

Synthesis of Mn-doped TiO₂ by novel route and photocatalytic mineralization/intermediate studies of organic pollutants

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Abstract

The doping of TiO₂ particles with various manganese (Mn) concentrations (0.25-1.0%) were synthesized using simple sol-gel and modified sol-gel technique. The characteristics of synthesized particles were found employing standard analytical techniques such as X-ray diffraction, scanning electron microscopy and UV-Vis spectroscopy. The photocatalytic activity of the synthesized particles was compared by investigating the mineralization of two selected organic pollutants like ketoprofen and chlorothalonil. The photocatalysts which were produced by improved sol-gel technique show the lower value of band gap energy and small size crystallite and, hence, exhibit better photocatalytic activity. The outcomes also designate that the concentration of dopant Mn 0.75% indicated the highest photocatalytic activity than other concentrations of dopant in the mineralization of both the compounds. The mineralization kinetics of both compounds was studied under various situations like reaction pH and catalyst dosage. The mineralization rates were highly affected by all the above parameters. An effort has also been performed to highlight the intermediates produced during the photooxidation of both the compounds using the GC-MS analysis method. Both compounds show the production of several intermediates. A possible pathway for the production of different products has been suggested.

Keywords Ketoprofen \cdot Chlorothalonil \cdot Doped-titanium dioxide \cdot Semiconductor \cdot Intermediate products

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Introduction

The formulation of new pharmaceutical compounds and pesticides plays a vital role and revolutionizes the life of human beings day by day. The pharmaceutical compounds are ultimately responsible for the treatment of various dangerous diseases. On the other hand, the use of pesticides protects the crops from pests and finally increases the productivity. Nowadays, global consumption of these compounds in human and veterinary medicine are now at very high levels which creates a lot of problems for the environment [1]. A drug derivative such as ketoprofen, (non-steroidal anti-inflammatory drug) is extensively employed to prevent rheumatoid arthritis, these molecules are highly soluble in the groundwater but insoluble and non-degraded in the subsoil, biotic and abiotic due to polar structure. Therefore, lengthy contact of these chemicals is probable and influences health [2-6]. Moreover, chlorothalonil is a non-systemic foliar fungicide employed in many agricultural crops, particularly fruits and vegetables [7, 8]. In addition, it has been used as an alternative to TBT additive agent in antifouling paints for the last few years [9]. To prevent the growth of algae, bacteria and other invertebrates, this type of paint is applied to the hulls of ships [10].

Key sources of pharmaceutical compounds polluting ground and surface water are the waste of manufacturing pharma-industries, human excretion [11] while for pesticides, urban areas runoff, agricultural fields return flows and leaching are accountable for water pollution [12]. Even a very small amount of these pollutants is very harmful to our living systems. For example, Chlorpyrifos (concentration, $1-10 \text{ mg } \text{L}^{-1}$) is enough to slow down the development in blue green algae Anabaena sp. and decrease ciliated protozoa in a naturally based microbial community [13, 14]. Therefore, degradation of these compounds has acquired increasing attention. In recent years, doping of metal ions with semiconductor has been made with the aim that they could do work in the visible region and also recognised as changing both photochemical reactivity and photophysical behaviour [15-17]. Although the sol-gel technique is an eye-catching technique and a simple method for synthesis of TiO₂ at low temperature, it is difficult to find uniform particles employing this technique. Due to some advantages, hydrothermal technique proved to be a potential technique such that (1) Crystalline product can be achieved directly (2) It also favours a decline in particles agglomeration. (3) Due to a recrystallization process, the purity of the obtained product is very high [15]. In literature, synthesis of nanocrystalline TiO₂ with doped metal ions/metal oxide using the sol-gel method has been proposed [18-20].

As far as the mechanism of photocatalysis is concerned, this involves the excitation of electrons from the valance band to the conduction band. As a result, the formation of a hole in the valance band and availability of electrons in the conduction band takes place. After that, if this charge separation continues, these electrons and holes may travel to the surface of catalyst where they react with water and oxygen to form radical ions [21–23]. In the case of doping metal ions with photocatalyts, it establishes a new energy level which reduces the band gap and inhibits electron-hole recombination. The doping also improves the absorption of visible light [16, 24].

The current paper investigates the production of Mn-doped TiO_2 with various methods followed by characterization employing an analytical standard. The comparison of photocatalytic activity for both photocatalysts synthesized by two different methods was examined by investigating the two organic pollutants mineralization (drug and pesticides) like ketoprofen and chlorothalonil under a source of visible light. A study on the photomineralization of ketoprofen and chlorothalonil sensitized by Mn-doped TiO_2 in aqueous solution was carried out by considering different parameters of reaction, like pH reaction and catalyst loading. To obtain the optimal condition of mineralizations. An effort has also been made to recognize the intermediate products produced during the photooxidation practise of both the compounds using the GC–MS analysis method.

Experimental

Materials and methods

Ketoprofen, chlorothalonil and titanium isopropoxide, were procured from Sigma-Aldrich. Mangnese (II) sulphate monohydrate and 2-propanol were obtained from Merck, Himedia Laboratories Pvt. Ltd. India, Central Drug House, India. Double distilled water was used in all experiments. TiO₂ particles were synthesized by the simple sol-gel method reported in our earlier paper [19] while to synthesize TiO₂ particles with modified sol-gel technique, the following procedure was used; a homogeneous solution I (10 mL of 2-propanol and 10 mL of water) was mixed slowly with solution II (titanium isopropoxide and 2-propanol) under constant stirring and maintaining temperature at 90 °C. After sometime, the turbidity in the solution occurred and later the formation of precipitation took place. The precipitation state may be due to hydrolysis of titanium isopropoxide. A solution III was prepared which consisted of known concentrations (0.25-1.0%) of manganese sulphate monohydrate, 2-propanol and water. Doping of TiO2 with Mn was performed by addition of solution III slowly with solution II. For hydrothermal treatment, the gel obtained was shifted into a 100-mL, autoclave Teflon-lined vessel at 350 °C for 5 h. Then the suspension was centrifuged, washed with absolute ethanol and dried at room temperature.

Catalysts characterization

The techniques like standard analytical XRD, SEM and UV–Vis spectroscopy were used to characterize the synthesized catalysts. XRD was carried out in the 2θ range of 20–80° (Rigaku Miniflex II) with Cu K α radiations (λ =1.5418 Å) at 30 kV and 15 mA to discover the structural characteristics of TiO₂ and doped TiO₂ particles. A Shimadzu UV–Vis spectrophotometer (Model 1601) was used to find the band gap

energy of synthesized particles in the range of 300–800 nm at room temperature. The surface morphology of synthesized material was recorded using SEM (LEO, 435 VF) at 1 K–100 K magnification, WD 15 mm at 20 kV voltage.

Irradiation procedure

Solutions of desired concentrations of each organic pollutant (ketoprofen and chlorothalonil) were synthesized in double distilled water and irradiated in the existence of Mn-doped TiO₂ (2 g L⁻¹) with regular supply of atmospheric oxygen and stirring. Pyrex glass was used to make an immersion cell photochemical reactor equipped with a water circulating jacket, magnetic stirring bar, and an opening for air supply. Aqueous solution of 250 mL of preferred organic pollutants was transferred into the reactor, and the desired quantity of photocatalyst was added. For system equilibration, the solution was stirred for 15 min in the dark. The blank solution was kept in the dark to obtain a zero time reading. A visible light halogen lamp (500 W, 9500 Lumens) was used to irradiate the solution. Samples were collected at regular time intervals during the experiment and examined after centrifugation.

For the intermediate products characterization, an aqueous solution of the organic pollutants ketoprofen (0.30 mM, 250 mL) was placed in a photochemical reactor. After that, Mn-doped TiO₂ (0.75%, 3 g L⁻¹) was added to the reactor. The solution was irradiated through visible light at different time intervals with continuous bubbling and stirring of atmospheric O₂. The photocatalyst was removed by filtration, and the filtrate was transferred into a separating funnel. After adding the chloroform to the separating funnel, two layers were formed, i.e., one organic layer and a second aqueous layer. The vigorous shaking of the separating funnel may be responsible for the displacement of intermediates compounds from aqueous to an organic layer, which was consequently dried over anhydrous sodium sulphate and investigated by GC/MS. The same procedure was used for another organic pollutant, i.e., chlorothalonil (0.20 mM, 250 mL).

Analysis

The mineralization of ketoprofen and chlorothalonil was checked by determining the total organic carbon (TOC) content using a Shimadzu TOC- V_{CH} analyser. For GC–MS investigation, a Perkin Elmer (GC-MASS CLARUS -680) which was equipped with a capillary column PE-5MS (length 30 m, i.d. (250 µm), operating temperature 50 °C, which was elevated to 250 °C at 10 °C min⁻¹), in a split less approach of injection volume (1.0 µL) with carrier gas as helium, was employed.

Results and discussion

Characterization of catalysts

XRD patterns of prepared doped and undoped TiO_2 with different concentrations of Mn calcinated at 350 °C for 5 h were measured. Figure 1 indicates the XRD arrangement of Mn-doped TiO₂ calcined at 350 °C as a representative example. The undoped and doped-TiO₂ XRD patterns do not show any noteworthy change. It is pertinent to mention here that XRD patterns do not show any peak corresponding to dopant, possibly the sample encloses the low concentration of dopant as compared to TiO₂. Moreover, ionic radii of Mn²⁺ (0.80 Å) is higher than Ti⁴⁺ (0.68 Å). Therefore, these dopants rarely to act as interstitial contamination, so they probably exist on the surface of TiO₂ [25–27]. For the calculation of the average crystallite size of synthesized particles (pure and doped TiO₂), the Debye Scherer formula was used which is expressed by the following Eq. 1:

$$D = \frac{K\lambda}{\beta\cos\theta}.$$
 (1)

This is in which D=size of crystallite, K=factor of shape, β =full width at half maximum, λ =wavelength, and θ =diffraction angle. The crystallites average size of pure and doped samples, synthesized by both the methods are shown in Table 1.

The size of crystallite was establish to be reduced with the rise in concentration of dopant. This decrease in size may be due to possible production of some interaction of dopants with titanium, which is responsible for the inhibition of the size of crystal grains [28]. It is important to mention here that the particles yielded by the



Fig. 1 XRD patterns of undoped and Mn-doped TiO₂ (0.25%, 0.50%, 0.75% and 1.0%). (H=post hydrothermally modified sol-gel method)

| S. no. | Dopant concent- ration (%) | Dopant/crystallite size (nm) (sim- ple sol-gel method) | Dopant/crystallite size (nm) (modified sol–gel method) |
|--------|-------------------------------|---|--|
| 1 | 0 | None/15.9 | None/13.6 |
| 2 | 0.25 | Mn/15.4 | Mn/11.7 |
| 3 | 0.50 | Mn/14.5 | Mn/9.9 |
| 4 | 0.75 | Mn/13.8 | Mn/8.1 |
| 5 | 1.00 | Mn/13.2 | Mn/7.7 |

Table 1 Crystallite size of undoped and Mn-doped TiO_2 with different concentrations of Mn synthesized by two different routes

Calcination temp: 350 °C calcination time: 5 h

modified sol-gel method show the smaller average crystallite size than the simple one.

UV–Vis light excitation creates photogenerated holes and electrons in the structure of band (or levels of molecular energy) of the material. So, the UV–Vis absorption spectra of doped TiO_2 and undoped TiO_2 synthesized by two different routes with different dopant concentrations of Mn were investigated and as a symbolic model, UV–Vis absorption spectra of Mn-doped TiO_2 are revealed in Fig. 2. The wavelength attained by pure and doped TiO_2 particles from UV–Vis spectra has been used to calculate the band gap energies using the following (Eq. 2) and are enumerated in Table 2.



Fig. 2 Absorption spectra of undoped and Mn-doped TiO_2 . (a) Undoped TiO_2 , (b) 0.25% Mn-doped TiO_2 , (c) 0.50% Mn-doped TiO_2 , (d) 0.75% Mn-doped TiO_2 and (e) 1.00% Mn- doped TiO_2 , (H=post hydrothermally modified sol-gel method)

| S. no. | Dopant concentration (%) | Dopant/band gap (eV) (simple sol-gel method) | Dopant/band gap (eV) (modified sol-gel method) |
|--------|--------------------------|---|--|
| 1 | 0.00 | None/3.16 | None/3.16 |
| 2 | 0.25 | Mn/3.07 | Mn/2.99 |
| 3 | 0.50 | Mn/2.97 | Mn/2.89 |
| 4 | 0.75 | Mn/2.79 | Mn/2.67 |
| 5 | 1.00 | Mn/2.88 | Mn/2.79 |

Table 2 Band gap energy of undoped and Mn-doped TiO_2 with different concentrations of Mn synthesized by two different routes

Calcination temp: 350 °C calcination time: 5 h

Band energy(eV) =
$$1240$$
/wavelength(nm) (2)

The UV–Vis absorption spectra of Mn-doped TiO_2 display a red shift in the band-gap alteration. This phenomenon may be understood so that the doping of metals introduces the new levels of energy in the TiO_2 particle, which reduces the band gap energy [27].

The morphological properties of doped and undoped TiO_2 were determined through SEM. Figure 3 shows the structural properties of undoped and Mn-doped TiO_2 (0.75%) synthesized by the modified sol–gel method while Fig. 4 shows images of undoped and Mn-doped TiO_2 (0.75%) produced by the simple sol–gel method. The SEM images of doped TiO_2 particles produced by the modified sol–gel technique show a complex and porous nature with a high irregular surface that would be the outcome in a high area of the surface. On the other hand, doped TiO_2 synthesized by the simple sol–gel technique presents an amorphous nature [24].



Fig.3 SEM images of a undoped TiO_2 , b Mn-doped TiO_2 (0.75%) calcination temp: 350 °C, modified sol-gel method, calcination time: 5 h



Fig. 4 SEM images of a undoped TiO₂, b Mn-doped TiO₂ (0.75%) calcination temp: 350 °C, simple solgel method, calcination time: 5 h

Photocatalytic activity

Photocatalytic action of Mn-doped-TiO₂ for the mineralization of organic pollutants

The Mn-doped TiO_2 based photocatalytic activity is synthesized by two different methods with various concentrations of metal ions ranging from 0.25 to 1.0% that was verified by determination of the mineralization of two various organic derivatives like ketoprofen (drug) and chlorothalonil (pesticide) under a source of visible light in aqueous suspension with the existence of O₂. Figures 5 and 6 illustrate the mineralization rate of both contaminants in the presence of doped TiO₂ and undoped (pure TiO₂). Figures show the mineralization rate of pollutants rises with escalation in dopant concentration from 0.20 to 0.75% and more growth in the dopant concentration leads to reduction in the mineralization rate.

The rise in the photocatalytic action by growing the concentration of dopant could be ascribed to the fact that the TiO_2 doping with dopant can introduce fresh sites of trapping. These innovative produced sites of trapping also affect the recombination process of the photo-generated moieties which increases the photo-oxidation proficiency [16]. The shortening of band gap may be another cause for the rise in the photocatalytic action by increasing the concentration of dopant thereby efficiently absorbing the longer wavelength light. Moreover, at upper concentrations of dopant there is incidence of many charge carriers trapping and hereafter the chance of electron-hole recombination rises [29, 30] which decreases the mineralization rate. It is also appropriate to discuss here that the TiO_2 particles which were prepared by the modified method show the higher activity as compared to the simple sol-gel method. The photocatalytic performance of particles depends on several factors like the morphology, distribution of particle size, electronic properties, surface area, conflicting surfaces hydroxylation, quantity of adsorbed reactant species, etc. [31].

In this case, the better activity of the particles which were prepared by the modified method can be elucidated on the basis of the fact that they have lower band



Fig. 5 Photocatalytic activity of undoped and Mn-doped TiO₂ [synthesized by the simple sol–gel method (ssg) and the modified sol–gel method (msg)] for the mineralization of ketoprofen and chlorothalonil. Experimental condition: reaction vessel: immersion well photochemical reactor made of Pyrex glass, ketoprofen (0.12 mM), volume (250 mL), dopant: Mn, dopant concentration (0, 0.25, 0.50, 0.75 and 1.0%), light source: halogen linear lamp (500 W, 9500 Lumens) continuous stirring and air purging, irradiation time: 300 min



Fig. 6 Photocatalytic activity of undoped and Mn-doped TiO₂ [synthesized by simple sol–gel method (ssg) and modified sol–gel method (msg)] for the mineralization of ketoprofen and chlorothalonil. Experimental condition: reaction vessel: immersion well photochemical reactor made of Pyrex glass, Chlorothalonil (0.15 mM), volume (250 mL), Dopant: Mn, Dopant concentration (0, 0.25, 0.50, 0.75 and 1.0%), light source: halogen linear lamp (500 W, 9500 Lumens) continuous stirring and air purging, irradiation time: 300 min

gap energy. Secondly, also they have small crystallite size which is accountable to increase surface area and the better activity observed.

In all following experiments, Mn-doped TiO₂ (0.75%, msg) was employed as the photocatalyst, meanwhile this material showed the maximum whole action for the mineralization of the organic pollutants.

Photolysis of aqueous suspension of organic pollutants in the presence of Mn-doped TiO_2

Aqueous suspension irradiation of desired compound (ketoprofen or chlorothalonil) in the presence of Mn-doped TiO₂ (0.75%) with continuous bubbling of atmospheric oxygen lead to reduction in content of TOC as a time function. Figures 7 and 8 depict the reduction in content of TOC as a time function on irradiation of aqueous suspensions of ketoprofen or chlorothalonil in the nonexistence and existence of doped TiO₂. Controlled experiments were performed by irradiating a solution of the compounds in the absence of photocatalyst where no visible depletion in the TOC content takes place as shown in the figure whereas in the presence of Mn-doped TiO₂ a mineralization of 83% and 72% take place in ketoprofen and chlorothalonil, respectively, in 300 min.

For each irradiation process, the rate constant for the mineralization of ketoprofen or chlorothalonil was measured from the natural logarithm plot of the TOC content as a function of time irradiation.



Fig. 7 Change in concentration as a function of time on irradiation of an aqueous solution of ketoprofen in the absence and presence of Mn-doped TiO_2 (0.75%), (simple sol–gel method, modified sol–gel method) respectively. Experimental conditions: reaction vessel: immersion well photochemical reactor made of Pyrex glass, ketoprofen (0.12 mM), volume (250 mL), light source: halogen linear lamp (500 W, 9500 Lumens) continuous stirring and air purging, irradiation time: 300 min



Fig. 8 Change in concentration as a function of time on irradiation of an aqueous solution of chlorothalonil in the absence and presence of Mn-doped TiO_2 (0.75%), (simple sol–gel method, modified sol–gel method) respectively. Experimental conditions: reaction vessel: immersion well photochemical reactor made of Pyrex glass, chlorothalonil (0.15 mM) volume (250 mL), light source: halogen linear lamp (500 W, 9500 Lumens) continuous stirring and air purging, irradiation time: 300 min

As a representative example, the mineralization curve (ln C vs time) of ketoprofen in the existence of doped TiO₂ shown in Fig. 9 which can be plotted rationally well by an exponential curve decay signifying pseudo first order kinetics. The



Fig. 9 Plot showing the linear regression curve fit for the natural logarithm of concentration of ketoprofen as a function of time on irradiation of an aqueous suspension of the pollutant in the presence of Mn-doped $\text{TiO}_2(0.75\%)$. (modified sol–gel method)

mineralization rate for the compounds was measured in term of mol L^{-1} min using formulas such as the following;

$$-d[TOC]/dt = kC^1$$
(3)

TOC = Total Organic Carbon, C = pollutant concentration, k = constant rate, n = 1.

Effect of initial pH

The pH of an aqueous solution of organic pollutants shows a significant role, as it effects the charge on the catalyst surface, the aggregation particles number and the position of conductance and valance band. To see the pH effect on the mineralization kinetics, the mineralization of both the pollutants was investigated at various pH values employing Mn-doped TiO₂ (0.75%) as photocatalyst. The mineralization rate for organic pollutants ketoprofen and chlorothalonil was investigated in the range of pH from 4 to 13. Figure 10 shows the mineralization rate for the organic pollutants ketoprofen and chlorothalonil as a function of pH. The solution initial pH was adjusted by adding the required amount of dilute HNO₃ or NaOH solution before irradiation.

The understanding of pH influence on the process of photocatalytic is very difficult because of its numerous roles like electrostatic interactions among solvent molecules, semiconductor surface, charged radicals and substrate produced during the reaction process. The surface ionization state of the photocatalyst can be



Fig. 10 Influence of pH on the rate for the mineralization of ketoprofen, chlorothalonil in the presence of Mn-doped TiO₂ (0.75%). Experimental condition: reaction vessel: immersion well photochemical reactor made of Pyrex glass, ketoprofen (0.12 mM), chlorothalonil (0.15 mM), volume (250 mL), reaction pH (4.7, 6.4, 8.7 10.8 and 12.9), light source: halogen linear lamp (500 W, 9500 Lumens) continuous stirring and air purging, irradiation time: 300 min



Fig. 11 Influence of catalyst concentration on the rate for the mineralization of ketoprofen, chlorothalonil in the presence of Mn-doped TiO₂ (0.75%). Experimental conditions: reaction vessel: immersion well photochemical reactor made of Pyrex glass, ketoprofen (0.12 mM), chlorothalonil (0.15 mM), volume (250 mL), photocatalyst: Mn-doped TiO₂ (0.5, 1.0, 2.0 3.0, 4.0 and 5.0 g L⁻¹), light source: halogen linear lamp (500 W, 9500 Lumens) continuous stirring and air purging, irradiation time: 300 min

deprotonated and protonated under alkaline and acidic conditions, respectively, as indicated in the given equations:

$$TiOH + H^+ \to TiOH_2^+, \tag{4}$$

$$TiOH + ^{-}OH \rightarrow TiO^{-} + H_2O.$$
(5)

In this study it has been shown that the rate of mineralization for both the pollutants was better under acidic pH. The zero point of charge (pHzpc) of Degussa P25 has been stated as 6.25 [32]. Hence, the surface of the particle is positively charged as pH moves to an acidic range whereas it is negatively charged at pH values above pHzpc. For ketoprofen because of low pK_a value (5.0) [33], this compound will be present in an anionic state within the studied pH range. The negative charges of TiO₂ would repel with pH rising, resulting in a reduction in the photomineralization competence. The better mineralization rate of chlorothalonil in acidic pH may be ascribed to the fact that the morphological alignment of the molecule is favored for reactive species attack under this condition.

Influence of catalyst dosage

In order to prevent extra amounts of catalyst, the maximum catalyst concentration has to be identified, which is important for any field application. The effect of catalyst concentration on the mineralization kinetics of organic pollutants ketoprofen and chlorothalonil was studied using various concentrations of Mn-doped TiO_2



Fig. 12 Gas chromatogram of ketoprofen [(**a**) unirradiated mixture (0 h)], [(**b**) irradiated mixture (9 h)]. Experimental conditions: ketoprofen (0.12 mM), V=250 mL, photocatalyst: Mn-doped TiO₂ (0.75%) (3 g L⁻¹)

ranging from 0.5 to 5 g L^{-1} . The result on the rate of mineralization of ketoprofen and chlorothalonil as a role of catalyst concentration is revealed in Fig. 11. The rate of both organic pollutants (ketoprofen and chlorothalonil) with Mn-doped TiO₂ was



Fig.13 Proposed photocatalytic degradation pathway of ketoprofen in presence of Mn-doped ${\rm TiO}_2$ (0.75%)

to indicate increase with rise in loading catalyst from 0.5 to 4 g L^{-1} for ketoprofen and from 0.5 to 3 g L^{-1} of chlorothalonil. Moreover, increase in loading catalyst moves to a slight reduction in the mineralization rate. The reason for the decrease in mineralization rate at higher catalyst dosage may be due to the fact that, at higher catalyst loading the interaction between particle-to-particle increases which is ultimately responsible for a agglomeration. This agglomeration reduces the surface area available for absorption of light and, hence, a drop in the mineralization rate occurred [34, 35].

Intermediate products

The unirradiated and irradiated samples of both the compounds under investigation were measured employing the GC–MS analysis method with a purpose to recognize the transitional yields generated during the process of photooxidation.

Transitional products of ketoprofen

An aqueous solution of ketoprofen (0.2 mM) with Mn-doped TiO₂ (3 g L⁻¹) was irradiated through a linear lamp of visible light halogen (500 W, 9500 Lumens) at different time intervals with continuous bubbling and stirring of atmospheric O₂. The GC–MS analysis of an unirradiated solution of Ketoprofen shows a single peak seeming at the time of retention (R_t) 14.62 min (Fig. 12a) which was categorized by



Fig. 14 Gas chromatogram of chlorothalonil [(a) unirradiated mixture (0 h)], (b) irradiated mixture (9 h). Experimental conditions: chlorothalonil (0.15) mM, V=250 mL, photocatalyst: Mn-doped TiO₂ (0.75%) (3 g L⁻¹)

paralleling the pattern of mass fragmentation and molecular ions. The analysis of a 9 h irradiated mixture of ketoprofen indicates the generation of several transitional products seeming at times of retention (R_t) 4.07, 5.28, 7.27, 10.75, 13.20 and 17.25 besides unaffected initial material Ketoprofen (1) appearing at R_t =14.62 as revealed in Fig. 12b. Two products appearing at R_t =5.28 and 10.75 min are characterized as



Fig. 15 Proposed photocatalytic degradation pathway of chlorothalonil in presence of Mn-doped ${\rm TiO_2}$ (0.75%)

benzoic acid (3) and 2-phenylpropanoic acid (4) on the basis of a pattern of mass fragmentation and the molecular ions. The generation of products 3 and 4 in the photocatalytic ketoprofen degradation could be agreed to be as pathways revealed in Fig. 13. The formation of these products from 1 involves the attack of electrons and followed by hydroxyl radicals which may in turn abstract hydrogen atom from the solvent to form the observed products 3 and 4.

Intermediate products of chlorothalonil

Aqueous solution irradiation of chlorothalonil (0.30 mM) was carried out with Mndoped TiO₂ (3 g L⁻¹) with a linear lamp of a visible light halogen (500 W, 9500 Lumens) at different time intervals with continuous stirring and bubbling with atmospheric O₂. Figure 14a, b shows the GC examination of unirradiated (0 h) and irradiated (9 h) mixture of chlorothalonil, respectively. Analysis of 9 h irradiated mixture of chlorothalonil indicates the generation of many transitional yields, of which two products seeming at retention time 14.15 and 17.01 has been characterized as **9** and **8** on the basis of the pattern of mass fragmentation and molecular ions, indicating the replacement of a cyanide group with a hydroxyl group in the benzene ring as revealed in Fig. 15.

Conclusion

The outcomes of these studies evidently designate that Mn-doped TiO_2 was successfully synthesized by two different routes, characterized and also catalyzed the photomineralization of organic pollutants ketoprofen and chlorothalonil. The modified sol–gel method proved to more efficient. Due to the lower value of band gap energy and small crystallite size, the photocatalysts, which were synthesized by modified sol–gel technique, exhibit better activity photocatalysis. The photocatalyst Mn-doped TiO₂ with 0.75% was found to be more efficient as compared to other dopant concentrations using visible light.

These investigations clearly shows that the selection of optimum degrading parameters is important to get a high mineralization rate, which is vital for any application of photocatalytic oxidation processes at the field level. The different transitional yields generated during the photo- mineralization processes of organic pollutants (ketoprofen and chlorothalonil) were reflected in valuable information for the pathways of degradation in heterogeneous photocatalysed reactions to understand the mechanism of reaction.

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