



# Photocatalytic Reaction Pathway and Mechanism of Degradation of Pesticide Using Nano Catalysts

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## ABSTRACT

Dichlorvos was degraded in this analysis using photocatalytically active p-type and n-type semiconductors. Nano-WO<sub>3</sub> was synthesised from sodium tungstate, and nano-TiO<sub>2</sub> was synthesised from titanium (IV) isopropoxide using a sol-gel technique by hydrothermal treatment. Different methods, such as XRD, FTIR, and SEM, were used to analyse the synthesised materials. The experiment was carried out in aqueous suspension under UV light to determine their photocatalytic potential and degradation of dichlorvos. The mechanism and pathway of the reaction is investigated. When compared to other catalysts, nano-TiO<sub>2</sub> showed higher activity in the evaluation.

**Keywords:** Dichlorvo; Degradation; Photocatalyst; Nano - TiO<sub>2</sub>.

## 1. INTRODUCTION

The environment and the whole lot connected with it's been a major difficulty of the general public, due to the fact maximum of our ecological structures, particularly water are being continuously contaminated by home and commercial pollution. At some stage in the past numerous many years, the boom of population and the hobby in industry and agriculture have drastically altered the environment and reduced the natural sources. The continual and toxic organic substrates present in wastewater effluent have to be removed or destroyed before discharge to the environment. Already existing methods like adsorption or biological treatment appear to have many drawbacks for the reason that the former entails only section transfer of the pollution without degradation, and the latter cannot be implemented to contaminants which can be toxic to the micro-organism (Hoffmann *et al.*, 1995). Semiconductor assisted photocatalysis is a promising environmentally benign technique that has been broadly and efficaciously used for the elimination of pollution (Ragnarsdottir, 2000).

The organophosphorus insecticides are comprised of the ten most broadly used insecticides all around the globe. They're extremely poisonous, appearing on acetylcholinesterase hobby (Miles *et al.*, 1998; Menear and Dichlorvos, 1998). Dichlorvos (2,2-dichlorovinyl-o,dimethyl phosphate) become commercially synthetic in 1961, and it is used for insect management in meals storage areas, greenhouses and barns. It's also used for controlling parasites and bugs in homes, aircraft and outside regions (as aerosols, liquid sprays).

On this take a look at, the photocatalytic degradation of dichlorvos using Graphite oxide (GO), Commercial TiO<sub>2</sub> (C-TiO<sub>2</sub>), WO<sub>3</sub>, nano TiO<sub>2</sub> as catalysts have been investigated. The objectives have been: (i) to assess the kinetics of pesticide disappearance (ii) to evaluate the photocatalytic efficiency of the catalysts. The photocatalytic degradation of dichlorvos, the use of TiO<sub>2</sub> has already been studied with the aid of other researchers. Harada *et al.* (1990) analyzed the charge of rutile TiO<sub>2</sub> and TiO<sub>2</sub>/pt as catalysts in the photocatalytic oxidation of dichlorvos. Naman *et al.* (2002), Lu *et al.* (1996) and Balkaya (1999) analyzed the effect of various parameters like the initial awareness of dichlorvos, the addition of salts, the addition of various sensitizers, and many others. No significant attempt has been made by previous researchers, which will take a look at the photocatalytic efficiency of nano-TiO<sub>2</sub> on dichlorvos oxidation and the elements affecting it.

## 2. EXPERIMENTAL METHODS

### 2.1 Reagents and Materials

Dichlorvos analytical grade (92% purity) was purchased from UPL Ltd (Gujarat) and was used without any further purification. Titanium dioxide P-25 Degussa (anatase/rutile: 65/35, non-porous, mean size 30 nm, surface area 56 m<sup>2</sup> g<sup>-1</sup>) was purchased from Loba Chemie Pvt Ltd. Sodium Nitrate and Potassium Permanganate was purchased from Emplura. Titanium (IV) Isopropoxide was obtained from Sigma -Aldrich. Doubly distilled water was used throughout the work.

## 2.2 Material Synthesis

The detailed synthesis procedure for pure GO is given in our previously published report (Yeh *et al.* 2010).

### 2.2.1 Preparation of WO<sub>3</sub>

The detailed synthesis procedure for pure WO<sub>3</sub> is as per the reported literature (Nogueira, 2004).

### 2.2.2 Preparation of TiO<sub>2</sub> nanoparticles

Titanium tetra isopropoxide was used as a precursor in the synthesis of TiO<sub>2</sub> particles, and it was mixed with HCl, ethanol, and deionized water for half an hour at room temperature, in a pH range of 1.5. 10ml of deionized water was applied to the above mixture and stirred for 2 hours at room temperature. Finally, the solution was cured at room temperature, and the powder was heated for 1 hour at 120 °C.

### 2.2.3 Catalysts characterization

High-resolution transmission electron microscopy (HRTEM; JEOL 2100F, Japan) and scanning electron microscope (SEM; JEOL JSM-6700F, Japan) was used to explore the microstructure of the GO composites specimens. Powder X-ray diffraction (XRD) was used to determine the crystal structure of the samples using a RIGAKU RINT-2000 (Japan) diffractometer with Cu K radiation excited at 40 kV and 40mA. A JASCO FTIR-4100 (Japan) spectrometer was used to do diffused reflectance Fourier-transform infrared (FTIR) spectroscopy.

## 2.3 Irradiation Procedure

Irradiation experiments were carried out in a Pyrex UV reactor with a 500 mL capacity and a diving Philips HPK 125 W high-pressure mercury lamp. The lamp was fitted with a water-cooled Pyrex filter that blocked wavelengths shorter than 290 nm. The suspension was kept cold (30–350 °C) by using a tap water cooling circuit to eliminate IR radiation. Before and during the illumination, the dichlorvos solution (10 mg L<sup>-1</sup>, unless otherwise stated) was magnetically stirred with the required volume of catalyst. Prior to lighting, the suspension was left in the dark for 30 minutes to ensure optimum pesticide adsorption onto the semiconductor surface. Unless otherwise mentioned, the pH was not modified. Samples were taken from the reactor at predetermined intervals.

## 3. PHYSICO-CHEMICAL CHARACTERIZATIONS

The XRD pattern of industrial P-25 titania, which has a 75:25 ratio of anatase and rutile stages. At a 2 theta value of 27.32, the presence of the rutile process is detected, and the remaining peaks correspond to

anatase. The 101 planes of anatase titania are represented by the high-intensity peak at 25.33. A monoclinic process may be assigned to all of the WO<sub>3</sub> reflection patterns.

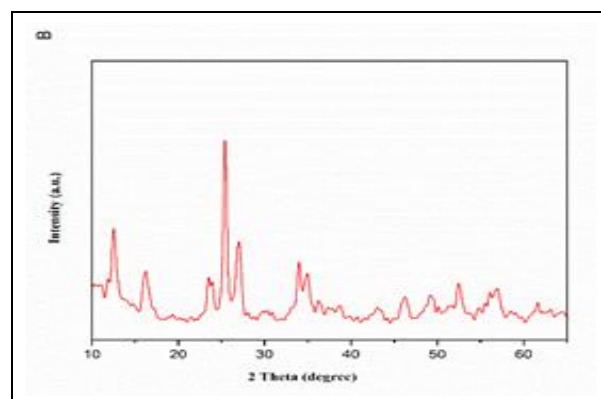


Fig. 1: X-Ray Diffraction pattern of TiO<sub>2</sub>

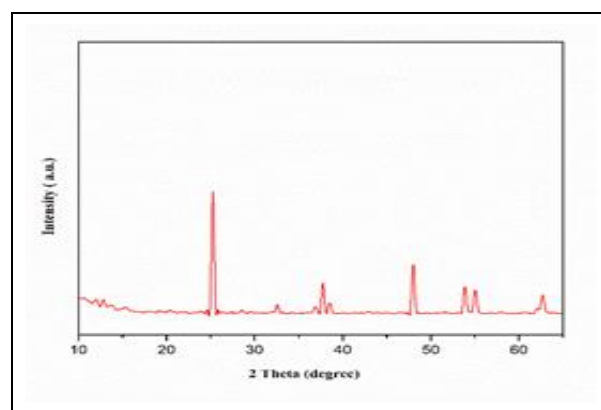


Fig. 2: X-Ray Diffraction patterns of WO<sub>3</sub>

Scanning transmission electron microscopy was used to examine the surface morphology of both catalysts, and the findings are seen in Figures 3, 4, and 5. The surface was coated in a significant number of TiO<sub>2</sub> nanoparticles, as seen in the photographs. In WO<sub>3</sub>, though the particle shapes are poorly defined, three different morphological patterns were clearly observed: irregular plates, nanowires, agglomerated particles.

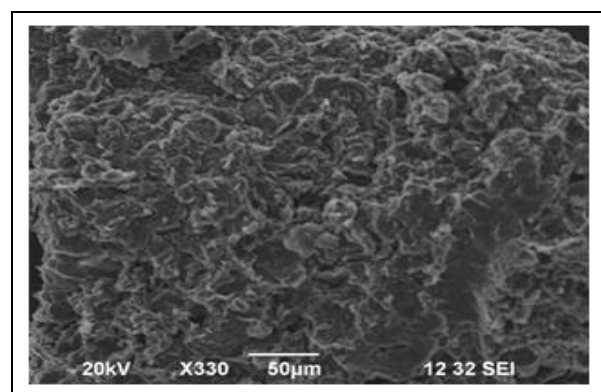


Fig. 3: Scanning Electron Microscopy image of GO

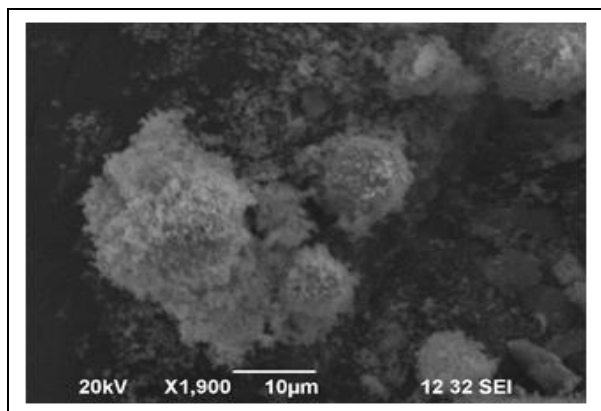


Fig. 4: Scanning Electron Microscopy image of TiO<sub>2</sub>

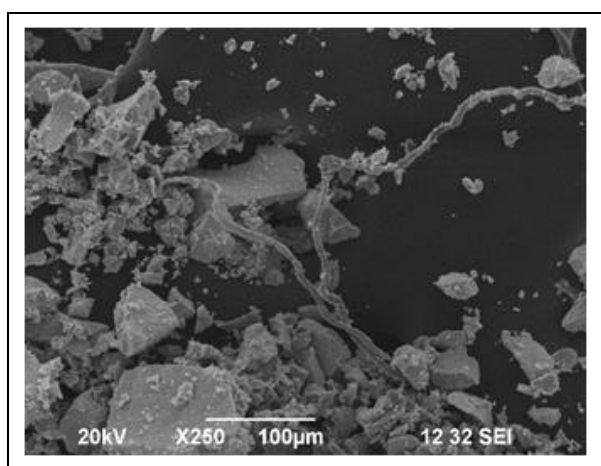


Fig. 5: Scanning Electron Microscopy image of WO<sub>3</sub>

In all the FTIR spectra (Fig. 6), a peak is observed at 3200-3500 cm<sup>-1</sup> corresponding to O-H stretching frequency (Paredes *et al.*, 2008), and this particular peak is broader in pure GO. The stretching frequency of C=O is found at 1690 cm<sup>-1</sup>. The tertiary alcoholic group is detected at 1390 cm<sup>-1</sup>. The peak for phenolic O-H is observed in GO at 1230 cm<sup>-1</sup>.

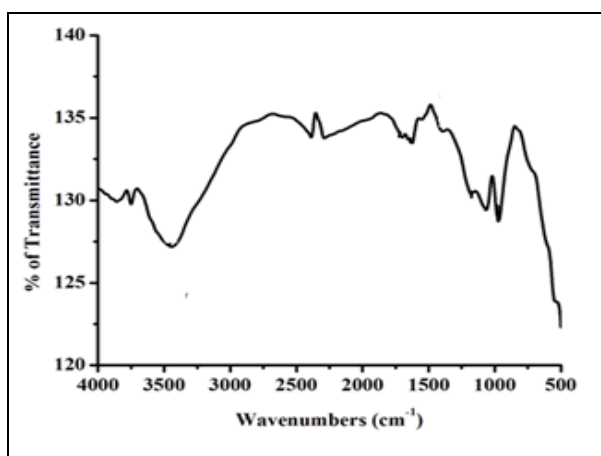
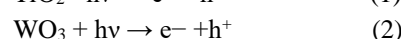
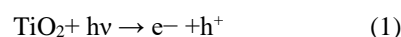


Fig. 6: FTIR spectra of pure GO.

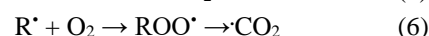
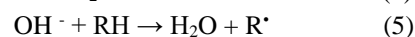
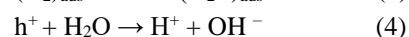
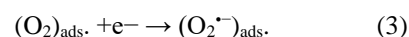
## 4. PHOTOCATALYTIC DEGRADATION PATHWAYS

### 4.1. Primary Degradation

The electronic structure of semiconductors, which is characterised by a filled valence band and an empty conduction band, is due to their ability to serve as sensitizers and, as a result, to improve the photodegradation of organic contaminants. Excited high-energy states of electron and hole pairs are formed when semiconductors are illuminated with energy greater than their bandgap energy (E<sub>g</sub>):



These generated species can either recombine and dissipate the input energy as heat or react with electron donors or electron acceptors, which are adsorbed on the semiconductor surface or trapped within the surrounding.



Electrical double layer of the charged particles (eq. (3) and (4)) to produce strong oxidizing hydroxyl radicals which can promote the oxidation of organic compounds (Eqs. (5) and (6)).

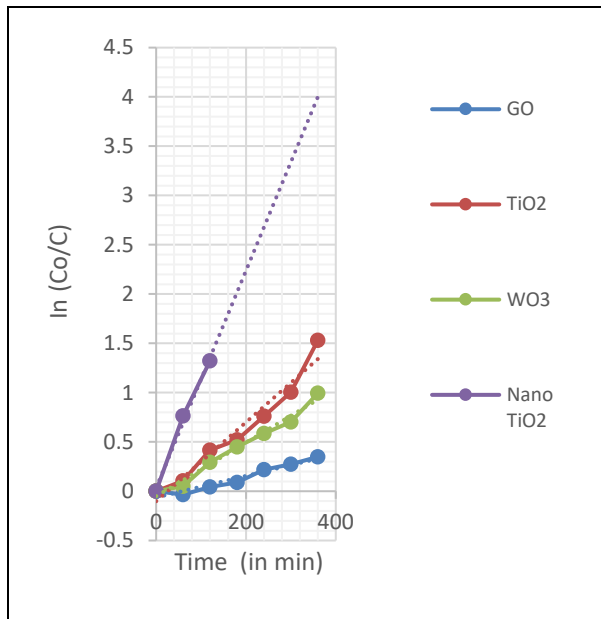
### 4.2. Photocatalytic Activity

In order to achieve effective degradation, factors influencing reaction such as catalyst concentration and reactant concentration were optimized. The catalyst amount of 0.025, 0.05 and 0.075 was tested, and the reactant concentration was varied with 5, 10 and 15 ppm of methylene blue. Catalyst concentration of 0.05g/L and reactant concentration of 10 ppm was chosen as the optimized condition for the photocatalytic activity. The concentration remained after attaining adsorption-desorption equilibrium was taken as the initial concentration for plotting the results.

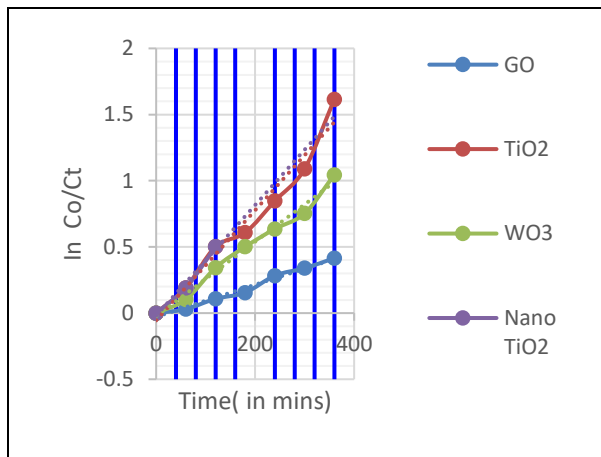
### 4.3. Effect of Different Catalysts

The linear transform of the kinetic plot showed that the reaction followed the pseudo-first-order kinetics. From the kinetic plot (Fig 7a, 7b), it is found that the increase in reaction time increased the activity of all the catalysts except GO. The activity of different catalysts follows the trend: nano- TiO<sub>2</sub>>C - TiO<sub>2</sub>> WO<sub>3</sub>> GO. photocatalytic degradation of dichlorvos was carried out using pure GO, and results showed that it does not

influence the activity. However, it showed higher adsorption than the other catalysts.

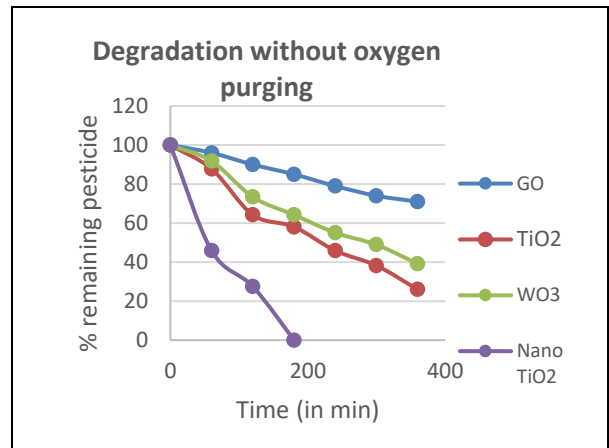


**Fig. 7a: Kinetics plot of dichlorvos on different catalysts without oxygen purging.**



**Fig. 7b: Kinetics plot of dichlorvos on different catalysts.**

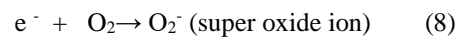
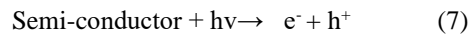
Fig.8 shows the degradation profile represented in percentage(%) of degradation. Among the other catalysts, nano-TiO<sub>2</sub> showed the fastest as well as complete degradation. The next highly active catalyst is C - TiO<sub>2</sub>. However, on comparing WO<sub>3</sub>with C - TiO<sub>2</sub>, the latter is the highly active one. Since C - TiO<sub>2</sub> and WO<sub>3</sub> have a lower surface area, they failed to show a significant increase in adsorption as well as photocatalytic degradation. Photocatalytic activity mainly depends on effective charge carrier separation.



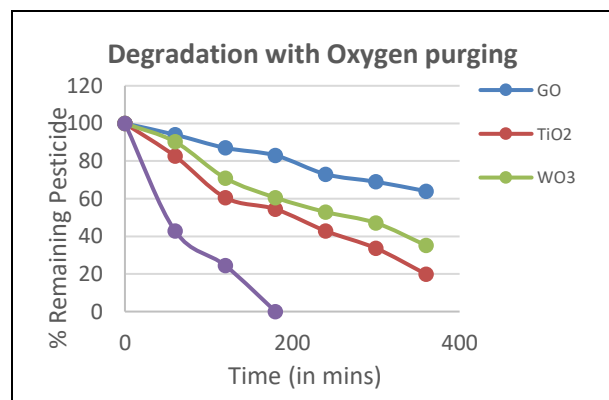
**Fig. 8: Degradation of dichlorvos on different catalysts.**

#### 4.4 Influence of External Oxygen

The air was purged during the reaction to research the effect of external oxygen. This extra air purification increases catalyst particle dispersion. The effects of external oxygen are shown in Figure 9. External oxygen is thought to play a role in photocatalysis by the formation of superoxide ion during the reaction, as seen in reactions 7 and 8.



The reactant molecules can be further oxidised by this superoxide ion. As a result, oxidation is predicted to occur in two ways: (i) Water is oxidised I by valence band hole (ii) Conduction band reduction of oxygen. As seen in reaction 8, GO has a higher conduction band, allowing it to effectively reduce oxygen. As a result, dichlorvos is oxidised from both hole and superoxide ion oxidations. This improved the photocatalytic activity of nano TiO<sub>2</sub>, C-TiO<sub>2</sub> and WO<sub>3</sub>.



**Fig. 9: Influence of external oxygen.**

## 5. CONCLUSIONS

Different physico-chemical techniques were used to classify the materials that were developed. The photocatalytic degradation of Dichlorvos was then examined on these samples. Characterization results showed that more number of TiO<sub>2</sub> particles are present over the surface, and WO<sub>3</sub> showed larger and irregular shaped particles seen on the surface. These were confirmed with FTIR and SEM analysis. Hence, nano-TiO<sub>2</sub> showed higher activity than C-TiO<sub>2</sub> and WO<sub>3</sub>.

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## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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