

Solar Photo-Fenton Induced Degradation of Combined Chlorpyrifos, Cypermethrin and Chlorothalonil Pesticides in Aqueous Solution

Augustine Chioma Affam, Shamsul Rahman M. Kutty and Malay Chaudhuri

Abstract—The feasibility of employing solar radiation for enhanced Fenton process in degradation of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides was examined. The effect of various operating conditions of the process on biodegradability improvement and mineralization of the pesticides were also evaluated. The optimum operating conditions for treatment of aqueous solution containing 100, 50 and 250 mg L⁻¹ chlorpyrifos cypermethrin and chlorothalonil, respectively were observed to be H₂O₂/COD molar ratio 2, H₂O₂/Fe²⁺ molar ratio 25 and pH 3. Under the optimum operating conditions, complete degradation of the pesticides occurred in 1 min. Biodegradability (BOD₅/COD) increased from zero to 0.36 in 60 min, and COD and TOC removal were 74.19 and 58.32%, respectively in 60 min. Due to mineralization of organic carbon, decrease in ammonia-nitrogen from 22 to 4.3 mg L⁻¹ and increase in nitrate from 0.7 to 18.1 mg L⁻¹ in 60 min were recorded. The study indicated that solar photo-Fenton process can be used for pretreatment of chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution for further biological treatment.

Keywords—Chlorpyrifos, Cypermethrin, Chlorothalonil, Solar photo-Fenton

I. INTRODUCTION

THE application of pesticide in agriculture during the last few decades has caused large scale development and increase in agrochemical industries [1]. During and after spraying in the field, pesticides can be adsorbed on stagnant, airborne surfaces or may dissolve in natural water due to their high solubility. As a result, they are deposited on vegetation, soil or may evaporate and remain on other surfaces. Deposits on soil remain in the top few centimeters, where they degrade or become adsorbed on the soil and inorganic particles. However, pesticide misuse, spillage, and/or inappropriate storage, handling and disposal, has been estimated to be responsible, in many cases, for water contamination at high concentration levels. More importantly, only a very minor fraction contaminates surface water and groundwater sources which are of concern in aquatic toxicology and drinking water quality [2]. Advanced oxidation process (AOP) such as Fenton has been proposed as an alternative for the treatment of water contaminated with pesticides.

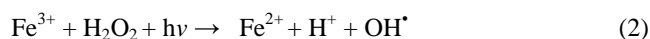
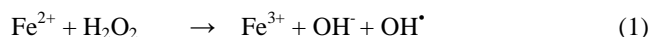
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This process is characterized by the production of hydroxyl radicals (OH[•]) by catalytic decomposition of hydrogen peroxide (H₂O₂) in reaction with ferrous ions (Fe²⁺) (Eq.1) [3]. Additional reactions occur in the presence of light that produce hydroxyl radicals or increase the production rate of hydroxyl radicals [4] as seen in Eq.(2)[5]. These radicals are extraordinarily reactive (oxidation potential 2.8 V) and attack most organic molecules. The obtained Fe³⁺ or its complexes subsequently act as the light absorbing species that produces another radical while the initial Fe²⁺ is regenerated as seen in Eq. (2- 3) [5].



It is noteworthy that in Eq. (3), which involves organic ligands, L (e.g. RCOO⁻, RO⁻, RNH⁺ etc.) is more efficient than the oxidation of organic substrates via OH[•]. The application of solar-radiation reduces the energy consumption required to generate UV radiation [6].

Removal of chlorpyrifos, cypermethrin and chlorothalonil from natural water and wastewater has been reported [7]–[14]. There is no study on degradation of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution by the solar photo-Fenton process. The tendency to combine a given number of chemically active but different pesticides indicates the need of treatment (degradation) of combined pesticides.

This study examined the optimized reaction conditions of the solar-Fenton process for chemical oxygen demand (COD) and total organic carbon (TOC) removal and biodegradability (BOD₅/COD) ratio improvement in treatment of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution. High performance liquid chromatography (HPLC) and Fourier transform infrared (FTIR) spectroscopy were used to estimate pesticide concentration and degradation of organic bonds in treatment.

II. MATERIALS AND METHODS

A. Chemicals and Pesticides

Hydrogen peroxide (30%, w/w) and ferrous sulphate heptahydrate (FeSO₄·7H₂O) were purchased from R&M Marketing, Essex, U.K. Analytical grade of chlorpyrifos was obtained from Dr. Ehrenstorfer, Germany and cypermethrin and chlorothalonil were obtained from Sigma-Aldrich, Germany. They were used for analytical identification and

determination of pesticide concentration by HPLC. The pesticides used to prepare aqueous solution were obtained from a commercial source and were used as received. Fig. 1 shows the chemical structure of the pesticides.

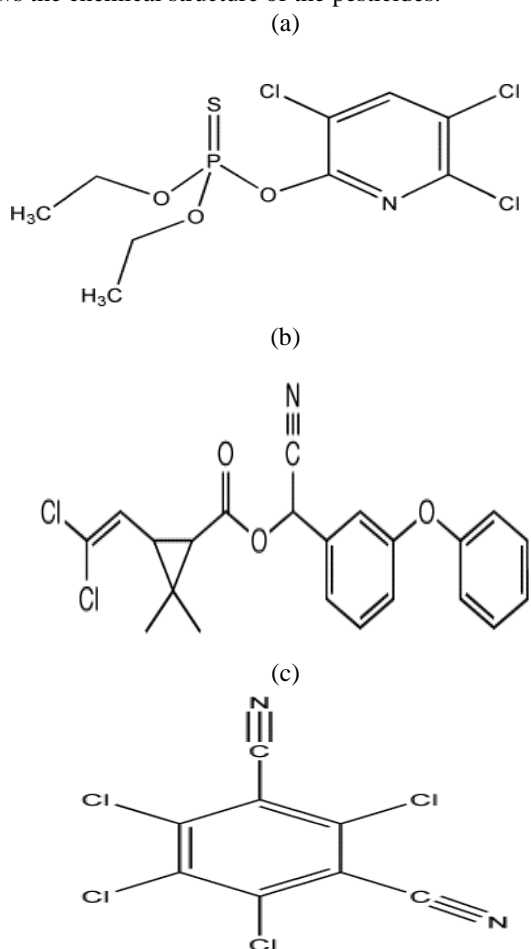


Fig. 1 Chemical structure of (a) chlorpyrifos (b) cypermethrin and (c) chlorothalonil

B. Analytical Methods

Pesticide concentration in treated samples was determined by HPLC (Agilent 1100 Series) equipped with micro-vacuum degasser (Agilent 1100 Series), quaternary pumps, diode array and multiple wavelength detector (DAD) at wavelength 230 nm. Chemstation software was installed and used for data recording. The HPLC detection column was ZORBAX SB-C18 (3.0 mm×250mm, 5μm). The column temperature was set at 30°C. Mobile phase was made up of 25% buffer solution (0.001M KH₂PO₄ in double distilled water) and 75% acetonitrile.

Chemical oxygen demand (COD) was determined according to the Standard Methods [15]. When the sample contained hydrogen peroxide (H₂O₂), to reduce interference in COD determination pH was increased to above 10 so as to decompose hydrogen peroxide to oxygen and water [16], [17].

TOC analyzer (Model 1010, O & I analytical) was used for determining total organic carbon (TOC). pH measurement was done using a pH meter (HACH sension 4) and a pH probe (HACH platinum series pH electrode model 51910, HACH Company, USA). Biodegradability was measured by 5-day

biochemical oxygen demand (BOD₅) test according to the Standard Methods [15]. DO was measured by YSI 5000 dissolved oxygen meter. The seed for BOD₅ test was obtained from a municipal wastewater treatment plant. Fourier transform infrared (FTIR) spectrum was taken by FTIR-8400S, SHIMADZU. Luzchem Solsim v1.2, (intensity approximately AM1.5 solar spectrum) provided simulated solar radiation, with a 300 W ceramic xenon lamp, wavelength 280-800 nm and maximum power 1.5 kW/m². It was preset to 0.85 kW/m² for the study. A hand held solar radiometer model 776E Dodge product, USA was used for measuring solar intensity and subsequent simulation of the reactor radiation.

C. Pesticide Aqueous Solution

Pesticide aqueous solution was 400 mg L⁻¹ of pesticides (100 mg L⁻¹ of chlorpyrifos (CPF), 50 mg L⁻¹ of cypermethrin (CPT) and 250 mg L⁻¹ of chlorothalonil (CTN)) in distilled water. It was prepared weekly and stored at 4 °C. The pesticide aqueous solution had a COD of 1130 mg L⁻¹.

D. Experimental Procedure

Batch experiments were carried out in Luzchem Solsim v1.2 reactor with 600 mL beaker containing 500 mL of the pesticide aqueous solution. A hand held portable solar radiation meter was used to measure the average daily irradiation and simulated in the reactor accordingly. The required amount of iron (FeSO₄·7H₂O) was added to the aqueous solution and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, the pH was adjusted to the required value using sulfuric acid (H₂SO₄) and then necessary amount of H₂O₂ was added. Duration of experiment was monitored by an inbuilt automatic timer. Samples were filtered through a 0.45 μm membrane filter for COD, BOD₅ and TOC measurement, and filtered through a 0.20 μm membrane filter for HPLC and FTIR spectra.

III. RESULTS AND DISCUSSION

A. Solar Irradiation

The photolysis of the pesticide aqueous solution due to simulated solar irradiation was studied. The experiment was conducted at pH 3.0, with pesticide aqueous solution of COD 1130 mg L⁻¹. There were 3.21, 5.13 and 8.95% removal of COD in 1, 2 and 3 h, respectively. The photolysis alone was not sufficient for complete degradation of the pesticides in aqueous solution (Fig. 2). Degradation does not proceed significantly under direct irradiation without a catalyst [18]. This is because the process depends on the adsorptive properties of the organic compound based on its chemical structure and also, the presence of dissolved organic matter (DOM) which may lead to competition in the energy absorption [19-20]. As a basic distinction, photodegradation reactions can be classified as being of direct or indirect nature. In the former, the compound is directly excited by absorbing energy from solar radiation (290-800 nm), while indirect photodegradation proceeds through the generation of reactive intermediates from matrix components which subsequently interact with the substrate [20-21].

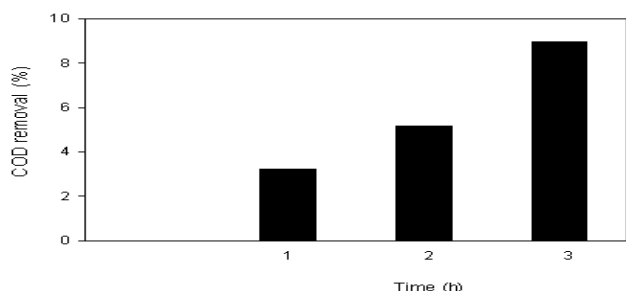


Fig. 2 COD removal during solar irradiation of pesticide aqueous solution at 1, 2 and 3 h duration

B. Effect of H_2O_2 /COD Molar Ratio

To obtain the optimum H_2O_2 /COD molar ratio, initial H_2O_2 concentration was varied in the range 35.31–123.59 mM at initial COD 1130 $mg L^{-1}$ (35.31mM). The corresponding H_2O_2 /COD molar ratios were 1, 1.5, 2, 2.5, 3 and 3.5. The other operating conditions were pH 3 and H_2O_2/Fe^{2+} molar ratio 25. Fig. 3 (a)–(c) shows the effect of H_2O_2 /COD molar ratio on pesticide degradation in terms of COD and TOC removal and BOD_5 /COD ratio. The COD removal after 60 min reaction time was 39.03, 51.35, 72.08, 54.16, 40.17 and 35.93% at H_2O_2 /COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively. The TOC removal after 60 min reaction time was 25.15, 34.27, 57.56, 39.96, 33.27 and 28.38% at H_2O_2 /COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively. BOD_5 /COD ratio after 60 min reaction time was 0.25, 0.33, 0.33, 0.29, 0.23, 0.19 and 0.14 at H_2O_2 /COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively.

The results indicate that the pesticide degradation increased with increasing concentration of H_2O_2 but the degradation did not improve above H_2O_2 /COD molar ratio 2. This may be due to scavenging of OH^\bullet by H_2O_2 as in Eq. (4) [22].



Maximum COD and TOC removal and biodegradability (BOD_5 /COD ratio) improvement was achieved at H_2O_2 /COD molar ratio 2.

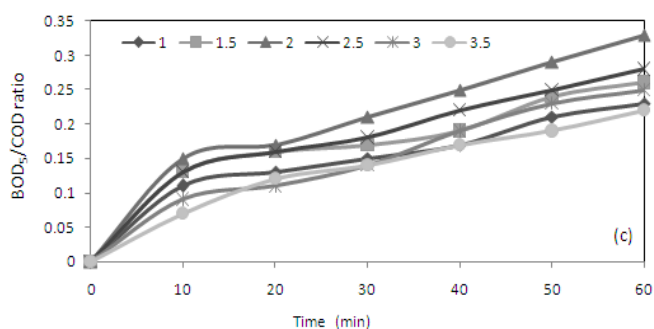
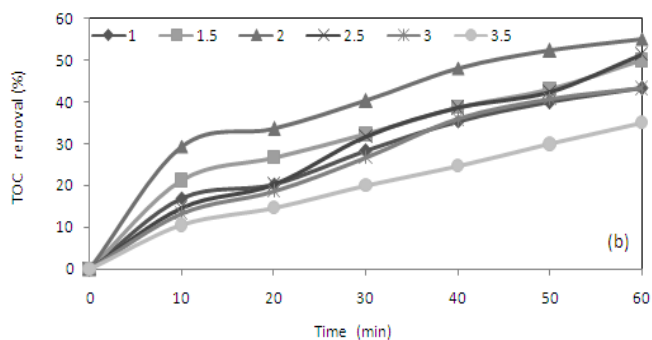
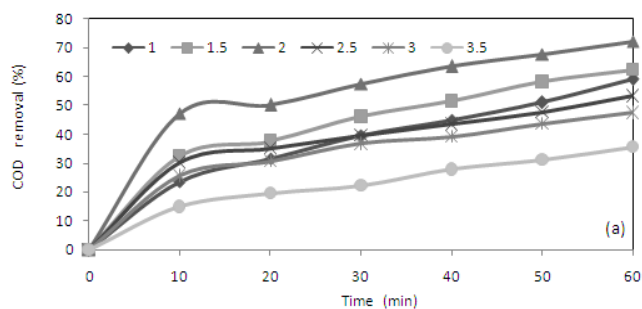


Fig. 3 Effect of H_2O_2 /COD molar ratio on (a) COD removal (b) TOC removal and (c) BOD_5 /COD ratio

C. Effect of H_2O_2/Fe^{2+} Molar Ratio

The effect of ferrous ion concentration was studied in order to obtain the optimum H_2O_2/Fe^{2+} molar ratio for degradation of the combined pesticide aqueous solution. Fe^{2+} concentration was varied from 0.94 to 28.25 mM under operating conditions of pH 3, H_2O_2 /COD molar ratio 2 and initial COD 1130 $mg L^{-1}$. Fig. 3 (a)–(c) indicates that COD and TOC removal efficiency and BOD_5 /COD ratio improvement increased with increasing Fe^{2+} concentration up to H_2O_2/Fe^{2+} molar ratio 25. Further addition of Fe^{2+} did not increase removal. This may be due to direct reaction of OH^\bullet radical with metal ions at high concentration of Fe^{2+} as seen in reaction (5) [23].



After 60 min reaction time, COD removal was 32.41, 48.39, 61.47, 74.19, 41.86, 34.88 and 30.31% at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 25, 50, 100 and 150, respectively. The TOC removal was 27.33, 33.27, 47.87, 58.32, 38.85, 30.84 and 23.8% at H_2O_2/Fe^{2+} molar ratio 5, 10, 25, 50, 100 and 150, respectively. The BOD_5 /COD ratio after 60 min reaction time was 0.19, 0.24, 0.31, 0.35, 0.24, 0.19 and 0.17 at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 25, 50, 100 and 150, respectively. The H_2O_2/Fe^{2+} molar ratio 25 was obtained as optimum to achieve maximum degradation of the pesticides aqueous solution.

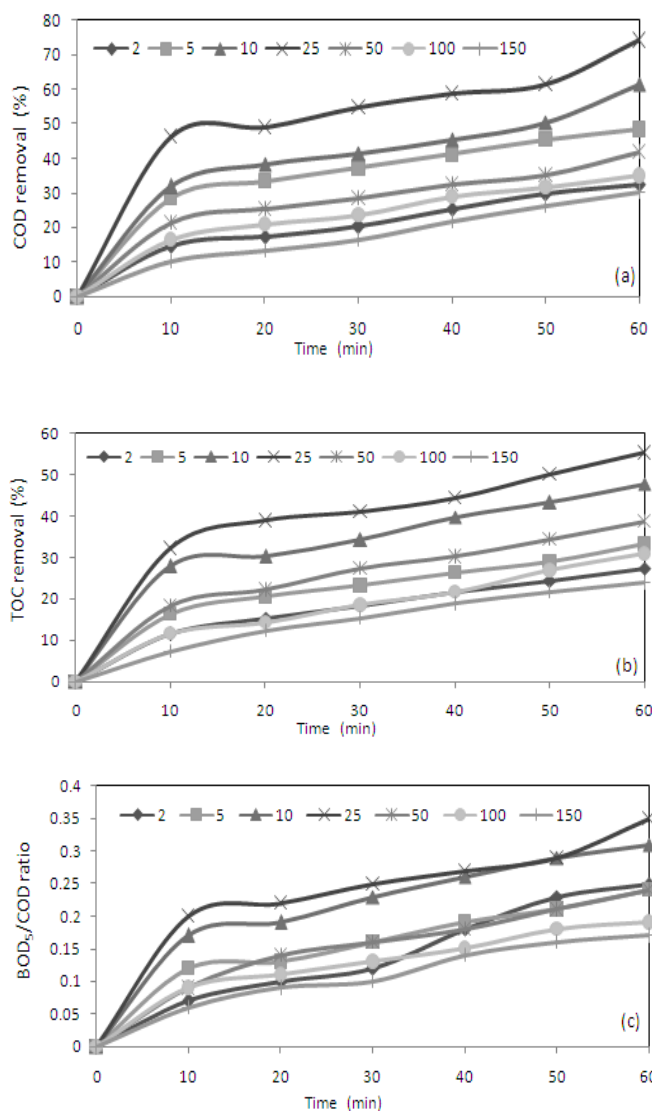


Fig. 4 Effect of H_2O_2/Fe^{2+} molar ratio on (a) COD removal (b) TOC removal and (c) BOD_5/COD ratio

D. Effect of pH

The solution pH is an important variable in the evaluation of aqueous phase mediated photocatalytic reactions. The pH of the solution influences adsorption and dissociation of the substrate, catalyst surface charge, oxidation potential of the valence band and other physico-chemical properties of the system [20]24. To obtain the optimum pH, experiments were conducted by varying the pH in the range 2-6. The other operating conditions were H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and initial COD 1130 $mg L^{-1}$. Fig. 5 (a)–(c) shows the effect of pH on COD and TOC removal and BOD_5/COD ratio. The COD removal after 60 min reaction time was 65.11, 74.19, 50.04, 41.23 and 32.39% at pH 2, 3, 4, 5 and 6, respectively. The TOC removal after 60 min reaction time was 45.47, 58.32, 48.87, 38.45 and 33.29% at pH 2, 3, 4, 5 and 6, respectively. BOD_5/COD ratio after 60 min reaction time was 0.27, 0.35, 0.29, 0.26 and 0.23 at pH 2, 3, 4, 5 and 6, respectively. From the experiment, the optimum pH for degradation of the pesticides in aqueous solution was 3.0.

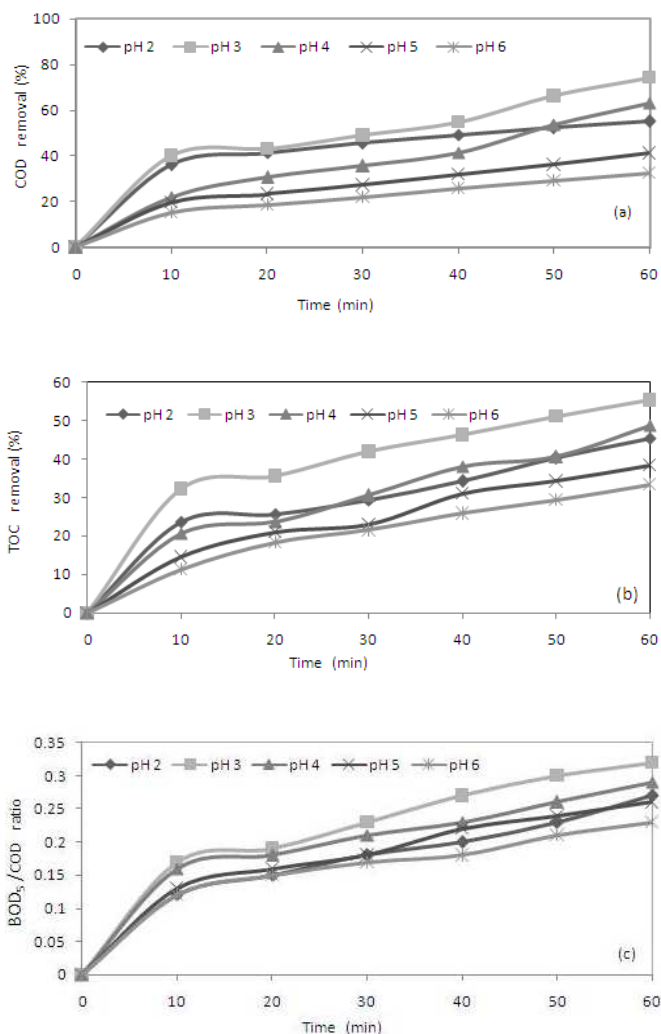


Fig. 5 Effect of pH on (a) COD removal (b) TOC removal and (c) BOD_5/COD ratio

E. Effect of Initial Pesticide Concentration

The investigation of the effect of initial pesticide concentration was conducted by using 400, 800 and 1200 $mg L^{-1}$ combined pesticides concentrations with equivalent COD of 1130, 2150 and 3280 $mg L^{-1}$, respectively. The optimum operating conditions used were H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and pH 3. Fig.6 (a)–(c) shows the effect of initial pesticides concentration on COD and TOC removal and BOD_5/COD ratio. After 60 min reaction time, COD removal was 74.19, 72.24 and 71.57%, TOC removal was 58.32, 56.98 and 55.01%, and BOD_5/COD ratio was 0.35, 0.34 and 0.33 at initial pesticide concentration 400, 800 and 1200 $mg L^{-1}$, respectively. At low concentration of substrate there was improved efficiency (high percentage degradation). Even though at high initial substrate concentration, net degradation was more but percentage degradation of the substrate appeared less. The presumed reason is that when the initial concentration of the pesticide increased, the hydroxyl radical (OH^*) concentrations remain constant for all pesticide molecules [25]. The efficiency of the Fenton process depends on the formation of hydroxyl radicals and less scavenging of

hydroxyl radicals occurs as initial organic substrate concentration increases [26]. The optimum operating condition H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and pH 3 were adequate to degrade the pesticides in aqueous solution.

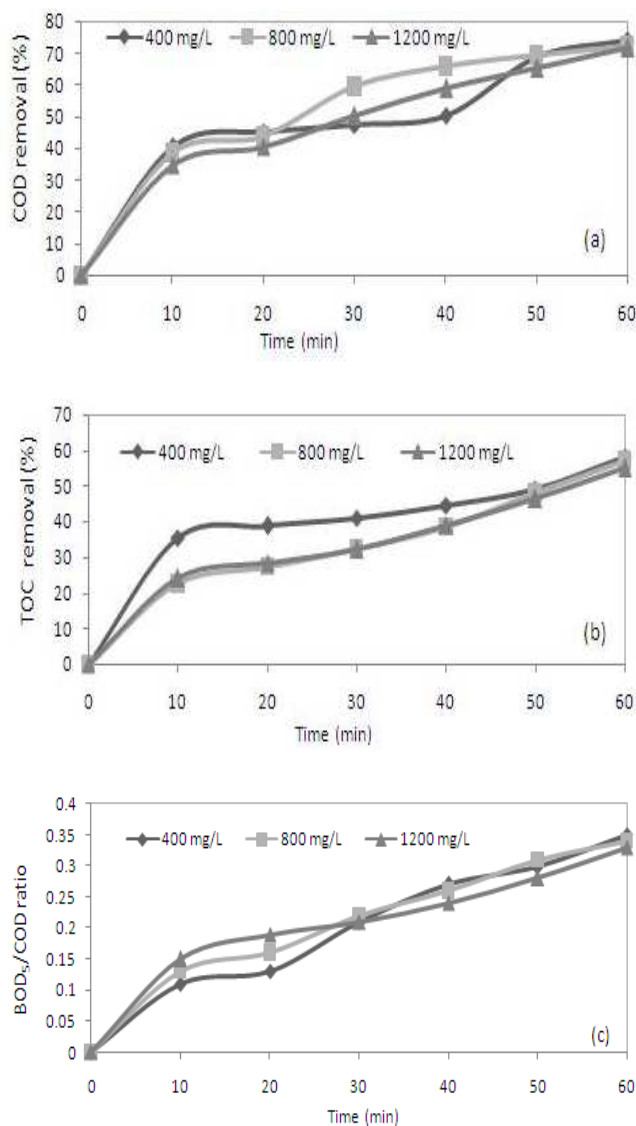


Fig. 6 Effect of initial concentration on (a) COD removal (b) TOC removal and (c) BOD₅/COD ratio

F. FTIR Spectra

In the Fourier transform infrared (FTIR) process, a tiny proportion of the photons incident on the aqueous solution interacts with vibrations in the pesticide and it is eventually scattered at higher or lower energy to represent the spectra. Untreated and solar-Fenton treated pesticide aqueous solution were analyzed by FTIR spectroscopy to check for presence of organic bonds. Identified tangential C–C stretching in benzene and hexa-substituted benzene derivatives of chlorothalonil was observed in the range of 1548 and 1265 cm^{-1} [27]. The cypermethrin spectrum showed absorption bands from 1742 to 1076 cm^{-1} due to carbonyl stretching, C=C stretching in chloroalkenes, ring vibration of benzene,

CH_2 deformation in R– CH_2 –CN structure and (C=O)–O–stretching, whereas the absorption bands of chlorpyrifos were located between 1549 to 968 cm^{-1} due to C=N stretching, pyridine stretching, ring vibration, ring breathing, Cl–C stretching, trigonal ring breathing and P=S stretching [28]. In the present study, the band at 1650.95 cm^{-1} and 1448.44 cm^{-1} in the untreated aqueous solution in Fig. 7 (a) was modified as seen in Fig.7 (b), indicating degradation of the pesticides.

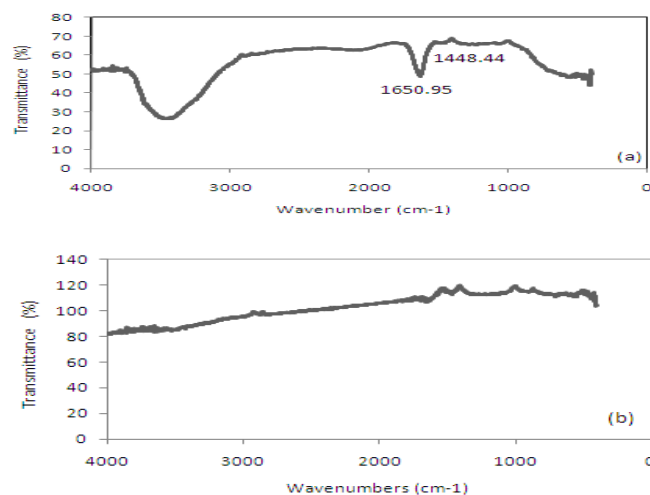
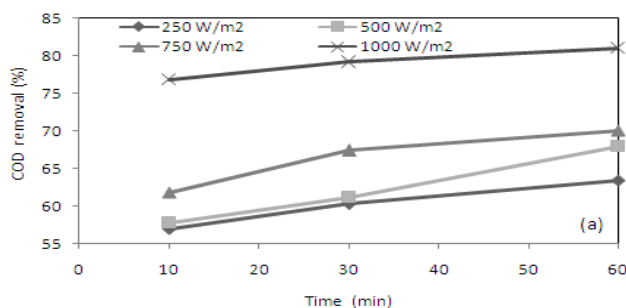


Fig. 7 FTIR spectra of (a) untreated and (b) treated pesticide aqueous solution

G. Effect of Incident Solar Radiation Intensity

The effect of solar radiation intensity was investigated for 250, 500, 750 and 1000 W/m^2 as seen in Fig. 8 (a)–(b). Radiation intensity distribution within the reactor invariably determines the overall pesticide conversion and degradation efficiency [29]. The rate of initiation of photocatalysis and electron-hole formation in the photochemical reaction is strongly dependent on the light intensity [30]. While increasing the intensity of incident light, the probabilities of excitation of electrons as well as the re-excitation of recombined electrons increase. Hence, increase in the degradation is observed with increase in the intensity of incident light [31]. The dependency of pollutant degradation rate on light intensity has been studied for various organic pollutants. In some cases, the reaction rate exhibited a square root dependency on the light intensity; others observed a linear relationship between the two variables [32, 33]. In this study, 1000 W/m^2 showed the highest COD and TOC removal efficiency of 81.05 and 60.11%, respectively.



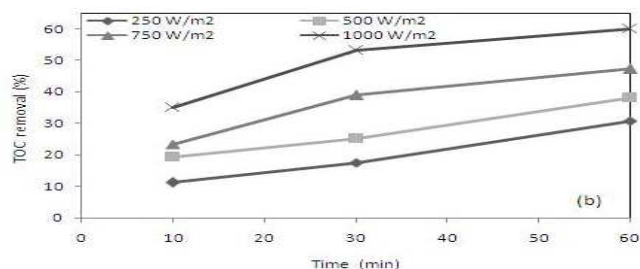


Fig. 8 Effect of incident solar radiation intensity on (a) COD removal and (b) TOC removal

H. Degradation of Pesticide in Aqueous Solution under the Optimum Operating Conditions

Fig. 9 shows the degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution under the optimum operating conditions (H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and pH 3). Complete degradation of the pesticides occurred in 1 min. Maximum COD and TOC removal were 74.19% and 58.32%, respectively, and the corresponding BOD_5/COD ratio was 0.36 after 60 min reaction time (Fig. 10) which is considered adequate for biological treatment as a wastewater is considered biodegradable if BOD_5/COD ratio is ~ 0.4 [34]. In terms of mineralization of organic carbon, concentration of ammonia-nitrogen (NH_3-N) decreased from 22 to 4.3 mg L^{-1} and nitrate (NO_3-N) increased from 0.7 to 18.1 mg L^{-1} in 60 min (Fig. 11).

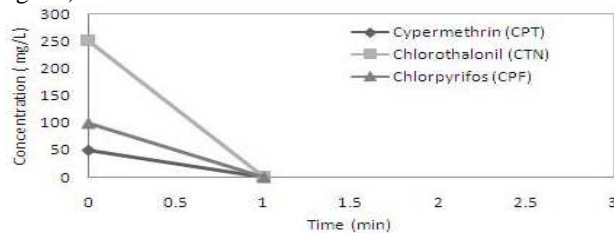


Fig. 9 Degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides under optimum operating conditions

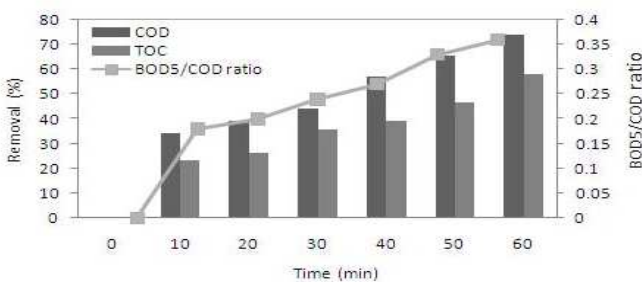


Fig. 10 Pesticide degradation under optimum operating conditions in terms of COD and TOC removal and BOD_5/COD ratio

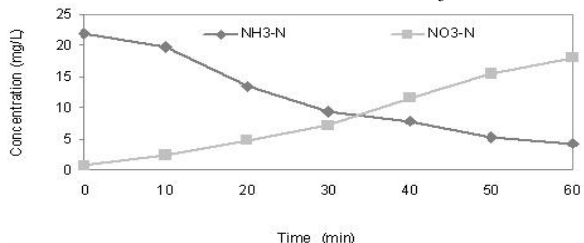


Fig. 11 Mineralization of pesticide in terms of NH_3-N and NO_3-N concentration

IV. CONCLUSIONS

Solar photo-Fenton process is effective in the treatment (degradation) of chlorpyrifos, cypermethrin, and chlorothalonil pesticides in aqueous solution. Under the optimum operating conditions, complete degradation of the pesticides occurred in 1 min. Biodegradability increased from zero to 0.36 in 60 min, and COD and TOC removal were 74.19 and 58.32%, respectively. Mineralization of organic carbon led to a decrease in ammonia-nitrogen concentration from 22 to 4.3 mg L^{-1} and an increase in nitrate concentration from 0.7 to 18.1 mg L^{-1} in 60 min. Solar photo-Fenton process can be used for pretreatment of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution or wastewater for biological treatment.

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REFERENCES

- [1] S. Kundua, A. Pala, A. K. Dikshit, "UV induced degradation of herbicide 2, 4-D: kinetics, mechanism and effect of various conditions on the degradation," *Separation and Purification Technology*, Vol. 44, no. 2, pp. 121-129, 2005.
- [2] A. Lagana, A. Bacaloni, I.D. Leva, A. Faberi, G. Fago, A. Marino, "Occurrence and determination of herbicides and their major transformation products in environmental waters," *Analytica Chimica Acta*, Vol. 462, no. 2, pp. 187-198, 2000.
- [3] E. Chamarro, E. Marco, S. Esplugas, "Use of Fenton reagent to improve organic chemical biodegradability," *Water Research*, Vol. 35, no. 4, pp. 1047-1051, 2001.
- [4] J.J. Pignatello, D. Liu, P. Houston, "Evidence for an additional oxidant in the photo assisted Fenton reaction," *Environmental science and Technology*, Vol. 33, no. 11, pp. 1832-1839, 1999.
- [5] H. Fallmann, Thomas Krutzler, Rupert Bauer, S. Malato, J. Blanco, "Applicability of the Photo-Fenton method for treating water containing pesticides," *Catalysis Today*, Vol. 54, no.2-3, pp. 309-319, 1999.
- [6] J. Fernandez, J. Bandara, A. Lopez, P. Albers, J. Kiwi, "Efficient photo-assisted Fenton catalysis mediated by Fe ions on Nafion membranes active in the abatement of non-biodegradable azo-dye," *Chemical Communications*, Vol. 14, pp. 1493-1484, 1998.
- [7] R. M. Sherrada, J.S. Bearrb, C.L. Murray-Guldec, J.H. Rodgers Jr., and Y.T. Shahd, "Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures," *Environmental Pollution*, Vol. 127, no. 3, pp. 385-394, 2004.
- [8] Y. Zhang, J. Lu, L. Wu, A. Chang, and W.T. Frankenberger Jr., "Simultaneous removal of chlorothalonil and nitrate by *Bacillus cereus* strain NS1," *Science of the Total Environment*, Vol. 382 no. 2-3, pp. 383-387, 2007.
- [9] Y. Samet, L. Agengui, R. Abdelhédi, "Anodic oxidation of chlorpyrifos in aqueous solution at lead dioxide electrodes," *Journal of Electroanalytical Chemistry*, Vol. 650, no.1, pp. 152-158, 2010.
- [10] Y. Samet, L. Agengui, R. Abdelhédi, "Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes," *Chemical Engineering Journal*, Vol. 161, no. 1-2, pp. 167-172, 2010.
- [11] A. Ghauch, A. Tuqan, "Catalytic degradation of chlorothalonil in water using bimetallic iron-based systems", *Chemosphere*, Vol. 73 no. 5, pp. 751-759, 2008.
- [12] F. Chen, L. Zeng, Y. Zhang, X. Liao, Y. Ge, X. Hua, L. Jiang, "Degradation behaviour of methamidophos and chlorpyrifos in apple juice treated with pulsed electric fields," *Food Chemistry*, Vol. 112, no. 4, pp. 956-961, 2009.
- [13] J.G. Wu, T.G. Luan, C.Y. Lan, W.H. Lo, G.Y.S. Chan, "Efficacy evaluation of low-concentration of ozonated water in removal of residual diazinon, parathion, methyl-parathion and cypermethrin on vegetable,"

- Journal of Food Engineering*, Vol. 79, no. 3, pp. 803–809, 2007.
- [14] C.F. Gromboni, M.Y. Kamogawa, A.G. Ferreira, J.A. N'Obrega, and A.R.A. Nogueira, "Microwave-assisted photo-Fenton decomposition of chlorfenvinphos and cypermethrin in residual water," *Journal of Photochemistry and Photobiology A: Chemistry*, Vol. 185, no.1, pp. 32–37, 2007.
- [15] APHA, AWWA, WPCF, "Standard Methods for the Examination of Water and Wastewater," 21st edition, American Public Health Association, Washington, DC, 2005.
- [16] I. Talinli, G.K. Anderson, "Interference of hydrogen peroxide on the standard COD test," *Water Research*, Vol. 26, no. 1, pp. 107–110, 1992.
- [17] Y.W. Kang, M.J. Cho, K.Y. Hwang, "Correction of hydrogen peroxide interference on standard chemical oxygen demand test," *Water Research*, Vol. 33, no. 5, pp. 1247–1251, 1999.
- [18] V. A. Sakkas, T. A. Albanis, "Photocatalyzed degradation of the biocides chlorothalonil and dichlofluanid over aqueous TiO₂ suspensions," *Applied Catalysis B: Environmental*, Vol. 46, no. 1, pp. 175–188, 2003.
- [19] L. Tong, P. Eichhorn, S. Pérez, Y. Wang, D. Barceló, "Photodegradation of azithromycin in various aqueous systems under simulated and natural solar radiation: Kinetics and identification of photoproducts," *Chemosphere*, Vol. 83, no.3, pp.340–348, 2011.
- [20] R.G. Zepp, G.L. Baughman, P.F. Schlotzhauer, "Comparison of photochemical behavior of various humic substances in water: I. Sunlight induced reactions of aquatic pollutants photosensitized by humic substances," *Chemosphere*, Vol. 10, no.1, pp.109–117, 1981a
- [21]] R.G. Zepp, G.L. Baughman, P.F. Schlotzhauer, 1981b. "Comparison of photochemical behavior of various humic substances in water: II. Photosensitized oxygenations," *Chemosphere*, Vol. 10, no.1, pp.119–126, 1981b.
- [22] M.I. Badawy, M. Y. Ghaly, T. A. Gad-Allah, "Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater," *Desalination* Vol. 194, no. 1-3, pp. 166–175, 2006.
- [23] E. Elmolla and M. Chaudhuri, "Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution," *Journal of Hazardous Materials*, Vol. 170, no. 2-3, pp. 666–672, 2009.
- [24] M.V. Shankar, S. Anandan, N. Venkatachalam, B. Arabindoo, V. Murugesan, "Novel thin-film reactor for photocatalytic degradation of pesticides in aqueous Solutions," *Journal of Chemical Technology and Biotechnology*, Vol. 79, no. 11, pp. 1279 – 1285, 2004.
- [25] E. Neyens, J. Baeyens, "A review of classic Fenton's peroxidation as an advanced oxidation technique," *Journal of Hazardous Materials*. Vol. 98, no. 1-3, pp. 33–50, 2003.
- [26] N. Modirshahla, M.A. Behnajady, F. Ghanbary, "Decolorization and mineralization of C.I. acid yellow 23 by Fenton and photo-Fenton processes," *Dyes Pigments*, Vol. 73, no.3, pp. 305–310, 2007.
- [27] D.A. Dhas, I. H. Joea, S.D.D. Roy, T.H. Freed, "DFT computations and spectroscopic analysis of a pesticide: Chlorothalonil," *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy Spectrochimica Acta Part A*, Vol. 77, no. 1, pp. 36–44, 2010.
- [28] S. Armenta, G. Quintás, S. Garrigues, M. de la Guardi, "A validated and fast procedure for FTIR determination of cypermethrin and chlorpyrifos," *Talanta*, Vol. 67, no. 3, pp. 634-639, 2005.
- [29] V. Pareek, S. Chong, M. Tade, A. Adesina, Light intensity distribution in heterogeneous photocatalytic reactors," *Asia-Pacific Journal of Chemical Engineering*, Vol. 3, no. 2, pp. 171-201, 2008.
- [30] A.E. Cassano, O.M. Alfano, "Reaction engineering of suspended solid heterogenous photocatalytic reactors," *Catalysis Today*, Vol. 58 no. 2-3, pp. 167-197, 2000.
- [31] M. Mahalakshmi, Banumathi Arabindoo, M. Palanichamy, V. Murugesan, "Photocatalytic degradation of carbofuran using semiconductor oxides," *Journal of Hazardous Materials*, Vol. 143 no. 1-2, pp. 240–245, 2007.
- [32] D. F. Ollis, E. Pelizzetti, N. Serpone, "Photocatalyzed destruction of water contaminants," *Environmental Science and Technology*, Vol. 25, no. 9, pp. 1522-1529, 1991.
- [33] R. Terzian, N. Serpone, "Heterogeneous photocatalysed oxidation of creosote components; mineralization of xylenols by illuminated TiO₂ in oxygenated aqueous media," *Journal of Photochemistry and Photobiology A: Chemistry* Vol. 89, no. 2, pp. 163-175, 1991.
- [34] F. Al-Momani, J.R. Touraud, J. R. Degorce-Dumas, J. Roussy, O. Thomas, "Biodegradability enhancement of textile dyes and textile wastewater by UV photocatalysis," *Journal of Photochemistry and*