Photocatalytic degradability of insecticide Chlorpyrifos over UV irradiated Titanium dioxide in aqueous phase
Anoop Verma, Poonam, Divya Dixit
Department of Biotechnology & Environmental Sciences,
Thapar University, Patiala, Punjab
anoop.kumar@thapar.edu
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ABSTRACT
Photocatalytic degradation of Chlorpyrifos in aqueous phase by using photocatalyst TiO$_2$ in the presence of artificial UV-light and sunlight was reported. Experiments were performed in both UV and solar light at optimized conditions. The degradation of insecticide was investigated in terms of reduction in COD. The effect of catalyst loading, pH, addition of oxidant on the reaction rate was ascertained and optimum conditions for maximum degradation were determined. In this case catalyst concentration was optimized at 4.0 gL$^{-1}$, pH 6.5 and oxidant concentration at 3.0 gL$^{-1}$, where 90% degradation of the insecticide was observed. Treatment under natural solar conditions showed better results as compared with UV treatment. The effect of sonication on the catalyst slurry was also studied for the better dispersion of the catalyst. The complete mineralization of pesticide from water or waste water followed first–order Langmuir-Hinshelwood (L-H) kinetic model.

Keywords: Photocatalysis, sun-light radiation, oxidant, Insecticide, Titanium dioxide.

1. Introduction
In recent years, using a semiconductor as the photocatalyst to degrade various organic and inorganic pollutants in wastewater has become a kind of water treatment technology. Heterogeneous catalysis which involves semiconductor developed in the last 10-15 years due to its potential applications to environmental problems. The strong potential of advanced oxidation processes (AOPs) for bio-recalcitrant wastewater treatment is universally recognized today. There are many studies focusing on the application of this technique for the degradation of many compounds (Nag and Raikwar, 2008; Kumari et al., 1996; Kumari, Madan, and Kathpal, 2007). AOPs are characterized by the production of hydroxyl radicals (•OH), the second largest known oxidant after fluorine which are able to oxidize and mineralize almost any organic molecule, yielding CO$_2$ and inorganic ions. While AOP operating costs are always higher than those of a biological treatment, their use as a pre-treatment for the enhancement of the 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 (Gupta, 2004; Ovez, Yuksel and Saglam, 2009).

The solar photocatalytic oxidation with TiO$_2$ as a catalyst uses only UV portion of the solar radiation, which forms about 4-6% of the total spectrum. A number of different designs of non-concentrating solar reactors have been proposed which includes thin film cascade (Chan et al., 2003), fixed bed reactor (Zayani et al., 2009) and shallow solar ponds (Biljana et al., 2004). Industries which generate large amount of effluent per day already use ponds for the
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microbiological treatment of wastewater and similar shallow solar ponds can be used for the front or back end of a combined solar/ microbiological treatment of wastewater.

The removal of persistent organic chemicals from water is a pressing ecological problem. Persistent contaminants include pesticides, solvents, detergents and a variety of industrial chemicals which, due to resistance to biodegradation are capable of penetration deep into the soil and of reaching groundwater. During the last few decades, the development of the agrochemical industry has dramatically increased due to widespread intensive agriculture. The problem of the pesticide pollution is increasing day by day due to its maximum use in the agricultural field and also pesticide contaminated water if taken above the permissible limits it may lead to the serious health problems such as vomiting, nausea, diarrhoea, hypertension and many others health related problems (Muszkat, Bir and Feigelson, 1995).

Synthetic insecticides have been popular with farmers, because of their widespread availability, simplicity in application, efficacy and economic returns besides having huge environmental costs. Insecticides are considered cumulative and toxic compounds. Their presence as contaminants in aquatic environments may cause serious problems to human beings and other organisms. Excessive and injudicious use of insecticide lead the environmental contamination in air, water, soil besides accumulating in food chain. The study revealed the contamination of milk with pesticide residues was observed in number of contaminated samples which exceed the tolerance level (Tiwana, 2007). The contamination problem is more serious in case of vegetables as these are often consumed either raw or without much processing or storage. (Altieri, 2005)

Chlorpyrifos is one of the world’s most widely used organophosphorus insecticide in agriculture (Affam et al., 2012; Devi et al., 2009; Murillo et al., 2010; Peñuuela and Barcelo, 1997). It shows a wide spectrum of biological activity and is used to control range and forage insect pests as well as soil dwelling grubs, rootworms, borers and subterranean termites. Symptoms of acute poisoning include headache, nausea, muscle twitching and convulsions and in some extreme cases even death. Human birth defects have also been associated with exposure to chlorpyrifos and its products. It also affects the male reproductive system. It is toxic to a variety of beneficial arthropods including bees, ladybird beetles and parasitic wasps. It kills fish at concentrations as low as a few parts per trillion (Racke et al., 1994). There are limited studies pertaining to catalyst recycling as well as effect of UV intensity to best of our knowledge. These parameters are very important for field scale applications of this technology. This present work is mainly aimed for the degradation of the technical grade insecticide chlorpyrifos used widely in the region, using AOP system. COD is used to measure the extent of degradation along with spectrophotometric studies. Process conditions were optimized by varying the concentration of the catalyst, pH, H₂O₂ etc.

2. Experimental

2.1 Chemicals

Chlorpyrifos is a crystalline organophosphate insecticide that inhibits acetyl cholinesterase and is used to control insects (Figure 1). The pesticide having purity >90% was collected from the Dhanuka group of pesticide industries [New Delhi, India] as a gift sample. This pesticide is widely used in the Haryana and Punjab [India] region.
The photocatalyst was TiO$_2$ P-25 (a mixture of Anatase and Rutile form of titanium dioxide in the ratio of 70:30, received from 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 30 nm. For the pH adjustment 0.1 N H$_2$SO$_4$ and 0.1 N NaOH were used. All chemicals were used as received. In all the experiments doubly distilled water was used.

### 2.2 Photoreaction apparatus and procedure

For the photocatalytic experiments the UV Chamber used was of rectangular in shape having dimensions of length 4.5 ft, width 3.0 ft and height 3.5 ft (Figure 2) and made up of GI sheet (Toor et al., 2006). It was 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 were drilled on the sidewall of the chamber to maintain a constant temperature and for proper circulation of air. The reactor (17 cm in diameter and 5.3 cm in height made up of borosil glass) was 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 to 35 Wm$^{-2}$ corresponding to the average intensity of UV radiation in sunlight. The process was carried out in open atmosphere and oxygen purging was done from time to time. Temperature inside the reactor was maintained by an exhaust fan.

A volume of 200 ml of stock solution (2 ppm) was taken in the batch reactor made up of borosil glass (diameter 7.5 inches and 2 inches in height) and the optimum amount of catalyst was added. The suspension was first stirred in 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. Before analysis, the aqueous samples were filtered through 0.45 µm membrane filter to remove TiO₂ agglomerates in suspension. All the experiments were carried out under the normal reaction conditions at UV intensity of 27-30 W m⁻².

2.3 Analysis

The mineralization of insecticide under study was analyzed by COD estimation. The initial COD of the pesticide sample was estimated to be 480 mg/l. The degradation was followed by the reduction in COD values representing the breaking the complex structure to simpler ones. Standard titration methods were used for calculating COD (APHA, 1989).

2.4 Photocatalytic kinetics

Several research paper results indicated that the destruction rates of photocatalytic oxidation of various organic contaminants over illuminated TiO₂ fitted the Langmuir–Hinshelwood (L–H) kinetics model i.e.

\[ r = \frac{dC}{dt} = kKC/1+KC \]

where \( r \) is the reaction rate (mg/l min), \( C \) the concentration of the reactant (mg/l), \( t \) the illumination time in minutes, \( k \) the reaction rate constant (min⁻¹), and \( K \) the adsorption coefficient of the reactant (l/mg).

When the chemical concentration \( C_0 \) is a millimolar solution (\( C_0 \) small) the equation can be simplified to a pseudo first-order equation

\[ r = kKC = k_{app}C \]

which on integration gives

\[ \ln \frac{C_0}{C} = k_{app}t \]

A plot of \( \ln C_0/C \) versus time represents a straight line, the slope of which upon linear regression equals the apparent first-order rate constant \( k_{app} \). Generally first-order kinetics is appropriate for the entire concentration range of ppb or few ppm (Konstantinou and Albanis, 2002).

3. Results and discussion

3.1 Preliminary studies

Dark adsorption studies were carried out with chlorpyrifos to correlate the results for adsorption and degradation under UV light (Toor et al., 2005). In this study, the required volume of insecticide was stirred for many hours with the addition of the catalyst in the dark conditions without pH adjustments. The sample was analysed after 8 h to estimate the percentage of COD reduction and it was found to be nearly 17% (Figure 3). Addition of catalyst TiO₂ leads to monolayer formation on the surface. As soon as the catalyst was added; insecticide from solution was adsorbed on the surface, thus lead to decrease in COD values in the solution. After monolayer formation, no free active sites were available for further adsorption so no further reduction in COD was observed. Thus results from adsorption experiment confirmed that decrease in COD was due to the adsorption of pesticide. Direct photolysis of the effluent yielded only 8% reduction in COD after 8 h of irradiations as clear
from Figure 3. The degradation of the insecticide using TiO$_2$ with UV light showed 55% 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 (Verma and Singh, 2009).

![Figure 3: Comparison between photolysis and percentage COD degradation of wastewater in the presence and absence of UV irradiations](image)

Consequently, the dark adsorption studies, photolytic treatment, photocatalytic treatment of the insecticide showed 17 %, 8% and 55% degradation respectively.

### 3.2. Effect of catalyst concentration

To study the effect of catalyst dose on the degradation of insecticide, TiO$_2$ was varied from 1.0 gL$^{-1}$ to 10 gL$^{-1}$. It was observed that degradation rate of insecticide increases with increased catalyst concentration and becomes constant above a certain level as shown in Figure 4 and then decreased after one particular optimum dose. This is because with the increasing concentration of TiO$_2$, the number of photons absorbed in UV light and the number of pollutant molecules absorbed on the surface of catalyst are increased owing to an increase in rate of photocatalytic reaction. Above a certain level, the pollutant molecules available are not sufficient for the adsorption by the increased number of TiO$_2$ particles. The other reason for this is clustering of catalyst particles at higher concentrations and thus causing a decrease in the number of active sites on its free surface.

The decrease in degradation is thus due to the decrease in surface area of catalyst due to aggregation of TiO$_2$ (Malato et al., 2000; Muhamad, 2010). The highest COD reduction was observed at the catalyst dose of 4.0 gL$^{-1}$, after this COD on decreased substantially.
3.3 Effect of operating pH

Another important parameter in the photocatalytic reactions taking place on the particulate surfaces is the pH of the solution, since it dictates the surface charge properties of the photocatalyst and size of aggregates it forms. Experiments were carried out at different pH values i.e. 3.5 to 8.5 to study the photodegradation as shown in Figure 5. The photodegradation of the insecticide under study increases reaches up to 80% with optimum catalyst dose, when the initial pH value increases from 3.5 to 6.5 and decreases thereafter in basic medium. This is attributed to the fact that TiO$_2$ shows an amphoteric character so that either a positive or a negative charge can be developed on its surface. The point of zero charge (pzc) of the used TiO$_2$ (Degussa P-25) is widely reported at pH≈6.5. The TiO$_2$ surface is positively charged in acidic solution and negatively charged in basic solution (Singh, Muneer, and Bahnemann, 2003) according to the following equations:

\[-\text{TiO}_2^- \leftrightarrow \text{TiOH} + \text{H}^+\]

\[-\text{TiOH} \leftrightarrow \text{TiO}^+ + \text{H}^+\]

![Figure 5: Effect of pH on rate constant k (reaction volume 200ml, TiO$_2$=4.0 gL$^{-1}$, UV intensity 28 Wm$^{-2}$)](image-url)
In our experiment, maximum degradation was obtained at pH 6.5, thus selected as optimum pH.

### 3.4 Effect of Oxidant addition

One practical problem in using TiO$_2$ as a photocatalyst is the undesired electron/hole recombination which, in the absence of proper electron or donor is extremely efficient and 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. They could have several different effects, such as (1) to increase the number of trapped electrons and, consequently, avoid recombination, (2) to generate more radicals and other oxidizing species, (3) to increase the oxidation rate of intermediate compounds and (4) to avoid problems caused by low oxygen concentration (Saquib and Muneer, 2003). At high concentrations of H$_2$O$_2$ it also acts as scavenger as shown in the following equation (Kavitha and Palanisamy, 2011).

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{HO}_2^- + \text{H}_2\text{O}
\]

\[
\text{H}_2\text{O}_2 + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{O}_2
\]

With this view, we have studied the effect of oxidant dose (H$_2$O$_2$) concentrations on the photocatalytic treatment from 0.375 to 4.875 gL$^{-1}$ with optimized concentration of catalyst and pH shown in Figure 6. The best result was obtained when oxidant addition came out to be 3.0 gL$^{-1}$, where insecticide degradation was observed to be nearly 90%. Above this, degradation decreases due to reasons cited above. This was selected as the optimum amount required for maximum effective degradation of insecticide under study.

![Figure 6: Effect of oxidant dose on rate constant k (reaction volume 200ml, TiO$_2$=4.0 gL$^{-1}$, pH =6.5, and UV intensity 28 Wm$^{-2}$)](image)

### 3.5 Effect of Sonication of TiO$_2$ slurry

Sonication helps in the uniform dispersion of catalyst particles in the suspension thus helps in creating more surface area for photocatalytic reactions. It is cited in many literatures that for
achieving uniform dispersion, TiO$_2$ slurry was sonicated by ultrasonic bath with ultrasonic frequency of 16-20 KHz. Ultrasound play a profound role due to substantial increase in the number of active sites and also the surface area available due to defragmentation of the catalyst agglomerates under the action of turbulence by acoustic streaming along with an increase in the diffusion rates of contaminants (Suslick et al., 1999). This sonicated catalyst was then added to the 200 ml sample with all optimized conditions, i.e. 4 gL$^{-1}$ TiO$_2$, 6.5 pH, 3.0 gL$^{-1}$ H$_2$O$_2$. It was observed (Figure 7) that the degradation of the insecticide was maximum i.e. 94% with sonicated catalyst slurry as compared with catalyst without sonication i.e. 89 % under same optimized conditions.

![Figure 7: Effect of Sonication of TiO$_2$ slurry for the degradation of Insecticide](image)

Figure 7: Effect of Sonication of TiO$_2$ slurry for the degradation of Insecticide

3.6 Comparative studies of degradation of pesticide under UV- light and solar radiations

![Figure 8: % photo degradation efficiency of pesticide under UV- light and solar radiations](image)

Figure 8: % photo degradation efficiency of pesticide under UV- light and solar radiations

Figure 8 shows the comparison between sample degradation by solar light and artificial UV light with all optimized parameters i.e. 4 gL$^{-1}$ TiO$_2$, 6.5 pH, 3.0 gL$^{-1}$ H$_2$O$_2$ addition. Results
obtained from the studies confirmed more degradation i.e. 83 %, under natural solar radiation as compared UV- light i.e. 70 % after 5 h of treatment. The average solar intensity was nearly 27-30 Wm$^{-2}$, same as kept during artificial UV treatment (measured with Radiometer). Similar kind of studies (Parra et al.,2000) have also been reported that the rate and extend of degradation of toxic/non- biodegradable is more in natural sunlight conditions as compared to artificial UV- light source.

### 3.7 Effect of UV intensity

For field applications of AOP, the variation in sunlight intensity is always an important factor. The solar intensity varies throughout the year in tropical region like India. Thus studies have been done with variation in UV intensity using aqueous solutions of chlorpyrifos. The height of the reactor was varied from the UV tubes with the help of lab jack to get the required intensity. Actually the number of photons increases as the intensity is increased, leading to formation of more number of hydroxyl radicals (OH$^*$), thus more degradation. In our study, the first order rate constant increases from 0.157 h$^{-1}$ to 0.308 h$^{-1}$ as intensity is varied from 15 Wm$^{-2}$ to 34 Wm$^{-2}$ (Figure 9).

![Figure 9: Effect of UV intensity on the first order degradation rate constant for chlorpyrifos](image)

### 3.8 Catalyst recycling

TiO$_2$ was reused in photocatalysis for treatment of insecticide waste water. TiO$_2$-catalyst suspensions worked efficiently in photocatalysis for wastewater treatment. Nevertheless, once photocatalysis is complete, separation of the catalyst from solution becomes the main challenge. The catalyst was reused after it had settled to the bottom and clear water had been removed. The catalyst was filtered by using wattmann filter paper no. 22 and it was activated at 105 °C. Photocatalytic efficiency worsens with successive runs when catalyst and water are reused without separation, whereas, when TiO$_2$ is separated, the photocatalyst is not deactivated.
There are two major causes behind the reduction in the efficiency i.e. catalyst fouling and loss of catalyst through filtration, during an experiment for catalyst recycling, TiO$_2$ was recycled for at least five times as shown in (Figure 10) but with the reduction in the degradation efficiency (Abo-Farha, 2010). The catalyst lifetime is an important parameter for industrial application of photo catalyst and also to reduce the cost of the catalyst significantly.

4. Conclusion

1. In advanced oxidation process, photocatalytic process can efficiently degrade the insecticides using artificial UV- light or sunlight radiation sources. The observations, clearly demonstrated the importance of cooling optimum degradation parameters to obtain high degradation rates. In this work, the photocatalytic oxidation of chlorpyrifos insecticide had been studied using TiO$_2$ as a photo catalyst and H$_2$O$_2$ as an oxidant. Studies reveal that photo catalytic oxidation of the insecticide in a shallow pond reactor can be efficiently done. The optimum conditions for the photo degradation of insecticides are 4 gL$^{-1}$ catalyst concentration, 3.0 gL$^{-1}$ H$_2$O$_2$ and 6.5 pH.

2. TiO$_2$ was recycled for at least five times but with the reduction in the degradation efficiency. The catalyst lifetime is an important parameter for industrial application of photo catalyst and also to reduce the cost of the catalyst significantly.

3. Results can be implemented with certain modifications at the large level, to effectively remove insecticides from water or wastewater, which can’t be removed by conventional treatment. Large shallow pond reactors can be made and implemented in conventional treatment to treat water containing pesticides. But, prior to developing a full scale pond reactor test or experiments should be conducted with a prototype system to calculate the typical values of the rate constant, because photocatalytic degradation process or rates are highly dependent on the molecular structure of the solute.

4. In overcoming one of the major challenges i.e. a treatment cost and advanced oxidation process there is a need of the future research that must lead to the reduction of the treatment cost. Future research must also investigate the effectiveness of these technologies in the combination with other cost effective treatments such as biological
treatment of bio-recalcitrant compounds, where each technology by itself may not be sufficiently effective for the degradation of toxic compounds.

5. References


