



Photo Catalytic Degradation of Chlorpyrifos in an Annular Slurry Reactor

K. Sivagami, R. Ravi Krishna, T. Swaminathan *

Department of Chemical Engineering,
Indian Institute of Technology Madras, Chennai 600 036, INDIA

ABSTRACT

Increasing use of pesticides is causing severe environmental impacts due to their toxicity and health effects. An effective treatment technique for their removal from wastewaters is necessary. The photo catalytic degradation of Chlorpyrifos, an Organo Phosphate Pesticide, using TiO_2 was investigated in suspended system under UV irradiation. Batch degradation experiments were carried out at initial concentrations ranging from 5 to 50 mg/L at a pH ranging from 3.5 – 10.5 and at a catalyst loading of 0.5 – 2 g/L. The studies on batch photo catalytic degradation of chlorpyrifos, showed about 80 – 99% degradation depending on the initial pesticide concentration, pH and the amount of catalyst. pH had a noticeable effect on removal efficiency in degradation. High removal efficiency obtained in 5 – 50 mg/L indicated effectiveness of this process and its potential for practical application. The photo-catalytic oxidation of Chlorpyrifos over illuminated TiO_2 fitted well with Langmuir-Hinshelwood (L-H) kinetics model. The values of the adsorption equilibrium constant, $K_{\text{pesticide}}$, and the rate constant, $k_{\text{L-H}}$ were 0.0218 L/mg and 65.78 mg/L. min, respectively.

Keywords: Photo catalysis; TiO_2 ; annular reactor; chlorpyrifos; L-H kinetics; UV irradiation

1. INTRODUCTION

Modern agricultural practices have relied heavily on large scale use of fertilizers and pesticides to increase crop yield. This has resulted in increasing levels of pesticides in the environment. A multitude of factors, viz physical, chemical and biological complicate the prediction of their fate and effects in the natural environment. Though pesticides are also typically hydrophobic compounds with low water solubility; they get magnified within food chains due to their higher solubility in fatty tissues (Kutz et al., 1991). The possible chronic health effects of these compounds, carcinogenicity, neuro toxicity and adverse reproductive effects have mandated the need

for eliminating pesticides from surface waters (Burrows, 2002). Limitations of conventional decontamination techniques have resulted in an intensive search for more efficient treatment techniques. Advanced Oxidation Processes (AOP), which is based on the principle of highly reactive hydroxyl radical generation, has emerged as a potential alternate technique for treatment of hazardous pollutants. Chlorpyrifos (CP) is a crystalline organo-phosphate insecticide that is widely used to control pests. As a result of crop and non-crop usage, chlorpyrifos residues may be present in a variety of environmental matrices, e.g., crops and crop products, air, soil and water. Mathur et al. (2003) reported that many of the raw water and bottled water samples contains exceeding level of chlorpyrifos concentra-

*Corresponding to: tswami@iitm.ac.in

tion in Delhi region. Penuela et al. (1997) studied the degradation kinetics of chlorpyrifos in water by natural photolysis and photocatalysis with TiO_2 and FeCl_3 and established the degradation pathway of chlorpyrifos in various degradation processes. The photocatalytic degradation of chlorpyrifos in different waters was studied by researchers, in which they observed that the rate of photocatalysis to be higher than photolysis. Muhmad (2010) also reported that the catalyst concentration showed an optimum level at which the degradation rate was maximum. Chlorpyrifos degradation using different advanced oxidation processes such as photo-Fenton, TiO_2 , $\text{TiO}_2/\text{H}_2\text{O}_2$, O_3 and $\text{O}_3/\text{H}_2\text{O}_2$ has been studied by Murillo et al. (2010). The photo-Fenton, TiO_2 and ozonation processes were optimized using a solar chamber as light source. Devi et al. (2009) have proposed a photo catalytic degradation pathway of chlorpyrifos involving several chloride intermediates. Much of the previous work reported on the photo catalytic treatment of chlorpyrifos was in very low concentration range (1-10 mg/L) normally observed in surface waters. However, wastewaters arising from pesticide manufacture and application may have much higher concentrations of pesticide. The main objectives of this work were to study the effectiveness of photo catalytic treatment at these higher concentrations of pesticides and to optimize the parameters for chlorpyrifos degradation.

2. MATERIALS AND METHODS

2.1 Materials

Technical grade pesticide Chlorpyrifos (98% purity) (Sriram Pesticides, India) and TiO_2 (pure anatase, surface area $15 \text{ m}^2/\text{g}$, CDH, India) were used in the experiments.

2.2 Experimental studies

Chlorpyrifos degradation studies were carried out in an annular photo reactor. CP was dissolved in methanol to increase its solubility in water. A schematic of the experimental setup is shown in Figure 1. It consisted of two concentric cylinders, a quartz inner cylinder of 2.5 cm diameter, 30 cm height and a glass outer cylinder of 3.82 cm diameter. A 11 W UV-C lamp (Philips, Holland) placed inside the inner cylinder provided the UV irradiation. TiO_2 was mixed with pesticide solution in a glass reservoir and stirred well for ten minutes. The slurry of the pesticide solution was continuously circulated through the annular reactor using a peristaltic pump (Ravel Hitech, India) at a flow rate of 300 ml/min. Hourly samples were collected from the reactor and analyzed by HPLC after filtration (Gelman GHP acrodisc $0.25 \mu\text{m}$) to separate titania particles. The degradation studies were carried out for five hours over different ranges of pH, initial CP concentration and catalyst concentrations.

2.3 Analytical method

Concentration of residual chlorpyrifos concentration in the samples was analyzed by gradient HPLC method (Jasco Pu-2089 plus, Japan) with PDA detector using Agilent Eclipse PAH $5 \mu\text{m}$ Column of dimension 10 x 150 mm. Acetonitrile and water (milli-Q) in the ratio of 70:30 was used as mobile phase at a flow rate of 1 ml/min. The pesticide concentration was determined by measuring absorbance of samples and reading the corresponding concentration from a standard calibration. Samples collected at different time intervals were extracted in hexane and analyzed in GC-MS (Shimadzu mass spectrometer) to identify the intermediates formed during the course of the reaction.

3. RESULTS AND DISCUSSION

3.1 Batch degradation experiments in slurry reactor

Batch studies on the photo catalytic degradation of Chlorpyrifos were done by varying the parameters, initial pesticide concentration (5 to 25 mg/L), catalyst concentration (0.5 to 2 g/L) and pH (3.5 to 10.5).

3.1.1 Effect of initial concentration

Initial concentration of reactants plays a significant role in determining the rates of most chemical and photochemical reactions. This was evident in the degradation patterns of the CP shown in Figure 2. The degradation patterns for all the concentrations were similar, with relatively faster degradation in the first two hours, followed by relatively slower removal rate at later stages. There was a signif-

icant reduction in the rate and extent of degradation of CP as the initial concentration was increased from 5 to 25 mg/L respectively. This may be attributed to several factors. At higher pesticide concentrations, there would be more adsorption of pesticide on TiO_2 resulting in a lesser availability of catalyst surface for hydroxyl radical generations. Similar result was observed by (Korman et al., 1991) and they suggested that this may be due to the formation of several layers of adsorbed pesticide on photo catalyst surface, at higher pesticide concentrations. Another possible reason may be that the intermediates formed from the initial breakdown of CP may be competing for the OH- radical resulting in slower degradation. Similar results were observed for photo catalytic degradation of another pesticide, Monocrotophos in our earlier study (Sivagami et al., 2011).

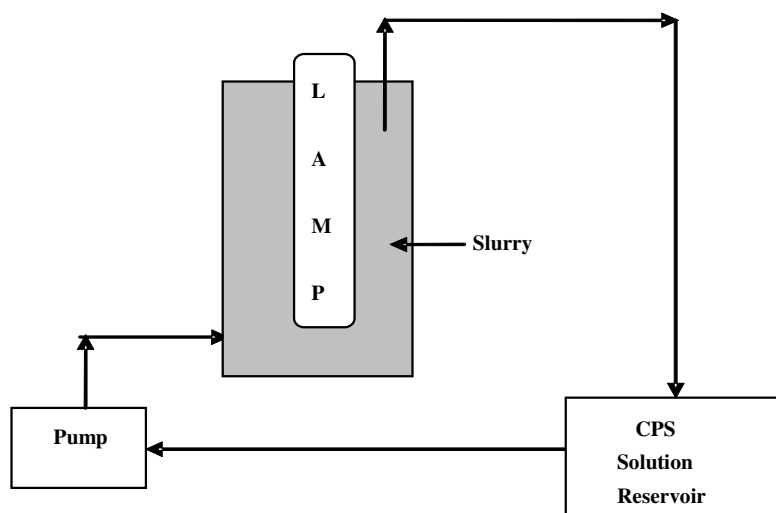


Figure 1 Schematic diagram of experimental setup

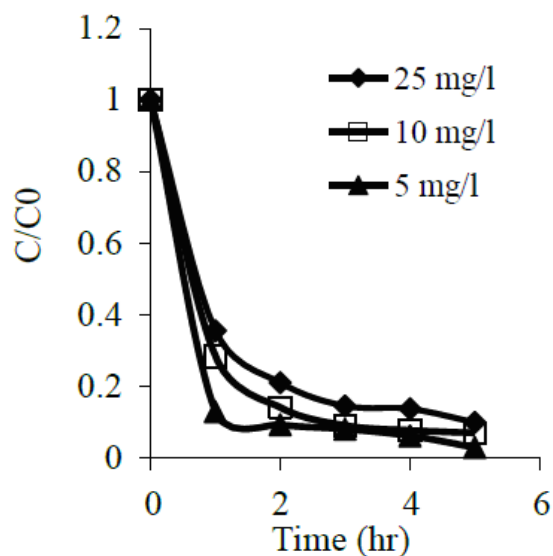


Figure 2 Effect of initial concentration on degradation of chlorpyrifos
TiO₂ load – 0.5 g/L, 7 pH

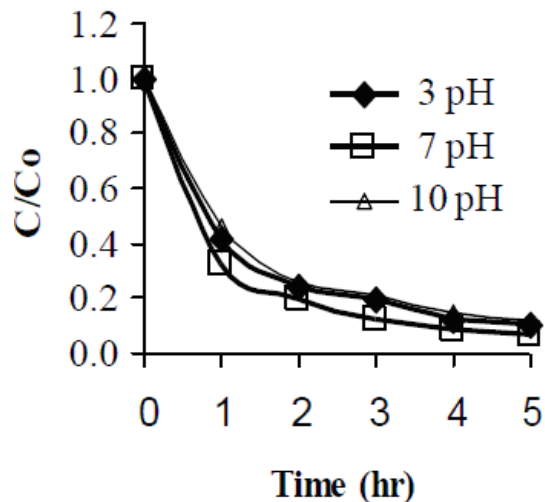


Figure 3 Effect of pH on degradation of chlorpyrifos
(CP concentration – 10 mg/L, TiO₂ load – 0.5 g/L)

3.1.2 Effect of pH

The amphoteric behaviour of titania influences the surface charge of the photocatalyst. The

role of pH on the photocatalytic degradation of chlorpyrifos was studied in the pH range 3-10. The results are shown in Figure 3. It was observed that the rate of degradation was maxi-

mum in the acidic pH and decreased as pH was increased. It was low at alkaline pH. The same behaviour was reported by (Murillo et al., 2010; Yadav et al., 2010) where the degradation of chlorpyrifos was more significant in acidic than in alkaline conditions. Pelizzetti et al. (1993) have reported that the acid-base behaviour of catalyst surface influences the photo catalytic degradation. The zero point charge, pH_{ZPC} for titania is around 6.9 and in acidic pH it is positively charged and in alkaline pH it is negatively charged. The pK_a value of chlorpyrifos is 4.55. At acidic pH, the protonated form predominates while at higher pH it exists in the anion form. Hence the electrostatic interaction between the positively charged surface and protonated chlorpyrifos favours adsorption and increases its removal.

3.1.3 Effect of catalyst concentration

In heterogeneous catalysis, the catalyst concentration has a significant effect on the process efficiency since the active sites are proportional to the catalyst concentration. Degradation patterns of chlorpyrifos at different catalyst concentrations of TiO_2 are shown in Figure 4. It was observed that the rate of degradation increased when the catalyst concentration was increased from 0.5 to 1 g/L. However, further increase in catalyst concentration to 2 g/L decreased the rate of degradation. Reduced degradation efficiency at higher catalyst concentrations has been observed in photo catalytic reactions by others also (Malato et al., 2010; Muhamad et al., 2010). This behavior may be attributed to the shielding effect of catalyst at higher concentrations where the suspended TiO_2 reduces the penetration of light to the solution. Konstantinou et al. (2004) have also observed that degradation of pesticide increased with increasing amount of photo catalyst reaching highest value at catalyst loading 1 g/L and then decreased.

3.2 Batch Kinetic studies

The photo catalytic degradation of a complex molecule like chlorpyrifos takes place in several steps involving a number of intermediates. Hence, the actual degradation kinetics is difficult to follow. However, since photo catalytic degradation usually involves an initial adsorption step followed by the chemical reactions, the Langmuir - Hinshelwood (L-H) kinetic model is usually preferred over the conventional rate kinetics. The Langmuir-Hinshelwood (L-H) kinetic model is represented by

$$r = \frac{dC}{dt} = \left[\frac{K C}{(1 + k K C)} \right] = k_{obs} C \quad (1)$$

The pseudo first order rate constants obtained at different initial concentration of CP were used to fit the L-H kinetic model. The result presented in Figure 5 shows a high degree of fit with regression coefficient of 0.99. The L-H kinetic parameters K and k_{L-H} were obtained from the slope and intercept of the straight line. The values were $K = 0.0218$ L/mg and $k_{L-H} = 65.789$ mg /L.min.

Navarro et al. (2009) studied the degradation of pesticides in leaching water using the tandem $ZnO/Na_2S_2O_8$ as photosensitizer/oxidant and compound under natural sunlight. They reported that the disappearance of pesticides followed first-order kinetics according to Langmuir-Hinshelwood model and complete degradation of eight pesticides occurred within 120 min. They also observed that for all the pesticides the rate constants were a function of the initial concentration and decreased with increasing initial concentration. The first order degradation of lindane and methyl parathion following Langmuir Hinshelwood kinetics has been reported by Senthilnathan and Philip (2009) as well.

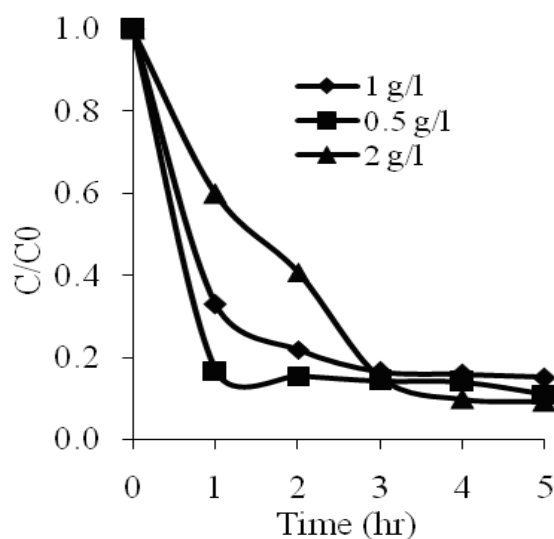


Figure 4 Effect of catalyst concentration on degradation of chlorpyrifos (CP conc.-10 mg/L, pH7)

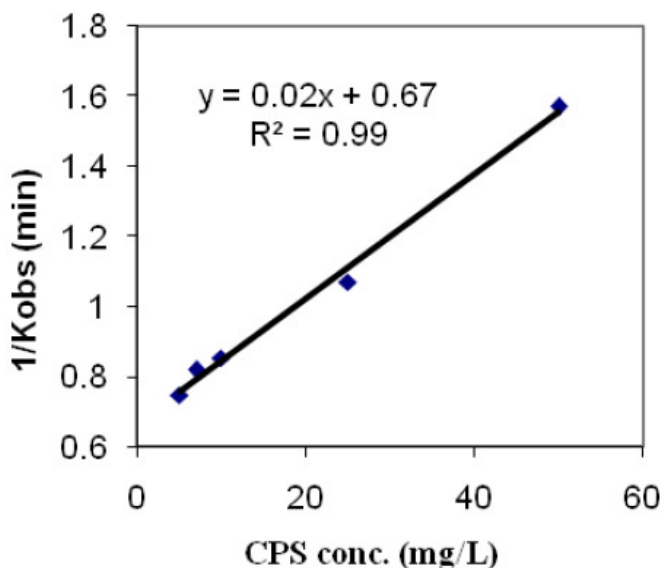


Figure 5 L-H kinetic model for photocatalytic degradation of CP

3.3 Identification of Chlorpyrifos intermediates in GC-MS

As mentioned earlier, the photo catalytic degradation pathway of CP involves a number of organic intermediates. An attempt was made to identify some of the intermediates. The GC

Mass spectrum of CP and its intermediates after 1 hour are shown in Figures 6, 7 and 8. Intermediate (1) was identified as Chlorpyrifos Oxon by a library search value with a fit value of 95%. The mass spectrum of this compound showed the characteristic ions at $m/z = 81$, $m/z = 109$ and $m/z = 197$ related with

di methyl group and phosphate respectively. This intermediate (1) formation is due to the result of hydroxyl radicals attack at the P-S bond converting to P-O (oxon derivative) which is a primary characteristic product formed during the photo catalytic oxidation of organo phosphorous compound. This indicates that the degradation proceeds through the loss of sulfur atom as sulfate group. Similar type of intermediate was found by (Evgenidou, 2007; Kerzhentsev, 1996). Intermediate 2 was iden-

tified as 1-O-Ethyl methyl phosphonothioate by a library search fit value of 97%. The mass spectrum of this compound characteristic ions at $m/z = 47$ and $m/z = 76$. Intermediate 3 was identified as 2-hydroxy 3, 5, 6 tri-chloro pyridine by a library search value with a fit of 80%. The mass spectrum of this compound showed the characteristic ions at $m/z = 199$. Similar products of chlorpyrifos degradation were reported by Devi et al. (2009).

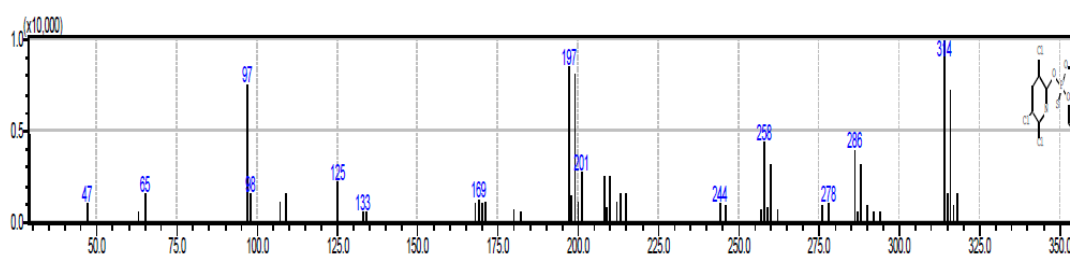


Figure 6 Mass spectrum of Chlorpyrifos at time t=0

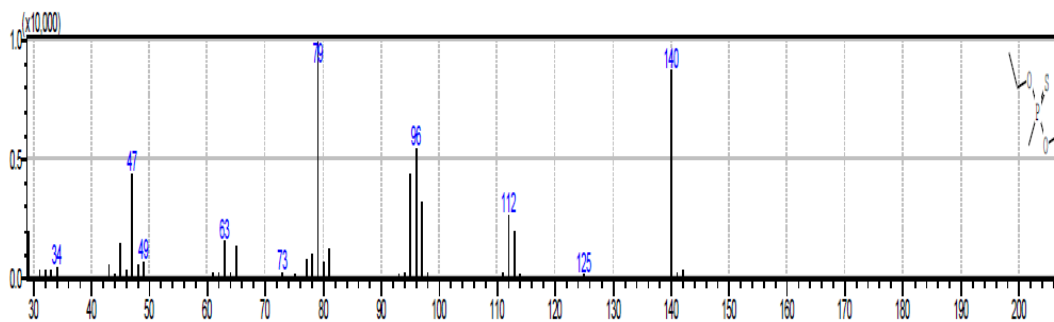


Figure 7 Mass spectrum of O-Ethyl methyl phosphonothioate

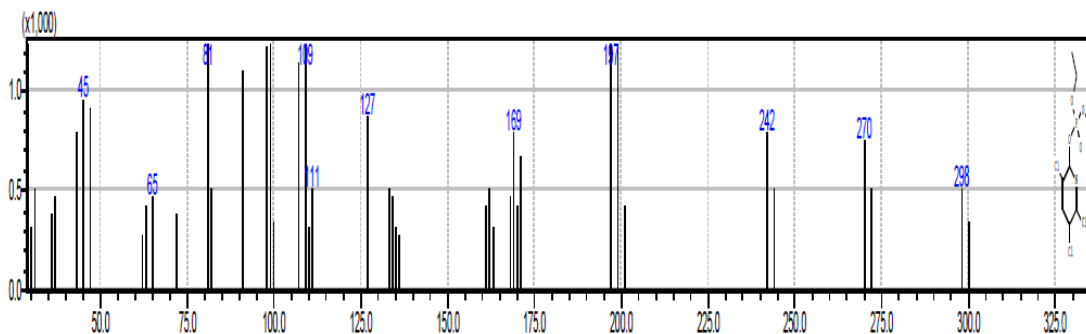


Figure 8 Mass spectrum of Chlorpyrifos oxon

CONCLUSION

This study shows that chlorpyrifos can be substantially (80-90%) degraded by photocatalysis in an annular slurry reactor even at relatively high initial concentrations. Degradation was a function of initial concentration, pH and the catalyst concentration in the solutions. Studies on slurry reactor exposed to UV radiation showed that pH plays significant role in degradation. Acidic pH giving better degradation compared to alkaline pH. The optimal catalyst concentration was 1 g/L above which the degradation was affected by shielding effect. The degradation reaction kinetics followed the L-H kinetics with high degree of correlation.

REFERENCES

- Burrows, H.D., Caule, L.M., Santaballa, J.A. and Steenken, S. (2002). Reaction pathways and mechanisms of photodegradation of pesticides. *Journal of Photochemistry and Photobiology B: Biology*, 67, 71-108.
- Devi, L.G., Murthy, B.N. and Kumar, G.S. (2009). Photocatalytic activity of V^{5+} , Mo^{6+} and Th^{4+} doped polycrystalline TiO_2 for the degradation of chlorpyrifos under UV/solar light. *Journal of Molecular Catalysis A: Chemical*, 308(1-2), 174-181.
- Evgenidou, E., Konstantinou, I., Fytianos, K., Poullos, I. and Albanis, T. (2007). Photocatalytic oxidation of methyl parathion over TiO_2 and ZnO suspensions. *Catalysis Today*, 124(3-4), 156-162.
- Kerzhentsev, M., Guillard, C., Hermann, J.M. and Pichat, P. (1996). Photo catalytic pollutant removal in water at room temperature: case study of the total degradation of the insecticide fenitrothion (Phosphorothioic acid O, O-dimethyl- O-(3-methyl-4-nitro-phenyl) ester). *Catalysis Today*, 27(1-2), 215-220.
- Kormann, C., Bahnemann, D.W. and Hoffmann, M.R. (1991). Photolysis of chloroform and other organic molecules in aqueous titanium dioxide suspensions. *Environmental Science and Technology*, 25(3), 494-500.
- Konstantinou, I.K. and Albanis, T.A. (2004). Photocatalytic transformation of pesticides in aqueous titanium dioxide suspensions using artificial and solar light: intermediates and degradation pathways. *Applied Catalysis B: Environmental*, 42(4), 319-335.
- Kutz, F.W., Wood, P.H. and Bottimore, D.P. (1991). Organochlorine pesticides and polychlorinated biphenyls in human adipose tissue. *Environment Contamination Toxicology*, 120, 1-82.
- Malato, S., Blanco, J., Caceres, J., Fernández-Alba, A.R., Agüera, A. and Rodríguez, A. (2002). Photocatalytic treatment of water-soluble pesticides by photo-fenton and TiO_2 using solar energy – review. *Catalysis Today*, 76.
- Mathur, H.B., Sapna, J., Rashmi, M., Avinash, K. and Bhupinder, S. (2003). Analysis of pesticide residues in bottled water. *India report on pesticide residues in bottled water in Delhi region*. Centre for Science and Environment (CSE) New Delhi, India, 1-51.
- Muhamad, S.G. (2010). Kinetic studies of catalytic photo degradation of chlorpyrifos insecticide in various natural waters. *Arabian Journal of Chemistry*, 3(2), 127-133.
- Murillo, R., Sarasa, J., Lanao, M. and Ovelleiro, J.L. (2010). Degradation of chlorpyrifos in water by advanced oxidation processes. *Water Science and Technology: Water Supply*, 10(1), 1-6.
- Navarro, S., Fenoll, J., Vela, N., Ruiz, E. and Navarro, G. (2009). Photocatalytic degradation of eight pesticides in leaching water by use of ZnO under natural sunlight. *Journal of hazardous materials*, 172(2-3), 1303-1310.
- Pelizzeti, E. and Minero, C. (1993). Mechanism of the photo-oxidative degradation of organic pollutants over TiO_2 particles. *Electrochimica Acta*, 38(1), 47-55.

- Peñueta, G.A. and Barceló, D. (1997). Comparative degradation kinetics of chlorpyrifos in water by photo catalysis with FeCl_3 , TiO_2 and photolysis using solid-phase disk extraction followed by Gas chromatographic techniques. *Toxicological and Environmental Chemistry*, 62(1-4), 135-147.
- Senthilnathan, J. and Philip, L. (2009). Removal of mixed pesticides from drinking water system by photo degradation using suspended and immobilized TiO_2 . *Journal of Environmental Science and Health, Part B*, 44(3), 262-270.
- Sivagami, K, Krishna, R.R. and Swaminathan, T. (2011). Studies on photocatalytic degradation of monocrotophos in an annular slurry reactor using factorial design of experiments. *Journal of water sustainability*, 1(1), 75-84.
- Yadav, P. (2010). *Titanium dioxide mediated photocatalytic degradation of Chlorpyrifos in aqueous phase*. M.Sc. Dissertation, Thapar University, Patiala, India.