



## Photo Catalytic Activity of Chromium Doped Nano Titania for the Mineralization of Dichlorvos

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### Abstract

Chromium doped (2, 4, 6 and 8 Molar ratio of M/Ti) nano Titania were synthesized through solgel technique followed by hydrothermal treatment using titanium (IV) isopropoxide as the precursor. The resulting nanocrystals were characterized by XRD, DRS-UV, ICP-AES, BET and TEM techniques. The photocatalytic activity of synthesized catalysts were tested for the mineralization of Dichlorvos in aqueous solution using air as an oxidant. The reaction products were collected at different intervals and analyzed with the help of HPLC and TOC analyzer. Chromium doped nanocrystalline titania shows better catalytic activity than both commercial and as synthesized pure titania. Among the various chromium doped titania 4 molar chromium doped titania is found to be the best for the mineralization of Dichlorvos. The catalytic activity will be correlated with physico-chemical properties and the results will be discussed in detail.

**Keywords:** Dichlorvos; Nano titania ; Photocatalysis; UV-Vis DRS.

### 1. INTRODUCTION

In recent years, the concentrations of organochlorine as well as organophosphorous pesticides have exceeded frequently the maximum contamination level in surface water and ground water. Organophosphorous pesticides are comprised within the 10 most widely used pesticides all over the world. They are considered as extremely toxic compounds acting on acetyl cholinesterase activity (Ragnarsdottir *et al.* 2000; Mileson *et al.* 1998). Among many organophosphorous compounds, Dichlorvos (DDVP) an insecticide is used widely for crop protection mainly in greenhouses and for controlling parasites and insects in houses, aircraft, and outdoor areas (as aerosols, liquid sprays). Dichlorvos is highly toxic by inhalation, dermal absorption, and ingestion. EPA has classified dichlorvos as a group B2, probable human, carcinogen. In the USA, its use was restricted on account of the leukaemia cases. Owing to its probable carcinogenic effect, this chemical was banned in Denmark, UK and Asian Countries.

This is not degradable by the conventional methods like adsorption, biological methods, thermal decomposition and photolysis. Since adsorption can recover the toxicant and it cannot be degraded, it is not feasible. These substances are highly toxic to microorganisms. So, a biological method is not fit for this degradation process. Thermal decomposition is not an environmentally benign process. Absorption maximum of this substance lies in UV region (210 nm). Hence it is not advisable to degrade by UV photolysis. However, photocatalysis is an advanced oxidation process and can be used for the effective mineralization of Dichlorvos. Few research works have been done on degradation of Dichlorvos by photocatalysis using solid oxidant like H<sub>2</sub>O<sub>2</sub> and K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (Evgenidou *et al.* 2005) and few works have been reported on using of organic sensitizers like p-nitro phenol and hydroquinone (Rahman *et al.* 2005). Oxidation of Dichlorvos with H<sub>2</sub>O<sub>2</sub> using Fenton's reagent has been carried out. This kind of oxidation leads to ecological deterioration. Semiconductor like titania and zinc oxide have been used and titania has been reported to be an efficient catalysts than any other semiconductor (Siva *et al.* 2012).

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Although many semiconductors used as a photocatalyst,  $\text{TiO}_2$  is far better than the others due to its non-toxicity, non-corrosive, favorable band gap and good redox property. However, titania has fast recombination of electron hole pairs. The enhancement of photo-degradation efficiency by the addition of metals may be attributed to the rapid transfer of the photo-generated electrons from the semiconductors to the metal particles, resulting in the effective separation of the electrons and holes. Unfortunately metal doped titania has not been widely used for mineralize Dichlorvos. Within our knowledge obtained from literature survey, only Mg- $\text{TiO}_2$  has been attempted to mineralize Dichlorvos (Naman *et al.* 2002). Hence, in this work, highly photoactive chromium doped nano  $\text{TiO}_2$  photocatalyst was prepared using sol-gel followed by hydrothermal method and used it for the effective mineralization of Dichlorvos.

## 2. MATERIALS & METHOD

Titanium tetra isopropoxide (TTIP) was purchased from Alfa Aesar. Anhydrous ethanol purchased from Hayman Limited, England. Chromium nitrate was purchased from SRL India limited. All the reagents were of analytical grade. Triply distilled water was used throughout this study.

### 2.1 Preparation of Bare and Doped $\text{TiO}_2$ nanoparticles:

Anatase nanostructured pure and chromium doped  $\text{TiO}_2$  particle were synthesized by adopting methodology used for the preparation of Fe- $\text{TiO}_2$  (Vijayan *et al.* 2009). The procedure reported in the literature was modified as follows.

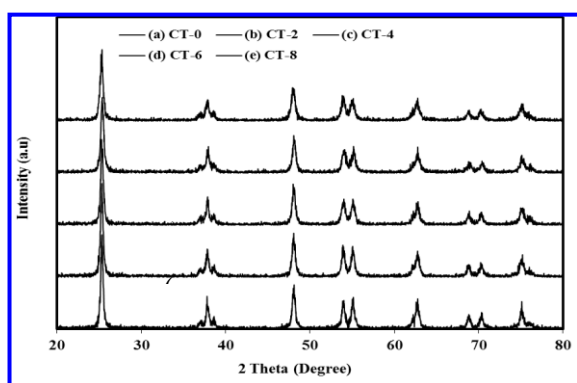


Fig. 1: X-ray diffraction patterns of Cr- $\text{TiO}_2$

$\text{TiO}_2$  nano particles were synthesized by hydrolyzing TTIP in a mixture of anhydrous ethanol

and water. The synthesis procedure is as follows: 10 mL of TTIP diluted in 40 mL anhydrous ethanol (A). 40 ml water mixed with 10 mL anhydrous ethanol (B). Solution A is added drop wise to solution B with constant and vigorous stirring. Required molar of dopant precursor was dissolved in ethanol and added drop wise to this solution. Hydrolysis and condensation were conducted at room temperature with 1 M sulphuric acid and stirred for 1hr. The amorphous precipitate was then subjected to hydrothermal treatment. The precipitate was transferred to autoclave and tightly closed. The autoclave was then subjected to hydrothermal treatment at 353K for 12 hrs. Then it was cooled and recovered by filtration, washed thoroughly with water and ethanol. It was then dried in an oven at 373K overnight. The sample was then ground and calcined at 773K. Catalysts with M/Ti molar ratio of 2,4,6 and 8 are denoted as CT-2, CT-4, CT-6 and CT-8 respectively.

### 2.2 Characterization of Bare and Doped $\text{TiO}_2$ nanoparticles

The catalysts were characterized by powder XRD with Phillips X'pert model using Cu-K $\alpha$  radiation. XRD pattern were obtained for 20-70° ( $2\theta$ ) by step scanning with a step size of 0.02  $\theta$ . to determine the average crystallite size, peak broadening analysis was applied to Anatase (101) diffraction using Scherer equation. DRS UV-Vis spectra of the powders were recorded using shimadzu UV2450 model with  $\text{BaSO}_4$  white plate as reference. Transmission electron micrographs of catalysts were taken by JEOL TEM instrument. Specific surface area (BET), pore volume and average pore diameter (BJH) of the catalysts were measured by nitrogen adsorption-desorption isotherms using Quadrasorb model surface area analyzer from Quantachrome inc. The calcined samples were degassed at 300 °C for 3 hrs prior to adsorption measurement. X-ray photoelectron spectra of these materials were recorded with ESCA-3 Mark II spectrometer (VG Scientific Ltd., U.K.) using Al K $\alpha$  radiation (1486.6 eV).

### 2.3 Photocatalytic reactor set-up

Photocatalytic reaction was carried out in an inner irradiation type photocatalytic reactor. The light source was 400 W high pressure mercury lamp. The temperature of reaction vessel was maintained at 18 °C by filling with flowing thermo stated cooling water. 1 M  $\text{NaNO}_2$  aqueous solution was used to filter out the UV light. External oxygen was fed by purging air. The reactor set-up was covered with aluminium foil followed by a black cloth to prevent UV light

leakage. 100 mL of 100 ppm DDVP taken and stirred for 30min to attain adsorption-desorption equilibrium then it was irradiated. The sample was collected at the interval of every one hour and filtered through 0.2  $\mu\text{m}$  filter. DDVP concentration was analyzed by HPLC (Shimadzu  $V_{\text{CPN}}$ ), in which aC-18 column was employed and a mobile phase of acetonitrile/water (60:40, v/v) was used at a flow rate of 1.0 ml/min. An injection volume of 20  $\mu\text{L}$  was used and the amount was determined by a UV detector. Extent of mineralization was measured by TOC analyser (Shimadzu, TOC  $V_{\text{CPN}}$ , Japan) by catalytic oxidation method (platinum was used as catalyst).

### 3. RESULTS & DISCUSSIONS

#### 3.1 Catalysts characterization

X-ray diffractograms were recorded for calcined Cr-TiO<sub>2</sub> catalysts. A complete analysis of the diffractograms for the crystallite size and phase formation was carried out. The broad diffraction lines of (101), (004), (200), (105), (211), (204), (116), (220) and (215) appeared at  $2\theta$  values of 25.32, 38.18, 48.30, 54.21, 55.25, 63.45, 69.34, 70.17 and 75.25 are for anatase phase (fig.1). The diffraction lines corresponding to rutile and brookite phases were not found. Cr-TiO<sub>2</sub> samples also did not show any additional peak corresponding to CT-8. This indicates that there is no detectable amount of metal oxide. This may be due to homogeneous distribution of Cr<sup>3+</sup> in the TiO<sub>2</sub> matrix. Since the ionic radius of Cr<sup>3+</sup> is 0.76 Å is close to the ionic radius of Ti<sup>4+</sup> (0.75 Å) it can easily enter into the anatase structure of titania without disturbing the crystal structure of titania. Such a substitution not only decreases the crystallization of TiO<sub>2</sub>, which is reflected by a weaker diffraction intensity of XRD pattern, but also restrains the growth of TiO<sub>2</sub> crystallite (Zhu *et al.* 2006) as shown in table 1. As the metal content is increased, the peak width increased slightly showing a small reduction in particle size. It is also understood that the dopant ion can restrict the crystallite growth and control the particle size (table 1).

Titanium dioxide is very efficient for the chemical conversion of light energy but its absorption does not fit with the solar spectrum. A possible way to extend its photo response to the visible region consists in doping with suitable foreign cations. Fig. 2 represents the UV-visible DR spectra of pure and Cr-TiO<sub>2</sub> samples. There are two absorptions bands observed in the diffused reflectance spectra. The first one between 380-390 nm is also observed in pure titania which is due to excitation of electron from valence band to conduction band. The second one is at

420-440 nm which is not observed in pure titania. This is due to excitation of electron from Cr<sup>3+</sup> to the conduction band of TiO<sub>2</sub>. As shown in the fig. 2, the dopant ion Cr<sup>3+</sup> caused significant absorption shift towards visible region. As the dopant ion concentration is increased, a shift in the absorption maximum to the visible region is observed.

There is no band edges observed after 450 nm. Formation of metal oxide is not also observed in the spectrum which is normally formed by dopant ion during heat treatment. The ionic size of Cr<sup>3+</sup> and Ti<sup>4+</sup> are very close to each other, i.e. 0.76 and 0.75 Å respectively, therefore, Cr<sup>3+</sup> ions can go into the lattice of TiO<sub>2</sub> as substitutional metal dopant.

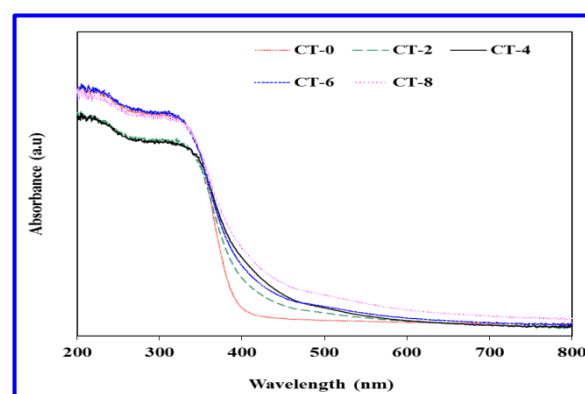
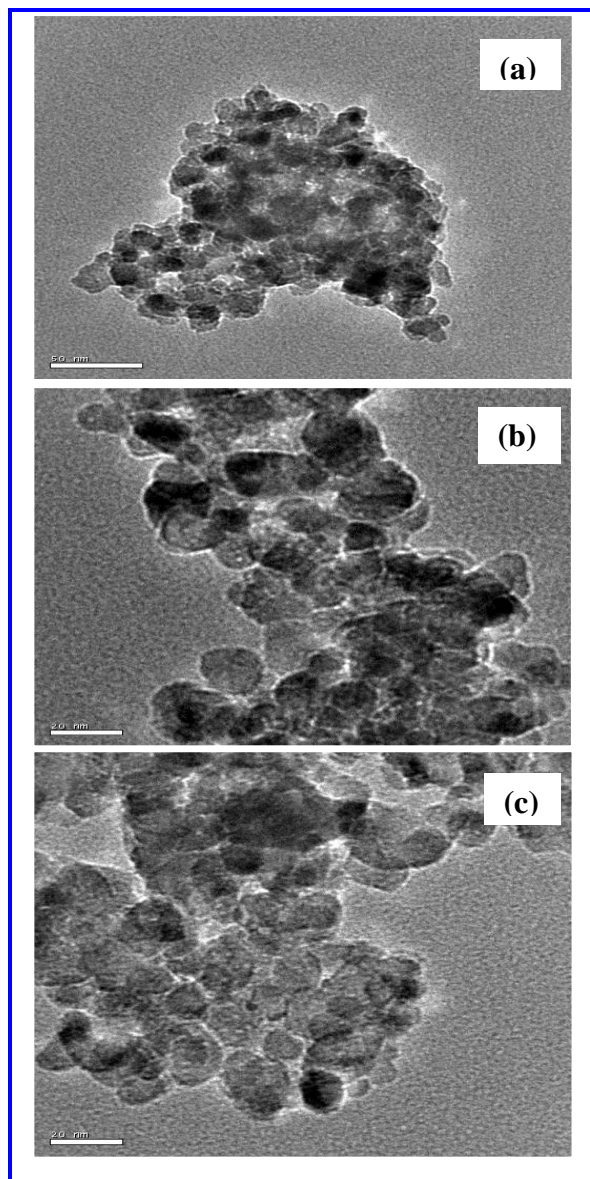


Fig. 2: UV-Visible diffused reflectance spectra of Cr-TiO<sub>2</sub>

The reason for the increased absorption maxima has been explained in the literature (Liu *et al.* 2005). The role of Cr<sup>3+</sup> ion in Cr-TiO<sub>2</sub> is mainly to improve charge separation of the photo produced electron-hole pairs by means of a permanent electric field. Cr<sup>3+</sup> ion doping can bring free negative charge ( $e_2$ ) and these free electrons can induce cavities ( $h_2$ ). The cavities induced by free negative charge have the same ionization energy value and form doping energy level ( $E_{\text{Cr}}$ ). When activated by visible light and ultraviolet, the induced cavities can escape from the 'bandage' of doping energy level and transfers. Hence, Cr<sup>3+</sup> doping effectively red shifts the absorption maximum of pure TiO<sub>2</sub>.

Any heterogeneous photocatalytic reaction is a surface process, because the surface to bulk ratio of smaller particles is much higher than that of larger ones. It can be expected that the particles with size ranging from 15 to 20 nm contribute strongly to the activity of the sample. The surface morphology, dispersion and particle size distribution were studied from transmission electron microscopic images. Typical electron micrographs of the Cr-TiO<sub>2</sub> calcined

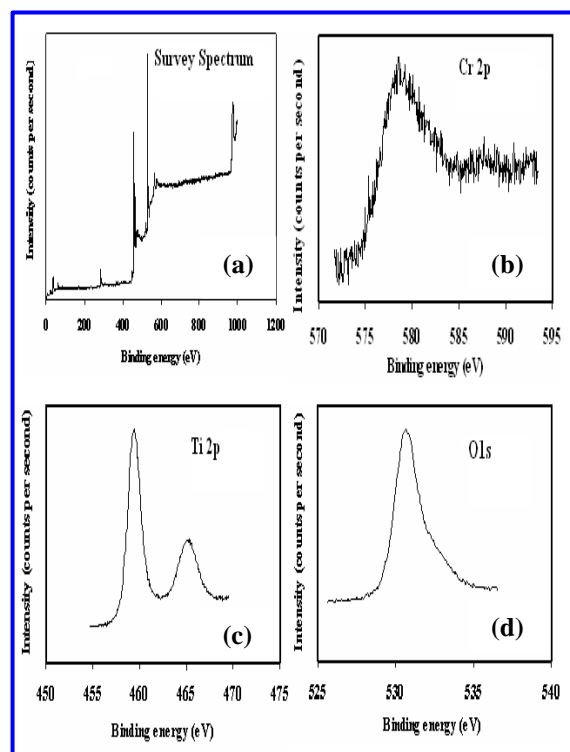
at 500 °C with various percentage of loading (CT-4, CT-6 and CT-8) are shown in fig. 3 (a-c). It is evident that the particle growth becomes restricted by the chromium doping, which is decisive not only for the design of the surface properties and surface area but also for the electronic structure. It can be understood from the TEM studies that all the particles are in nanometer range and are well dispersed. The picture clearly shows that the particles are distributed between 10 - 25 nm.



**Fig. 3:** Transmission electron microscopy of Cr-TiO<sub>2</sub> (a) CT-4(b) CT-6 and (c) CT-8

The core level Ti 2p, O 1s and Cr 2p X-ray photoelectron spectra of CT-6 are shown in fig.5 (a-d). The peak position for Cr 2p is located at 458 eV.

Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub> spin-orbital splitting photoelectrons are located at binding energies of 460 and 465 eV respectively which are in good agreement with the values of Ti<sup>4+</sup> in pure TiO<sub>2</sub>. The measured FWHM of Ti 2p<sub>3/2</sub> signal is about 1.4 eV which is a strong evidence for the presence of Ti<sup>4+</sup> and absence of Ti<sup>3+</sup> (Zhang *et al.* 2003). The results show that there is a shift in Ti 2p signal towards higher energy side. The enhancement of Cr 2p level binding energy may be due to the diffusion of Cr<sup>3+</sup> ion into TiO<sub>2</sub> lattice and the formation of Cr-O-Ti bond. The shift in binding energy indicates that there is a charge transfer taking place from Ti to Cr ions, and therefore, the work function of host material increases (Bernasik *et al.* 1993). The incoming oxygen molecules form bond with Cr metal ions having low dissociation energy. Additional peaks around 288.5 eV is corresponding to carbon impurities arising probably from the thermal decomposition of the precursors during firing process. From the survey spectrum it is evident that the peak intensity of O 1s is two times greater than (almost ratio is 2.0) the peak intensity of Ti 2p<sub>3/2</sub>, indicating that the surface of the samples are either hydrated or hydroxylated.



**Fig. 4:** X-ray photoelectron spectroscopy of Cr-TiO<sub>2</sub> (a) survey spectrum(b) Cr 2p peak (c) Ti 2p peak and (d) O 1s peak

Fig. 5 (a-d) shows the N<sub>2</sub> adsorption-desorption isotherms of Cr-TiO<sub>2</sub>. It can be understood

from the isotherms that hysteresis loop occurs at relatively high pressures confirming the irregularity of the mesopores. All the catalysts have shown type IV isotherm with H<sub>2</sub> hysteresis loop implying that pores are distributed in the range of meso and macroporosity. There is an increase in surface area value was observed from 52-75 m<sup>2</sup>g<sup>-1</sup> as the chromium content is increased from CT-2 to CT-4 (table 1).

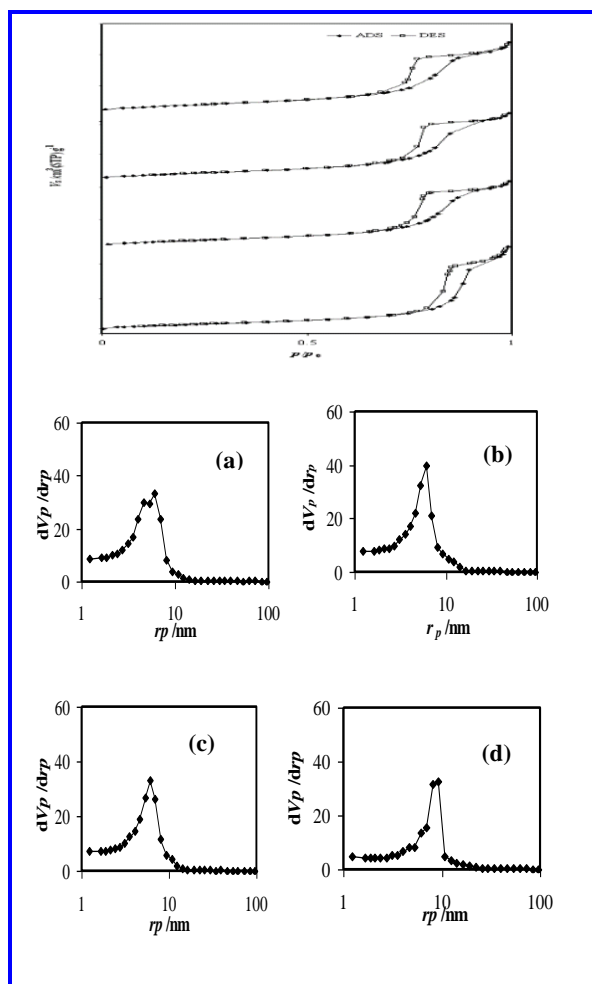


Fig. 5: N<sub>2</sub> adsorption-desorption isotherms of (a) CT-2 (b) CT-4 (c) CT-6 and (d) CT-8

The hysteresis loop of the Cr doped TiO<sub>2</sub> is steeper than pure mesoporous TiO<sub>2</sub> indicating the cylindrical shape of pore in Cr-TiO<sub>2</sub>. Fig.6 (right) illustrates that the pore size distribution of metal doped TiO<sub>2</sub> is more uniform with a peak centred at 6 nm. It has been suggested that incorporation of transition metals into TiO<sub>2</sub> could restrain the growth speed of the particles with temperature (Zhang *et al.* 2001; Zhang *et al.* 2002). The metal incorporation might prevent the pore walls from excessive collapse (or) distortion by limiting the grain

growth on heating. This property may help to explain the observed high specific surface area and the uniform pore distribution of metal doped titania.

### 3.2 Influence of chromium doping on the photocatalytic degradation of DDVP

It is interesting to study the photocatalytic activity of Cr-TiO<sub>2</sub> for photodegradation of hazardous organic compounds as it depends on various factors such as crystal size, surface area band gap energy and structure. Fig. 6 (a, b) present the results of photocatalytic mineralization of DDVP. The experimental results demonstrate that Cr-TiO<sub>2</sub> catalysts can mineralize much faster than pure TiO<sub>2</sub>. It is observed from the fig. 6 that the increase in chromium content increased the extent of mineralization of DDVP upto 4 and 6 molar % Cr loading respectively. Further increase in chromium content decreased the mineralization as seen in the degradation profiles. DDVP showed increased degradation and mineralization when irradiated with 4 molar ratio of Cr. In the case of other doped catalysts, both activity is slow. As the chromium loading increases to 6 and 8 molar ratio, the activity is decreased. On comparison of pure titania with higher loading of chromium, latter has shown same trend in activity upto 20 mins of irradiation.

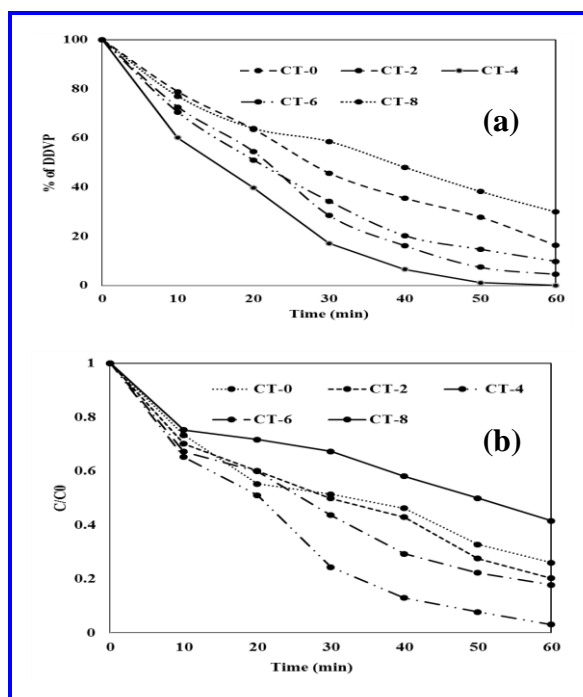


Fig. 6: (a) Extent of Dichlorvos degradation (b) Extent of mineralization of Dichlorvos

Catalyst: Cr-TiO<sub>2</sub>, Catalyst dosage: 100 mg/L, pH: 4, Reactant: 100 mL of 50 ppm Dichlorvos and Wavelength: 400 nm

**Table 1. Physico-chemical properties of Cr -TiO<sub>2</sub>**

Cr-TiO <sub>2</sub> (mole %)	Crystallite size (nm) <sup>a</sup>	Band gap Energy (eV) <sup>b</sup>	Surface area (m <sup>2</sup> g <sup>-1</sup> ) <sup>c</sup>	Pore volume (cm <sup>3</sup> g <sup>-1</sup> ) <sup>f</sup>	Pore diameter (nm) <sup>f</sup>
0.0	16	3.06	59	0.21	6
2	20	3.10	52	0.19	9
4	19	3.02	65	0.17	6
6	16	2.92	71	0.17	6
8	14	2.84	75	0.16	6

a-Calculated using Debye-Scherrer equation for (101) anatase peak.

b-Obtained from UV-Vis DRS

c-Obtained from the linear plot of BET

f -Obtained from the desorption branch of isotherm

After that the pure titania dominates. Initial increase in mineralization activity of CT-8 catalyst may be due to the availability of more number of Cr<sup>3+</sup> ions. Beyond 20 mins, the population of intermediate increased and prevents the surface of the catalyst from light penetration. Pure titania shows lower activity than CT-2, CT-4 and CT-6 and higher activity than CT-8.

Cr<sup>3+</sup> doped catalysts showed higher mineralization than pure TiO<sub>2</sub>. Interestingly the Cr doping upto 8 molar % greatly restricts the pore size within 6 nm which is beneficial for further reaction of fragmented products during the reaction which enhanced the mineralization. The maximum degradation of DDVP achieved with 4 molar. % Cr. As the metal content is increased, the crystallite size and band gap energy decreased and with increase in surface area up to 6 molar % (table 1). The increased adsorption of reactant molecules and enhancement of degradation upto the level of 4/6 molar % are attributed due to the increased surface area and decreased crystallite size and band gap energy (table 4.3). Increased degradation of DDVP upto 4 molar. % may be due to shorter reaction time and adsorption of more reactant molecules from the reaction mixture. However, prolonged irradiation of 6 molar % Cr-TiO<sub>2</sub> decreased the TCP degradation due to the increase in recombination rate fig. 6 (a, b).

From the study on effect of chromium doping on photocatalytic activity of TiO<sub>2</sub>, it can be broadly concluded that an appropriate amount of the doped ions is necessary for effective capture of the photo induced electrons and holes. An optimum metal may inhibit the recombination of photo induced carriers and improve the photocatalytic activity of the photocatalysts. However, beyond an optimum level can induce recombination centers of the photo induced electrons and holes and decrease the surface area and light harvesting efficiency (shielding of core

species by dopant atom) as they are unfavorable for photocatalytic reaction.

## 5. CONCLUSION

Different molar percentage of chromium doped titania were prepared by sol-gel followed by hydrothermal method. Cr/TiO<sub>2</sub> has been found to possess higher activity than pure titania for photocatalytic mineralization of DDVP. The doping ions caused significant absorption shift towards visible region compared to pure titania. The photocatalytic activity has been found to strongly depend on Cr doping concentration. 4 molar % which is having crystallite size of 16 nm was the optimal loading for the photocatalytic mineralization of DDVP. 100mg/L of catalyst was used to mineralize 50 ppm of DDVP at pH 4. The complete mineralization was achieved with 4 molar % Cr doped titania within 1h of irradiation. This study confirms the potential of heterogeneous photocatalysis to purify wastewaters containing aromatic pollutants, particularly chlorinated substances, which are often toxic for microorganism in biological treatments.

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## CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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