



UV Photo-Fenton Treatment of Combined Chlorpyrifos, Cypermethrin and Chlorothalonil Pesticides Aqueous Solution

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ABSTRACT

The study examined the effect of the operating conditions of the UV photo-Fenton process on COD and TOC removal, biodegradability improvement and mineralization of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution. The optimum operating conditions for treatment of an aqueous solution containing 100 mg/L of chlorpyrifos, 50 mg/L of cypermethrin and 250 mg/L of chlorothalonil were observed to be H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and pH 3. Under the optimum operating conditions, complete degradation of the pesticides occurred in 1 min. Biodegradability (BOD_5/COD ratio) increased from zero to 0.38 and COD and TOC removal were 78.56 and 63.76%, respectively in 60 min. The treatment resulted in release and mineralization of organic carbon and nitrogen from the pesticide molecules as evident from TOC degradation (removal), and decrease in NH_3-N from 22 to 3.9 mg/L and increase in NO_3-N from 0.7 to 19.3 mg/L in 60 min. The study shows that UV photo-Fenton process is effective in pretreatment of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides aqueous solution for biological treatment.

INTRODUCTION

Compliance with stringent discharge standards is required for the toxic substances that are non-biodegradable or inhibitory to biological degradation processes. Among these substances, pesticides are considered to be significant surface and ground water contaminants introduced through crop disinfection and pesticide wastewater discharge (Shawaqfeh & Al Momani 2010). Pesticide residues have been detected in inland waterways (Huat et al. 1991, Cheah 1996, Chea et al. 1996, Ipen 2005, Leong et al. 2007, Pan Asia 2010). Pesticides aldrin, heptachlor and DDT have been detected in Malaysian river water (Kimura et al. 2005).

Degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides in water has been reported. Chlorpyrifos and chlorothalonil were removed from aqueous mixture in constructed wetlands (Sherrarda et al. 2004), chlorothalonil was degraded by *Bacillus cereus* strain NS1 (Zhang et al. 2007), chlorpyrifos was degraded by anodic oxidation at lead dioxide and boron-doped diamond electrodes (Samet et al. 2010a, 2010b), chlorothalonil was degraded by bimetallic iron-based systems (Ghauch & Tuqan 2008), chlorpyrifos was degraded by pulsed electric fields (Chen et al. 2009) and cypermethrin was removed by ozonation (Wu et al. 2007).

Advanced oxidation processes (AOPs) constitute a promising technology for the treatment of wastewaters

containing non-easily removable organic compounds with high toxicity and low biodegradability (Pera-Titus et al. 2004). Experiences with different oxidation technologies and substrates have shown that a partial oxidation of toxic water may increase its biodegradability up to high levels (Kiwi et al. 1994, Scott & Ollis 1995). Oxidation with Fenton's reagent is based on hydroxyl radical (OH^\bullet) produced by catalytic decomposition of hydrogen peroxide (H_2O_2) in reaction with ferrous ion (Fe^{2+}) (Walling 1975). In the UV photo-Fenton process, the rate of OH^\bullet radical formation is increased by photoreactions of H_2O_2 and/or Fe^{3+} that produce OH^\bullet radical directly or regenerate Fe^{2+} (Pignatello et al. 1999), thus increase the efficiency of the process. Degradation of cypermethrin by microwave irradiated photo-Fenton reaction has been reported (Gromboni et al. 2007). However, there has been no study on degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides aqueous solution by the UV photo-Fenton process.

This study examined the operating conditions (H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and pH) of the UV photo-Fenton process for COD and TOC removal, biodegradability (BOD_5/COD ratio) improvement and mineralization of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides aqueous solution. High performance liquid chromatography (HPLC) was used to determine pesticide concentration and Fourier transform infrared (FTIR) spectroscopy to estimate degradation of organic bonds in the pesticides.

MATERIALS AND METHODS

Chemicals and pesticides: Hydrogen peroxide (30%, w/w) and ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from R&M Marketing, Essex, U.K. Analytical grade of chlorpyrifos was obtained from Dr. Ehrenstorfer, Germany, and cypermethrin and chlorothalonil from Sigma-Aldrich, Germany. They were used for analytical determination of pesticide concentration by HPLC. The pesticides used to prepare aqueous solution were obtained from a commercial source, and were used as received.

Analytical methods: Pesticide concentration 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 (λ) 230 nm. Chemstation software was installed and used for data recording. The HPLC detection column was ZORBAX SB-C18 (3.0 mm \times 250mm, 5 μ m). The column temperature was set at 30°C. Mobile phase was made up of 25% buffer solution (0.001M KH_2PO_4 in double distilled water) and 75% acetonitrile.

Chemical oxygen demand (COD) was determined according to the standard methods (APHA 2005). Where the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose hydrogen peroxide to oxygen and water (Talini & Anderson 1992, Kang et al. 1999). TOC analyzer (Model 1010, O & I Analytical) was used for determining total organic carbon (TOC). pH was measured by a pH meter (HACH sension 4) and a pH electrode (HACH platinum series pH electrode model 51910, HACH Company, USA). Biodegradability was measured by 5-day biochemical oxygen demand (BOD_5) test according to the standard methods (APHA 2005). Ammonia nitrogen ($\text{NH}_3\text{-N}$) was measured by the Nessler method and nitrate-nitrogen ($\text{NO}_3\text{-N}$) by the cadmium reduction method (Hach 2002). DO was measured using YSI 5000 dissolved oxygen meter. The seed for BOD_5 test was obtained from a municipal wastewater treatment plant. Fourier transform infrared spectrum was taken by FTIR-8400S, Shimadzu.

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

Experimental procedure: Batch experiments were carried out in a 600 mL Pyrex reactor with 500 mL of the pesticide aqueous solution. The required amount of iron ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) was added to the aqueous solution and the pH was adjusted to the required value using sulphuric acid (H_2SO_4) and mixed

by a magnetic stirrer to ensure complete homogeneity. Thereafter, the necessary amount of H_2O_2 was added to the mixture and the mixture was subjected to UV irradiation at room temperature ($23 \pm 2^\circ\text{C}$) by placing a UV lamp 5 cm above the reactor. The UV lamp (Spectroline model EA-160/FE; 230V 0.17A, Spectronics Corporation, New York, USA) had a nominal power of 6 W, emitting radiation at $\lambda \sim 365$ nm. Samples were taken at pre-selected time intervals, filtered through a 0.45 μm membrane filter for COD, BOD_5 and TOC measurement, and filtered through a 0.20 μm membrane syringe filter for determination of pesticide concentration by HPLC and estimation of degradation of organic bonds in the pesticides by FTIR spectroscopy.

RESULTS AND DISCUSSION

Effect of UV irradiation: The photolysis of the pesticides in the pesticide aqueous solution due to UV irradiation ($\lambda \sim 365$ nm) at pH 3 was studied. Pesticide degradation (COD removal from the pesticide aqueous solution) by UV irradiation *per se* was 4.1, 6.96, 7.61 and 8.79% in 1, 2, 3 and 4 h, respectively. Further, it is known that H_2O_2 has a maximum absorbance at λ 210-230 nm and H_2O_2 proteolysis takes place to a small extent at λ 365 nm (Pignatello et al. 1999) and iron photo-redox also takes place under λ 365 nm (Al Momani 2006). Consequently, degradation of the pesticides when subjected to UV photo-Fenton reaction will be mainly due to the OH^\bullet radical produced by the UV photo-Fenton reactions

Effect of H_2O_2 /COD molar ratio: In order to obtain the optimum H_2O_2 /COD molar ratio, initial H_2O_2 concentration was varied in the range 35.31-123.58 mM at initial COD 1130 mg/L (35.31 mM). The corresponding H_2O_2 /COD molar ratios were 1, 1.5, 2, 2.5, 3 and 3.5. The other operating conditions were $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 50 and pH 3.

Fig. 1 shows the effect of H_2O_2 /COD molar ratio on pesticide degradation in terms of COD and TOC removal and biodegradability (BOD_5 /COD ratio) improvement. The COD removal after 60 min irradiation was 58.98, 62.34, 77.82, 53.24, 47.37 and 35.71% at H_2O_2 /COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively. The TOC removal after 60 min irradiation was 50.03, 54.45, 61.15, 43.27, 40.23 and 35.09% 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 irradiation was 0.26, 0.28, 0.37, 0.25, 0.23 and 0.22 at H_2O_2 /COD molar ratio 1, 1.5, 2, 2.5, 3 and 3.5, respectively. The results show increase in pesticide degradation with H_2O_2 /COD molar ratio up to 2 and reduced degradation with further increase in H_2O_2 /COD molar ratio. This was presumably due to scavenging of the OH^\bullet radical by H_2O_2 as in Reaction (1) (Kavitha & Palanivelu 2005).

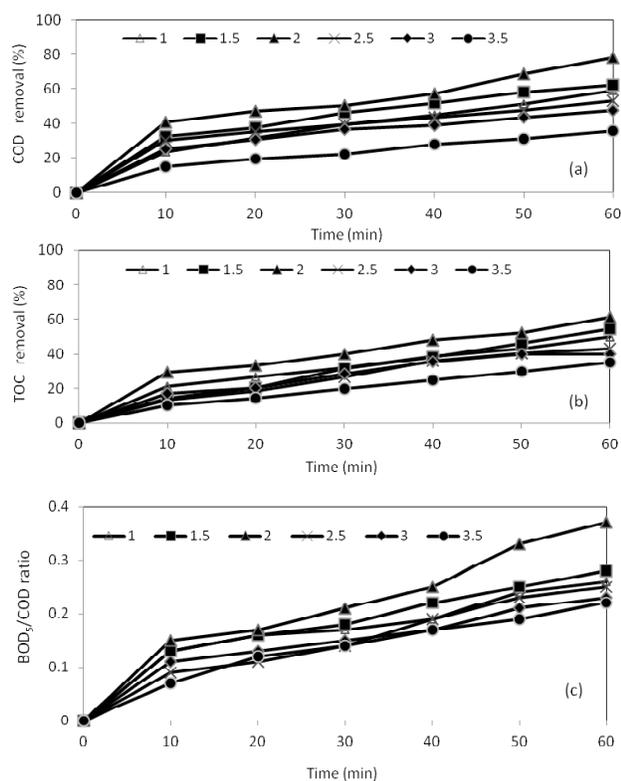


Fig. 1: Effect of $\text{H}_2\text{O}_2/\text{COD}$ molar ratio on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD_5/COD ratio.



Maximum removal of COD (77.82%) and TOC (61.15%) and biodegradability improvement (0.37) was achieved after 60 min irradiation at $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 2. Optimum $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 1.5 has been reported for degradation of antibiotics in aqueous solution (Elmolla & Chaudhuri 2009) and 2.5 for treatment of antibiotic wastewater (Emad & Chaudhuri 2010).

Effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio: To determine the optimum $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio for pesticide degradation, Fe^{2+} concentration was varied from 0.47 to 14.12 mM with constant H_2O_2 concentration (70.62 mM). The other operating conditions were $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 2, initial COD 1130 mg/L (35.31 mM) and pH 3. Fig. 2 shows the effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio on pesticide degradation in terms of COD and TOC removal and biodegradability (BOD_5/COD ratio) improvement. The results show increase in pesticide degradation with decrease in $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio up to 25 and reduced degradation with further decrease in $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (increase in Fe^{2+} concentration). This was presumably due to direct reaction of OH^\cdot radical with Fe^{2+} ion at high concentration as in Reaction (2) (Joseph et al. 2000).

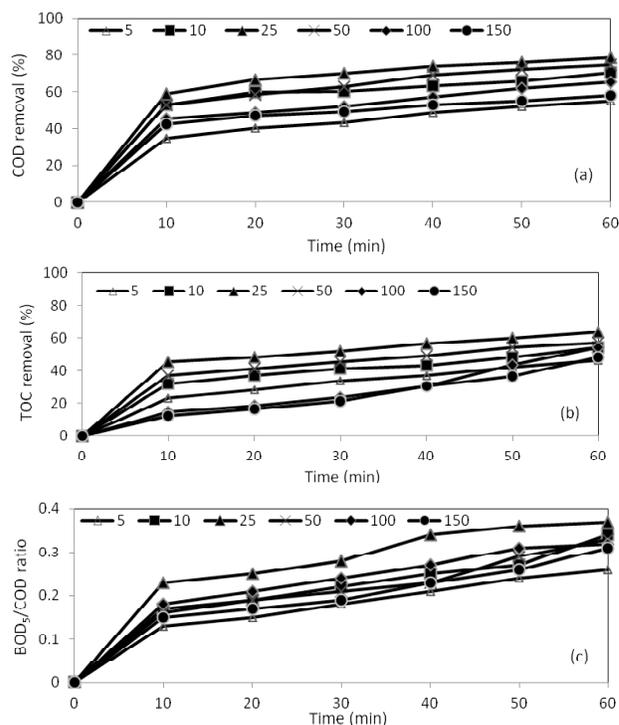


Fig. 2: Effect of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD_5/COD ratio

Maximum removal of COD (78.56%) and TOC (63.76%), and biodegradability improvement (0.37) was achieved after 60 min irradiation at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 25. Optimum $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 20 has been reported for degradation of antibiotics in aqueous solution (Elmolla & Chaudhuri 2009) and treatment of antibiotic wastewater (Elmolla & Chaudhuri 2010).

Effect of pH: The pH value influences the generation of OH^\cdot radical and hence the oxidation (degradation) efficiency. To obtain the optimum pH, experiments were performed by varying pH in the range 2-6. The other operating conditions were $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 2, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 25 and initial COD 1130 mg/L (35.31 mM). Fig. 3 shows the effect of pH on pesticide degradation in terms of COD and TOC removal and biodegradability (BOD_5/COD ratio) improvement. The COD removal after 60 min irradiation was 73.82, 78.56, 76.14, 65.13 and 59.08% at pH 2, 3, 4, 5 and 6, respectively. The TOC removal after 60 min irradiation was 52.35, 63.55, 58.12, 50.02 and 43.41% at pH 2, 3, 4, 5 and 6, respectively. The BOD_5/COD ratio after 60 min irradiation was 0.31, 0.38, 0.34, 0.29 and 0.24 at pH 2, 3, 4, 5 and 6, respectively. From the results obtained, the optimum pH for treatment of the pesticides in aqueous solution was 3. Elmolla & Chaudhuri (2009) also observed optimum pH 3 for degradation of antibiotics in aqueous solution.

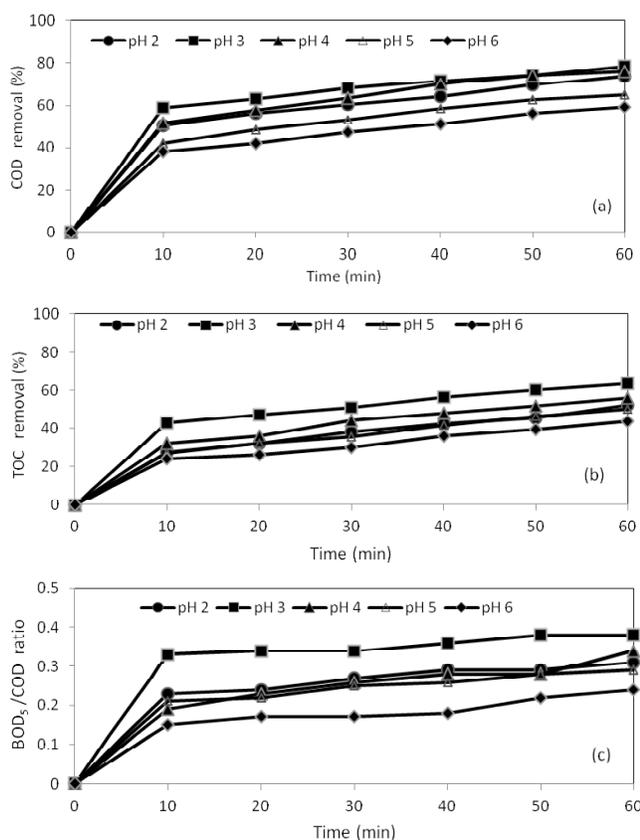


Fig. 3: Effect of pH on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD₅/COD ratio.

The results show that pH significantly influenced pesticide degradation. Maximum degradation was achieved at pH 3 and it decreased at lower and higher pH. This can be explained by taking into consideration the effect of pH on the formation of ferric iron complex species in solution. At pH 2-3 the main ferric iron species is $[\text{Fe}(\text{OH})(\text{H}_2\text{O})_5]^{2+}$ which has the largest light absorption coefficient and quantum yield for OH^\cdot radical production, along with Fe^{2+} regeneration in the λ range 280-370 nm (Benkelberg & Warnek 1995). At lower pH, $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ is more predominant and so the effectiveness of light absorption, regeneration of Fe^{2+} and pesticide degradation is lower. In addition, H_2O_2 gets solvated in presence of high concentration of H^+ to form stable oxonium ion (H_3O_2^+), thus reducing substantially its reactivity with Fe^{2+} ion (Kwon et al. 1999). At higher pH, $[\text{Fe}(\text{OH})_2(\text{H}_2\text{O})_4]^+$ dominates, but the solution becomes unstable with $\text{Fe}(\text{OH})_3$ precipitation (Benkelberg & Warnek 1995).

Effect of initial pesticide concentration: To determine the effect of initial pesticide concentration on pesticide degradation, experiments were conducted by varying concentration of the pesticides in aqueous solution as 400 mg/L (100

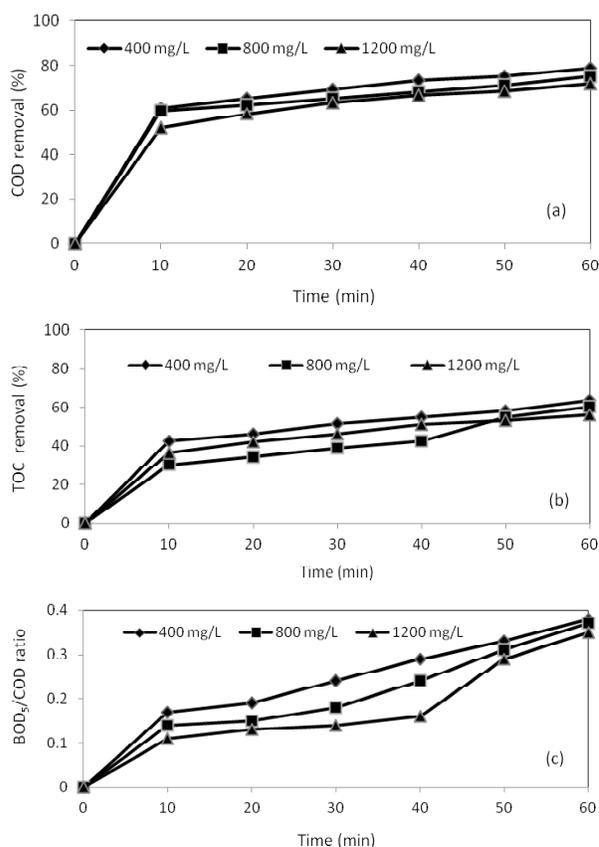


Fig. 4: Effect of initial concentration on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD₅/COD ratio.

mg/L of chlorpyrifos, 50 mg/L of cypermethrin and 250 mg/L of chlorothalonil), 800 mg/L (200 mg/L of chlorpyrifos, 100 mg/L of cypermethrin and 500 mg/L of chlorothalonil) and 1200 mg/L (300 mg/L of chlorpyrifos, 150 mg/L of cypermethrin and 750 mg/L of chlorothalonil). The corresponding COD were 1130, 2150 and 3280 mg/L, respectively. The operating conditions were $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 2, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 25 and pH 3. Fig. 4 shows the effect of initial pesticide concentration on pesticide degradation in terms of COD and TOC removal and biodegradability (BOD₅/COD ratio) improvement. After 60 min irradiation, COD removal was 78.56, 78.15 and 76.88%, TOC removal was 63.76, 60.12 and 58.23% and BOD₅/COD ratio was 0.38, 0.37 and 0.35 at initial pesticide concentration 400, 800 and 1200 mg/L, respectively. This indicates that the optimum operating conditions ($\text{H}_2\text{O}_2/\text{COD}$ molar ratio 2, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 25 and pH 3) are adequate for UV photo-Fenton treatment of such aqueous solutions or wastewater.

Degradation of pesticides in aqueous solution, biodegradability improvement and mineralization under optimum operating conditions: Degradation of the pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous so-

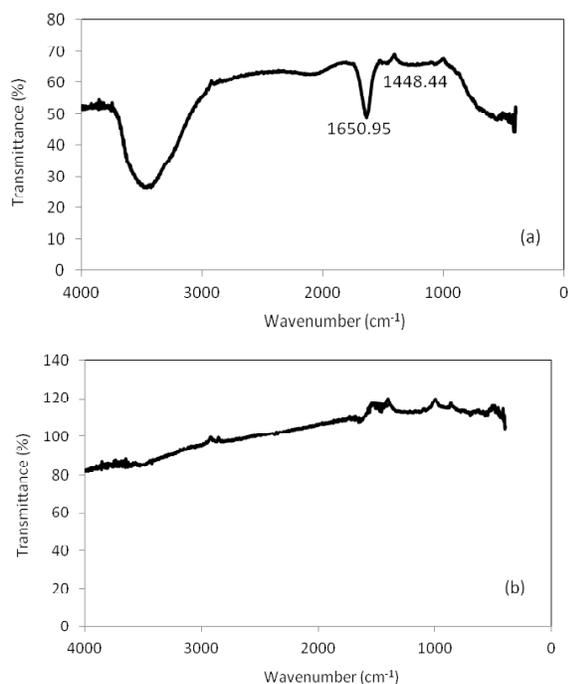


Fig. 5: FTIR spectra of (a) untreated and (b) treated pesticide solution

lution (COD 1130 mg/L; 35.31 mM) under the optimum operating conditions (H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and pH 3) was studied. Complete degradation of all the three pesticides was achieved in 1 min.

In the FTIR spectrum, the absorption bands of chlorpyrifos are 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; the cypermethrin absorption bands appear 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; and tangential C-C stretching in benzene and hexa-substituted benzene derivatives of chlorothalonil is observed in the range of 1548 and 1265 cm^{-1} (Armenta et al. 2005, Dhas et al. 2010). Fig. 5 shows the FTIR spectra of the untreated and treated pesticide aqueous solution. The absorption bands at 1650.95 cm^{-1} and 1448.44 cm^{-1} in the untreated aqueous solution were modified in the treated aqueous solution, indicating degradation of the organic bonds in the pesticide.

Fig. 6 shows pesticide degradation under the optimum operating conditions in terms of COD and TOC removal and biodegradability (BOD_5/COD ratio) improvement. Maximum COD and TOC removal were 78.56 and 63.76%, respectively after 60 min irradiation and BOD_5/COD ratio was 0.38 which is considered adequate for biological treatment (Al-Momani et al. 2002).

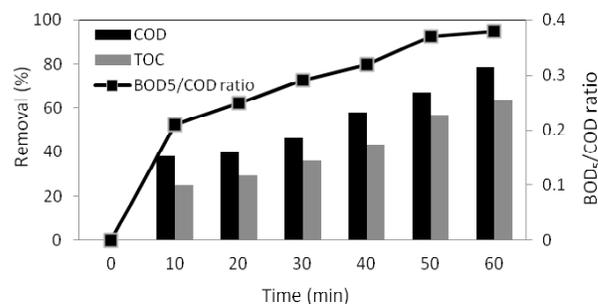


Fig. 6: Pesticide degradation under optimum operating conditions in terms of COD and TOC removal and BOD_5/COD ratio.

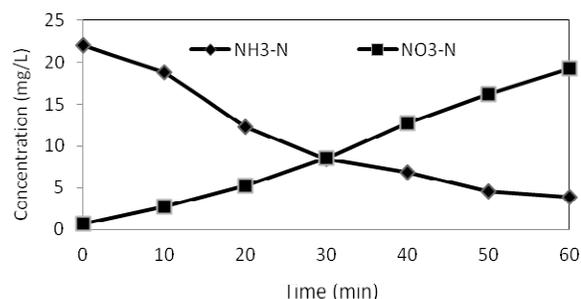


Fig. 7: Mineralization of organic nitrogen in terms of NO_3 -N formation.

UV photo-Fenton treatment resulted in release and mineralization of organic carbon and nitrogen from the pesticide molecules. Mineralization of organic carbon is evident from TOC degradation (removal) as shown in Fig. 6. Mineralization of organic nitrogen is evident from decrease in NH_3 -N from 22 to 3.9 mg/L and increase in NO_3 -N from 0.7 to 19.3 mg/L in 60 min (Fig. 7).

CONCLUSIONS

- Under optimum operating conditions (H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 25 and pH 3), UV photo-Fenton treatment of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides aqueous solution resulted in complete degradation of the pesticides in 1 min. Biodegradability increased from zero to 0.38, and COD and TOC removal were 78.56 and 63.76%, respectively in 60 min.
- UV photo-Fenton treatment resulted in release and mineralization of organic carbon and nitrogen from the pesticide molecules as evident from TOC degradation (removal), and decrease in NH_3 -N from 22 to 3.9 mg/L and increase in NO_3 -N from 0.7 to 19.3 mg/L.
- UV-photo-Fenton process can be used for pretreatment of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides aqueous solution for biological treatment.

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