Titanium dioxide mediated photocatalytic degradation of malathion in aqueous phase

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Received 5 January 2011; accepted 17 September 2012

The photocatalytic degradation of technical grade pesticide ‘malathion’ has been studied in aqueous suspensions of TiO2. The main aim of using this process is to degrade the toxic complex structure of the pesticide to harmless products by treating the sample in the UV-reactor. The COD measurements are carried out in order to study the percentage mineralization and degradation is studied under different parameters like varying pH, catalyst concentration, and oxidant addition (H2O2). The degradation of the pesticide is found to be maximum at optimum catalyst loading of 3.0 g/L, pH of 6.0 and oxidant concentration of 2.5 mL/200 mL. Adsorption is negligible as compared to photocatalytic degradation of the pesticide.

Keywords: Biodegradability, Chemical oxygen demand, Mineralization, Malathion, Pesticide, Photocatalysis, Titanium dioxide

After India’s green revolution started, the consumption of pesticides in India has increased several hundred folds, from 154 MT in 1954 to 88,000 MT in 2000-2001. Therefore, the problem of the pesticide pollution is increasing day by day due to its maximum use in the agricultural field. The pesticide contaminated water if taken above the permissible limits it may lead to the serious health problems such as vomiting, nausea, diarrhea, hypertension and many others health related problems. Synthetic pesticides have been popular with farmers, because of their widespread availability, simplicity in application, efficacy and economic returns. But they also have huge environmental costs. Mostly pesticides are used for cotton and rice in India. While cotton is planted on about 5% of the total cultivable area (on about 8 million hectares out of a total of 170 million), it accounts for about 45% of pesticide application. Rice accounts for another 23% of application. Vegetables and fruit also account for a significant proportion. Many of the pesticides currently being used have a tendency to survive in plants for a long time. They also enter the food chain and are found in metal and dairy products. The problem of pesticide residue is already a serious threat to health and environment in India. Jumanah stated in his study that more than 80% of milk samples tested in India have residues of pesticide. The amount of residue is very high and babies are ingesting 21 times more amount of these chemicals then that considered acceptable through their mother’s milk.

Malathion is a pesticide that is widely used in agriculture, residential landscaping, public recreation areas, and in public health pest control programs such as mosquito eradication. Malathion itself is of low toxicity; however, the absorption or ingestion into the human body readily results in its metabolism to malaoxon, which is substantially more toxic. Acute exposure to extremely high levels of malathion will cause body-wide symptoms whose intensity will be dependent on the severity of exposure. Possible symptoms include skin and eye irritation, cramps, nausea, diarrhea, excessive sweating, seizures and even death. Most symptoms tend to resolve within several weeks. Malathion present in untreated water is converted to malaoxon during the chlorination phase of water treatment, so malathion should not be used in a source for drinking water, or any upstream waters.

Several processes including biological techniques are available today for the treatment of process effluents. The effluent containing pesticides/other complex compounds cannot be treated by
conventional techniques due to their recalcitrant nature to biodegradation.\textsuperscript{6,7} Research and development in innovative technologies during the last decade have shown that advanced oxidation processes (AOP) that are combination of powerful oxidizing agents, like UV light, UV/TiO\textsubscript{2}, O\textsubscript{3}/UV, Fenton and Photo-fenton to mention a few, are highly promising for the remediation of complex organic compounds which are present in contaminated water/effluent systems. These processes do not generate any sludge or solid material of hazardous character. AOP include homogeneous and heterogeneous photocatalytic processes. AOP with the highly reactive hydroxyl radicals ($\bullet$OH) as the main oxidative species and either hydrated electrons or hydrogen atoms as reducing species can degrade these biorefractory compounds. However, to ensure that the AOP treatment process occurs efficiently and quantitatively, a full understanding of the reaction kinetics and destruction mechanism involved under various conditions is necessary.

While the operating cost of AOP is always higher than those of a biological treatment, its use as a pre-treatment for the enhancement of biodegradability of pesticides/wastewater containing recalcitrant or treatment-inhibiting compounds might be justified. The intermediate reaction products could then be degraded by microorganisms in a biological post-treatment.\textsuperscript{8-10}

This work is mainly aimed for the degradation of technical grade pesticide malathion used widely in the region, using well defined AOP system. Parameter COD is used to measure the extent of degradation along with spectrophotometric studies. Process conditions are optimized by varying the concentration of catalyst, pH, and an oxidant (H$\textsubscript{2}$O$\textsubscript{2}$).

2 Experimental Procedure

Chemicals

Technical grade pesticide having $>$90% purity of malathion was collected from the Dhanuka group of pesticide industries, New Delhi, India. It is an aliphatic organothiophosphate insecticide (Fig. 1) widely used in the Haryana and Punjab regions of India.

The photocatalyst used in the study was TiO\textsubscript{2} P-25 (a mixture of anatase and rutile form of titanium dioxide in the ratio of 70:30), received form Evonik Industries India Pvt. Ltd, Mumbai Branch, as a gift sample, with a BET surface area of 50±15 m$^2$g$^{-1}$ and average particle size of 30nm. For the adjustment of pH, 0.1 N H$\textsubscript{2}$SO$\textsubscript{4}$ and 0.1N NaOH were used. All chemicals were used as received. In all the experiments doubly distilled water was used.

Laboratory photoreactor and light source

The experimental set-up consists of batch UV reactor (Fig. 2), rectangular in shape having dimensions of length 4.5 m, width 3.0 m and height 3.5 feet and made up of GI sheet. Reactor was mounted with wooden roof and equipped with seven 36 W UV tubes (Philips) attached to the roof having wavelength of 365 nm fitted in parallel on the top of the chamber. Small holes are given on the sidewall of the chamber to maintain a constant temperature and for proper circulation of air. The reactor is placed on a lab jack so that required intensity could be attained by adjusting the distance of the reactor from the UV tubes. The UV intensity in the reactor can be varied from 10 Wm$^{-2}$ to 30 Wm$^{-2}$ corresponding to the average intensity of UV radiation in sunlight. The process is carried out in open atmosphere and oxygen purging is done from time to time. Temperature inside the reactor was maintained by an exhaust fan.

Fig. 1−Chemical structure of malathion

Fig. 2−Schematic diagram of laboratory scale set-up [(1) UV chamber, (2) reactor, (3) lab jack, (4) UV lamps, and (5) holes]
**Procedure**

In a typical study, stock solution of pesticide (2 ppm) was prepared based on the survey done in different regions of Punjab and Haryana. Then 200 mL of stock solution was taken in the batch reactor made up of borosil glass (diameter 7.5 inches and height 2 inches) and the optimum amount of catalyst was added. The solution was maintained in the dark for at least one hour to reach complete adsorption equilibrium. This solution was then irradiated under UV lamp with continuous stirring using a magnetic stirrer in the UV chamber for the required period. An aliquot of 5 mL was taken from the reactor at regular interval of time with the help of a syringe. The catalyst was filtered from the sample by millipore filter (0.45 µm). These samples were analyzed for COD estimation as well as with UV-Vis spectrophotometer (Hitachi model U-2800). Standard methods were used for calculating COD and other parameters. All the experiments were carried out under the normal reaction conditions at an average intensity of 27-30 W m$^{-2}$.

**3 Results and Discussion**

**Preliminary Studies**

The photodegradation of malathion in the presence and absence of semiconductor is shown in Fig. 3. Direct photolysis of the selected pesticide yields only 5.0% reduction in COD after 10 h of irradiations. Consequently, the photolysis of the pesticide is negligible and the decomposition that is observed in the presence of the catalyst (TiO$_2$) is ascribed to the catalyst activity. Moreover, blank experiments in the absence of UV light exhibite negligible adsorbance of the pesticide on the catalyst’s surface. The results observed from the adsorption experiment confirm 18% reduction in COD values i.e. negligible degradation of the compound is observed. The reduction in COD values is mainly due to the formation of pesticide monolayer on the catalyst surface. After monolayer formation, no free active sites remain available for further adsorption and hence no further reduction in COD is observed, which is supported by adsorption curve (Fig 3). The degradation of the organic compound using TiO$_2$ with UV light shows 60% reduction in COD, thus assuming that adsorption-desorption of substrate and reaction intermediate is relatively slow as compared to the formation of electron/hole pairs$^{11}$.

**Effect of catalyst concentration**

It has been reported that the increase in the number of TiO$_2$ particles increases the number of photons absorbed and the number of contaminated molecules absorbed$^{12,13}$. Therefore, the degradation efficiency can be enhanced with increasing TiO$_2$ concentration due to the increase in total surface area available for contaminant adsorption. Experiments were performed to study the variations in the rate of degradation at different catalyst concentration ranging from 1.0 g/L to 10.00 g/L at a constant UV intensity of 28Wm$^{-2}$. It is observed that as the catalyst concentration increases from 1.0 g/L to 3.0 g/L, the photodegradation of malathion increases rapidly from 22% to 60% at normal pH of 3.5. The efficiency decreases slightly (Fig. 4a-c) when the amount of TiO$_2$ is above 3.0 g/L. The reasons for this decrease in degradation rate are (i) aggregation of TiO$_2$ particles at high concentrations causing a decrease in the number of surface active sites and (ii) decrease in opacity and light scattering of TiO$_2$ particles at high concentration.

**Effect of operating pH**

The pH plays an important role in the photocatalytic process of various pollutants$^{14}$. The influence of the initial pH value on the photodegradation rate of malathion for the TiO$_2$ suspensions is demonstrated in Fig. 4b. The photodegradation of selected pesticide increases from 53% to 77% at 2 ppm with optimum catalyst dose of 3.0 g/L, when the initial pH value increases from 2.0 to 6.0 and decreases thereafter in basic medium.

It is reported that in the illuminated TiO$_2$ system, the effect of the solution pH on the degradation rate can be explained mainly by the surface charge of

![Fig. 3—Comparison between photolysis and percentage reduction in COD of malathion in the presence and absence of UV irradiations (♦→ UV, ■→ TiO$_2$, ▲→ UV+TiO$_2$)](image-url)
TiO$_2$. The point of zero charge (pzc) of the TiO$_2$ is widely reported at pH=6.5. The TiO$_2$ surface is positively charged in acidic solution and negatively charged in basic solution$^{16}$. Electrostatic attraction or repulsion between the catalyst’s surface and the organic molecule is taking place, depending on the ionic form of the organic compound (anionic or cationic) and thus consequently enhances or inhibits the photodegradation efficiency respectively. In our study, the degradation of pollutant significantly increases in acidic suspension compared to that in alkaline suspension.

**Effect of addition of oxidant**

In order to enhance the photodegradation rate of the malathion under UV light, an oxidant (H$_2$O$_2$) is added into a semiconductor suspension. The experiments are conducted by varying the hydrogen peroxide concentration from 0.5 to 5.0 mL per 200 mL of the pesticide sample (Fig. 4c). The degradation of the pesticide under study increases from 77% to 93% as the oxidant dose varies from 0.5 mL to 2.5 mL and overdose of H$_2$O$_2$ retards the malathion photocatalytic rates. The slight rate improvement at lower H$_2$O$_2$ dosages is probably due to the enhancement of the photocatalytic activity by providing an additional oxidant source and by reducing the rate of recombination between holes and electrons in the activated titanium dioxide particles.

Hydrogen peroxide shows two main functions in the process of photocatalytic degradation. It accepts a photo generated electron from a conduction band and thus promotes the charge separation. It also forms OH radical, as shown in Eq. (1). At high concentration of H$_2$O$_2$, it acts as a scavenger, as shown in the following equations:

\[
\text{H}_2\text{O}_2 + \text{OH} \rightarrow \text{HO}_2 + \text{H}_2\text{O} \quad \cdots(1)
\]

\[
\text{HO}_2 + \text{OH} \rightarrow \text{H}_2\text{O} + \text{O}_2 \quad \cdots(2)
\]

Our observations are in agreement with those reported in the literature$^{17-19}$.

**Solar studies**

Results obtained from the degradation studies of pesticide using artificial UV light source are compared with the treatment under natural solar conditions. After optimizing the conditions with UV source i.e. 0.3 g/L TiO$_2$, 6 pH, 2.5 mL H$_2$O$_2$ addition, the degradation studies are carried out under natural solar conditions. The average solar intensity is nearly 27-30 Wm$^{-2}$ (measured using radiometer in the months of May-June), same as was kept during artificial UV treatment. After each hour, degradation is more in case of sunlight as compared with lab conditions. Overall degradation of the pesticide is found to be approx. 80% after 7-8 h of
treatment under sunlight as compared to 65% in artificial UV conditions in the same duration of time and under same intensity. Similar kind of work has also been reported that, the rate and extent of degradation of toxic/non-biodegradable is more in natural sunlight conditions as compared to that in artificial UV-light source.

Catalyst recycling
The catalyst lifetime is an important parameter for industrial applications of photocatalytic and also to reduce the cost of the catalyst significantly. During photocatalytic treatment catalyst recycling is one of the major challenges towards the large scale applications. Catalyst fouling and loss during filtration is the major cause behind the drop in the efficiency of the catalyst. During our studies, the catalyst was effectively recycled for at least four times (Fig. 5), but with at least 15% reduction in the degradation efficiency. After the each run, the catalyst was filtered using Wattmann filter paper (no. 22) and then activated at 105°C.

Conclusion
It is inferred that photocatalytic process is a convenient means of degrading the pesticides. In this work, the direct photolysis and the photocatalytic oxidation of pesticide malathion has been studied using TiO₂ as a photocatalyst. Photolysis of the malathion pesticide causes less than 10% reduction in its initial concentration after 10 h of treatment. Malathion is easily degraded by TiO₂ assisted photocatalysis in aqueous dispersion under irradiation by UV light. The optimum concentration of TiO₂ photocatalyst is found to be 3.0 g/L. Variation in the initial pH of the sample reveals that acidic conditions are favorable for the degradation of target compound with maximum at 6.0 pH. With the addition of an oxidant into illuminated semiconducting suspensions, a positive effect is observed that leads to the enhancement of the photodecomposition of the parent compound with 2.5 mL dose of H₂O₂ per 200 mL of the sample as optimum. The observations clearly demonstrate the importance of choosing optimum degradation parameters to obtain high degradation rates which is most essential for any practical applications of photocatalytic oxidation processes.

Results can be implemented with certain modifications at large level to efficiently remove pesticide from water/wastewater which are not conveniently removed by conventional treatment. Shallow pond reactors can be made and incorporated as pre or post treatment in conventional methods to treat water containing pesticides.

Acknowledgement
The study is supported by grant from Defence Research and Development Organisation (DRDO), New Delhi, India. The authors are also thankful to Degussa India Pvt. Ltd, Mumbai Branch (Evonik Industries) for providing free samples of TiO₂ for the present study.

References
2 Ghayur A, A Study of Biopesticides and Biofertilisers in Haryana, India (Gatekeeper Series No.SA93), 2000, 3.
VERMA et al.: TiO$_2$ MEDIATED PHOTOCATALYTIC DEGRADATION OF MALATHION
