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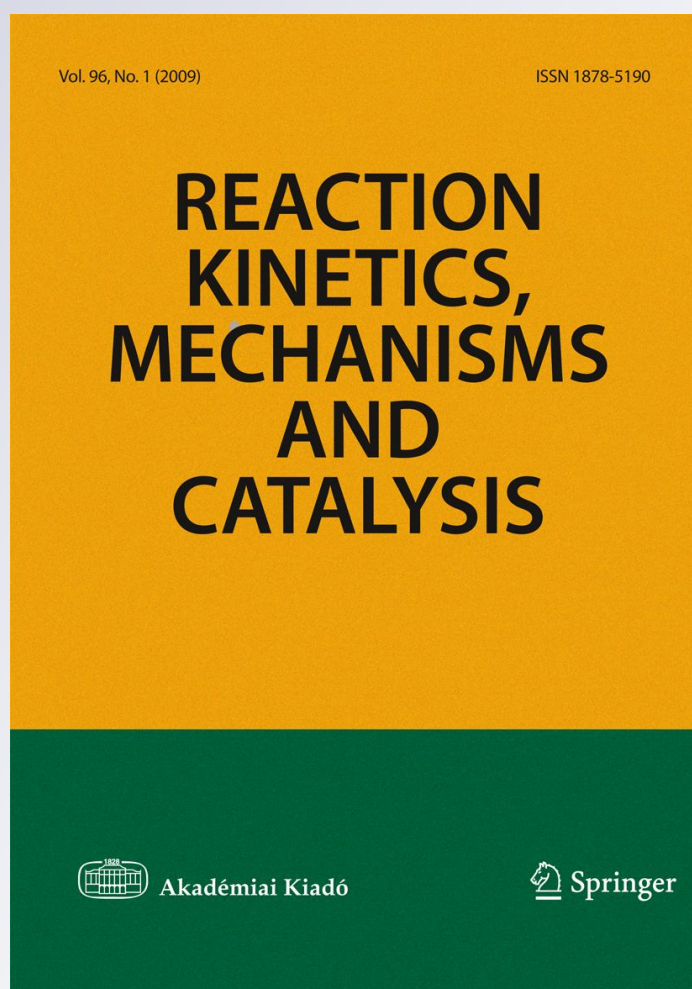
V. Gnana Glory Kanmoni, Sheeba Daniel & G. Allen Gnana Raj

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Photocatalytic degradation of chlorpyrifos in aqueous suspensions using nanocrystals of ZnO and TiO$_2$

**V. Gnana Glory Kanmoni · Sheeba Daniel ·
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Abstract The photocatalytic degradation of an organophosphorus insecticide chlorpyrifos (*O,O*-diethyl *O*-3,5,6-trichloro-2 pyridyl phosphorothioate) in aqueous suspensions of nano ZnO and nano TiO$_2$ under sunlight is reported in this study. Nanocrystals of ZnO (34.3 nm) were prepared by the wet chemical method and TiO$_2$ nanocyrstals (7.5 nm) were synthesized from titanium tetraisopropoxide by hydrolysis and peptization. The synthesized nanocrystals were characterized by X-ray diffraction, FT-IR, SEM–EDS and UV–Visible analytical techniques. The degradation of the insecticide was studied by monitoring the change in substrate concentration employing UV–Visible spectroscopy. The influence of catalyst loading, substrate concentration and pH were studied. The intermediates of the degradation process were identified by GC–MS. The synthesized nano ZnO and nano TiO$_2$ demonstrated high photocatalytic activity under solar light. The results show that nanocrystals of TiO$_2$ exhibit a better photocatalytic activity on the degradation of Chlorpyrifos than nanocrystals of ZnO.

Keywords Photodegradation · Chlorpyrifos · Nano ZnO · Nano TiO$_2$

Introduction

Chlorpyrifos is an organophosphate insecticide, acaricide and miticide used to control foliage and soil-borne insect pests on a variety of food and feed crops. It is the fourth highest consumed pesticide in India [1]. It is moderately toxic to humans and highly toxic to plants and animals. Poisoning from chlorpyrifos may affect the central nervous system, the cardiovascular system and the nervous system. It also inhibits acetylcholinestearase enzyme, an enzyme required for proper nerve functioning [2].

V. G. G. Kanmoni (✉) · S. Daniel · G. A. G. Raj
Department of Chemistry and Research Centre, Scott Christian College (Autonomous),
Nagercoil 629003, Tamil Nadu, India
e-mail: kanmoni2010@gmail.com

Extensive use of chlorpyrifos contaminates air, ground water, rivers, lakes, rainwater and fog water. In the environment, it is slowly hydrolyzed to other toxic chemical species, but they are quite persistent in aqueous solution [3]. It kills fish at concentrations as low as a few parts per trillion [4].

There are several methods to remove organophosphorous compounds from water. Chemical oxidation is one such method but it is expensive and leads to the contamination of water [5] with other toxic pollutants. Biological treatment processes are very slow or ineffective and have inherent limitations in applicability and effectiveness [6]. Therefore photocatalysis seems to be an ideal method for removal of insecticides since it is rapid and non-selective. The photo-catalytic process breaks down the organic compounds such as alcohols, carboxylic acids, amines, insecticides, herbicides and aldehydes into carbon dioxide, water and simple mineral acids. The main advantage of photocatalysis is that there is no further requirement for secondary disposal methods [7]. Heterogeneous photocatalysis using semiconductor oxides has been demonstrated to be very effective to treat pollutants both in gas and in liquid phase [8]. In the last few years, there have been a number of studies and reviews about this process [9–11]. Various researchers compared the efficiency of different semiconductor photocatalysts such as ZnO, TiO_2, SnO_2, ZrO_2 and CdS in the photodegradation of organic pollutants in aqueous solutions [12]. ZnO and TiO_2 are widely used due to their high photocatalytic activity under UV light, low cost, non-toxicity and high stability in aqueous solutions [13]. Photocatalysis based on the TiO_2 semiconductor is very promising and it has attracted extensive interest for the mineralization of pollutants both in air and water. Titania based photocatalysis has advantages such as strong resistance to chemicals, resistance to photocorrosion, ambient operational temperature and its low cost have led the relevant applications to the stage of commercialization [4]. They require UV light to generate the photocatalytic activity due to their wide band gap energy (~ 3.3 eV) [14]. Numerous studies have attempted to extend the photosensitivity of these semiconductors towards the visible light by performing modifications such as anion doping [15], metal doping [16], and generating oxygen deficiency [17]. Nanoparticles exhibit better photocatalytic activity under sunlight because of their large surface area and narrow size distribution than their counterparts [18]. Pelentridou et al. [19] investigated the photocatalytic activity of nanocrystalline TiO_2 film under sunlight illumination. Similarly, nanoparticles of V-doped and V and C60 co-doped titania showed better photocatalytic activity in the degradation of paraquat under visible light [20]. In the present study, nanocrystals of ZnO and TiO_2 were prepared by suitable methods and a series of photocatalytic experiments were conducted to examine their catalytic activity on the degradation of chlorpyrifos. The intermediate products formed in the photodegradation process were analyzed by GC–MS techniques.

Materials and methods

Chemicals

Chlorpyrifos (99.5 %) and titanium tetraisopropoxide (97 %) were purchased from Sigma Aldrich. Acetonitrile and methanol were purchased from Merck chemicals.

All other chemicals were of analytical grade and were used without further treatment. Double distilled water was used throughout the experiment.

Synthesis of catalysts

Nanocrystals of ZnO were prepared from wet chemical method using zinc acetate and sodium hydroxide precursors. Zinc acetate (2.2 g) and sodium hydroxide (0.8 g) were dissolved in 100 mL double distilled water. The solution was heated in a microwave oven at 80 °C for 20 min. The precipitate obtained was cooled, centrifuged, filtered, dried and annealed at 800 °C for 2 h. Nanocrystals of TiO_2 were synthesized by hydrolysis and peptization method from Titanium tetraiso-propoxide and isopropanol at pH 2 [21].

Analytical instruments

Several techniques were used to characterize the ZnO and TiO_2 nanocrystals. The crystallite phases of the photocatalysts were determined by X-ray diffraction (XRD) measurements using X' Pert Pro PANalytical diffractometer with Cu K_α radiation. FT-IR spectra were recorded using Thermo Nicolet Avatar 370 FTIR spectrometer, over the range of frequencies from 4,000 to 400 cm^{-1} using KBr pellets. UV–Visible absorption spectroscopy was employed on a SYSTRONICS 2203 double beam spectrophotometer. Surface morphology was analyzed by SEM–EDS analysis using a JEOL JSM-6390LV microscope with an energy dispersive spectrometer. GC–MS analysis was run on a Thermo MS DSQ II system. Separation was carried on a TR5-MS capillary standard non-polar column with 0.25 μm thick film.

Photodegradation experiment

The experiments were carried out under clear sky conditions. The light intensity was measured by Lux meter (LX-1102). The sunlight intensity was recorded from 900 to 950 W m^{-2} and the mean temperature was 30 °C. The sunlight photodegradation experiments were conducted in a laboratory made photoreactor. The experimental setup consists of a 250 mL Pyrex glass beaker containing 100 mL of the sample placed in a water bath. The sample was agitated with an electromagnetic stirrer at a constant speed of 400 rpm. The sample solution was directly exposed to sunlight irradiation in open atmosphere.

The desired concentrations of chlorpyrifos were prepared from 10 to 30 ppm in double distilled water containing 10 % acetonitrile. 100 mL of the chlorpyrifos solution in desired concentration was taken in the 250 mL Pyrex glass beaker and required amount of the catalyst (nano ZnO or nano TiO_2) was added. The solution was stirred for at least 15 min in the dark to allow equilibration of the system. Then the first sample (3 mL) was taken out and centrifuged to remove the suspended catalyst. The initial concentration (C_0) was monitored by measuring the absorbance on a UV–Visible spectrophotometer at 290 nm. After that, the aqueous suspension was placed in the water bath for sunlight irradiation with constant stirring. Aliquots (3 mL) were collected at regular intervals (30 min) for analysis. The change in the

concentration of chlorpyrifos was monitored by measuring the absorbance. The influence of catalyst concentration, substrate concentration and pH were investigated. The degradation followed pseudo-first order kinetics. The photocatalytic degradation efficiency of chlorpyrifos was calculated according to the following equation.

$$\text{Efficiency}\,(\%) = \frac{C_0 - C}{C_0} \times 100 \tag{1}$$

where C_0 represents the concentration of the chlorpyrifos solution before irradiation and C is the concentration of the chlorpyrifos solution after irradiation.

For the characterization of intermediate products, an aqueous solution of chlorpyrifos (25 ppm) containing the photocatalyst (1 g L^{-1}) was irradiated for 60 min and centrifuged to remove the photocatalyst. The filtrate was extracted with chloroform, dried over anhydrous sodium sulfate and the solvent was removed under reduced pressure to give a residual mass. The residual mass was dissolved in methanol and then analyzed by GC–MS.

Results and discussion

XRD analysis

Fig. 1b shows the XRD pattern of nano ZnO. The sharp diffraction peaks indicate the nanocrystalline nature. These peaks at scattering angles (2θ) of 31.8°, 34.4°, 36.3°, 47.5°, 56.6°, 62.9°, 67.9°, 69.1° correspond to the reflection from 100, 002, 101, 102, 110, 103, 200 and 112 crystal planes [22]. The XRD pattern of nano TiO_2 (Fig. 1a) shows five primary peaks at 25.4°, 38°, 47.7°, 54° and 62.8°. These peaks are attributed to different planes 101, 112, 200, 105 and 204 of anatase TiO_2 [23]. The 101 plane diffraction peak is used for both photocatalysts to determine the crystallite size. From the XRD patterns of nano ZnO and nano TiO_2, the average crystallite size (D in nm) was calculated in accordance with the Scherrer equation [24].

$$D = k\lambda/\beta \text{Cos}\theta \tag{2}$$

where k is the constant (shape factor, about 0.9), λ is the X-ray wavelength (0.15418 nm), β is the full width at half maximum (FWHM) of the diffraction line and θ is the diffraction angle.

The crystallite size for nano ZnO and TiO_2 are 34.3 and 7.5 nm.

FT-IR analysis

The FT-IR spectrum of synthetic ZnO nanocrystals (Fig. 2b) shows a broad band with low intensity at 3,436 cm^{-1} indicating the presence of small amount of water adsorbed on the ZnO nanocrystal surface. The strong band at 500 cm^{-1} is attributed to the Zn–O stretching band which is consistent with that reported before [25].

The FT-IR spectrum of nano TiO_2 is shown in Fig. 2a. The band at 3,400 cm^{-1} for the stretching vibration of −OH group and the band around 1,626 cm^{-1} for the
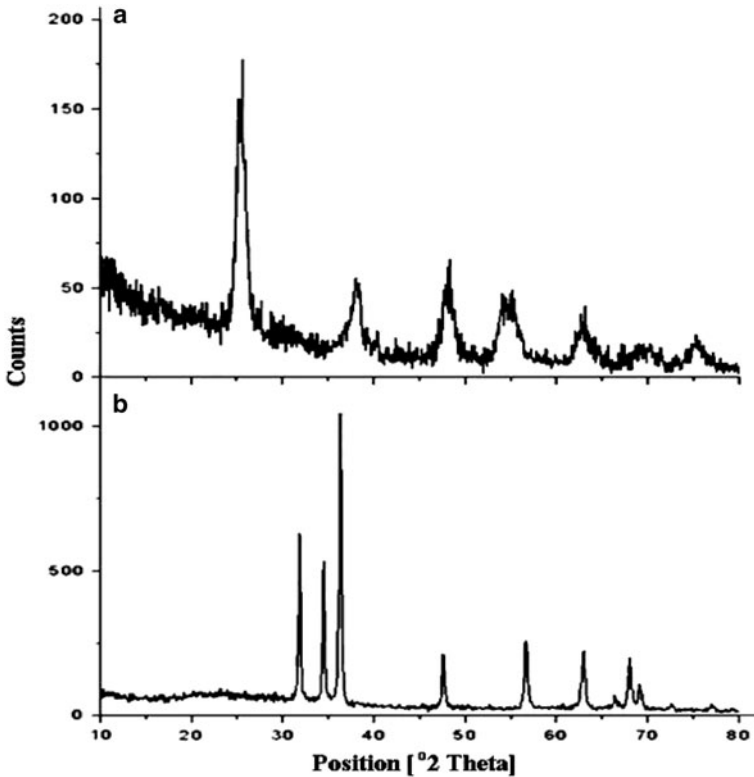
Fig. 1 XRD patterns of **a** nano TiO_2 and **b** nano ZnO

bending vibration of H–O–H group. The band at 460 cm^{-1} corresponds to the Ti–O–Ti stretching vibrations.

SEM–EDS analysis

The SEM image of ZnO nano crystals (Fig. 3) reveals the single phase primary particles are spherical in shape with the average size of 34–40 nm which is in good agreement with that estimated by the Scherrer formula. The SEM picture of nano TiO_2 is shown in Fig. 4. It shows irregularly shaped particles which are the aggregation of tiny crystals. The size of the primary particle is 8 nm which is in good agreement with that of XRD. The purity of nano crystal of ZnO and TiO_2 were also confirmed by EDS elemental analysis.
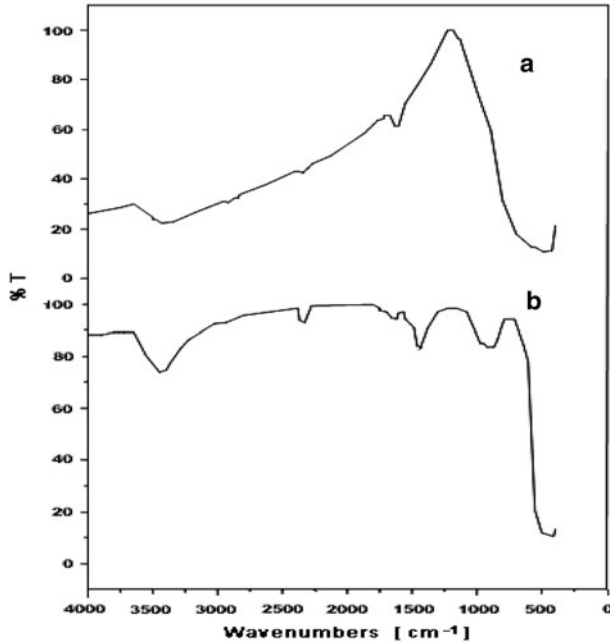
Fig. 2 FT-IR of **a** nano TiO$_2$ and **b** nano ZnO

UV–Visible absorption spectra

The UV–Visible absorption spectra (Fig. 5) shows that the nanocrystals of ZnO and TiO$_2$ are photocatalyst with the capability of photocatalysis under visible light irradiation. The band gap energy of the samples were determined by the equation

$$E_g = 1239.8/\lambda \tag{3}$$

where E_g is the band gap (eV) and λ (nm) is the wavelength of the absorption peak or edge in the spectrum. The photocatalyst nano TiO$_2$ has a narrower band gap (2.9 eV) than nano ZnO (3.2 eV).

Degradation of chlorpyrifos in the presence and absence of photocatalyst

To study the effectiveness of nano ZnO and TiO$_2$ on the photocatalytic degradation of chlorpyrifos under sunlight, two sets of experiments were performed. One set was performed by exposing chlorpyrifos alone (25 mg L^{-1}) to sunlight without catalyst. The second set was performed by exposing chlorpyrifos solution with nano ZnO and nano TiO$_2$ to sunlight. In the absence of photocatalysts, no significant degradation was observed within 150 min. The degradation proceeds rapidly in the presence of nano ZnO and nano TiO$_2$ showing sharp decrease in the concentration of
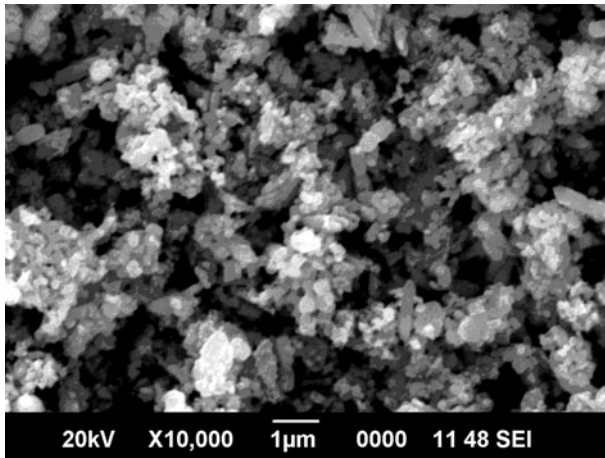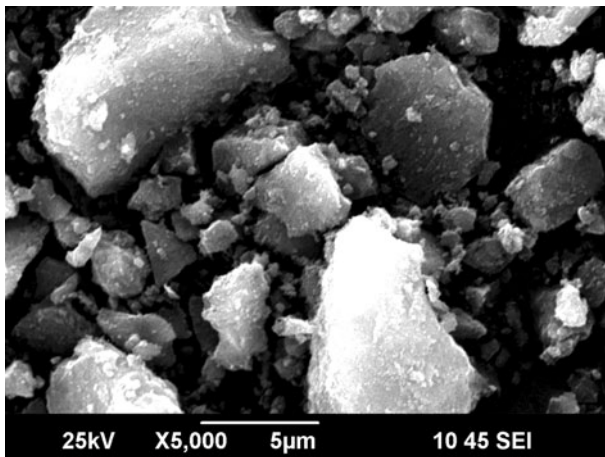
Fig. 3 SEM image of nano ZnO

Fig. 4 SEM image of nano TiO$_2$

chlorpyrifos for the first 30 min, further proceeding slowly; this is shown in Fig. 6. The activity of the photocatalyst depends on the type of pollutant under investigation and the oxidative reactions results in the degradation of the pollutant. Hence, the efficiency of degradation depends upon the oxygen concentration. As the oxidation proceeds, the concentration of oxygen in the sample decreases, and, consequently, the degradation rate decreases with an increase in the irradiation time [26]. So the last stage of the degradation was slow. Similar results were obtained in the degradation of an aqueous solution of chlorpyrifos solution by advanced oxidation processes [27]. Nano TiO$_2$ is more efficient compared to nano ZnO causing maximum degradation (100 %) within 120 min, which was not accomplished by nano ZnO.
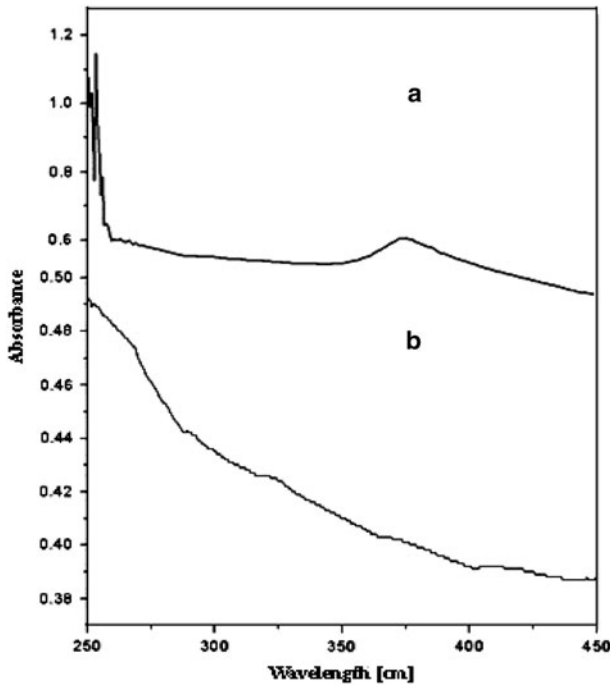
Fig. 5 UV–Visible absorption spectra of **a** nano ZnO and **b** nano TiO$_2$

Effect of catalyst concentrations

The influence of catalyst loading on the degradation of chlorpyrifos was investigated by changing the catalyst concentration from 0.1 to 1 g L^{-1}. The catalyst concentration increases the rate of degradation and reaches the maximum and then decreases (Fig. 7). The maximum rate of degradation was found in the optimum dosage of the photocatalyst. The reason for this decrease in degradation rate beyond the optimum dosage might be due to the aggregation of the photocatalyst at high concentrations causing a decrease in the number of surface active sites and the increase in opacity and light scattering of photocatalyst at high concentration leading to decrease in the passage of irradiation through the sample [28]. The optimum dosages of nano ZnO and nano TiO$_2$ were found to be 0.25 and 0.75 g L^{-1}.

Effect of substrate concentration

Fig. 8 shows the effect of substrate concentration on the rate of degradation of chlorpyrifos at constant concentration of the photocatalyst (0.25 g L^{-1}) by varying the concentration of chlorpyrifos from 10 to 30 mg L^{-1}. With nano ZnO, the degradation rate tends to drop after a particular substrate concentration 25 mg L^{-1}, whereas the degradation proceeds at a remarkable rate using nano TiO$_2$ without showing an optimum.
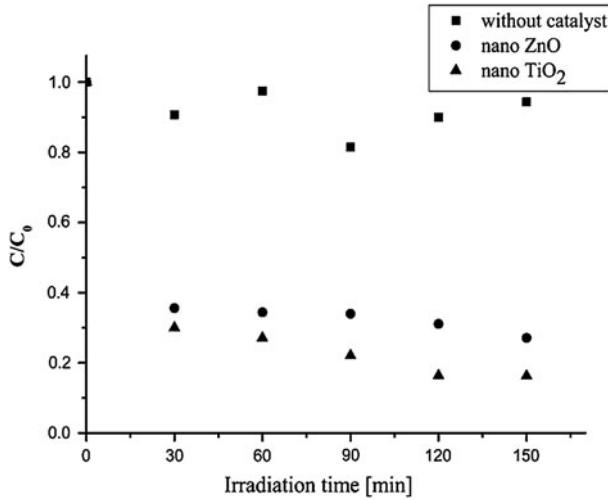
Fig. 6 Variation of concentration of chlorpyrifos as a function of irradiation time
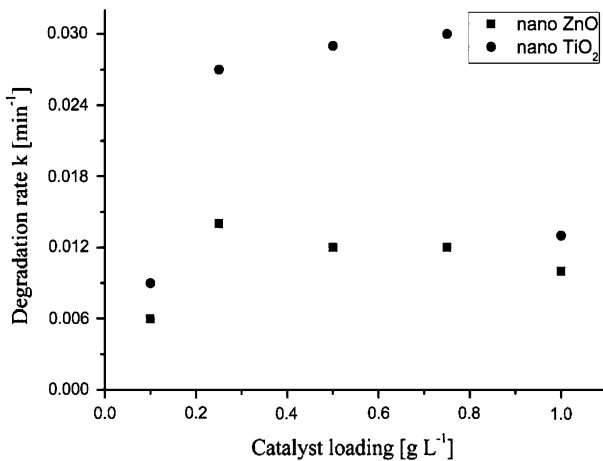

Fig. 7 Effect of catalyst concentration on the degradation rate of chlorpyrifos

Effect of pH

The pH has an influence on the rate of degradation of some organophosphorous compounds in photocatalytic process [29, 30]. The degradation of chlorpyrifos was studied at a pH range from 2 to 11 under sunlight using constant substrate concentration (25 mg L^{-1}) and catalyst concentration (0.25 g L^{-1}). The optimum pH (Fig. 9) for nano ZnO and nano TiO$_2$ were 6.4 and 4.2. The result shows that the rate of degradation of chlorpyrifos in the presence of photocatalysts is maximum in acidic medium.
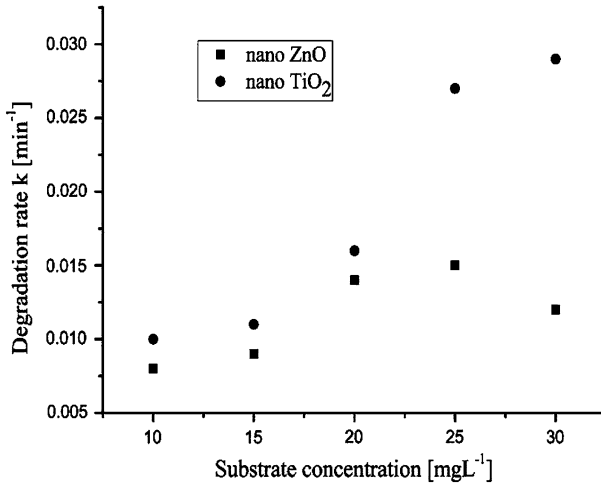
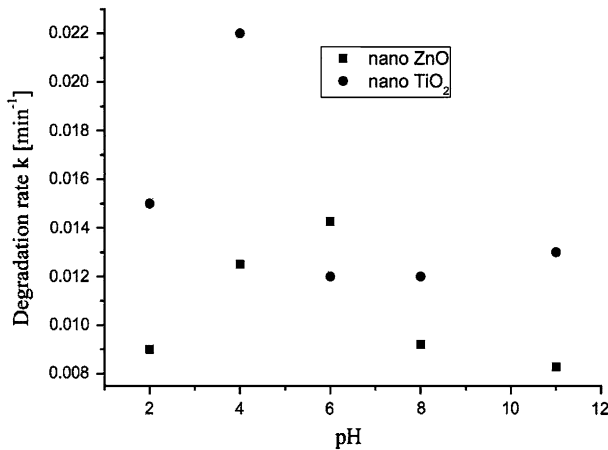**Fig. 8** Effect of substrate concentration on the degradation rate of chlorpyrifos

Fig. 9 Effect of pH on the degradation rate of chlorpyrifos

Kinetics of the photocatalytic degradation of chlorpyrifos

In order to determine the order of the reaction, the photodegradation reaction of chlorpyrifos (25 mg L^{-1}) with photocatalyst (0.25 g L^{-1}) was carried out at pH 6.4. The rate constant for the photocatalytic degradation of chlorpyrifos was obtained from the first order rate equation (Eq. 4).

$$-\ln C/C_0 = kt \tag{4}$$

where C and C_0 are the concentrations of substrate at time t and time 0 in minutes, k is the first order rate constant (min^{-1}).
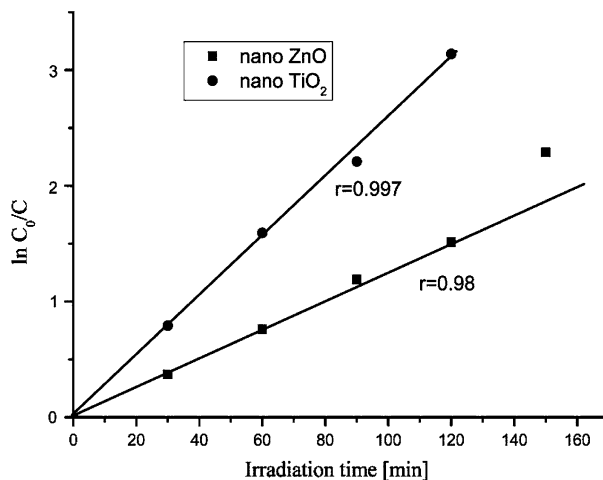
Fig. 10 Plot of ln C_0/C versus irradiation time of the degradation of chlorpyrifos using nano ZnO and nano TiO_2
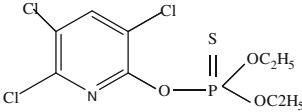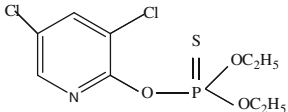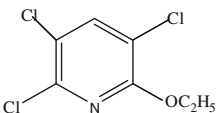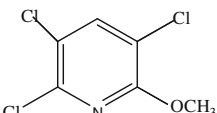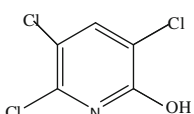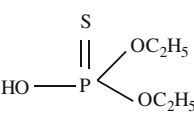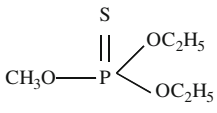
$$t_{1/2} = 0.693/k \qquad (5)$$

$t_{1/2}$ is the half-life.

The plot of lnC_0/C versus irradiation time shows a straight line behavior and the rate constants were determined from the slope of the straight line. The photocatalytic degradation of chlorpyrifos with nano ZnO and nano TiO_2 is shown in Fig. 10. It shows that the degradation proceeds through first order kinetics. The rate constants and the half life obtained for the photodegradation of chlorpyrifos with nano ZnO and nano TiO_2 were 0.014 min^{-1}, 49.5 min; 0.027 min^{-1}, 25.6 min. These results also show that the photodegradation was faster in nano TiO_2 than in nano ZnO. Complete degradation takes place within 120 min in the presence of nano TiO_2. The degradation efficiency is nearly two times greater in nano TiO_2 than in nano ZnO. A similar trend in the photocatalytic activity of modified TiO_2 is observed in the degradation of malachite green in aqueous solution under visible light [31].

GC–MS analysis

The photocatalytic degradation of chlorpyrifos gives a number of transient organic intermediates. Hydrolysis, oxidation and dechlorination were the main reactions involved in the photodegradation of chlorpyrifos. The chlorpyrifos solution showed intense m/z peak at 350.7. The intermediate products with retention time are mentioned in Table 1. The photodegradation takes place through free radical mechanism and the possible degradation pathways are shown in Scheme 1.

Table 1 GC–MS retention times and spectral characteristics of intermediate products of the photo-degradation of chlorpyrifos

Structure	Retention time (min)	M^+	Main fragment ions (m/z)
	19.408	351	336, 316, 304, 288, 276, 260, 244, 208, 197, 183, 180, 169, 144, 135, 153, 144,135, 125, 97, 81, 65, 47, 29
	19.224	316	288, 260, 243, 208
	17.44	226	183, 127, 95, 79
	16.965	213	199, 143
	15.29	199	183, 127
	15.15	169	141, 113, 97
	5.051	184	155, 127, 97

Conclusion

One of the major challenges for the scientific and industrial community involved in photocatalytic research is to increase the spectral sensitivity of semiconductor based photocatalysts from UV to visible light. The semiconductor catalysts synthesised in the present study have smaller particle size with narrow size distribution. Hence they showed better photocatalytic behavior in the degradation of chlorpyrifos under sunlight. Nano TiO_2 shows better photocatalytic activity than nano ZnO due to its small crystallite size and the higher capacity to adsorb surface water and hydroxyl
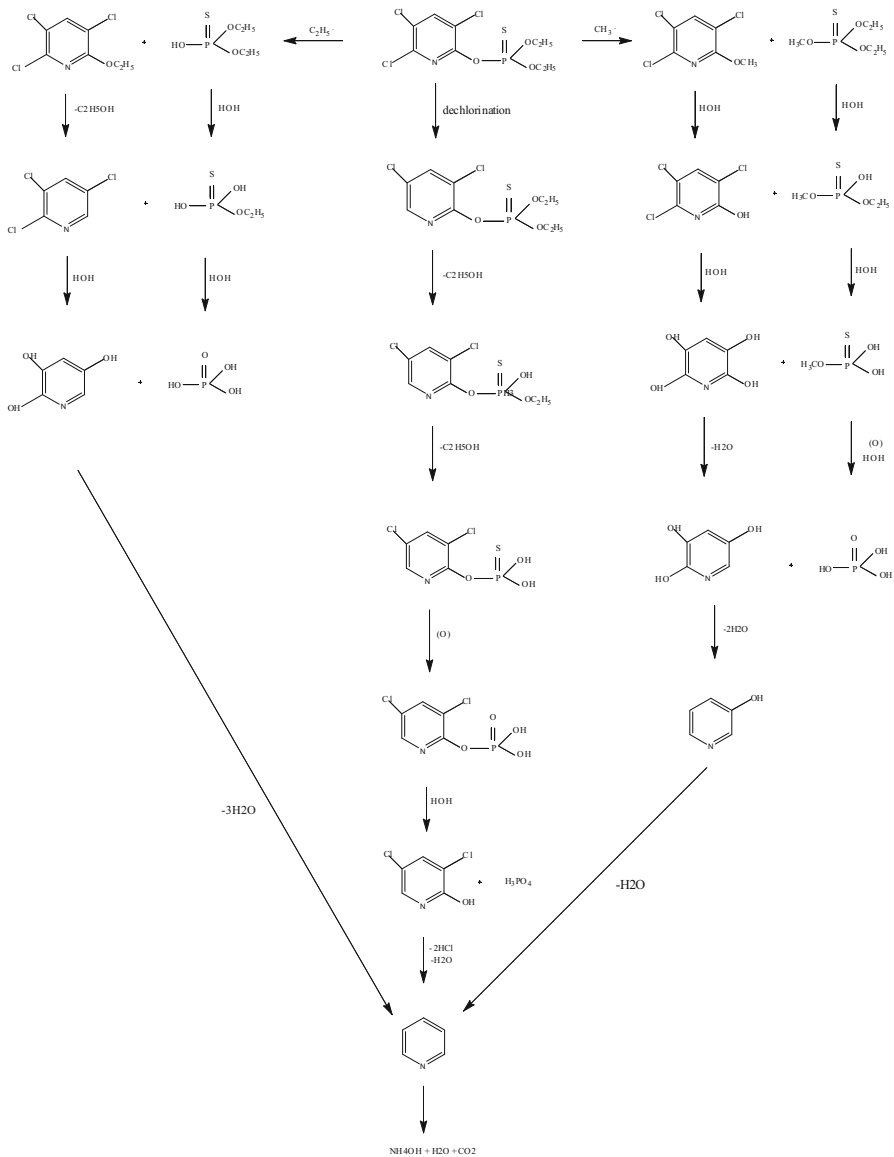
Scheme 1 Photodegradation of chlorpyrifos

groups. The degradation efficiency is also high for nano TiO$_2$ than nano ZnO. The photocatalysts worked more efficiently in acidic environment. The analysis of the intermediate products could be useful source of information on the degradation pathways. The photodegradation of chlorpyrifos under sunlight generates excess free radicals and destroyed the intermediates at a faster rate. Hence, it can be concluded that the use of solar energy is advantageous, it enhances the

photocatalytic process and avoids the complexity in the degradation mechanism owing to the formation of less number of intermediates.

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