

# Chapter 2

## Sunlight-Assisted Photo-Fenton Process for Removal of Insecticide from Agricultural Wastewater

Amrita Dutta, Sanjukta Datta, Mahua Ghosh, Debasish Sarkar,  
and Sampa Chakrabarti

### 1 Introduction

Pesticides and insecticides are harmful and toxic organic chemicals that are used for controlling pests and insects in agriculture, thereby considered as necessary evil. Agricultural wastewater, contaminated with such toxic pesticides, pollutes surface and groundwater. Pesticides are able to reach surface waters either directly or indirectly via the discharge of agricultural drainage water from treated land and via runoff after application on hard surfaces (Leu et al. 2004). Organophosphorus pesticides are produced in mass and are widely used in the developing country. 2,2 dichlorovinyl dimethyl phosphate, commonly referred as Dichlorvos (Fig. 2.1) is an organophosphorous insecticide, which is highly toxic, non-biodegradable and difficult to remove by conventional methods. During 2006–2010 period, consumption of Dichlorvos in India was 5833 metric tons. Due to its fairly good solubility [ $\sim 10$  g.  $L^{-1}$  (at 20 °C)] in water (WHO 1978, 1994) it is highly mobile in aquatic environment. Various technologies and processes have been proposed for the treatment of pesticide-contaminated waters. Some conventional techniques including flocculation, filtration and adsorption of activated carbon are only based on a phase transfer of the pollutant. These treatment procedures are either of high cost or a source of secondary pollution due to sludge formation: therefore, there is a need to seek better alternatives (Evgenidou et al. 2005). Advanced oxidation processes (AOPs) are attractive methods for the treatment of wastewaters containing

---

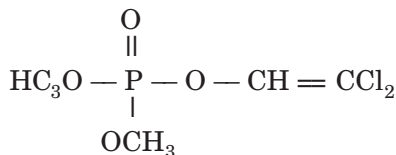
A. Dutta • D. Sarkar • S. Chakrabarti (✉)

Department of Chemical Engineering, University of Calcutta, 92, Acharya P.C. Road, Kolkata 700 009, India  
e-mail: scchemengg@caluniv.ac.in

S. Datta • M. Ghosh

Department of Chemical Technology, University of Calcutta, 92, Acharya P.C. Road, Kolkata 700 009, India

**Fig. 2.1** Structure of Dichlorvos (2, 2 dichlorovinyl dimethyl phosphate)



refractory organics due to their efficiency to oxidize a great variety of organic contaminants by the generation of highly reactive hydroxyl radicals ( $\text{OH}\cdot$ ) (Espulgas et al. 2002). Many pollutants, including pesticides, pharmaceuticals and dyes can be completely mineralised by AOP as reported in the works of Chiron et al. (2000), Perez-Estrada et al. (2005) and Lucas and Peres (2006). Heterogeneous photocatalysis using titanium dioxide ( $\text{TiO}_2$ ) and solar/UV radiation, combined with hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and homogeneous processes such as Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2$ ) and photo-Fenton ( $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}/\text{sunlight}$ ) reactions are proved to be useful techniques for the treatment of pesticide-contaminated wastewater. There are different ways to produce  $\text{HO}\cdot$ , among which solar photo-Fenton process is one of the most efficient ones for the treatment of contaminated wastewater (Malato et al. 2002; Oller et al. 2006; Maldonado et al. 2007; Ortega-Liébaná et al. 2012; Klammerth et al. 2013).

Degradation of triazine herbicides was reported by Burrows et al. (2002), methylparathion by Chiron et al. (2000), fenuron by Acero et al. (2002) and diuron by Burrows et al. (2002). Sakugawa et al. (2013) reported the degradation of three pesticides at pH 2.8 and 7.2 in pure and natural waters using  $\text{Fe}^{2+}/\text{H}_2\text{O}_2/\text{UV}$ -visible light and  $\text{Fe}^{3+}/\text{H}_2\text{O}_2$  UV-visible light oxidation systems.

Dichlorvos is among the 24 insecticides registered and used in India. It has been classified in category 'C' by US-EPA as potential carcinogen. Hence the present work has been undertaken in order to explore the efficacy of sunlight-assisted photo-Fenton oxidative degradation of dichlorvos pesticide in water in a batch process. Process parameters studied were (i) dosing of  $\text{H}_2\text{O}_2$ , (ii) ferrous sulphate dosing, (iii) pH and (iv) initial concentration of the insecticide. FTIR spectroscopy was used to identify the functional groups resulting from degradation reaction. Chemical oxygen demand (COD) was monitored to examine the extent of mineralization of the insecticide. Additionally, a kinetic model, representing the initial rate of degradation as a function of initial reactant concentration, was proposed and validated by experimental results.

## 2 Materials and Methods

### 2.1 Chemicals Used

Dichlorvos (76 % purity) (molecular formula  $\text{C}_4\text{H}_7\text{Cl}_2\text{O}_4\text{P}$ , molecular weight 220.9 g/mol) was obtained from United Phosphorus Limited, India. Structure is

given in Fig. 2.1. Crystalline ferrous sulphate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), was obtained from Sisco Research Laboratories, India. For this experiment 0.5 % of  $\text{FeSO}_4$  solution has been used. Hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 50 % v/v) was obtained from Merck Specialities, India. Sodium bi-sulphite ( $\text{NaHSO}_3$ ) was obtained from Loba Chemie. 5(N)  $\text{NaHSO}_3$  solutions have been used to stop the Fenton reaction at desired point. All solutions were prepared using fresh distilled water.

## 2.2 *Experimental Procedure*

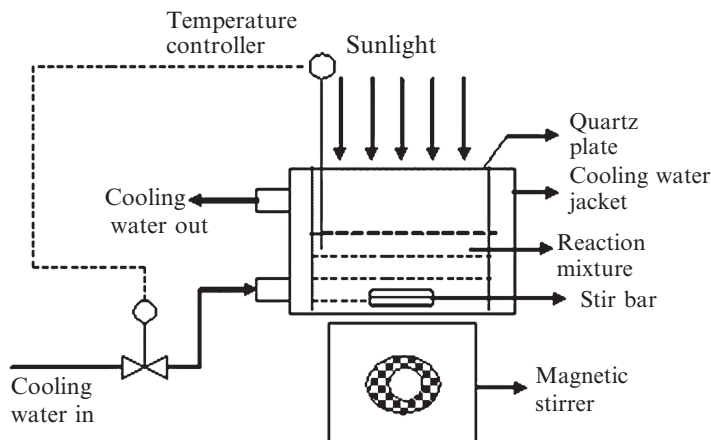
Solar photo-Fenton experiments were performed in a stainless steel box-shaped batch reactor with a 3 mm thick quartz plate as its lid through which sunlight could enter. The reactor was provided with cooling water circulation to maintain the temperature at 30–32 °C. The schematic of the present experimental setup is shown in Fig. 2.2. Simulated wastewater was prepared by adding Dichlorvos insecticide into deionised water. Freshly prepared solutions of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$  was added in the synthetic wastewater. The solutions were continuously stirred using a magnetic stirrer. Intensity of solar radiation was approximately 60–66 kLux (24.12–26.53  $\text{mW} \cdot \text{cm}^{-2}$ ). Samples were withdrawn from time to time to measure the extent of degradation. The reaction was stopped by adding sodium bisulphite and analyzed for the residual pollutant with HPLC. All the experiments were carried out within the time span between 12 noon and 2 pm during May-June in eastern part of India.

## 2.3 *Analytical Methods*

Residual concentrations of the pollutant were analyzed at different time intervals using WATERS 2487 HPLC equipped with a C18 Column (ZORBAX SB-C18 5  $\mu\text{m}$ ,  $46 \times 150$  mm). Mixture of acetonitrile and Milli-Q water (50/50 v/v for dichlorvos) was used as the mobile phase with a flow rate of 1  $\text{mL} \cdot \text{min}^{-1}$  (Rice et al. 2005). Chemical oxygen demand (COD) was determined by the APHA standard total reflux method. FTIR analysis was performed in a Jasco-6300 instrument using KBr pellet.

## 3 *Result and Discussions*

Time-concentration data was collected for all the experiments varying different process parameters. Each experiment was repeated more than once and the standard deviation was less than  $\pm 5$  %.



**Fig. 2.2** Schematic of experimental set-up

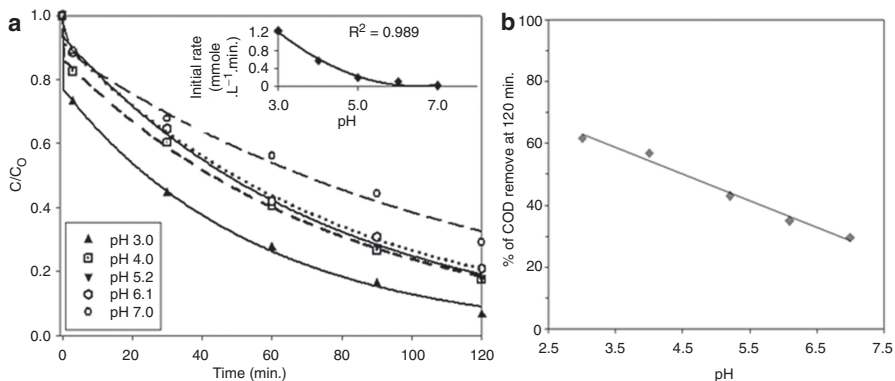
### 3.1 Effect of pH

Photo-Fenton reactions are strongly dependent on pH (Tamimi et al., 2011). Experiments were carried out in pH range of 3–7. From Fig. 2.3a it can be seen that the photo Fenton oxidation efficiency monotonically decreases with increasing pH. This is because pH value influences both the generation of hydroxyl radicals as well as the oxidation efficiency. The degradation decreased at pH values higher than 5, because ferrous sulphate gets precipitated as hydroxide, resulting in a reduction in the penetration of solar radiation in the reaction mixture (Faust and Hoigne 1990). Moreover, Dichlorvos in acidic solution is more susceptible to hydrolysis than that in alkaline solution (Jiangtong 1981).

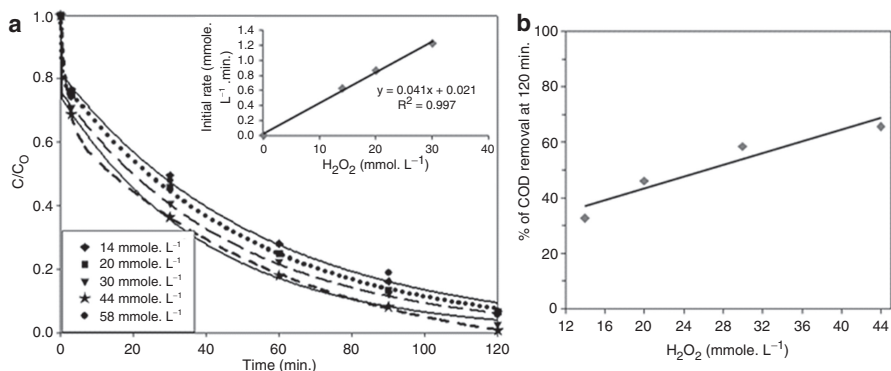
Figure 2.3b shows the effect of pH on the reduction of COD of wastewater containing Dichlorvos. The results show that the percent removal of COD is more at acidic pH. Raising pH from 3 to 7 decreased the removal efficiency of Dichlorvos from 83 to 57 %. Corresponding decrease in the removal of COD was from 86.6 to 61.8 % respectively. Initial rate also followed the same trend.

### 3.2 Effect of Hydrogen Peroxide Concentration

$\text{H}_2\text{O}_2$  itself generates active oxygen species. In this experiment, the concentration of  $\text{H}_2\text{O}_2$  was changed from 14 to 58  $\text{mmol.L}^{-1}$ , but the concentration of ferrous sulphate dosage was held constant (0.28  $\text{mmol.L}^{-1}$ ). Other process parameters, initial concentration of insecticide (0.133  $\text{mmol.L}^{-1}$ ), pH (3) and temperature (30 °C) were kept constant. From Fig. 2.4a it is observed that 95.33 % of 0.133  $\text{mmol.L}^{-1}$  Dichlorvos degraded after 120 min under sunlight of 66 kLux

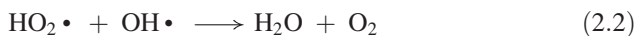


**Fig. 2.3** (a) Effect of pH on degradation of pesticide in water. Inset shows initial reaction rate at different pH and (b) Effect of the pH on the COD removal



**Fig. 2.4** (a) Effect of  $H_2O_2$  dosage for the degradation of pesticide contaminated water. Inset shows initial reaction rate vs.  $H_2O_2$  dosage and (b) Effect of dosing of  $H_2O_2$  on the COD removal

using 30 mmol. $L^{-1}$  of  $H_2O_2$ . Degradation of Dichlorvos was observed to increase from 93.24 to 95.33 with increasing the dosing concentration of hydrogen peroxide from 14 to 30 mmol. $L^{-1}$ . With the increase in  $H_2O_2$ -dosing, the initial reaction rate of pesticide increased up to a particular dosing of 30 mmol. $L^{-1}$ . After that it decreased due to the scavenging of hydroxyl radical by  $H_2O_2$ . Similar finding was reported by Ghaly et al. (2001) who found that the recombination of hydroxyl radicals and also hydroxyl radicals reaction with  $H_2O_2$ , contributes to the scavenging of  $OH\cdot$  (Eqs. 2.1, 2.2, 2.3).

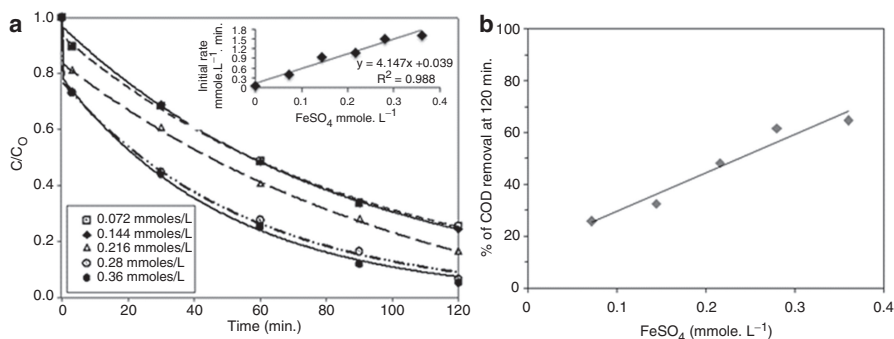




It can be postulated that  $\text{H}_2\text{O}_2$  should be added at an optimum concentration to achieve the best degradation. Hence,  $30 \text{ mmol.L}^{-1}$  of  $\text{H}_2\text{O}_2$  was selected as the optimal dosage for the degradation of Dichlorvos in wastewater. Rongxi et al. (2009) reported that 75 mL per litre of 30 %  $\text{H}_2\text{O}_2$  solution was the optimal dosage for the treatment of industrial triazophos pesticide wastewater. Figure 2.4b shows that percent of COD removal has increased with increasing  $\text{H}_2\text{O}_2$  concentration from 14 to  $30 \text{ mmol.L}^{-1}$ .

### 3.3 Effect of Ferrous Sulphate Dosing Concentration

Dosing of ferrous sulphate is one of the major parameters to influence the photo-Fenton processes. Solar-assisted photo-Fenton experiments were executed with different doses of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  ranging from 0.072 to  $0.36 \text{ mmol.L}^{-1}$ . The results of these experiments are shown in Fig. 2.5a, b. It can be seen that 11 % of  $0.133 \text{ mmol.L}^{-1}$  insecticide degraded without ferrous sulphate solution, when  $\text{H}_2\text{O}_2$  dosage was  $30 \text{ mmol.L}^{-1}$  and pH was 3. Moreover, the degradation and initial reaction rate decreased with decrease in the concentration of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  upto a critical value. Further increase in the concentration of ferrous sulphate resulted in decrease of the initial degradation rate of substrate because production of a large amount of  $\text{Fe}^{3+}$ .  $\text{Fe}^{3+}$  decomposes  $\text{H}_2\text{O}_2$  and produces  $\text{Fe}(\text{OH})^{2+}$  in acidic condition. Tamimi et al. (2008) reported that higher the concentration of  $\text{Fe}^{2+}$ , more was the amount of  $\text{Fe}^{3+}$  generated from the process of  $\text{H}_2\text{O}_2$  decomposition by  $\text{Fe}^{2+}$ , thus making  $\text{Fe}^{2+}$  unavailable for reaction.



**Fig. 2.5** (a) Effect of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosage for the degradation of pesticide contaminated water. Inset panel shows initial reaction rate vs.  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  dosage and (b) Effect of dosing of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  on the COD removal

### 3.4 Effect of Initial Concentration of Insecticide

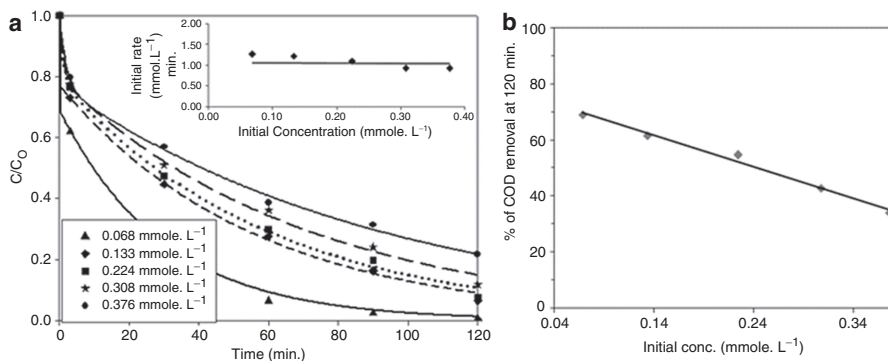
Degradation of pesticide and COD removal at various initial concentrations by photo-Fenton oxidation is shown in Fig. 2.5a, b respectively. After 120 min reaction time, degradation of pesticide were observed to be 99.42 %, 93.49 %, 95.42 %, 88.08 % and 88.22 % at initial pesticide concentration 0.069, 0.133, 0.224, 0.308 and 0.376 mmol.L<sup>-1</sup> respectively when the other parameters were fixed at FeSO<sub>4</sub>·7H<sub>2</sub>O: 0.28 mmol.L<sup>-1</sup>, H<sub>2</sub>O<sub>2</sub>: 30 mmol.L<sup>-1</sup> and pH 3. Initial rate remained almost independent of the initial concentration within the experimental range of concentration (0.068–0.224 mmol.L<sup>-1</sup>). Percent degradation decreased with increasing initial concentration of substrate.

It can be seen that the removal of COD clearly increased with the decreasing amount of pesticides (Fig. 2.6).

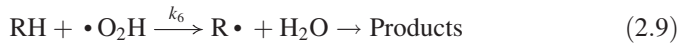
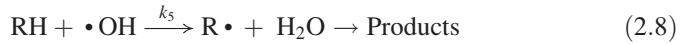
### 3.5 Rate Equation and Kinetics

Degradation of the oxidation reaction is assumed to proceed via hydroxyl and peroxyhydroxyl radical attack to the pesticide molecule (represented as RH). Hence rate of degradation is the rate of free-radical attack on pesticide.

In acidic medium, the scheme of the reaction can be represented as follows:



**Fig. 2.6** (a) Effect of initial concentration for the degradation of pesticide contaminated water. The inset panel shows reaction rate vs. initial concentration. (b) Effect of initial pesticide concentration on the COD removal



Here rate constants  $k_1$  and  $k_4$  are considered to be dependent on the intensity of sunlight i.e.,  $I_S$ . Hence  $k_1 = k_1(I_S)$  and  $k_4 = k_4(I_S)$ .

From Eqs. (2.5) and (2.6), initial rate of degradation of pesticide,  $-r_{\text{RH}}$  becomes:

$$-\frac{d}{dt}[\text{RH}] = k_5[\text{RH}][\bullet\text{OH}] + k_6[\text{RH}][\bullet\text{O}_2\text{H}] \quad (2.10)$$

Active oxidant,  $\bullet\text{OH}$  radical is generated by the reaction steps (2.1), (2.2) and (2.4) and is consumed in the step (2.5). So the net rate of generation of  $\bullet\text{OH}$  radical is:

$$\begin{aligned} -\frac{d}{dt}[\bullet\text{OH}] = & k_1(I_S)[\text{H}_2\text{O}_2] + k_2[\text{Fe}^{2+}][\text{H}_2\text{O}_2] \\ & + k_3[\text{Fe}^{3+}][\text{H}_2\text{O}_2] + k_4(I_S)[\text{Fe}^{3+}][\text{H}_2\text{O}] + k_5[\text{RH}][\bullet\text{OH}] \end{aligned} \quad (2.11)$$

Similarly the other reaction intermediates and oxidizing species,  $\text{O}_2\text{H}\bullet$ ,  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  have their own pathways of generation and consumption as described in the scheme. According to well known theory of non-elementary reaction, concentration of all the intermediates are in pseudo-steady state, that is net rate of each of them is zero. Therefore, the expression for the initial rate becomes:

$$-r_{\text{RH}} = -\frac{d}{dt}[\text{RH}] = k_1(I_S)[\text{H}_2\text{O}_2] + 2k_2[\text{Fe}^{2+}][\text{H}_2\text{O}_2] \quad (2.12)$$

For constant intensity of sunlight and constant dosing of  $\text{Fe}^{2+}$  ( $0.28 \text{ mmol.L}^{-1}$ ),

$$-r_{\text{RH}} = m[\text{H}_2\text{O}_2] \quad (2.13)$$

where  $m = \{k_1(I_S) + 2k_2[\text{Fe}^{2+}]\}$ ,

Initial rate varies with variation in dosing of  $\text{H}_2\text{O}_2$ . A plot with initial dosing of  $\text{H}_2\text{O}_2$  and corresponding initial rates is a straight line passing through (0,0) the slope of which is  $m$  (Fig. 2.4a inset).

Similarly at constant dosing of  $\text{H}_2\text{O}_2$  ( $30 \text{ mmol.L}^{-1}$ ) and constant intensity of sunlight,



$$-r_{RH} = p[\text{Fe}^{2+}] + q \quad (2.14)$$

where  $p = 2k_2 [\text{H}_2\text{O}_2]$  and  $q = k_1(I_S) [\text{H}_2\text{O}_2]$ .

Here initial rate varies with variation of initial dosing of  $\text{Fe}^{2+}$ . A plot with initial dosing of  $\text{Fe}^{2+}$  and corresponding initial rates [Fig. 2.5a inset] results in a straight line with slope  $p$  and intercept  $q$ .

Solving, we get,  $k_1(I_S) = 1.3 \times 10^{-3} \text{ min}^{-1}$  at  $I_S = 26.53 \text{ mW.m}^{-2}$ . Value of  $k_2$  was determined from both the equations. The average value of  $k_2$  is reported.

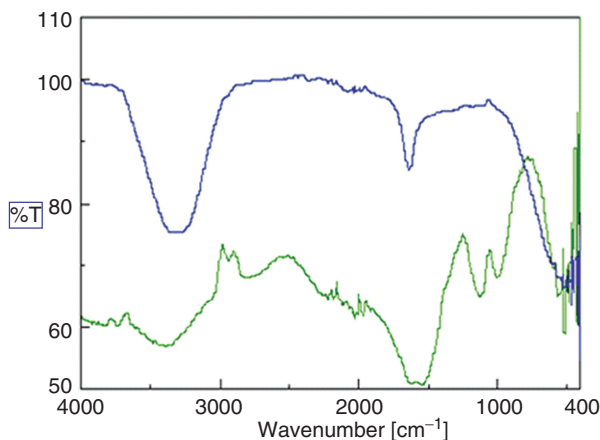
$$k_2 (\text{average}) = 0.0705 \left( \frac{\text{mM}}{\text{L}} \right)^{-1} \text{ min}^{-1}$$

### 3.6 FTIR Spectra Analysis

Untreated and solar-Fenton treated pesticide aqueous solution were analyzed by FTIR spectroscopy to check for presence of organic bonds. Evgenidou et al. (2006) proposed a tentative degradation scheme of Dichlorvos during the photocatalytic oxidation of the same over  $\text{TiO}_2$ . Since this was also a case of  $\text{OH}\cdot$  radical attack, the products and intermediates are expected to be the same in nature. In the mentioned scheme, formation of aldehydes, ketones and alcohols were proposed in addition to the ultimate oxidized products like carboxylic acid, carbon dioxide and water. Peak for  $\text{P}=\text{O}$  in  $1175\text{--}1300 \text{ cm}^{-1}$  was present in the Dichlorvos solution before reaction, but not in the product; indicating breakage of the bond. After reaction, strong peaks at  $2200\text{--}2300 \text{ cm}^{-1}$  indicate  $\text{CO}_2$  and medium peaks at  $2600\text{--}3000 \text{ cm}^{-1}$  along with strong peaks at around  $1700 \text{ cm}^{-1}$  indicate carboxylic acids (Fig. 2.7).

Strong peaks at  $3200\text{--}3700 \text{ cm}^{-1}$  and in  $620\text{--}680 \text{ cm}^{-1}$  indicate presence of alcoholic and hydrogen bonded  $\text{--OH}$  group.  $\text{--OH}$  in  $\text{--COOH}$  is indicated by peak at

**Fig. 2.7** FTIR spectra of untreated and treated insecticide aqueous solution (%T = percent of transmittance)



2400–3400  $\text{cm}^{-1}$  and  $\text{O}-\text{C}=\text{C}$  in carboxylic acid is indicated by strong peak in 590–700  $\text{cm}^{-1}$ . From the structure of the Dichlorvos molecule (Fig. 2.1), formation of dichloroacetic acid was envisaged. Strong peaks at 600–800  $\text{cm}^{-1}$ , indicating  $\text{Cl}-\text{C}$  bond vibration, confirmed the proposition. Strong peaks of aldehydes and ketones were observed at 520–565  $\text{cm}^{-1}$  and 510–560  $\text{cm}^{-1}$  respectively. Peaks for organic ethers, indicated by medium strong peaks at 430–520  $\text{cm}^{-1}$  and very strong peaks at 1070–1150  $\text{cm}^{-1}$ , became more intense than that in the unreacted compound. Peaks for vinyl ethers at 1000  $\text{cm}^{-1}$  became more intense after reaction.

All the above evidences prove well that the insecticide Dichlorvos was oxidized by sunlight-assisted photo-Fenton oxidative degradation into alcohols, aldehydes, ketones and carboxylic acid with mineralization into carbon dioxide and water. The mineralization was also evidenced by the decrease in COD as well.

## 4 Conclusion

Sunlight-assisted photo-Fenton oxidation reaction has been established as a very good and rapid method for the degradation of Dichlorvos insecticides. The degradation rate of insecticides and the respective COD were observed to increase with the increasing amount of ferrous sulphate and  $\text{H}_2\text{O}_2$ . The COD removal efficiencies of Dichlorvos wastewater treated by Fenton reagent are greatly influenced by the pH value, dosage of  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ . FTIR analysis of the insecticide before and after reaction indicates its degradation into lower organic fragments. In a tropical country like India with abundant solar energy, this may be considered as an economic and eco-friendly technology. The results of this work may be used to design a continuous reactor, which may be suitably scaled up to meet industrial requirement.

**Acknowledgements** This research was funded by the Department of Science & Technology, Government of West Bengal for their R&D grant number 749 (Sanc.)/ST/P/S&T/4G-1/2010 dated 2.2.2012. The authors are thankful to the Centre for Research in Nanoscience & Nanotechnology, CU and Prof. Arup Mukherjee, Department of Chemical Technology, CU for FTIR.

## References

- Acero, J., Benitez, F., Gonzalez, M. and Benitez R. (2002). Kinetics of fenuron decomposition by single-chemical oxidants and combined systems. *Ind. Eng. Chem. Res.*, **41**(17): 4225–4232.
- Burrows, H., Canle, M., Santaballa, J. and Steenken, S. (2002). Reaction pathways and mechanisms of photodegradation of pesticides. *J. Photochem. Photobiol. B: Biol.*, **67**(2): 71–108.
- Chiron, S., Fernandez-alba, A., Rodriguez, A. and Garcia-calvo, E. (2000). Pesticide chemical oxidation: State-of-the-art. *Water Res.*, **34**(2): 366–377.
- Espulgas, S., Giménez, J., Contreras, S., Pascual, E. and Rogríquez, M. (2002). Comparison of different advanced oxidation processes for phenol degradation. *Wat. Res.*, **36**(4): 1034–1042.

- Evgenidou, E., Fytianos, K. and Poullos, I. (2005). Semiconductor-sensitized photodegradation of Dichlorvos in water using  $\text{TiO}_2$  and  $\text{ZnO}$  as catalysts. *Appl. Catal. B-Environ.*, **59**(1–2): 81–89.
- Evgenidou, E., Konstantinou, I., Fytianos, K. and Albanis, T. (2006). Study of the removal of Dichlorvos and dimethoate in a titanium dioxide mediated photocatalytic process through the examination of intermediates and the reaction mechanism. *J. Hazard. Mater.*, **137**(2): 1556–1564.
- Faust, B. and Hoigne, J. (1990). Photolysis of Fe(III)-hydroxyl complexes as sources of OH radicals in clouds, fog and rain. *Atmos. Environ.*, **24**(1): 79–89.
- Ghaly, M., Hartel, G., Mayer, R. and Haseneder, R. (2001). Photochemical oxidation of p-chlorophenol by  $\text{UV/H}_2\text{O}_2$  and photo-Fenton process: A comparative study. *Waste Manage.*, **21**(1): 41–47.
- Jiangtong, Y. (1981). Organic Chemistry and Biochemistry of Organophosphorus Pesticides. Chemical Industry Publisher, Beijing.
- Klamerth, N., Malato, S., Agüera, A. and Fernández-Alba, A. (2013). Photo-Fenton and modified photo-Fenton at neutral pH for the treatment of emerging contaminants in wastewater treatment plant effluents: A comparison. *Water Research*, **47**: 833–840.
- Leu, C., Singer, H., Stamm, C., Muller, S. and Schwarzenbach, R. (2004). Simultaneous assessment of sources, processes, and factors influencing herbicide losses to surface waters in a small agricultural catchment. *Environ Sci Technol.*, **38**(14): 3827–3834.
- Lucas, M. and Peres, J. (2006). Decolorization of the azo dye reactive black 5 by Fenton and photo-Fenton oxidation. *Dyes Pigm.*, **71**(3): 236–244.
- Malato, S., Blanco, J., Caceres, J., Fernández-Alba, A., Agüera, A. and Rodriguez, A. (2002). Photocatalytic treatment of water-soluble pesticides by photo-Fenton and  $\text{TiO}_2$  using solar energy. *Catal. Today.*, **76**(2–4): 209–220.
- Maldonado, M., Passarinho, P., Oller, I., Gernjak, W., Fernandez, P., Blanco, J. and Malato, S. (2007). Photocatalytic degradation of EU priority substances: A comparison between  $\text{TiO}_2$  and Fenton plus photo-Fenton in a solar pilot plant. *J. Photochem. Photobio. A: Chem.*, **185**(2–3): 354–363.
- Oller, I., Gernjak, W., Maldonado, M., Perez-Estrada, L., Sanchez-Perez, J. and Malato, S. (2006). Solar photocatalytic degradation of some hazardous water-soluble pesticides at pilot-plant scale. *J. Hazard. Mater.*, **138**(3): 507–517.
- Ortega-Liébana, M.C., Sánchez-López, E., Hidalgo-Carrillo, J., Marinas, A., Marinas, J.M. and Urbano, F.J. (2012). A comparative study of photocatalytic degradation of 3-chloropyridine under UV and solar light by homogeneous (photo-Fenton) and heterogeneous ( $\text{TiO}_2$ ) photocatalysis. *Applied Catalysis B: Environmental*, **127**: 316–322.
- Perez-Estrada, L., Malato, S., Gernjak, W., Agüera, A., Thurman, E., Ferrer, I. and Fernandez-Alba, A. (2005). Photo-Fenton degradation of diclofenac: Identification of main intermediates and degradation pathway. *Environ. Sci. Technol.*, **39**(21): 8300–8306.
- Rice, E., Baird, R., Eaton, A. and Clesceri, L. (Eds) (2005). Standard Methods for the Examination of Water and Wastewater. American Public Health Association, AWWA (American Water Works Association), Water Environment Federation, USA, 21st ed.
- Rongxi, L., Chunping, Y., Hong, C., Guangming, Z., Guanlong, Y. and Junyuan, G. (2009). Removal of triazophos pesticide from wastewater with Fenton reagent. *J. Hazard Mater.*, **167**(1–3): 1028–1032.
- Sakugawa, H., Hasan, N., Olasehinde, E., Takeda, K. and Kondo, H. (2013). Applicability of solar photo-Fenton process to the remediation of water polluted with pesticides. *Nat Sci.*, **11**(1): 144–152.
- Tamimi, M., Qourzal, S., Barka, N., Assabbane, A. and Ait-Ichou, Y. (2008). Methomyl degradation in aqueous solutions by Fenton's reagent and the photo-Fenton system. *Sep. Purif. Technol.*, **61**(1): 103–108.
- WHO (1978). Dichlorvos. Geneva, World Health Organization (Data Sheets on Pesticides No. 2, rev. 1).
- WHO/FAO (1994). Dichlorvos. In: Pesticide residues in food: 1993 evaluations. Part II Toxicology. Food and Agriculture Organization of the United Nations and World Health Organization, Geneva (WHO/PCS/94.4; <http://www.inchem.org/documents/jmpr/jmpmono/v93pr05.htm>)

Trends in Asian Water Environmental Science and  
Technology

Kurisu, F.; Ramanathan, A.; Kazmi, A.A.; Kumar, M. (Eds.)

2017, XIV, 250 p. 85 illus., 31 illus. in color., Hardcover

ISBN: 978-3-319-39257-8