

Research Article

Titanium Dioxide-Mediated Photocatalysed Degradation of Two Herbicide Derivatives Chloridazon and Metribuzin in Aqueous Suspensions

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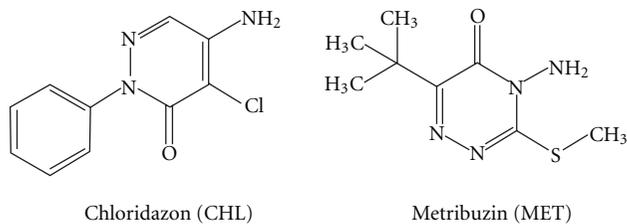
The aim of this paper is to find out the optimal degradation condition for two potential environmental pollutants, chloridazon and metribuzin (herbicide derivatives), employing advanced oxidation process using TiO₂ photocatalyst in aqueous suspensions. The degradation/mineralization of the herbicide was monitored by measuring the change in pollutant concentration and depletion in TOC content as a function of time. A detailed degradation kinetics was studied under different conditions such as types of TiO₂ (anatase/anatase-rutile mixture), catalyst concentration, herbicide concentration, initial reaction pH, and in the presence of electron acceptors (hydrogen peroxide, ammonium persulphate, potassium persulphate) in addition to atmospheric oxygen. The photocatalyst, Degussa P25, was found to be more efficient catalyst for the degradation of both herbicides as compared with two other commercially available TiO₂ powders like Hombikat UV100 and PC500. Chloridazon (CHL) was found to degrade more efficiently under acidic condition, whereas metribuzin (MET) degraded faster under alkaline medium. All three electron acceptors tested in this study were found to enhance the degradation rate of both herbicides.

1. Introduction

Clean and safe drinking water is vital for human health, wildlife, and also for a stable environment. Yet, water is being polluted at alarming rates, with chemicals, nutrients, metals, pesticides, and other contaminants from industrial effluents, chemical spills, and agricultural runoffs [1, 2]. A wide variety of herbicides and other chemicals are applied to agricultural field and lawns mainly to control undesirable vegetation. A fraction of herbicides applied to these sites end up as runoff. This runoff goes into the streams, rivers, and lakes. Some of the herbicides also end up in groundwater systems by percolating down through the soil. As a result, herbicides are widely found in rivers, streams, lakes, and even in drinking water [3]. These chemicals due to their toxicity, stability to natural decomposition, and persistence in the environment have been the cause of much concern to the

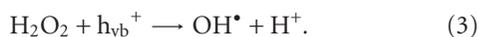
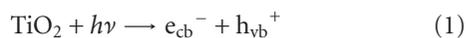
societies and regulatory authorities around the world [4]. The development of appropriate methods to treat these contaminated water is necessary before it is used for any useful purpose.

The photocatalysed degradation of various organic systems employing irradiated TiO₂ is well documented in the literature [5–14]. Briefly, when a semiconductor such as TiO₂ absorbs a photon of energy equal to or greater than its band gap energy, an electron may be promoted from the valence band to the conduction band (e_{cb}^-) leaving behind an electron vacancy or “hole” in the valence band (h_{vb}^+), as shown in (1). If charge separation is maintained, and the reaction is carried out in water and oxygen, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h_{vb}^+ may react with surface-bound H₂O to produce the hydroxyl radical and e_{cb}^- is picked up by oxygen to



SCHEME 1

generate superoxide radical anion ($O_2^{\bullet-}$), as indicated in the following equations (1)–(3)



It has been suggested that the hydroxyl radicals and superoxide radical anions are the primary oxidizing species in the photocatalytic oxidation processes. These oxidative reactions would result in the degradation of the pollutants.

CHL is a herbicide currently used for selective control in beets. It belongs to the class of Hill reaction inhibitors, whereas MET is used primarily to discourage growth of broadleaf weeds and annual grasses among vegetable crops and turf grass [15, 16]. CHL and MET possess high mobility in soil and thus have great potential to leach and pollute surface and groundwater [17]. Few studies relating to the degradation of chloridazon and metribuzin in UV and sunlight have been reported recently in the literature [18–20]. No major efforts have been made to study the detailed degradation kinetics of these two herbicide derivatives. Therefore, in this paper we present a detailed degradation of these compounds as shown in Scheme 1 in aqueous suspensions of TiO_2 under a variety of conditions such as different types of TiO_2 , reaction pH, catalyst and substrate concentration, and also in the presence of electron acceptors like hydrogen peroxide, potassium persulphate, and ammonium persulfate besides atmospheric oxygen.

2. Experimental

2.1. Reagents and Chemicals. Laboratory grade chloridazon was kindly supplied by Parijat Industries India Pvt. Ltd., Ambala whereas, the pesticide derivative metribuzin was obtained from Rallis India Ltd., and they were used as such for our studies without any further purification. All the solutions were made in double-distilled water for the irradiation experiments. Degussa P25 was used as catalyst in most of the experiments performed to carry out the photocatalytic degradation of these two model compounds. Other catalyst powders, namely, Hombikat UV100 (Sachtleben Chemie GmbH) and PC500 (Millennium Inorganic Chemicals), were used for comparative study. Degussa P25 contains 80% anatase and 20% rutile with a specific BET surface area

of $50\text{ m}^2\text{g}^{-1}$ and a primary particle size of 20 nm [21]. Hombikat UV100 consists of 100% pure anatase with a specific BET surface area of $250\text{ m}^2\text{g}^{-1}$ and a primary particle size of 5 nm [22]. The photocatalyst PC500 has a BET-surface area of $287\text{ m}^2\text{g}^{-1}$ with 100% anatase and primary particle size of 5–10 nm [23]. All other chemicals such as sodium hydroxide, nitric acid, hydrogen peroxide, potassium persulphate, and potassium bromate were obtained from Merck.

2.2. Procedure. An immersion well photochemical reactor consisting of inner and outer jacket made of Pyrex glass was used for the irradiation experiments. The detailed design of the photoreactor has been illustrated elsewhere [24]. Prior to illumination, stock solutions of CHL and MET were prepared in double-distilled water with desired concentration. The irradiation experiments were carried out in aqueous suspensions of TiO_2 using a pyrex-filtered output of 125 W medium pressure mercury lamp (Philips). The light intensity was measured by UV light intensity detector (Lutron UV-340) and was found to be in the range of 4.86–4.88 mW/cm^2 . The experimental runs were carried out by using the following procedure for both the herbicide derivatives: firstly 125 mL solution of the herbicide derivative was taken into the reactor and required amount of photocatalyst was added. The suspension was magnetically stirred and purged with atmospheric oxygen in the dark for 10 min to attain adsorption-desorption equilibrium between herbicide derivatives and TiO_2 . The zero time reading was obtained from blank solution kept in the dark. Samples (5 mL) were taken at regular time intervals from the reactor and analysed after centrifugation. The pH of the reaction mixture was adjusted by adding dilute NaOH and HNO_3 .

2.3. Analysis. The analysis was carried out after removal of photocatalyst by centrifuging the samples at 4000 rpm for 1 h using Remi centrifuge (model R24). The degradation of CHL and MET was followed by measuring the change in absorption intensity at their respective λ_{max} 238 nm (CHL) and 295 nm (MET) using Shimadzu UV-Vis Spectrophotometer (Model 1601), and mineralization was monitored by measuring the depletion in Total Organic Carbon (TOC) content with a Shimadzu TOC_{VCSH} Analyzer. The pH of the reaction mixture was measured using HI 2210 pH meter.

3. Results and Discussion

3.1. Photolysis of CHL and MET in Aqueous Suspensions of TiO_2 . Irradiation of an aqueous suspensions of CHL (0.18 mM, 125 mL, pH 6.2) and MET (0.30 mM, 125 mL, pH 6.5) in the presence of TiO_2 (Degussa P25, 1 g L^{-1}) using 125 W medium pressure mercury lamp in an immersion well photochemical reactor with constant stirring and bubbling of air led to a decrease in absorption intensity as a function of time as shown in the inset of Figures 1(a) and 1(b), respectively. The change in the concentration of the pollutant was calculated from standard calibration curve obtained from the absorption intensity of the herbicide derivatives at different

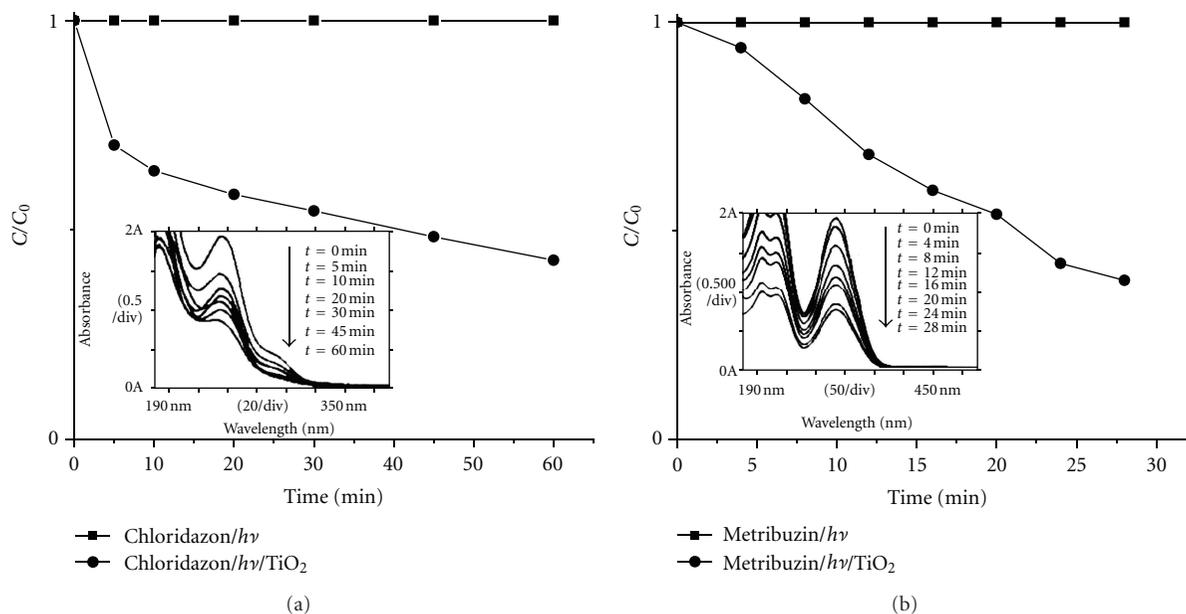


FIGURE 1: (a) Change in concentration as a function of time on irradiation of an aqueous solution of CHL in the presence and absence of photocatalyst. *Inset*: Change in absorption intensity at 238 nm on irradiation of aqueous suspension of CHL containing TiO_2 . *Experimental conditions*: CHL (0.18 mM), $V = 125$ mL, 125 W medium pressure mercury lamp, light intensity: 4.88 mW/cm^2 , irradiation time: 60 min. (b) Change in concentration as a function of time on irradiation of an aqueous suspension of MET in the presence and absence of photocatalyst. *Inset*: Change in absorption intensity at 295 nm on irradiation of aqueous suspension of MET containing TiO_2 . *Experimental conditions*: MET (0.30 mM), $V = 125$ mL, 125 W medium pressure mercury lamp, light intensity: 4.88 mW/cm^2 , Irradiation time: 28 min.

concentration. The change in concentration in the presence and absence of photocatalyst as a function of time is shown in Figures 1(a) and 1(b), for herbicide derivatives, CHL and MET, respectively. The results demonstrate that 62% degradation of CHL and 55% degradation of MET could be achieved in 60 min and 28 min, respectively, whereas in the absence of photocatalyst no significant degradation was observed as shown in the Figure 1. Control experiments were carried out to show that there was no appreciable loss of the compound in unirradiated blank solutions and also due to adsorption on the surface of the photocatalyst. In order to see the effect of change in initial volume, experiments were carried out (data not shown), where samples were withdrawn initially at zero min and then directly after 60 min (CHL) and 28 min, (MET). There was no significant effect of volume alteration on the reaction rate.

For each experiment, the degradation rate constant of the compound was calculated from the linear regression of a plot of the natural logarithm of the compound concentration as a function of irradiation time. The degradation rate of the herbicide derivatives was calculated using the formula given below

$$-\frac{d[c]}{dt} = kc^n, \quad (4)$$

k equals rate constant (min^{-1}), c equals concentration (mol L^{-1}) of the pollutant, n is order of reaction.

The degradation rate for both the herbicides was found to follow pseudo-first-order reaction kinetics, and the degradation rate was calculated in terms of $\text{mmol L}^{-1} \text{ min}^{-1}$.

3.2. Comparison of Photocatalytic Activity of Different TiO_2 Powders. Titanium dioxide is the most widely used photocatalyst in heterogeneous photocatalysis due to its low cost, high photocatalytic activity, nontoxic nature, photostability, and chemical and biological inertness [14]. The photocatalytic activity of three commercially available TiO_2 powders, namely, Degussa P25, Hombical UV100, and PC500, was tested on the degradation kinetics of herbicide derivatives CHL and MET. The rates obtained for the degradation of CHL and MET in the presence of different types of TiO_2 powders by continuous purging of air are shown in Table 1. It has been observed that the degradation of CHL and MET proceeds much more rapidly in the presence of Degussa P25 as compared to other TiO_2 powders. The photocatalysts UV100 and PC500 showed a comparable photocatalytic activity for the degradation of MET.

The photocatalyst Degussa P25 has been found to be a better photocatalyst for the degradation of a large number of compounds reported earlier [25–27]. The reason for the better photocatalytic activity of Degussa P25 is attributed to its anatase/rutile mixture as reported earlier [28, 29]. In all following experiments, Degussa P25 was used since this material exhibited the highest photocatalytic activity as compared to other photocatalyst tested for the degradation of herbicides under investigation.

3.3. Effect of pH. The pH of the reaction mixture in surface reactions significantly influences the physicochemical properties of titanium dioxide, including the charge on its

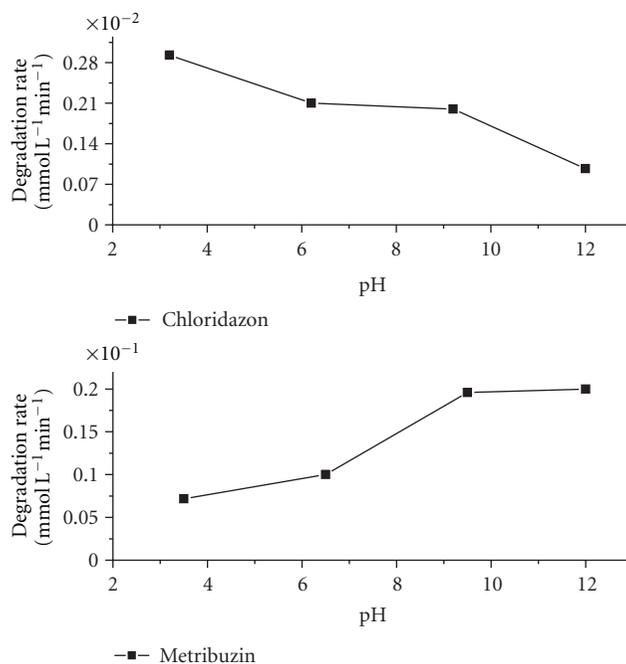


FIGURE 2: Influence of pH on the degradation rate of CHL and MET. *Experimental conditions:* CHL (0.18 mM), MET (0.30 mM), initial reaction pH of CHL (3.2, 6.2, 9.2, and 12), initial reaction pH of MET (3.5, 6.5, 9.5, and 12), $V = 125$ mL, photocatalyst: TiO₂ Degussa P25 (1 gL⁻¹), irradiation time: 60 min (CHL), 28 min (MET).

TABLE 1: (a) Comparison of degradation rate of CHL and MET in the presence of different types of TiO₂ samples. *Experimental conditions:* CHL (0.18 mM), MET (0.30 mM), $V = 125$ mL, photocatalysts: Degussa P25 (1 gL⁻¹), Sachtleben Hombikat UV100 (1 gL⁻¹), PC500 (1 gL⁻¹), irradiation time: 60 min (CHL), 28 min (MET). (b) Comparison of mineralization rate of CHL and MET in the presence of TiO₂ and TiO₂/H₂O₂. *Experimental conditions:* CHL (0.55 mM), MET (0.11 mM), $V = 125$ mL, photocatalysts: Degussa P25 (1 gL⁻¹), irradiation time: 60 min (CHL), 28 min (MET).

	(a) Rate of photodegradation (mmol L ⁻¹ min ⁻¹)			(b) Rate of photomineralization (mmol L ⁻¹ min ⁻¹)	
	P25	UV100	PC500	$h\nu$ /P25	$h\nu$ /P25/H ₂ O ₂
Chloridazon	0.0021	0.0018	0.0011	0.0003	0.0022
Metribuzin	0.036	0.025	0.025	0.0003	0.0008

surface, the aggregation numbers of particles it forms, and the position of the conductance and valence bands [30]. The effect of pH on the degradation of CHL and MET employing Degussa P25 was studied in the pH range between 3 and 12. The rate obtained for the degradation of herbicide derivatives CHL and MET as a function of reaction pH is shown in Figure 2. It is interesting to note that in the case of compound CHL, the highest degradation rate was observed at pH 3.2, which slowly decreases with the increase in reaction pH, whereas in the case of MET, the degradation rate was found to increase with the increase in reaction pH.

The zero point of charge (pHzpc) of Degussa P25 has been reported as 6.25 [31]; hence, at more acidic pH values, the TiO₂ particle surface is positively charged; while at pH values above pHzpc, it is negatively charged. The pKa for CHL and MET has been reported as 2.96 and 7.0, respectively [32, 33]. The higher degradation rate for CHL at lower pH

values and MET at higher pH values could be explained on the basis of the fact that the structural orientation of the compound at these pH values are favoured for the reactive species.

3.4. Effect of TiO₂ Concentration. The optimal amount of TiO₂ has to be found out in order to avoid unnecessary excess catalyst and also to ensure total absorption of light for efficient photodegradation. In order to find out the optimal catalyst concentration, we have investigated the influence of different concentrations of Degussa P25 (0.5 to 4 gL⁻¹) on the degradation kinetics of CHL and MET, and the results are shown in Figure 3. As expected, the rate of degradation for the model compound CHL was found to increase with the increase in catalyst concentration up to 2 gL⁻¹ after which a further increase in catalyst concentration led to a decrease in degradation rate. The degradation rate for MET

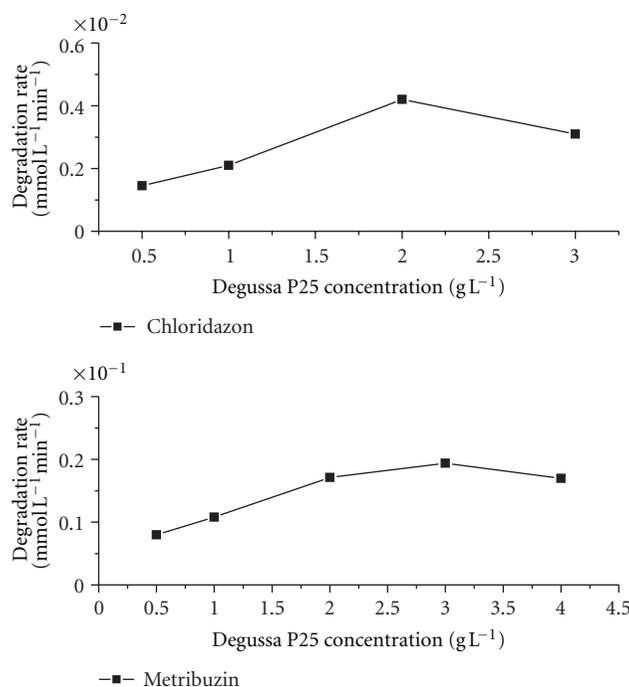


FIGURE 3: Influence of Degussa P25 concentration on the degradation rate of CHL and MET. *Experimental conditions:* CHL (0.18 mM), MET (0.30 mM), TiO₂ Degussa P25 (0.5, 1, 2, and 3 and 4 g L⁻¹), V = 125 mL, irradiation time: 60 min (CHL), 28 min (MET).

was found to increase linearly up to 3 g L⁻¹ followed by a decrease in degradation rate on further increase in catalyst concentration.

The decrease in degradation rate at a higher catalyst concentration may be due to the fact that when the catalyst concentration is very high, after traversing a certain optical path, turbidity impedes further penetration of light in the reactor (incidence of the combined phenomena of particle masking and scattering), lowering the efficiency of the catalytic process. The results are in agreement with the studies reported earlier by our group [34].

3.5. Effect of the Initial Herbicide Concentrations. The study of the dependence of the photocatalytic degradation rate on the substrate concentration is very important for the application of the photocatalytic process to waste-water treatment. Hence the effect of initial herbicide concentration, varying from 0.14 to 0.20 for CHL and 0.24–0.33 for MET on the photocatalytic degradation was studied, and the results, are shown in Figure 4.

As expected, the rate of degradation of CHL was found to increase gradually with the increase in substrate concentration from 0.14 to 0.18 mM. Further increase in substrate concentration led to a slight decrease in the rate of the reaction. Similar results were obtained for the degradation of MET, that is, the rate was found to increase with the increase in substrate concentration from 0.24 to 0.30 mM, and a further increase in the concentration led to more or less

same degradation rate within experimental error limits. The results are in agreement with earlier reported studies [35].

3.6. Effect of Electron Acceptors. Charge recombination of the photogenerated electron hole pairs is the major bottleneck in semiconductor photocatalysis. Due to the process of electron-hole recombination, both charge carriers annihilate each other. As a result, the rates of the photocatalytic transformations are limited by the rates of electron-hole recombination in the bulk of TiO₂ or at the surface. In order to enhance the formation of hydroxyl radicals and also inhibit undesired electron/hole pair recombination, electron acceptors such as hydrogen peroxide (10 mM), ammonium per sulphate (3 mM), and potassium per sulphate (3 mM) were used in addition to Degussa P25 in order to see their effect on the degradation kinetics of the herbicide derivative CHL and MET. The rate obtained for the decomposition of herbicide derivatives in the presence and absence of additives is shown in Figure 5.

All employed additives were found to enhance the degradation of both compounds, CHL and MET. The highest degradation rate for the decomposition of MET was observed in the presence of hydrogen peroxide as an electron acceptor in the presence of Degussa P25. In addition, the effect of different concentrations of hydrogen peroxide on the degradation kinetics of both herbicides have also been studied, and the rates are shown in the inset of Figure 5. In both compounds, the rates were found to increase as the H₂O₂ concentration increases from 5 to 15 mM (markedly in the

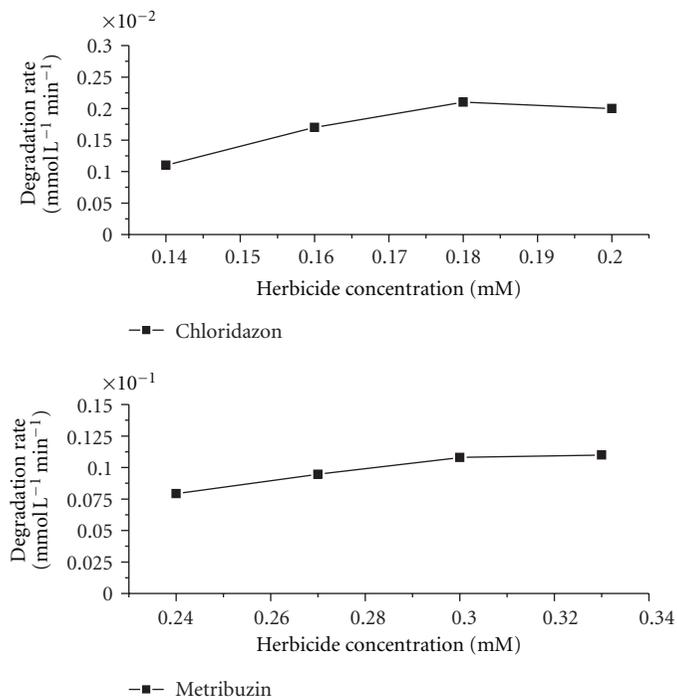


FIGURE 4: Effect of initial herbicide concentration on the degradation rate. *Experimental conditions:* Herbicide concentration: CHL (0.14, 0.16, 0.18, and 0.20 mM), MET (0.24, 0.27, 0.30, and 0.33 mM), $V = 125$ mL, photocatalyst: TiO₂ Degussa P25 (1 gL⁻¹), irradiation time: 60 min (CHL), 28 min (MET).

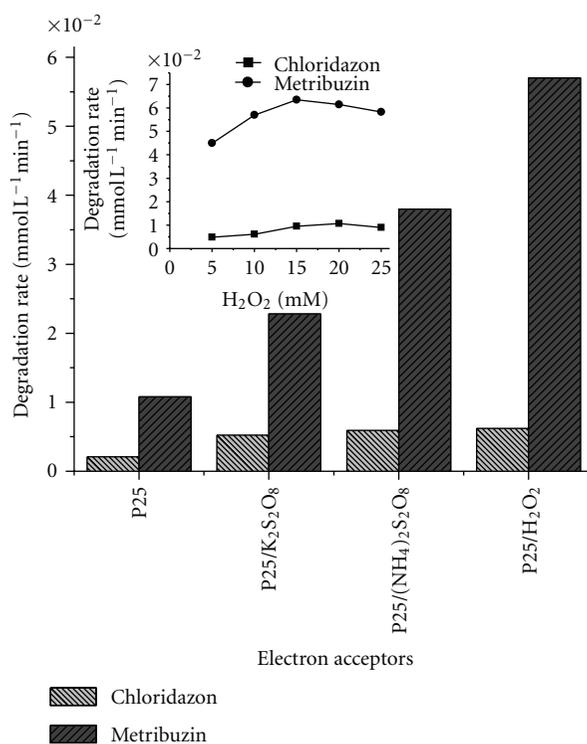
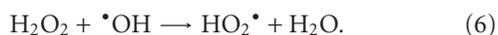
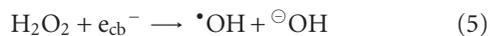


FIGURE 5: Influence of electron acceptors on the the degradation rate of CHL and MET. *Experimental conditions:* CHL (0.18 mM), MET (0.30 mM), electron acceptors, K₂S₂O₈ (3 mM), (NH₄)₂S₂O₈ and H₂O₂(10 mM), $V = 125$ mL, photocatalyst: TiO₂ Degussa P25 (1 gL⁻¹), irradiation time: 60 min (CHL), 28 min (MET).

case of MET). A further increase in the H_2O_2 concentration leads to a slight decrease in the degradation rate of MET and more or less same in the case of CHL.

The rate enhancement by H_2O_2 addition could be attributed to its better electron acceptance (5), thereby reducing electron hole recombination. Above the optimum value, the competitive reactions between hydroxyl radical and peroxide lead to the generation of less reactive hydroperoxide radicals, which does not contribute to the oxidative degradation of CHL (6)



3.7. Photomineralization of CHL and MET in Aqueous Suspension of TiO_2 . The photocatalytic mineralization of CHL and MET was studied in aqueous suspensions of TiO_2 in the presence and absence H_2O_2 . Table 1 shows the mineralization rate of CHL and MET in aqueous suspension of Degussa P25 in the presence and absence of H_2O_2 . Blanks experiments were carried out by irradiating the pesticide solutions in the absence of TiO_2 containing H_2O_2 where no appreciable loss of the compounds was observed (data not shown). It is obvious from the table that the mineralization rate was enhanced in the presence of TiO_2 containing hydrogen peroxide due to the efficient generation of hydroxyl radicals with the addition of H_2O_2 .

4. Conclusion

TiO_2 can efficiently catalyze the degradation and mineralization of herbicide derivatives chloridazon, and metribuzin in the presence of UV light. All parameters have been found to markedly influence the overall efficiency of degradation. Degussa P25 showed greater photocatalytic activity for the degradation of both herbicides, CHL and MET. In the case of chloridazon the highest efficiency was observed at pH 3.2, whereas metribuzin showed better degradation under alkaline condition. All the electron acceptors markedly enhanced the degradation of MET, and the highest rate was achieved with H_2O_2 , whereas in the case CHL all acceptors enhanced the degradation at comparable rate. The observations of these investigations clearly demonstrate the importance of choosing the optimum degradation conditions to obtain high degradation and mineralisation, which is essential for any practical application of photocatalytic oxidation processes.

Acknowledgments

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