Photocatalytic degradation of monocrotophos pesticide—An endocrine disruptor by magnesium doped titania

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ABSTRACT

Mg-doped TiO_2 with different Mg concentrations were prepared using sol–gel method and characterized by XRD, UV–visible, XPS, SEM and FT-IR. The XRD results revealed that Mg^{2+} goes into the TiO_2 lattice. SEM images of the doped and pure TiO_2 indicated that there is a smaller particle size for the doped catalyst compared to that of the pure TiO_2. UV–visible absorption spectra indicated that upon doping with Mg^{2+} ion, the catalyst exhibits absorption in visible region. FT-IR and XPS spectra demonstrated that the presence of Mg^{2+} ion in the TiO_2 lattice as substitutional dopant. Photocatalytic activity of doped TiO_2 has been evaluated by degradation of the monocrotophos (MCP) pesticide. The effect of solution pH, catalyst dosage and initial concentration of MCP on the photocatalytic activity of Mg-doped TiO_2 with different loadings was studied. It was observed that the rate of degradation of MCP over Mg-doped TiO_2 is better than Pure TiO_2 and Degussa P-25.

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1. Introduction

In the present day scenario, industrial, agricultural and domestic activities have adversely affected the water with both inorganic and organic pollutants. These contaminants are often toxic and cause harmful effects to human and animal life. Water contamination is likely to be the primary source of human contact with toxic chemicals emanating from more than 70% of the hazardous waste sites [1]. Problems related to waste remediation have emerged as a high national and international priority. It has therefore, become important to treat waste water for the removal of toxic substances before they are discharged into natural water bodies. Pesticides such as monocrotophos, ethyl parathion, and malathion are widely used because of their rapid rate of versatile action on pests and allies.

Monocrotophos (MCP), a widely used insecticide for cotton, has contact, systemic and residual activities. The prolonged use of this compound has recently found its way into the waterways in the proximity of its application [2]. Monocrotophos is identified as endocrine disrupting chemical (EDC), an exogenous agent present in the environment, disrupt the endocrine functions such as: growth, development and reproduction of humans and animals. A few adverse effects of EDCs are early maturity, defect in child birth and impotence [3]. Recent research reports have highlighted the existence of these chemicals in surface and ground water via point and non-point sources [4], because they are more soluble in water.

The pesticides in aquatic environment are potentially toxic and are hard to be decomposed by conventional treatment processes. Growing public concern on the contamination of drinking water supplies and the aquatic environment with organic pollutants has stimulated vigorous research activity for their treatment [5–7]. Hence, the degradation of monocrotophos, is imperative. But, the existing treatment processes are not effectively combating the problem.

In the past several decades, photocatalytic reaction has attracted much interest in the degradation of organic pollutants in water to less harmful materials [8], due to energy and environmental issues [9,10]. It has several advantages, especially low price, non-toxic and chemically stable. The efficiency of titanium dioxide (anatase) photocatalyst is experimentally proved for decomposition of most of organic substances in water [11,12].

Although TiO_2 is superior to other semiconductors for many practical uses, but two types of defects limit its photocatalytic activity. Firstly, TiO_2 is active only under UV light ($\lambda < 380$ nm) because of its high band gap (3.2 eV), which is only 4–5% of the overall solar spectrum. Thus, this restricts the use of sunlight or visible light. Secondly, the high rate of electron–hole recombination at TiO_2 par-

ticles results in low photoquantum efficiency. In order to overcome these limitations of TiO_2, many attempts have been made among which doping selective metal ions into TiO_2 is noteworthy. There have been many studies on transition metal, nobel and rare earth metal ions as dopants [13–15].

But, doping with alkaline earth metal ions has been less explored compared with other metal ions and also limited literature reports [16] are available that the doped catalyst was tested only in the UV range of radiation. Hence, in the present study doping of TiO_2 with magnesium (Mg^{2+}) ion has been taken up because its favorable size to charge ratio (+2/0.78 Å) [29] and it was tested in visible light.

2. Experimental

2.1. Preparation of photocatalysts

Titanium tetra-butoxide [Ti(O–Bu)$_4$] and magnesium nitrate obtained from E. Merck (Germany) were used as titanium and magnesium sources for preparing anatase TiO_2 and Mg^{2+}–TiO_2 photocatalysts. Monocrotophos obtained from Devi Agro Chemicals, was used as a model compound for degradation. All chemicals used in this work are of analytical grade and doubly distilled water was used for the solution preparation.

Initially 21.0 ml of titanium tetra-butoxide was dissolved in 80.0 ml absolute ethanol (100%) and the resulting solution was stirred vigorously. Then 2.0 ml of water and 0.5 ml of acetic acid (50%) were added to another 80.0 ml of ethanol to make an ethanol–water–acetic acid solution. The latter solution was slowly added to the Ti(O–Bu)$_4$–ethanol solution under vigorous stirring. When the resulting mixture turned to sol, the magnesium nitrate solution (0.25, 0.5, 0.75 and 1.0 wt.%) was added drop-wise.

The resulting transparent colloidal suspension was stirred for more than 2 h and was aged at 25 °C until the formation of gel. The gel was dried at 70 °C in vacuo at a pressure of 600 psi and then ground. The resulting powder was calcined at 400 °C for 2 h. The calcined powders were crushed using an agate mortar and pestle under similar conditions to produce powders with similar 'fineness' and particle size distributions.

A pure TiO_2 (anatase) sample was also prepared by adopting the above procedure without adding the metal nitrate and is subsequently referred to as pure TiO_2. The doping concentrations are expressed as weight percentage. The powders are stored in black coated air-tight glass containers and were used for XRD analysis, UV–visible absorption studies, XPS, SEM, FT-IR studies and for photocatalytic activity testing.

2.2. Characterization of photocatalysts

The crystal phase composition of the prepared photocatalysts (TiO_2, Mg^{2+}–TiO_2) was determined by X-ray diffraction measurement carried out at room temperature using a PANalytical, D/Max-III A diffractometer with CuK_α radiation ($\lambda = 0.15148$ nm) with a liquid nitrogen gas-cooled germanium solid state detector. The accelerating voltage of 35 kV and emission current of 30 mA were used, and studied in the range of 2–65° 2θ with a step time of 0.1°/s. To study the composition of the photocatalysts, X-ray photoelectron spectroscopy (XPS) was recorded with the PHI quantum ESCA microprobe system, using the AlK_α line of a 250 W X-ray tube as a radiation source with the energy of 1253.6 eV, 16 mA × 12.5 kV and a working pressure lower than 1×10^{-8} Nm^{-2}. As an internal reference for the absolute binding energies, the C 1s peak of hydrocarbon contamination was used as reference to 284.8 eV. The fitting of XPS curves was analyzed with Multipak 6.0 A software. UV–visible absorption spectra of the samples were obtained using a Schimadzu, UV-2101 spectrophotometer, to study

the optical absorption properties of the photocatalysts. The spectra were recorded at room temperature in the wavelength range 200–800 nm enabling to understand the spectral properties of metal-doped TiO_2 catalysts. The infrared spectra of the synthesized samples are recorded on Thermo Nicolet Nexus 670 Spectrometer, with resolution of 4 cm^{-1} in KBr pellets.

2.3. Photocatalytic activity of the catalysts

The photoreactor system is given elsewhere [17] used to accomplish the photocatalytic degradation of monocrotophos pesticide in the presence of visible light, using doped and un-doped TiO_2 photocatalysts. The required amount of catalyst was suspended in 100 ml of standard aqueous solution in a 150 ml Pyrex glass vessel with constant stirring, for uniform illumination of all the catalyst particles.

The suspensions were then irradiated under visible light (wavelength range 400–800 nm) using a UV filtered Osram high pressure mercury vapour lamp with power 400 W and 35,000 lm. Before irradiation of the sample solution the catalysts were agitated along with monocrotophos for 45 min in the absence of light to attain the adsorption/desorption equilibrium on the catalysts surface. The distance between the light and the reaction vessel was 20 cm. At regular intervals, 5 ml of the aliquots were taken by 0.45 μm Millipore syringe filter and transferred into quartz cuvette for absorbance measurements. Cooling water is circulated around the sample container continuously to keep the reaction solution at room temperature and to filter the IR fraction of the light [18].

The major degradation products of organophosphorus pesticides are PO_4^{3-}, CO_2 and NO_3^- ions, and their formation during the progress of the degradation of MCP is confirmed by the simple qualitative analysis tests [19]. The rate of formation of PO_4^{3-} in the solutions can thus express the rate of degradation of organophosphorus pesticides [20–22]. The determination of PO_4^{3-} was performed colorimetrically by the molybdenum blue method [22–24].

3. Results and discussions

3.1. Characterization

3.1.1. X-ray diffraction studies

The crystalline phases of the synthesized pure TiO_2 and Mg^{2+}–TiO_2 were examined by XRD and the diffractograms are given in Fig. 1a–e. The XRD patterns of TiO_2 and all other samples of Mg^{2+}–TiO_2 (Mg/Ti = 0.25, 0.5, 0.75 and 1.0 wt.%) calcined at 400 °C shows only anatase form [25], indicating that Mg^{2+} ions in TiO_2 did not influence the crystal patterns of TiO_2 particle, peaks corresponding to $Mg(NO_3)_2$, $MgCO_3$ and MgO are not detected.

Since Mg^{2+} is more electropositive, the electronic cloud in each TiO_2 might be loosely held, favoring the formation of less dense anatase phase. In other words, the tight packing arrangement required for rutile phase formation is fully suppressed by the addition of magnesium nitrate in water which enhances the polarity of water, thus facilitating the formation of anatase phase exclusively. The presence of residual alkyl groups can also reduce the rate of crystallization of TiO_2 which favored the formation of less dense anatase phase [26]. The acetate anion adsorbed on the surface of TiO_2 could also suppress the growth of TiO_2 particles. This type of complexation of acetate anion on the surface of anatase form of TiO_2 may be responsible for the decrease in the crystallite size of TiO_2 in the sol–gel synthesis. The XRD patterns of all the percentages of Mg^{2+}–TiO_2 did not show any MgO peaks which indicated that there may be Mg^{2+} ion introduced into TiO_2 crystal lattice substitutionally.
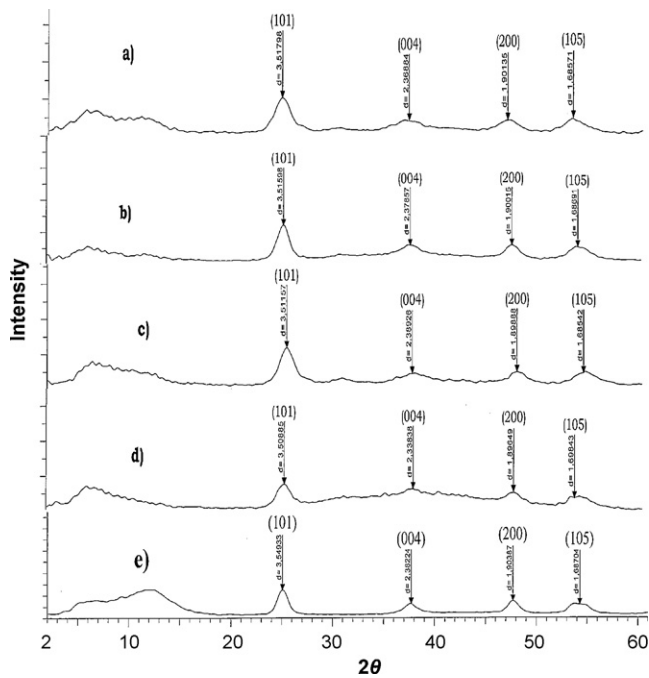
Fig. 1. XRD patterns of (a) 1.0 wt.%, (b) 0.75 wt.%, (c) 0.5 wt.%, (d) 0.25 wt.% of Mg^{2+}–TiO_2 and (e) pure TiO_2 gel powder heat treated at 400 °C for 2 h.

Fig. 2. UV–visible absorption spectra of (a) pure TiO_2 and (b) 1.0 wt.% Mg^{2+}–TiO_2.

Based on the trial photocatalytic degradation patterns of different pollutants with Mg^{2+}–TiO_2 samples have shown less catalytic activity except 1.0 wt.% Mg^{2+}–TiO_2. Hence, further characterization have been made only for 1.0 wt.% Mg^{2+}–TiO_2, which is having intense anatase phase formation and better photocatalytic activity.

3.1.2. UV–visible absorption study

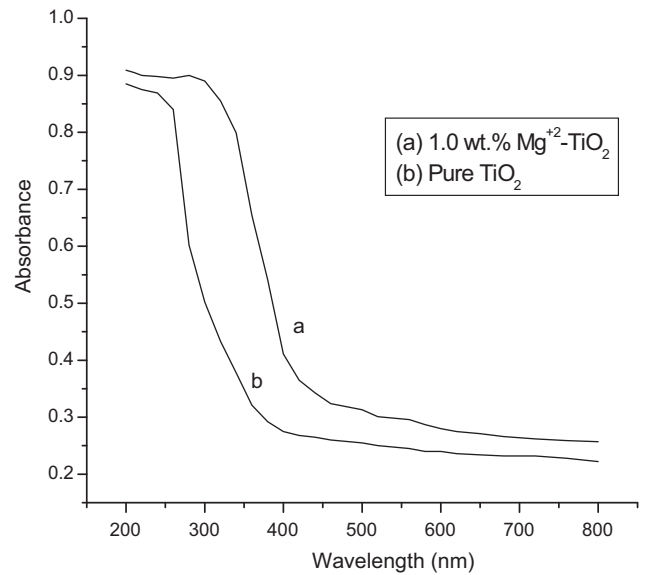Comparative UV–visible absorption spectra of doped and pure TiO_2 samples are given in Fig. 2. Figure illustrates that there is a shift in the absorption spectra of doped TiO_2 towards visible region.

The absorption spectrum of pure TiO_2 consists of a single and broad intense absorption band below 400 nm due to charge-transfer from the valence band (mainly formed by 2p orbitals of the oxide anions) to the conduction band (mainly formed by 3d t_{2g} orbitals of the Ti^{4+} cations) [27]. But in the doped TiO_2 absorption shifted to higher wavelength region of 400–550 nm. The absorption shift is due to the reduced band gap, with the energy band assumed to be between the top of Mg^{2+} 3s band and the bottom of the Ti^{4+} 3d bands. Thus the absorption spectra extend to longer wavelengths.
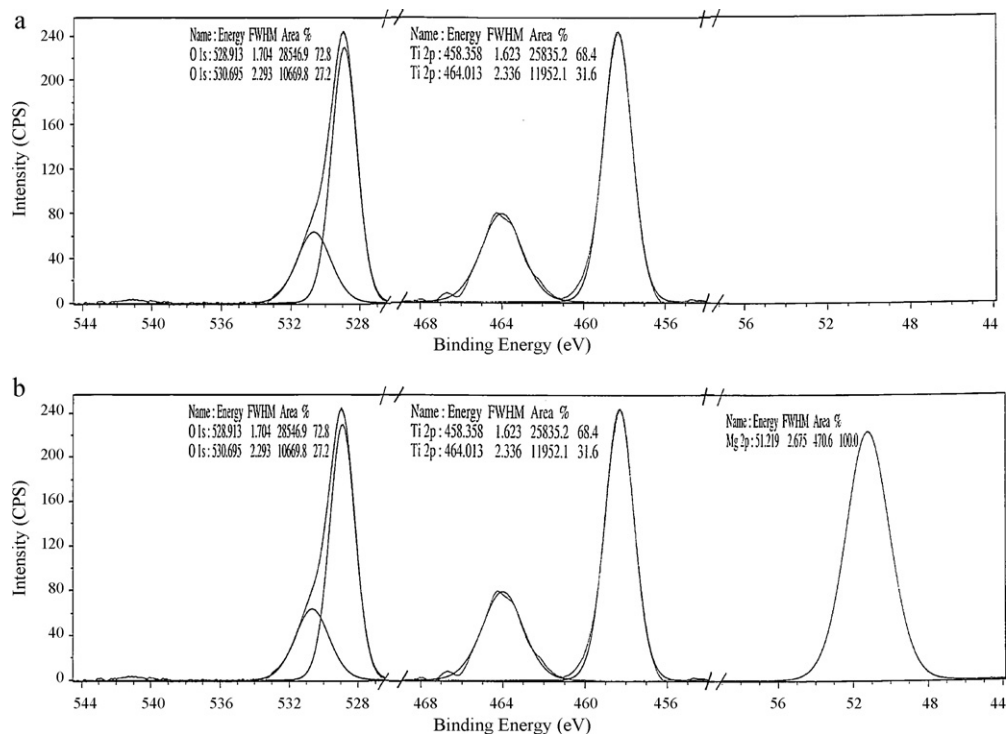

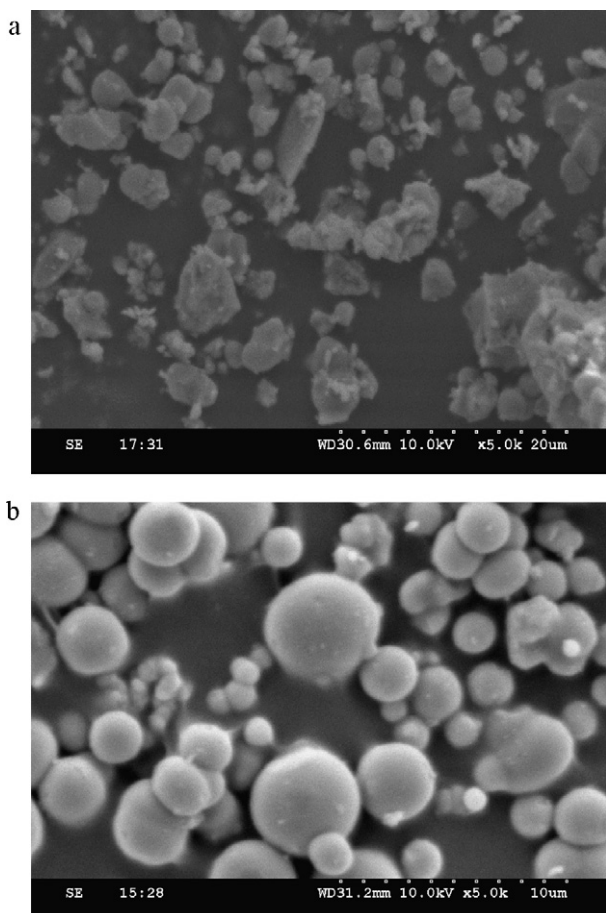**Fig. 3.** XPS spectra of (a) pure TiO_2 and (b) 1.0 wt.% Mg^{2+}–TiO_2.

Fig. 4. SEM images of (a) pure TiO$_2$ and (b) 1.0 wt.% Mg^{2+}–TiO$_2$.

Fig. 5. FT-IR spectra of (a) pure TiO$_2$ and (b) 1.0 wt.% Mg^{2+}–TiO$_2$.

3.1.3. X-ray photoelectron spectroscopic study

The XPS analysis was carried out for pure TiO$_2$ and 1.0 wt.% of Mg^{2+}–TiO$_2$ to determine the chemical composition and the recorded spectra was given in Fig. 3a and b. In both the spectra, the Ti 2p peaks are narrow with slight asymmetry and have binding energies of 458.63 eV and 464.013 eV, attributable to Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$. These values are consistent with those reported for titanium in TiO$_2$ [28,29]. For the 1.0 wt.% Mg^{2+}–TiO$_2$, a binding energy of 51.21 eV (FWHM = 2.675) was observed for Mg$_{2P}$, which is typical of Mg^{2+} that bonds with oxygen atom [29]. There was no any fitting peak of Ti^{3+}. The O 1s peak can be resolved into two peaks, one is peaked at 528.9 eV and the other at 530.6 eV.

The experimental results of XPS concluded that the entry of Mg^{2+} ion into TiO$_2$ lattice is substitutional. It is further evidenced by the reports of Serpone and Lawless [30] and Kiwi et al. [31], that the metal dopants are conveniently substituted into the TiO$_2$ lattice if their ionic radii are identical or nearly identical to that of the Ti(IV) cation. The ionic radius [32] of Mg^{2+} is 0.72 Å which is 19.2% larger than Ti^{4+} (0.605 Å). This clearly indicated that the Mg^{2+} is introduced into TiO$_2$ lattice as substitutional dopant.

3.1.4. Scanning electron microscopic study

The SEM images of Pure TiO$_2$ and 1.0 wt.% Mg^{2+}–TiO$_2$ catalysts are shown in Fig. 4a and b. The SEM image of samples containing 1.0 wt.% Mg^{2+} ion show the morphological changes induced by the addition of alkaline earth metal cation. The catalysts are found to contain irregular particles shape which is again aggregates of tiny crystals. Fig. 4a shows anatase SEM image of pure TiO$_2$ which appears as large blocks of coarse material of average particle size
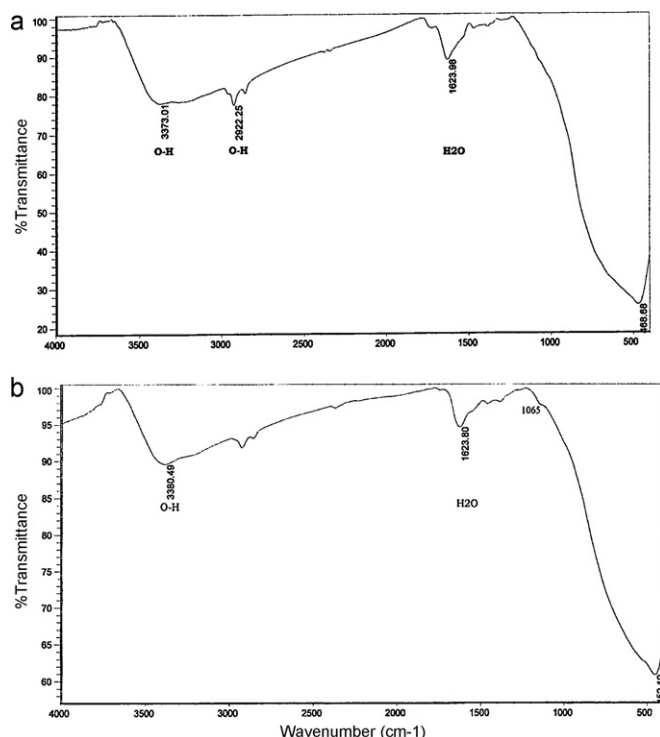
3.8 μm. Fig. 4b shows similar features to Fig. 4a, with change in the average particle size of 1.04 μm. This clearly illustrates the altered size and morphology of the catalyst powders and enhanced photocatalytic activity, due to decrease in particle size and increase in surface area of the catalyst.

3.1.5. FT-IR spectral study

FT-IR spectra of pure TiO$_2$ and 1.0 wt.% Mg^{2+}–TiO$_2$ given in Fig. 5a and b, have shown peaks corresponding to stretching vibrations of O–H and bending vibrations of adsorbed water molecules around 2910–3380 cm^{-1} and 1620–1625 cm^{-1}, respectively. The intensity of the peaks became less in 1.0 wt.% Mg^{2+}–TiO$_2$, indicating the removal of large portion of adsorbed water from TiO$_2$.

The broad band below 1200 cm^{-1} is due to Ti–O–Ti vibration. A peak has been observed at 1065 cm^{-1} which can be assigned to Ti–O–Mg vibration. Hence the FT-IR spectral study along with XPS established the clear substitution of Mg^{2+} into TiO$_2$ lattice.

3.2. Photocatalytic degradation of monocrotophos

To determine the photocatalytic efficiency of the prepared catalyst, the process was extended to degradation of MCP. Experiments are carried out in the presence and absence of catalysts under visible light. One of the final degradation products of MCP is observed as phosphate (PO$_4^{3-}$). The rate of formation of PO$_4^{3-}$ corresponds to the rate of degradation of MCP. The percentage of MCP degradation is significantly less in the absence of catalyst (0.02% for 10 h irradiation). A blank experiment was carried out in the absence of irradiation along with catalysts demonstrated that no significant change in the MCP concentration was observed. The efficiency of photocatalytic degradation process depends on various experimental parameters such as catalyst dosage, initial concentration of pollutant and pH. Hence, it is important to establish optimum conditions to achieve higher degradation efficiency of the catalyst.
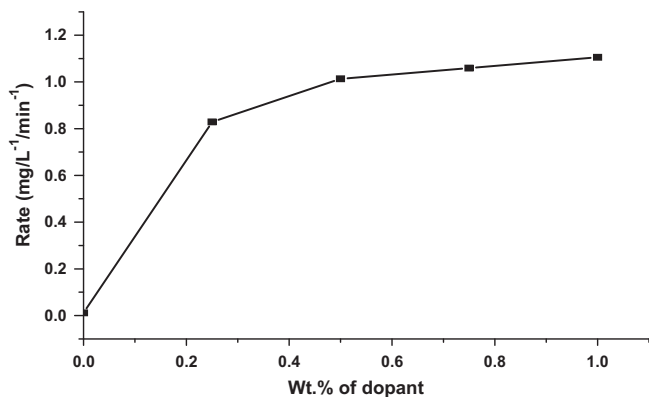
Fig. 6. Effect of dopant concentration on the rate of MCP degradation. Concentration of MCP = 50.0 mM (PO$_4^{3-}$ = 515.3 mg); catalyst = pure TiO$_2$ and Mg^{2+}–TiO$_2$; weight of catalyst = 0.1 g; pH = 6.5.

3.2.1. Effect of dopant concentration on MCP degradation

In order to determine the photocatalytic efficiency of Mg^{2+}–TiO$_2$ at an optimum dopant concentration of Mg^{2+} ions, for photocatalytic degradation of MCP, a set of experiments were carried out using 0.25, 0.5, 0.75 and 1.0 wt.% Mg^{2+}–TiO$_2$ and pure TiO$_2$. The percentage of phosphate formed is corresponding to the percentage of degradation of MCP at different irradiation time intervals, quantified by the absorption studies and the results are shown in Fig. 6. The results indicated that, the rate of MCP photodegradation increased with increase in the concentration of magnesium ions and it was maximum at 1.0 wt.%.

The experimental results also revealed that the dopant (Mg^{2+}) had a significant role in the enhancement of photocatalytic activity of TiO$_2$. Even though the concentration of the doped magnesium ions is small, it still gives much influence on the photocatalytic activity of TiO$_2$ particles.

3.2.2. Effect of pH

Since, solution pH influences the adsorption and desorption of the substrate, catalyst surface charge, oxidation potential of the valence band and other physico-chemical properties, the catalyst assisted photodegradation of MCP has been monitored by in situ measurements of pH of the aqueous suspension with irradiation time, at a fixed weight of catalyst and MCP concentration at different pH values are carried out. The required solution pH value was adjusted by the addition of NaOH or HCl solutions of 0.1 M concentration [33] and the results are given in Fig. 7. It can be observed that the rate of degradation is higher in the acidic pH range (pH = 3.0 and 6.0) than in alkaline pH (pH = 8.0).

On the surface of TiO$_2$, titanol (Ti–OH) is present, which is amphoteric and occurs in an acid–base equilibrium as indicated
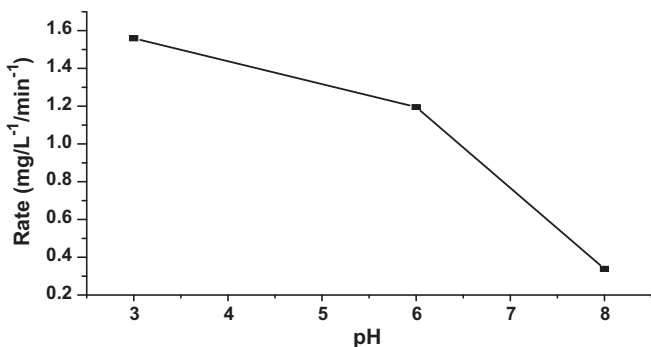

Fig. 7. Effect of pH on the rate of MCP degradation. Concentratin of MCP = 50.0 mM (PO$_4^{3-}$ = 515.3 mg); catalyst = 1.0 wt.% Mg^{2+}–TiO$_2$; weight of catalyst = 0.1 g.
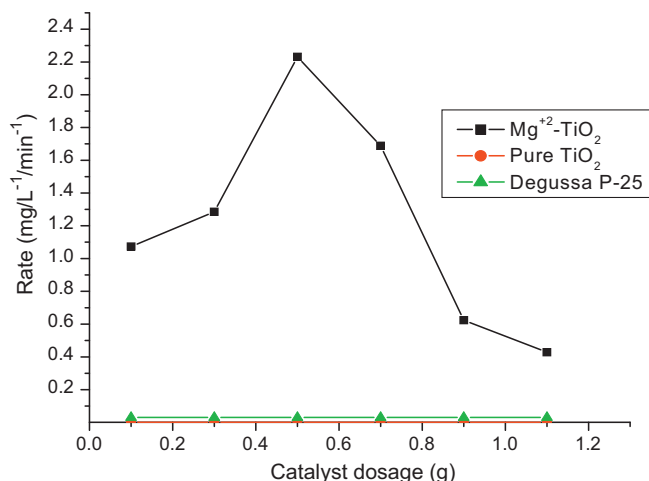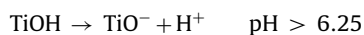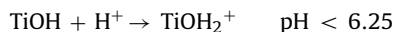

Fig. 8. Effect of catalyst dosage on the rate of MCP degradation. Concentration of MCP = 50.0 mM (PO$_4^{3-}$ = 515.3 mg); catalyst = 1.0 wt.% Mg^{2+}–TiO$_2$; pH = 3.0,

by the following equations:

$$TiOH + H^+ \rightarrow TiOH_2^+ \qquad pH < 6.25$$

$$TiOH \rightarrow TiO^- + H^+ \qquad pH > 6.25$$

In acidic environment, H$^+$ ions adsorbed onto the surface of TiO$_2$, which has large proton exchange capacity. The photogenerated electrons can be captured by the adsorbed H$^+$ to form H$_{ads}$$^\bullet$. At higher pH, the surface of catalyst has a net negative charge due to a significant fraction of total surface sites present as TiO$^-$ and hence the degradation rate was found to be less. During the experiment it is observed that drop in pH may be due to the formation of acidic intermediates.

3.2.3. Effect of catalyst dosage

The effect of the amount of catalyst on the rate of photodegradation of MCP was investigated, at a fixed pH and initial concentration of MCP. To determine the optimal catalyst dosage, experiments were carried out by varying concentration of Mg^{2+}–TiO$_2$ from 0.1 to 1.1 g in 100 ml aqueous solution of MCP. The degradation pattern of these experiments have been given in Fig. 8, which reveals that the rate of degradation increases linearly with increase in the amount of catalyst up to 0.5 g, and then decreases (leveling off).

As the amount of catalyst increases, the number of photons and the number of MCP molecules adsorbed also increased due to an increase in the number of catalyst particles leading to the increase in photocatalytic activity. However, as the catalyst dosage is increased beyond an optimum concentration, the increase in the number of available catalyst particles is offset by a decrease in the penetration depth of radiation, due to higher opacity of the suspension and scattering effects by the catalyst particles. This leads to a decrease in the degradation rate. The deactivation of activated molecules by collision with ground state molecules may also hinder the photocatalytic efficiency [34]. Hence, at a certain level, additional catalyst amount may not involve in catalysis and thus the rate levels off.

Degradation of monocrotophos is also carried out with Pure TiO$_2$ and Degussa P-25, shows that no appreciable degradation is observed (Fig. 8) particularly in visible region and no distinguishable photocatalytic activity reports are available in the literature for these two catalysts in visible light.
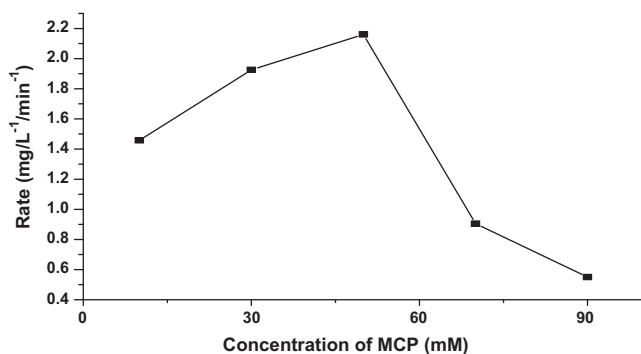
Fig. 9. Effect of initial MCP concentration on the rate of degradation. Catalyst = 1.0 wt.% Mg^{2+}–TiO_2; weight of catalyst = 0.5 g; pH = 3.0.
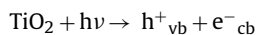
3.2.4. Effect of MCP concentration

At a fixed weight of Mg^{2+}–TiO_2 and pH, the effect of various initial MCP concentrations on photodegradation of MCP was studied and the results are presented in Fig. 9. It is observed that the degradation rate increases with increase in MCP concentration up to 50.0 mM (PO_4^{3-} = 515.3 mg) and a further increase leads to a decrease in the rate of MCP degradation. The decrease in degradation by increasing pollutant concentration is due to the reduction of generation of radicals ($^\bullet$OH) on the catalyst surface as the active sites are covered by the pollutant molecules.

3.2.5. Photocatalytic mechanism

Based on the experimental results the following mechanism is proposed for the photocatalytic reactions of magnesium doped TiO_2.
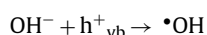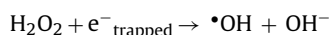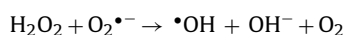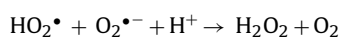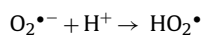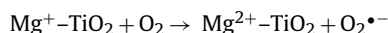
(i) Upon visible light illumination of photocatalyst, electrons are ejected from the valence band to the conduction band leaving positive holes in the valence band.

$$TiO_2 + h\nu \rightarrow h^+_{vb} + e^-_{cb}$$

(ii) When the metal ion is doped into TiO_2 lattice, these ejected electrons are trapped by dopant ions eliminating the recombination process.

$$Mg^{2+}\text{–}TiO_2 + e^- \rightarrow Mg^+\text{–}TiO_2 (unstable)$$

(iii) The trapped electrons can be subsequently scavenged by molecular oxygen, which is adsorbed on the TiO_2 surface, to generate the superoxide radical, and this in turn produce hydrogen peroxide (H_2O_2), hydroperoxy ($HO_2^\bullet$) and hydroxyl ($^\bullet$OH) radicals [35].

$$Mg^+\text{–}TiO_2 + O_2 \rightarrow Mg^{2+}\text{–}TiO_2 + O_2^{\bullet-}$$

$$O_2^{\bullet-} + H^+ \rightarrow HO_2^\bullet$$

$$HO_2^\bullet + O_2^{\bullet-} + H^+ \rightarrow H_2O_2 + O_2$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow {}^\bullet OH + OH^- + O_2$$

$$H_2O_2 + e^-_{trapped} \rightarrow {}^\bullet OH + OH^-$$

$$OH^- + h^+_{vb} \rightarrow {}^\bullet OH$$

The positive holes in the valence band act as good oxidizing agents available for degradation of pollutants in the solution

$${}^\bullet OH(orh^+_{vb}) + Red \rightarrow Red^+$$
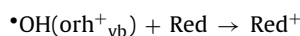
where 'Red' is the pollutant an electr on donor (reductant).

Thus, the pollutant is attacked by the hydroxyl radicals formed both by trapped electrons and hole in the VB as given in the above equations, to generate organic radicals or other intermediates.

Degradation results of the MCP with Mg^{2+}–TiO_2 catalyst shows the effective degradation of the molecular structure of MCP. It can be attributed that the C=C is supposed to be easily broken by $^\bullet$OH free radicals or electron holes to form phosphorus and nitrogen containing intermediates. Subsequently, the intermediates were gradually decomposed by $^\bullet$OH free radicals to form phosphates and nitrates. The organophosphates were converted almost to phosphate indicating that the CH_3O–P bond was effectively destroyed. And the MCP degradation products are NO_3^-, PO_4^{3-}, CO_2 and H_2O [22].

4. Conclusions

In the present study Mg^{2+} doped and undoped TiO_2 photocatalyst has been synthesized by using sol–gel method. Characterization of both the catalysts are carried out by XRD, UV–visible absorption spectra, XPS, SEM and FT-IR. The XRD data has shown anatase phase indicating that the Mg^{2+} ions in TiO_2 did not influence the crystal patterns of TiO_2 particle. The absorption spectrum of Mg^{2+}–TiO_2 has been shifted to higher wavelength when compared with pure TiO_2. XPS spectra shows the presence of Mg^{2+} ion in TiO_2 lattice, which is further confirmed by the FT-IR data where there is a presence of Mg–O peak at approximately 1065 cm^{-1} has established the Mg^{2+} ion introduced into TiO_2 lattice as substitutional dopant. The SEM image of Mg^{2+}–TiO_2 shows decrease in particle size compared to undoped TiO_2. Due to decrease in particle size, increase in surface area, leads to enhanced photocatalytic activity of the catalyst.

In addition to the above, the maximum degradation of MCP was observed at 1.0 wt.% of Mg^{2+} dopant concentration. The catalyst dosage, MCP concentrations and the solution pH are 0.5 g, 50.0 mM and 3.0, respectively, are the optimum conditions for maximum degradation.

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