Photocatalysed degradation of a fungicide, thiram in aqueous suspension of titanium dioxide

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Photocatalysed degradation of a fungicide derivative, thiram has been investigated in aqueous suspensions of titanium dioxide as a function of irradiation time under a variety of conditions. The degradation kinetics were studied under different conditions such as pH, catalyst concentration, substrate concentration, different types of TiO₂ and in the presence of electron acceptors such as hydrogen peroxide (H₂O₂), potassium bromate (KBrO₃) and ammonium persulphate (NH₄)₂S₂O₈ besides molecular oxygen. The degradation rates were found to be strongly influenced by all the above parameters. The photocatalyst, Degussa P25 was found to be more efficient as compared to other photocatalysts tested. All the electron acceptors markedly enhanced the degradation of the compound under investigation. The efficiency of degradation was found to be slower under sunlight as compared to the artificial light source. The degradation products were analyzed by GC-MS technique and probable pathways for the formation of products are proposed.

Keywords: Photocatalysis, fungicide, thiram, titanium dioxide, semiconductor.

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Water contamination is mainly caused by industrial effluents, agricultural runoff and chemical spills. These effluents contain several non-biodegradable substrates that can be harmful to the environment. Their toxicity, stability to natural decomposition and persistence in the environment have been the cause of much concern to the societies and regulation authorities around the world.

Among many processes proposed and/or being developed for the destruction of the organic contaminants, biodegradation has received the greatest attention. However, many organic chemicals, especially those that are toxic or refractory, are not amendable to microbial degradation. During the past two decades, photocatalytic process involving TiO₂ particles under UV light illumination have shown to be potentially advantageous and useful in the treatment of waste water pollutants. Earlier studies have shown that a wide range of organic substrates such as alkanes, alkenes, aromatics, surfactants, pesticides, etc., can be completely photomineralized in presence of TiO₂ and oxygen.

The photocatalysed degradation of various organic substrates employing irradiated TiO₂ is well documented. The mechanism constituting heterogeneous photocatalytic oxidation processes has also been discussed extensively.

Thiram (1) is a toxic compound, belonging to the ethylene bisdithiocarbamate (EBDC) class. The EBDCs, in general, are fungicides used to prevent crop damage in the field and to protect harvested crops from deterioration in the storage or transport. Thiram is used as an animal repellent to protect fruit trees and ornamentals from damage by rabbits, rodents and deer. The soil half life for thiram is reported as 15 days.

The biodegradation of thiram in composting process, its photolysis and photocatalysed degradation has been studied earlier. But detailed studies have not been done for this pollutant. Therefore, a detailed study on the photodegradation of thiram is proposed.
thiram (1) sensitized by TiO$_2$ in aqueous solution has been undertaken in the present work. An attempt has also been made to identify the intermediate products formed during the photooxidative process through GC-MS analysis.

**Experimental Procedure**

Laboratory grade thiram was obtained from Swarup Chemicals Pvt. Ltd., Lucknow, India and used as such without any further purification. Double distilled water was employed in this study to make stock solution for irradiation experiments. The photocatalyst, TiO$_2$ Degussa P25 was used in most of the experiments, other catalyst powders, namely, Hombikat UV100 (Sachtleben Chemie GmbH), PC500 (Millennium Inorganics) and TiO$_2$ obtained from Travancore Titanium Products (TTP), India, were also used for comparative studies. The other chemical used in this study such as NaOH, HNO$_3$, hydrogen peroxide, potassium bromate and ammonium persulphate were obtained from Merck.

For experiments under UV light, the desired concentrations of thiram were prepared in double distilled water. An immersion well photochemical reactor made of Pyrex glass was used in this study. For irradiation experiment 250 mL of the desired solution was filled into the reactor and required amount of TiO$_2$ was added. The solution was stirred for at least 15 min in the dark to allow equilibration of the system. The zero time reading was obtained from blank solution kept in the dark but otherwise treated similarly to the irradiated solution. The suspensions were continuously purged with molecular oxygen throughout each experiment. Irradiations were carried out using a 125 W medium pressure mercury lamp. IR radiation and short wavelength UV radiation were eliminated by a water circulating pyrex glass jacket. Samples (10 mL) were collected before and at regular intervals during the irradiation for analysis.

The sunlight experiments were carried out between 9.00 A.M to 2.30 P.M during the month of June at Aligarh City. The solution (250 mL) of desired concentration of thiram containing required amount of photocatalyst was taken in a round bottom flasks (250 mL) made of Pyrex glass and stirred for 15 min in the dark in presence of oxygen. The solution was then placed on flat platform with continuous stirring and purging of molecular oxygen. Samples (10 mL) were collected before and at regular intervals during the illumination for analysis.

The degradation of thiram was monitored by measuring the absorbance on a Shimadzu UV-Vis Spectrophotometer (Model 1601) at 278 nm wavelength. The degradation rate of thiram was calculated from the initial slope obtained by linear regression from a plot of the natural logarithm of the absorbance of the compound as a function of irradiation time, i.e. first order degradation kinetics.

For characterization of intermediate products, aqueous solution (250 mL) of thiram containing TiO$_2$ (Degussa P25, 1 gL$^{-1}$) was taken in the immersion well photochemical reactor. The mixture was irradiated for 60 min and the photocatalyst was removed through filtration. The filtrate was extracted with chloroform, dried over anhydrous sodium sulphate and the solvent was removed under reduced pressure to give a residual mass, which was analyzed by GC-MS.

**Results and Discussion**

**Photolysis of TiO$_2$ suspensions containing thiram**

Figure 1 shows the change in absorption intensity of an aqueous solution of thiram (1, 0.25 mM) in the absence and presence of the photocatalyst (TiO$_2$, 1 gL$^{-1}$) under oxygen, irradiated by the "Pyrex" filtered output of a 125 W medium pressure mercury lamp. It has been observed that 98.6 % degradation of thiram takes place after 45 min of irradiation, whereas no degradation takes place, when the irradiation was carried out in the absence of TiO$_2$. The degradation curve can be fitted reasonably well by an exponential

![Fig. 1 — Variation of absorption intensity at 278 nm as a function of irradiation time for an aqueous solution of thiram. Experimental conditions: 0.5 mM thiram, V = 250 mL, photocatalyst (P25, 1 gL$^{-1}$), immersion well photoreactor, 125 W medium pressure Hg lamp, pH 8.4, cont. O$_2$ purging and stirring, irradiation time = 45 min.](image-url)
decay curve suggesting first order kinetics. The degradation rate was calculated using following equation,

\[-d[A]/dt = k c^n\]

where \(k\) = rate constant, \(c\) = concentration of the pollutant, \(n\) = order of reaction. Control experiments were carried out in all cases, employing unirradiated blank solutions.

**Comparison of different photocatalysts**

It has been demonstrated that degradation by photocatalysis can be more efficient than by other wet-oxidation technique\(^{18}\). To determine the best photocatalyst among different TiO\(_2\) materials and find further means to accelerate the efficiency of the photocatalytic process, the degradation of thiram was tested with Degussa P25, Hombikat UV100, PC500 and TTP. Fig. 2 shows the degradation rate for the decomposition of thiram in presence of different photocatalysts. It has been observed that the degradation of the fungicide proceeds much more rapidly in presence of Degussa P25 as compared to other employed photocatalyst powders. In all the subsequent experiments, Degussa P25 was used as the photocatalyst since this material exhibited the highest activity for the degradation of thiram.

**pH Effect**

The pH of the solution may affect the surface charge properties of the catalyst and, therefore, the adsorption behavior of compound. The degradation of thiram in aqueous suspensions of TiO\(_2\) was studied at a pH range between 3 and 11 under UV light source. Fig. 3 shows the degradation for thiram as a function of reaction pH. The degradation rate was found to be highest at pH 4, whereas lower and more or less similar rates were observed at pH 6.2, 8.4 and 10.

**Effect of substrate concentration**

The influence of thiram concentration on the degradation rate was studied at concentrations varying from 0.25 to 0.75 mM. Fig. 4 shows the degradation rate for the decomposition of thiram as a function of substrate concentration. It was observed that the degradation rate increases with the increase in the substrate concentration.

**Effect of catalyst concentration**

The influence of catalyst concentration on the degradation kinetics of thiram was investigated using Degussa P25 concentrations varying from 0.5 to 5 g L\(^{-1}\). Fig. 5 shows the variation of the degradation rate for thiram as a function of catalyst concentration. It could be seen from the figure that the increase in the catalyst concentration improves the degradation rate of thiram.
Effect of electron acceptors

Since hydroxyl radical appears to play an important role in the photocatalysis, electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate were added into the solution in order to enhance the formation of hydroxyl radicals and also to inhibit the \((e^-/h^+)\) pair recombination. The degradation rate for thiram in the presence of various electron acceptors is shown in Fig. 6. Each additive showed a beneficial effect on the degradation of thiram.

One practical problem in using (TiO\(_2\)) as a photocatalyst is the undesired electron/hole recombination, which, in the absence of proper electron acceptor or donor, is extremely efficient. It represents the major energy wasting step thus limiting the achievable quantum yield. One strategy to inhibit electron-hole pair recombination is to add other (irreversible) electron acceptors to the reaction. In highly toxic wastewater where the degradation of organic pollutants is the major concern, the addition of inorganic ions to enhance the degradation rate may often be justified. Hence, the effect of electron acceptors such as hydrogen peroxide, potassium bromate and ammonium persulphate on the photocatalytic degradation of the thiram under investigation has been studied.

Photolysis of thiram under sunlight

For practical applications of wastewater treatment based on these processes, the utilization of sunlight is preferred. Aqueous suspension of thiram containing TiO\(_2\) was exposed to solar radiation as well as UV light source. Fig. 7 shows the change in absorption intensity at 278 nm as a function of irradiation time under sunlight in the presence of Degussa P25. The degradation of thiram was found to be slower under sunlight as compared with that of the UV light source.

Intermediate products

An attempt was made to identify the products formed as a result of thiram degradation. The GC-MS
analysis of the irradiated mixture showed the formation of several products out of which, three products 4, 5 and 8 appearing at retention times (tR) 8.07, 6.92 and 10.06 min were identified based on their molecular ion and mass spectrometric fragmentation peaks, which are indicated below:

**Compound 4:** m/z : 226 (M⁺), 222, 197, 183, 169, 155, 141, 127, 113, 99, 85, 71 and 57.

**Compound 5:** m/z: 212 (M⁺), 169, 154, 140, 126, 113, 99, 85, 71, 57 and 46.

**Compound 8:** m/z: 234 (M⁺), 219, 203, 191, 185, 171, 149, 143, 129, 115, 102, 85, 73, 57 and 47.

A possible mechanism for the formation of these products could be understood in term of the pathways involving electron transfer reactions and reaction with hydroxyl radicals shown in two self explanatory Schemes (Scheme 1 and 2).

![Scheme 1](image1)

![Scheme 2](image2)

Fig. 7—Change in absorption intensity at 278 nm as a function of irradiation time under sunlight in the presence of photocatalyst Degussa P25. Experimental conditions: 0.5 mM thiram, V = 250 mL, photocatalysts: Degussa P25 (1 g L⁻¹), round bottom flask (250 mL), cont. O₂ purging and stirring, irradiation time = 45 min.
Briefly, when a semiconductor such as TiO\textsubscript{2} absorbs a photon of energy equal to or greater than its band gap width, an electron may be promoted from the valence band to the conduction band (e\textsuperscript{-}\textsubscript{cb}) leaving behind an electron vacancy or “hole” in the valence band (h\textsuperscript{+}\textsubscript{vb}). If charge separation is maintained, the electron and hole may migrate to the catalyst surface where they participate in redox reactions with sorbed species. Specially, h\textsuperscript{+}\textsubscript{vb} may react with surface-bound H\textsubscript{2}O or OH to produce the hydroxyl radical and e\textsuperscript{-}\textsubscript{cb} is picked up by oxygen to generate superoxide radical anion (O\textsubscript{2}\textsuperscript{-}), as indicated in the following Eqs 1-3,

\[
\begin{align*}
\text{TiO}_2 + h^\ast v & \rightarrow e^-_{\text{cb}} + h^+_{\text{vb}} & \ldots (1) \\
O_2 + e^-_{\text{cb}} & \rightarrow O_2^- & \ldots (2) \\
H_2O + h^+_{\text{vb}} & \rightarrow OH + H^+ & \ldots (3)
\end{align*}
\]

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 pollutant and the efficiency of degradation will depend upon the oxygen concentration, which determines the efficiency with which the conduction band electrons are scavenged and the (e\textsuperscript{-}/h\textsuperscript{+}) recombination is prevented. It has been reported earlier\textsuperscript{19} that Degussa P25 owes its high photoreactivity to a slow recombination between electron and holes, whereas Sachtleben Hombikat UV100 has a high photoreactivity due to fast interfacial electron transfer rate. Since Degussa P25 was found to be the most active photocatalyst, it is obvious that the rate limiting step cannot be the interfacial electron transfer reaction but rather the life time of electron-hole pair. Earlier studies\textsuperscript{20-22} have shown that Degussa P25 was found to show better activity for degradation of a large number of organic compounds. Lindner\textsuperscript{23} showed that Hombikat UV100 was almost four times more effective than P25 when dichloroacetic acid was used as the model pollutant. In a recent study, Hombikat UV100 was found to be better for the degradation of benzidine and 1,2-diphenyl hydrazine\textsuperscript{24}. These results indicate that the activity of the photocatalyst also depends on the type of compound under investigation.

As oxidation proceeds, less and less of the surface of the TiO\textsubscript{2} particle is covered as the pollutant is decomposed. Evidently, at total decomposition, the rate of degradation is zero and a decreased photocatalytic rate is to be expected with increasing irradiation time. In all cases, the expression for the rate equation is similar to that derived from the L-H model, which has been useful in modeling the process, although it is not possible to find out whether the process takes place on the surface, in the solution or at the interface. Present results, on the effect of the initial concentration on the degradation rate, are in agreement with the assumption of the Langmuir Hinshelwood model.

Whether in static, slurry or dynamic flow reactors, the initial reaction rates were found to be directly proportional to catalyst concentration, indicating a heterogeneous regime. However, it has been observed that above a certain concentration, the reaction rate levels off and becomes independent of the catalyst concentration. This limit depends on the geometry and working conditions of the photoreactor and for a definite amount of TiO\textsubscript{2} in which all the particles, i.e., the entire surface exposed, are totally illuminated. When the catalyst concentration is very high, after traveling a certain distance on an optical path, turbidity impedes further penetration of light in the reactor. In any given application, this optimum catalyst concentration [(TiO\textsubscript{2})\textsubscript{OPT}] has to be found, in order to avoid excess catalyst and ensure total absorption of efficient photons. The results on the effect of catalyst concentration on the degradation rate for the decomposition of thiram, shown in Fig. 5 are in agreement with studies reported in the literature\textsuperscript{20}.

As expected, all the additives showed beneficial effect on the photocatalytic degradation of thiram. However, the addition of bromate ions markedly enhanced the degradation rate of the compound, indicating that this additive is the most effective electron acceptor as compared with the other oxidants employed in this study. The respective reduction potential of different species formed from these additives are: E (O\textsubscript{2}/O\textsubscript{2}^-\textsuperscript{−}) = -155 mV, E (H\textsubscript{2}O\textsubscript{2}/OH\textsuperscript{−}) = 800 mV, E (BrO\textsubscript{2}/BrO\textsubscript{2}^-) = 1150 mV, E (S\textsubscript{2}O\textsubscript{8}\textsuperscript{2−}/SO\textsubscript{4}\textsuperscript{−}) = 1100mV\textsuperscript{25}. From the thermodynamic point of view all employed additives should, therefore, be more efficient electron acceptors than molecular oxygen.

**Conclusion**

TiO\textsubscript{2} can efficiently catalyze the photodegradation thiram in the presence of light and oxygen. The results of this study clearly demonstrate the importance of choosing the optimum degradation parameters to obtain high degradation rates of the compound, which is essential for any practical
application of photocatalytic oxidation processes. Although the best degradation condition depends strongly on the kind of pollutant, but pH markedly influence the overall efficiency of the degradation. Degussa P25 was found to be more active as compared to other TiO₂ powders. The electron acceptors have been found to enhance the degradation rate of thiram. The efficiency of degradation of thiram under sunlight is slower than under the artificial light. The analysis of the intermediate products could be useful source of information on the degradation pathways.

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