis was done by EDAX (Energy Dispersive X-Ray Spectroscopy) analysis. Field Emission Gun-Scanning Electron Microscopes (FEG-SEM) JSM-7600F model was used for analysis, operating at accelerating voltage 0.1 to 30 kV, Magnification $\times 25$ to 1,000,000 and having resolution 1.0 nm - 1.5 nm (15kV). The shape of TiO_2 particles was obtained by SEM and depicted in the fig. 2.5 shows agglomeration of TiO_2 particles. The resultant EDAX image of TiO_2 (fig. 2.5) shows presence of only titanium and oxygen elements in prepared TiO_2 .

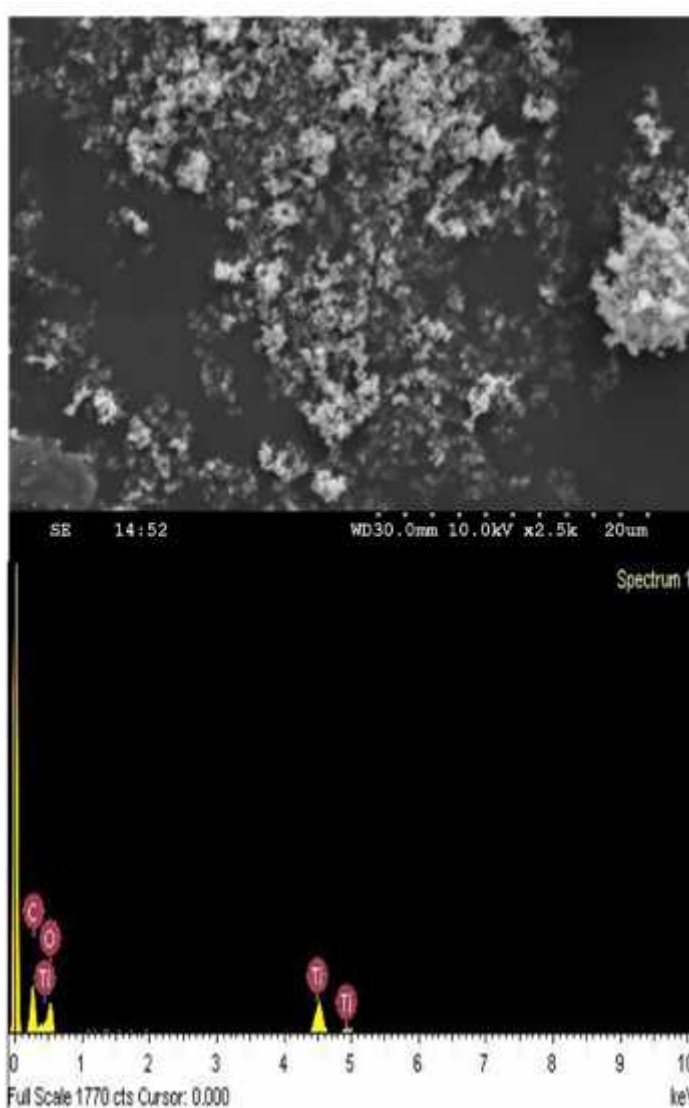


Fig. 2.5 SEM and EDAX spectra of nano TiO_2

2.2.3.4 FT-IR Analysis

To analyze the chemical structure, the FT-IR spectrum was recorded by using the Fourier Transform Infra-Red Spectroscopy (FT-IR) in the range of 400-4000 cm^{-1} frequency range on a Perkin-Elmer Spectrophotometer (100 Spectrochem Series). The IR spectra for the TiO_2 in the range of 400-4000 cm^{-1} is shown in fig. 2.6. No organic species. The stretching vibration of Ti-OH group was observed as broad absorption peak appearing near 3300 cm^{-1} . At 1620 cm^{-1} , a band for water also appears. It is reported that the decrease in the OH band intensities bonded to TiO_2 may be ascribed to the OH population due to dehydroxylation of the surface TiO_2 [21].

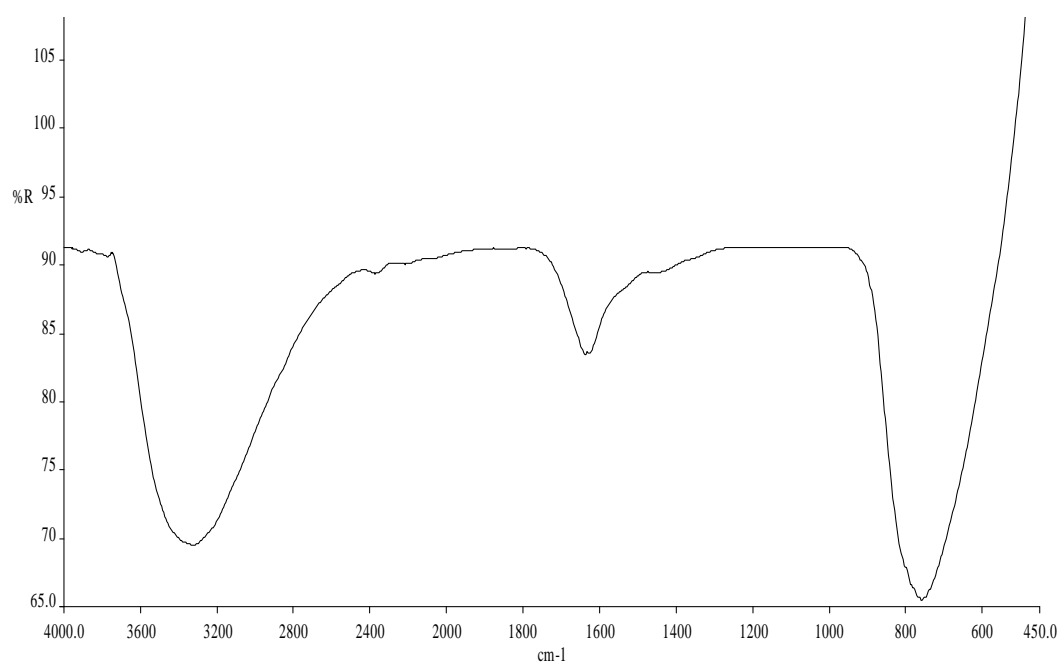


Figure 2.6 FT-IR of Nano TiO_2

2.3 Result and Discussion

2.3.1 Effect of Amount of TiO_2

The effect of catalyst concentration on the degradation of DDVP was investigated by employing different concentration of TiO_2 varying from 0.0 to 100 mg. The DDVP concentration is 10 ppm. The results are shown in fig. 2.7. The irradiation was carried out for 60 minutes. The degradation was found to increase with increase in catalyst concentration. The results show that photodegradation efficiency increases rapidly with 75 mg of TiO_2 and then decreases for 100 mg.

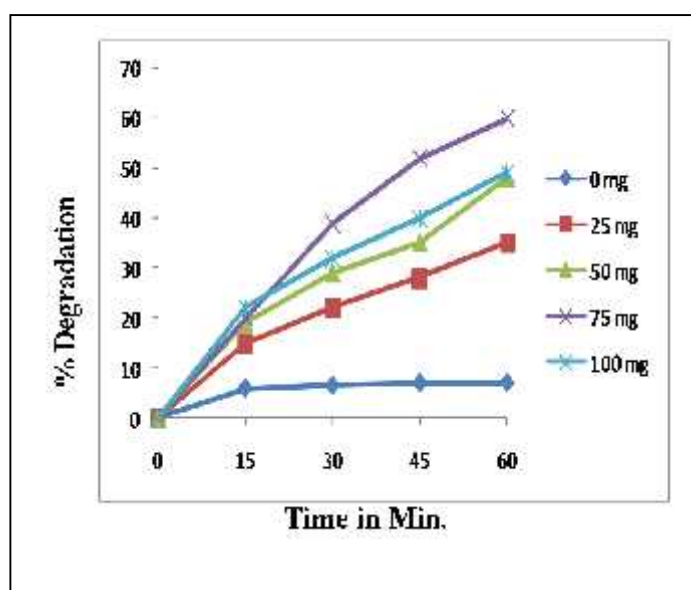


Figure 2.7 Effect of catalyst concentration on degradation of DDVP

2.3.2 Effect of initial concentration of DDVP

It can be seen from fig. 2.8 a, b that as the initial concentration of DDVP increases, photo-degradation decreases. The reason for this was the surface provided by the catalyst, intensity of the light and illumination times were constant. The numbers of adsorbing species on the catalytic surface were also constant. As the initial concentration increases, more and more amount of DDVP was adsorbed on the surface of the photocatalyst depending on the surface provided by the catalyst. In such cases the OH^\cdot and $\text{O}_2^{\cdot-}$ formed on the surface of the photocatalyst are also constant, so the strength of OH^\cdot and $\text{O}_2^{\cdot-}$ Vs increasing concentration of DDVP become less hence the photo-degradation efficiency decreases.

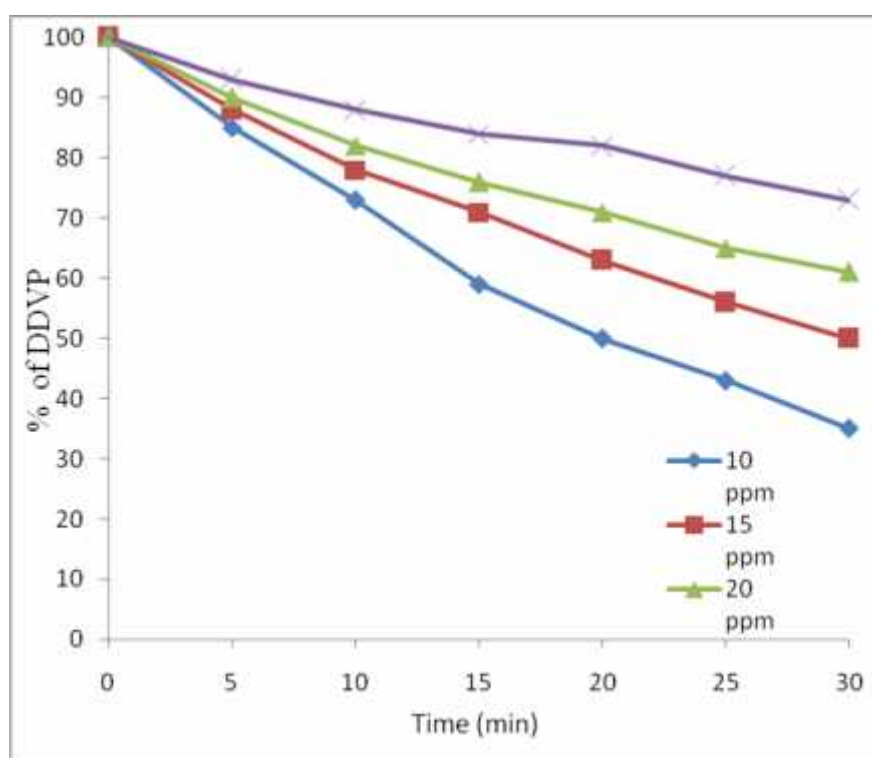


Figure 2.8 a Effect of different initial concentration of DDVP on degradation

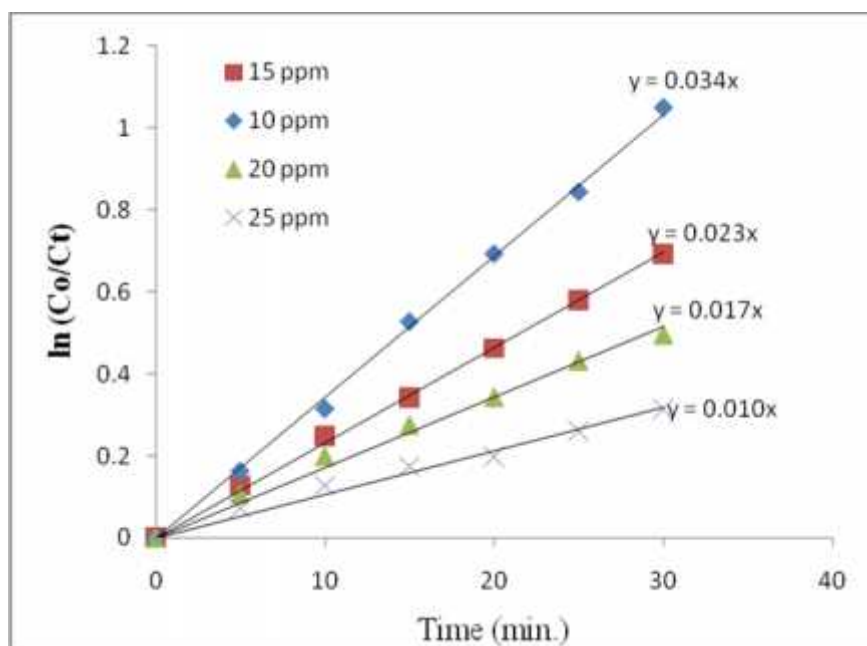
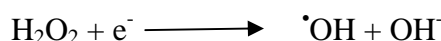
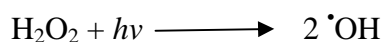


Figure 2.8 b Effect of different initial concentration of DDVP on degradation

2.3.3 Effect of H₂O₂ concentration of DDVP

Hydroxyl radicals play an important role since they greatly influence degradation reaction in forward direction. H₂O₂ was added into the solution as electron acceptor species in order to enhance the formation of hydroxyl radicals and also inhibit the electron/hole pair recombination. H₂O₂ is a strong oxidizing agent. Under UV illumination it helps to trap the conduction band electron, produce OH[•] radical from H₂O₂ [22].



H₂O₂ helps to trap the conduction of the electrons, prevents the recombination of electron hole pair, hence increases the chances of formation of OH[•]. Therefore, when adding the small amount of H₂O₂, the photo-oxidation efficiency increases. H₂O₂ also shows an adverse effect. When the concentration is higher, H₂O₂ can act as the trapping matter of OH[•], decreasing the photo-oxidation efficiency.

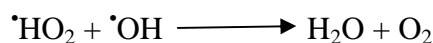
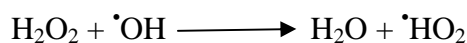


Figure 2.9 shows the effect of the H₂O₂ concentration on the photo-catalytic oxidation of DDVP. Small amount of H₂O₂ (up to 0.75 mmol; 30%; density 1.12) addition rapidly increases the photo-degradation efficiency, but if the concentration of H₂O₂ is more than 0.75 mmol, the photo-oxidation efficiency decreases gradually.

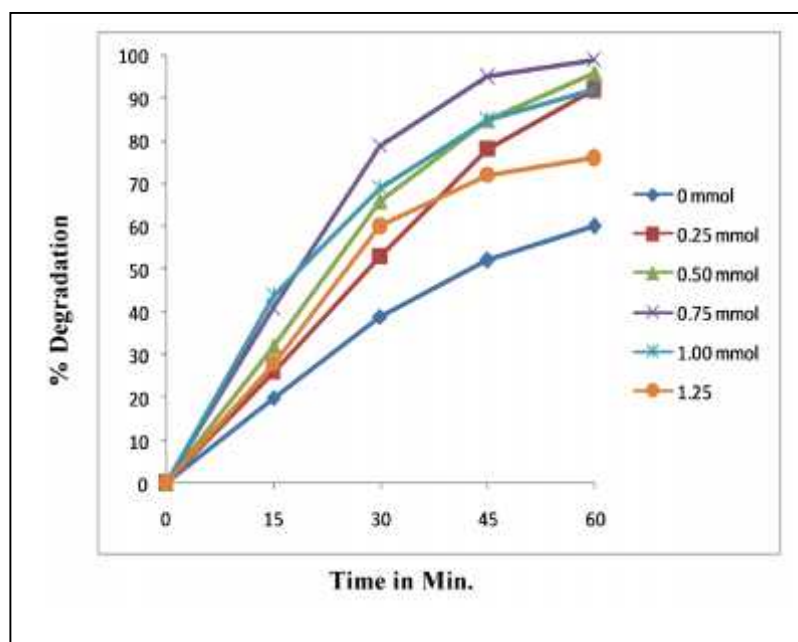


Figure 2.9 Effect of H₂O₂ concentration of DDVP on degradation

2.3.4 Effect of different initial pH

pH plays an important role in the photodegradation process of DDVP. The effect of the initial pH on the initial photodegradation rate of dichlorvos is shown in fig. 2.10. The higher degradation rate of the DDVP was observed at higher pH values. The higher reaction rate at higher pH is due to the high hydroxylation of the catalytic surface because of the presence of large no of OH^- . Consequently, it gives large no of hydroxyl radicals [12].

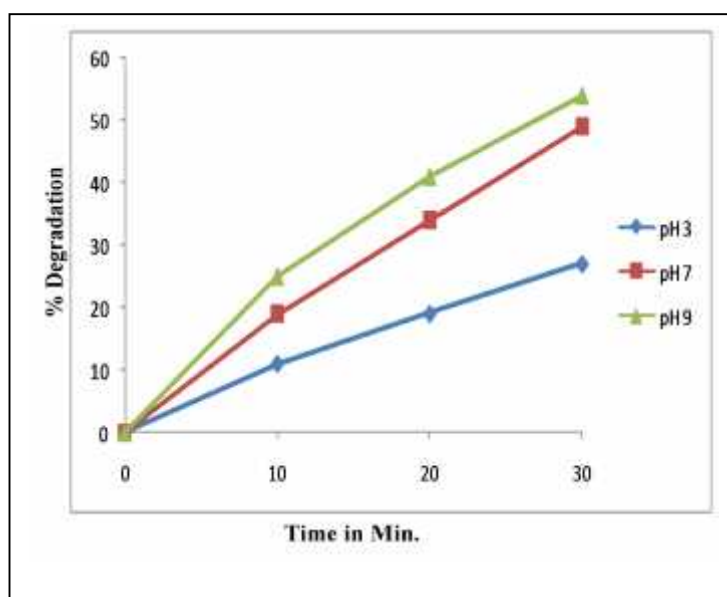


Figure 2.10 Effect of different initial pH on degradation of DDVP

Table 2.2 Optimized conditions for degradation of DDVP

Conditions	Methyl orange / Rhodamine b
Catalyst Concentration	75 mg
Initial pH	Basic
H ₂ O ₂ Concentrations	Sulphate

2.4 Conclusions

Photodegradation of DDVP in water was studied using TiO_2 photocatalyst. Some of the salient features of the photodegradation are enlisted below:

1. The present methodology does not require air or oxygen purging to achieve maximum degradation.
2. DDVP degrade efficiently with TiO_2 catalyst. The results show that the 75 mg of the catalyst gives 60% of degradation.
3. Presence of oxidizing agent lead to increase the degradation rate. 0.75 mmol of H_2O_2 is needed along with catalyst for complete degradation.
4. Degradation of DDVP follows first order reaction kinetics.
5. The maximum degradation is observed in alkaline pH.

2.5 References

1. S.B. Mathew, A.K. Pillai, V.K. Gupta, *Spectrochim. Acta, Part A.* **67** (2007) 1430.
2. M.P. Montgomery, F. Kame, T.M. Saldana, M.C.R. Alavanja, D.P. Sandler, *Am. J. Epidemiol.* **167** (2008) 1235–1246.
3. US Department of Health and Human Services, Public Health Service Agency for Toxic Substances and Disease Registry, *ToxFAQs*, September 1997.
4. X.P. Hu, Comeback story for an old chemical in fighting a new pest problem in home, *Entomology Series Timely Information Agriculture and Natural Resources* (June) (2010).
5. C. Liu, Z. Quing, C. Adams, F. Tian, T. Zang, *Water Research*, **43** (2009) 3435-3442.
6. Agency For Toxic Substances and Disease Registrar *Toxfaqs* September 1997; U.S. Environmental Protection Agency, Integrated Risk Information System (IRIS) on Dichlorvos (CASRN 62-73-7), Environmental Criteria and Assessment Office, Office of Health and Environmental Assessment, Office of Research and Development, Cincinnati, OH, 1994.
7. B.K. Binukumar, A. B. Ramesh, J.L. Kandimalla, K.D. Gill, *Mol. Brain* **3** (2010) 35.
8. Z. Mengyue, C. Shifu, T. Yaowu, J. *Chem. Tech. Biotechnol.* **64** (1995) 339-344.
9. N. Balkaya A Study of Optimal Experimental Conditions in the Photocatalytic Degradation of an Organophosphorous Insecticide *Environmental Technology*, 1999, **20**:6, 617-623
10. J. D. Schramm, I. Hua, *Wat. Res.* **35** (2001) 665-674.
11. S.A. Naman, Z.A.-A. Khammas, F.M. Hussein, *J. of Photochem. Photobiol. A: Chem.* **153** (2002) 229–236.
12. E. Evgenidou, I. Konstantinou, K. Fytianos, T. Albanis, *App. Cat. B: Environ* **59** (2005) 81–89.

13. M. A. Rahman, M. Muneer, *Desalination* 181 (2005) 161-172.
14. E. Evgenidou, I. Konstantinou, K. Fytianos, T. Albanis, *J. of Haz. Mater. B137* (2006) 1056–1064.
15. P. Oancea, T. Oncescu, *J. Photochem. Photobio. A: Chem.* 199 (2008) 8–13.
16. Mohd. Sleiman, C. Onto and J-M Chovelon, *Environ. Sci. Technol.* 42 (2008) 3018–3024.
17. J. Senthilnathan, Ligy Philip, *Chem. Engg. J.* 172 (2011) 678– 688.
18. T. Siva Rao, T. A. Segne, T. Susmitha, A. BalaramKiran, and C. Subrahmanyam, *Adv. Mater. Sci. Engg.*, 2012, doi:10.1155/2012/168780.
19. R. K. Joshi, P. R. Gogate, *Ultrasonics Sonochemistry* 19 (2012) 532–539.
20. Std. Vogel Method for determination of phosphate ion as phosphomolybdic acid, *Vogel textbook of quantitative inorganic analysis*, fourth edition, pp. 756.
21. D. A. Ward, W. I. Ko, *Ind. Eng. Chem. Res.* 34 (1995) 421.
22. S. Chen, G. Cao, *Chemosphere* 60 (2005) 1308-1315.