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Fenton Treatment of Chlorpyrifos, Cypermethrin and Chlorothalonil Pesticides in Aqueous Solution

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ABSTRACT

The study examined the effect of operating conditions of the Fenton process on degradation, biodegradability improvement and mineralization of chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution. Also, the degradation of the pesticides under optimum operating conditions was evaluated. The optimum operating conditions for Fenton treatment of an aqueous solution containing 100, 50 and 250 mg L⁻¹ of chlorpyrifos, cypermethrin and chlorothalonil, respectively were observed to be H₂O₂/COD molar ratio 3, H₂O₂/Fe²⁺ molar ratio 10 and pH 3. Pesticide degradation increased with temperature. Under the optimum operating conditions, complete degradation of the pesticides occurred in 1 min. Biodegradability (BOD₅/COD ratio) increased from zero to 0.35 and COD and TOC removal were 69.03 and 55.61%, respectively in 60 min. Due to mineralization of organic carbon, decrease in ammonia-nitrogen from 22-6.1 mg L⁻¹ and increase in nitrate from 0.7-15.2 mg L⁻¹ in 60 min were observed. The study indicated that Fenton process can be used for pretreatment of combined chlorpyrifos, cypermethrin and chlorothalonil aqueous solution or wastewater for biological treatment.

Key words: Pesticide, chlorpyrifos, cypermethrin, chlorothalonil, Fenton process

INTRODUCTION

Pest control is a worldwide problem in agriculture, forest ecosystem and environmental management (Bhattacharyya and Bhattacharya, 2006). In an effort to combat the menace of pests, industrial use of pesticides has become prevalent which has led to widespread contamination of the environment including surface water and groundwater (Foo and Hameed, 2010). Groundwater pollution is of increasing concern, especially because about 70% of drinking water comes from groundwater (Tariq *et al.*, 2006). Infiltration of pesticide effluent into groundwater, promoted by spray drift, soil leaching, tile drainage outflow, base-flow seepage, surface run-off, volatilization (diffuse-source inputs), sewer overflows, improper handling of tank mix leftovers, leaking of faulty equipments, incorrect storage of canisters, drippings from agricultural practices, accidental spillage and farmyard deposition (point source pathways) from agriculture, horticulture, forestry, chemical industry and domestic activities (Reichenberger *et al.*, 2007), constitutes persistent and accumulative deterioration of the aquatic environment (Gentz, 2009). Reports have indicated that a minimum of 50 µg L⁻¹ concentration of pesticide is toxic to guppy fish (Sharbidre *et al.*, 2011) and pesticide residues in soil surface layer are higher in concentrations than in soil subsurface layer (Al-Wabel *et al.*, 2011). With agricultural

modernization in developing countries in the mid 1960s, the global pesticide industry witnessed a tremendous growth (Binswanger *et al.*, 1998). The increasing concern over pesticides in surface and groundwater has required evaluation of their mobility as a basis of risk assessment (Abdel-Nasser *et al.*, 2011). Detection of pesticide compounds in inland waterways (Leong *et al.*, 2007) and natural waters (Somchit *et al.*, 2009) have been reported. Classification of pesticides is broadly based on their structure with the dominant ones including organochlorines, organophosphates, pyrethroids and carbamates (Al-Masri *et al.*, 2009). Chlorpyrifos (CPF) is a broad-spectrum organophosphate insecticide for use in plant protection and belongs to class II of World Health Organization classification of pesticides (Cox, 1997). It is moderately toxic and prolonged exposure to CPF has been reported to cause anemia although the mechanism has not been elucidated (Ambali *et al.*, 2010). Cypermethrin (CPT) is of the family of pyrethroid and belongs to class II. Pyrethroid pesticides were developed as a synthetic version of the naturally occurring pesticide pyrethrin. They have been modified to increase their stability in the environment (Eneh, 2011). Chlorothalonil (CTN) (a fungicide) belongs to class IV. Degradation/removal of CPF, CPT and CTN in natural water and wastewater has been reported. CPF was degraded by soil microbial action (Hua *et al.*, 2009), CPF and CTN were removed from simulated storm water runoff in constructed wetland (Sherrarda *et al.*, 2004) and CTN was degraded by *Bacillus cereus* (Zhang *et al.*, 2007). Anodic oxidation at lead dioxide or boron-doped diamond electrode was used to degrade CPF (Samet *et al.*, 2010a, b). Another report compared the effectiveness between UV/O₃ Advanced Oxidation Process (AOP) and Poly Aluminium Chloride (PACl) as a coagulant for the removal of chlorpyrifos, diazinon and carbaryl from drinking water (Samadi *et al.*, 2011). CTN was degraded by bimetallic iron based systems and pulsed electric field (Ghauch and Tuqan, 2008; Chen *et al.*, 2009) and CPT alone was degraded by microwave irradiated photo-Fenton reaction (Gromboni *et al.*, 2007). However, from an economic and technical point of view, the use of electrodes is not ideal, especially when oxidizing organic waste where fouling of the electrode can occur (Brillas *et al.*, 2009). The use of oxidative processes for pesticide degradation in natural, wastewater and residual waters has been reported by De Laat *et al.* (1999). Research has demonstrated that effects of combined pesticides should be taken into account to assess the actual impact of their application and degradation feasibility (Xiaoqiang *et al.*, 2008). This is because some pesticides naturally have little or no toxicity but chemicals they degenerate into during fermentation are highly toxic and dangerous (Gareth *et al.*, 2006). Typical pesticide wastewater characteristics collected from a pesticide company in China were COD 22,000±1000 mg L⁻¹, pH 13-14, BOD₅ 650 mg L⁻¹ and BOD₅/COD ratio 0.03 (Zhenglong *et al.*, 2011). Another pesticide wastewater taken from the production process in China had a COD value of 3242 mg L⁻¹ and pH 6 (Rongxi *et al.*, 2009).

Advanced Oxidation Processes (AOPs) are highly effective for degradation/removal of majority of water pollutants (Pera-Titus, 2004). Oxidation with Fenton's reagent is based on ferrous ions, hydrogen peroxide and hydroxyl radicals produced by the catalytic decomposition of hydrogen peroxide in acidic solution (Chamarro *et al.*, 2001). Fenton's reagent has been reported to be effective in the treatment of recalcitrant wastewater (Lodha and Chaudhari, 2007; Gulkaya *et al.*, 2006; Lin and Jiang, 2003) and degradation/removal of single pesticide in aqueous solution (Rongxi *et al.*, 2009; Tamimi *et al.*, 2008; Badawy *et al.*, 2006). The purpose of this study was to examine the effect of operating conditions (H₂O₂/COD molar ratio, H₂O₂/Fe²⁺ molar ratio, pH, temperature and reaction time) of the Fenton process on degradation, biodegradability improvement (BOD₅/COD ratio) and mineralization of a combined chlorpyrifos (CPF), cypermethrin

(CPT) and chlorothalonil (CTN) pesticides in aqueous solution. High Performance Liquid Chromatography (HPLC) and Fourier Transform Infrared (FTIR) spectroscopy were also used to estimate pesticide concentration and degradation of organic bonds after treatment.

MATERIALS AND METHODS

Reagents: Hydrogen peroxide (30%, w/w) and ferrous sulphate heptahydrate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) were purchased from R and M Marketing, Essex, U.K. Analytical grade of and chlorpyrifos (CPF) was obtained from Dr. Ehrenstorfer, Germany and cypermethrin (CPT) and chlorothalonil (CTN) 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. Figure 1 shows the chemical structure of the pesticides.

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 (3.0×250 mm, 5 μm). The column temperature was set at 30°C. Mobile phase was made up of 25% buffer solution (0.001 M KH_2PO_4 in double distilled water) and 75% acetonitrile. Chemical Oxygen Demand (COD) was measured according to the standard methods (APHA *et al.*, 2005). Where the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 so as to decompose hydrogen peroxide to oxygen and water (Talinli and Anderson, 1992; Kang *et al.*, 1999). TOC analyzer (Model 1010, O and 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,

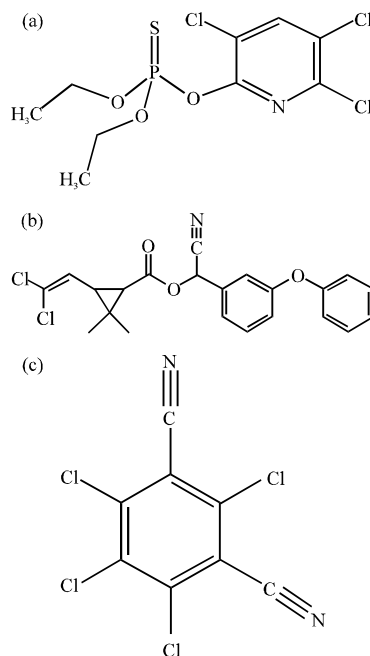


Fig. 1(a-c): Chemical structure of (a) Chlorpyrifos, (b) Cypermethrin and (c) Chlorothalonil

USA). Biodegradability was measured by 5-day biochemical oxygen demand (BOD₅) test according to the standard methods. DO was measured using YSI 5000 dissolved oxygen meter. The seed for BOD₅ test was obtained from a municipal wastewater treatment plant. Fourier Transform Infrared (FTIR) spectrum was obtained using FTIR-8400S, SHIMADZU.

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 1130 mg L⁻¹.

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 (FeSO₄·7H₂O) was added to the aqueous solution with pH adjustment to the required value using sulfuric acid (H₂SO₄) and mixed by a magnetic stirrer to ensure complete homogeneity. Thereafter, the necessary amount of H₂O₂ was added to the pesticide aqueous solution. Samples were taken at pre-selected time intervals using a syringe. The 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.

RESULTS AND DISCUSSION

Effect of H₂O₂/COD molar ratio: In determining the optimal H₂O₂/COD molar ratio, initial H₂O₂ concentration was varied in the range 35.31-141.25 mM at initial COD 1130 mg L⁻¹ (35.31 mM). The corresponding H₂O₂/COD molar ratios were 1, 1.5, 2, 2.5, 3, 3.5 and 4. The other operating conditions were pH 3 and H₂O₂/Fe²⁺ molar ratio 50. Figure 2a-c show the effect of H₂O₂/COD molar ratio on pesticide degradation in terms of COD and TOC removal and BOD₅/COD ratio. The COD removal after 60 min reaction time was 28.91, 30.26, 37.31, 46.88, 50.23, 42.26 and 37.88% at H₂O₂/COD molar ratio 1, 1.5, 2, 2.5, 3, 3.5 and 4, respectively. The TOC removal after 60 min reaction time was 17.85, 27.54, 29.73, 34.40, 40.26, 32.03 and 30.09% at H₂O₂/COD molar ratio 1, 1.5, 2.0, 2.5, 3, 3.5 and 4, respectively. The BOD₅/COD ratio after 60 min reaction time was 0.17, 0.21, 0.26, 0.31, 0.33, 0.17 and 0.14 at H₂O₂/COD molar ratio 1, 1.5, 2, 2.5, 3, 3.5 and 4, respectively. The results indicate that the pesticide degradation increased by increasing the concentration of H₂O₂ but above H₂O₂/COD molar ratio 3, the degradation did not improve. This may be due to auto-decomposition of H₂O₂ to oxygen and water and the recombination of hydroxyl radicals (OH•) radicals as in reactions 1 and 2 (Badawy *et al.*, 2006). Moreover, excess H₂O₂ reacts with ferric ions to form hydroperoxyl radical as in reaction 3 (Kavitha and Palanivelu, 2005). Maximum COD and TOC removal and biodegradability (BOD₅/COD ratio) improvement was achieved at H₂O₂/COD molar ratio 3:



The results agree with the reported results-the optimum H₂O₂/COD molar ratio was 4.4 for (Fenitrothion, diazinon and profenofos) insecticide aqueous solution and wastewater (Badawy *et al.*, 2006) and 6.5 for palm oil mill effluent (Sinnaraprasat and Fongsatitkul, 2011).

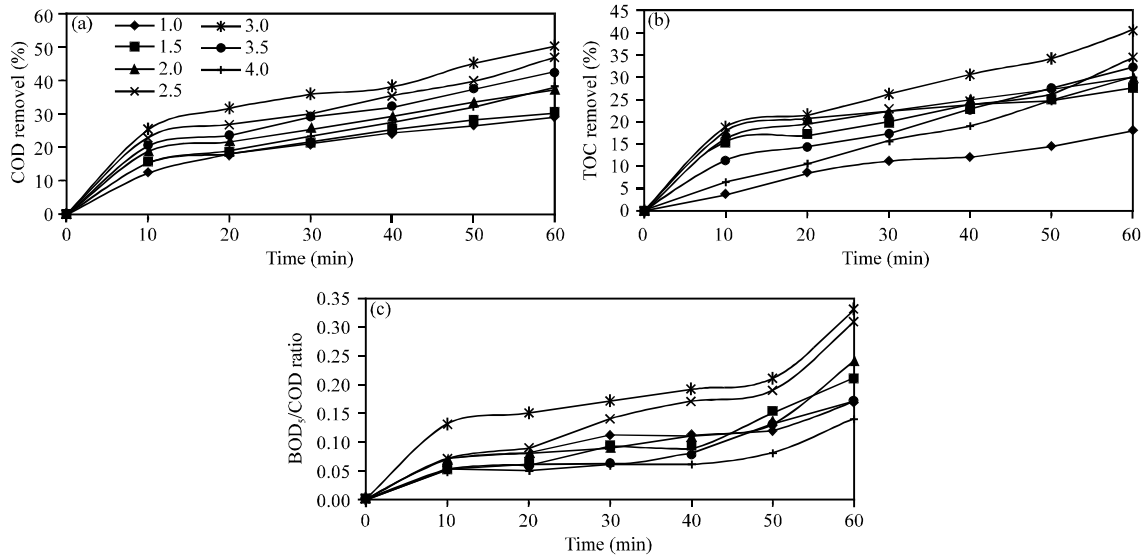


Fig. 2(a-c): Effect of H_2O_2 /COD molar ratio on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD_5 /COD ratio

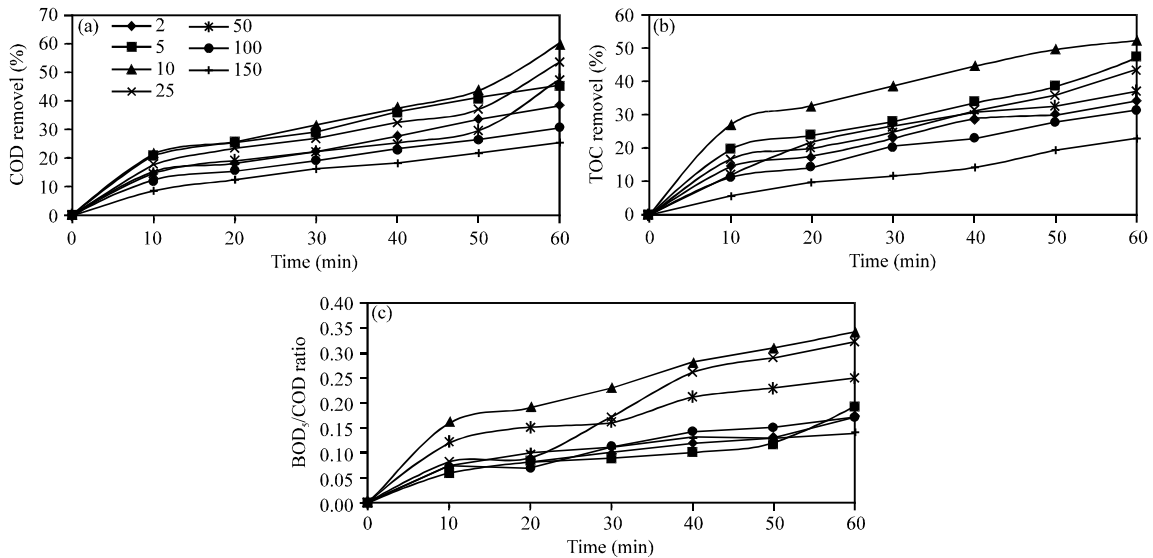


Fig. 3(a-c): Effect of H_2O_2 /COD molar ratio on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD_5 /COD ratio

Effect of H_2O_2/Fe^{2+} molar ratio: To study the effect of increasing ferrous ion concentration (decreasing H_2O_2/Fe^{2+} molar ratio) and to obtain the optimum H_2O_2/Fe^{2+} molar ratio for degradation of the pesticides in aqueous solution, Fe^{2+} concentration was varied from 0.94 to 70.62 mM under operating conditions of pH 3, H_2O_2 /COD molar ratio 3 and initial COD 1130 mg L⁻¹. The results shown in Fig. 3a-c indicate that COD and TOC removal efficiency and BOD_5 /COD ratio improvement increased with increasing Fe^{2+} concentration. The COD removal after 60 min reaction time was 38.12, 45.06, 60.16, 53.32, 47.11, 30.44 and 25.31% at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 25,

50, 100 and 150, respectively. The TOC removal after 60 min reaction time was 34.31, 47.12, 52.59, 43.66, 37.18, 31.35 and 23.02% at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 25, 50, 100 and 150, respectively. The BOD_5/COD ratio after 60 min reaction time was 0.17, 0.19, 0.32, 0.36, 0.25, 0.17 and 0.14 at H_2O_2/Fe^{2+} molar ratio 2, 5, 10, 25, 50, 100 and 150, respectively. The degradation did not improve with decreasing H_2O_2/Fe^{2+} molar ratio below 10. Presumably, this resulted from direct reaction of OH^\bullet radical with metal ions at high concentration of Fe^{2+} (Joseph *et al.*, 2000) as in reaction 4. The H_2O_2/Fe^{2+} molar ratio 10 was optimum for degradation of the pesticides in aqueous solution:



The results agree well with the reported results for different pollutants-the optimum H_2O_2/Fe^{2+} molar ratio was 10 and 40 for degradation of chlorophenol and chlorinated aliphatics (Pera-Titus *et al.*, 2004; Tang and Huang, 1997), 6.5 for cresols destruction (Kavitha and Palanivelu, 2005), 5-40 for degradation of aromatic amines (Casero *et al.*, 1997), 1.9-3.7 for degradation of trihalomethanes (Tang and Tassos, 1997) and 2.5 for landfill leachate treatment (Tengrui *et al.*, 2007). In the present of study COD and TOC degradation and BOD_5/COD ratio improvement for low H_2O_2/Fe^{2+} molar ratio is higher than that for high H_2O_2/Fe^{2+} molar ratio. This may be explained by taking into consideration the intermediates formed during reaction. Lower H_2O_2/Fe^{2+} molar ratio (higher Fe^{2+} concentration) causes a high removal of the target compound and formation of early intermediates (Pera-Titus *et al.*, 2004; Gonzalez *et al.*, 2007).

Effect of pH: The pH value has a decisive effect on the generation of OH^\bullet radicals and hence the oxidation (degradation) efficiency. It is known that OH^\bullet radical generation occurs in acidic condition. To determine 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 3, H_2O_2/Fe^{2+} molar ratio 10 and initial COD 1130 mg L^{-1} . Figure 4a-c show the effect of pH on pesticide degradation in terms of COD and TOC removal and BOD_5/COD ratio. The COD removal after 60 min reaction time was

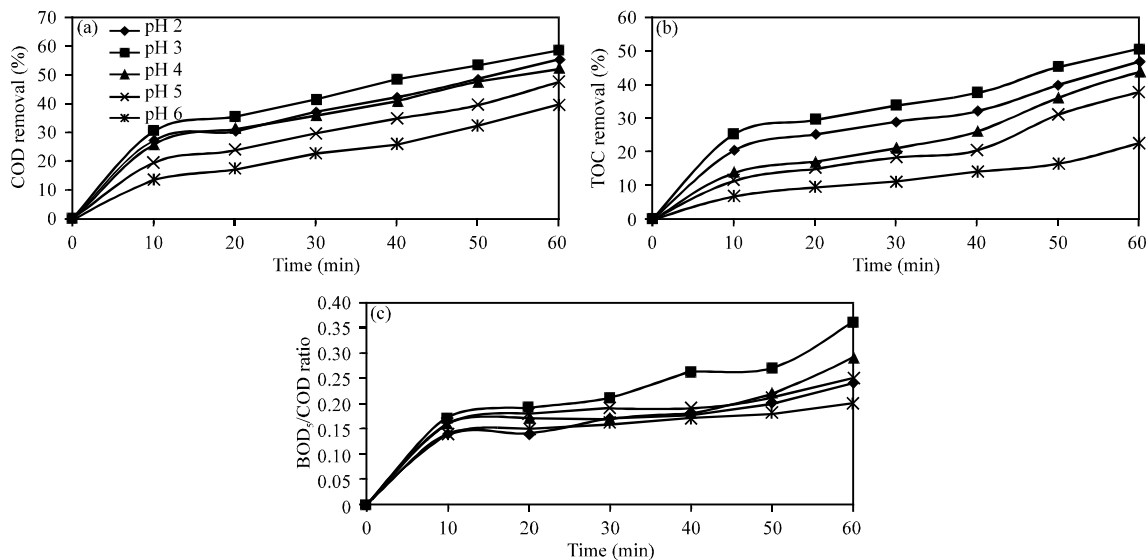


Fig. 4(a-c): Effect of pH on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD_5/COD ratio

55.17, 58.48, 52.33, 47.67 and 39.15% at pH 2, 3, 4, 5 and 6, respectively. The TOC removal after 60 min reaction time was 46.86, 50.34, 43.72, 37.55 and 22.41% at pH 2, 3, 4, 5 and 6, respectively. BOD₅/COD ratio after 60 min reaction time was 0.24, 0.36, 0.29, 0.25 and 0.20 at pH 2, 3, 4, 5 and 6, respectively. Therefore, pH is an important parameter in Fenton process and studies have shown that acidic pH levels near 3 are usually optimum for Fenton oxidation (Arnold *et al.*, 1995; Pignatello *et al.*, 1992). Based on the results, the optimum pH for degradation of the pesticides in aqueous solution was 3.0.

Effect of temperature: To study the effect of temperature, experiments were performed at 10, 20, 30 and 40°C. Initial COD was maintained at 1130 mg L⁻¹. The other operating conditions were H₂O₂/COD molar ratio 3, H₂O₂/Fe²⁺ molar ratio 10 and pH 3. Figure 5a-c shows the results of pesticide degradation at different temperature in terms of COD and TOC removal and BOD₅/COD ratio. After 60 min reaction time COD removal was 28.39, 50.93, 59.02 and 69.03%, TOC removal was 15.95, 48.73, 52.33 and 55.61% and BOD₅/COD ratio was 0.08, 0.17, 0.32 and 0.35 at temperature 10, 20, 30 and 40°C, respectively. This is because the number of molecular collisions and reactivity increase as a function of temperature according to the kinetic theory (Loftin *et al.*, 2008). At 10°C there was obvious reduction in degradation because of slow reaction rate between OH• radical and the organic structure of the substrate (Kavitha and Palanivelu, 2005). The results agree well with the findings of Kandil *et al.* (2011) in their investigation of chlorfenapyr degradation.

Degradation of pesticides in aqueous solution under the optimum operating conditions:

Figure 6 shows the degradation of the pesticides CPF, CPT and CTN in aqueous solution under the optimum operating conditions (H₂O₂/COD molar ratio 3, H₂O₂/Fe²⁺ molar ratio 10, pH 3 and temperature 40°C). Complete degradation of the pesticides occurred in 1 min. Maximum COD and TOC removal were 69.03 and 55.61%, respectively. The corresponding BOD₅/COD ratio was 0.35 after 60 min reaction time (Fig. 7) which is considered adequate for biological treatment as a wastewater is considered biodegradable if BOD₅/COD ratio is ~0.4 (Al-Momani *et al.*, 2002). In

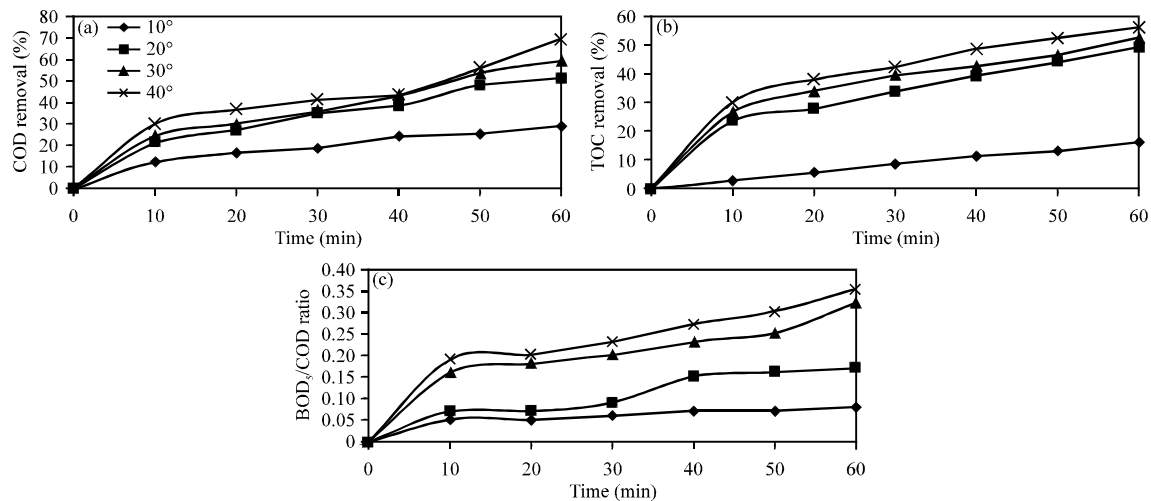


Fig. 5(a-c): Effect of temperature on pesticide degradation in terms of (a) COD removal, (b) TOC removal and (c) BOD₅/COD ratio

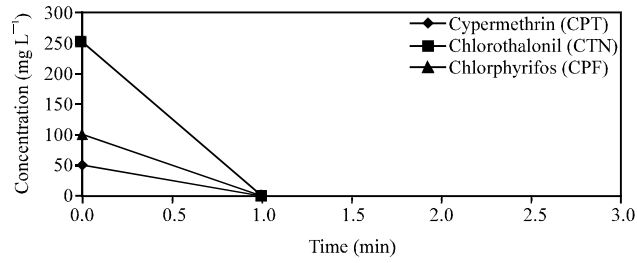


Fig. 6: Degradation of CPT, CTN and CPF pesticide under optimum operating conditions

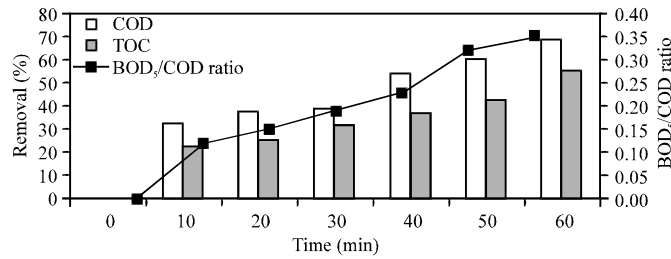


Fig. 7: Pesticide degradation under optimum operating conditions in terms of COD and TOC removal and BOD₅/COD ratio

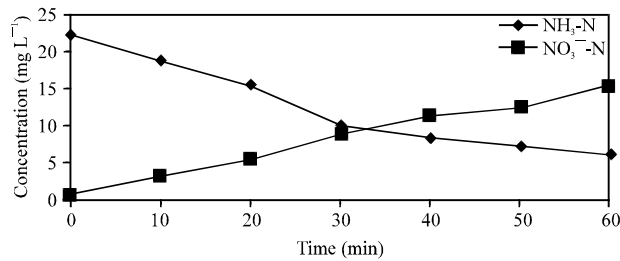


Fig. 8: Mineralization of pesticide in terms of NH₃-N and NO₃⁻-N concentration

terms of mineralization of organic carbon, concentration of ammonia-nitrogen (NH₃-N) decreased from 22 to 6.1 mg L⁻¹ and nitrate (NO₃⁻-N) increased from 0.7 to 15.2 mg L⁻¹ in 60 min (Fig. 8).

FTIR spectra: Untreated and Fenton treated pesticide aqueous solution was 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 is observed in the range of 1548 and 1265 cm⁻¹ (Dhas *et al.*, 2010). 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, CH₂ deformation in R-CH₂-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 (Armenta *et al.*, 2005). In the present study, the band at 1650.95 cm⁻¹ in the untreated aqueous solution in Fig. 9a shifted to 1622.02 cm⁻¹ in the treated aqueous solution in Fig. 9b and the band at 1448.44 cm⁻¹ in Fig. 9a was modified as seen in Fig. 9b, indicating degradation of the pesticides.

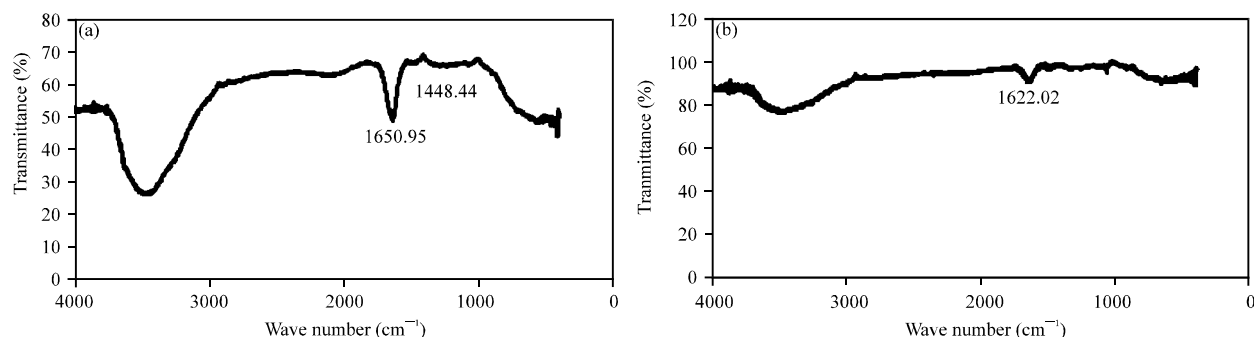


Fig. 9(a-b): FTIR spectra of (a) Untreated and (b) Treated pesticide aqueous solution

It can be deduced that, a reduction or an increase of H_2O_2 and Fe^{2+} above a certain dose led to a decrease in degradation of the selected combined pesticides. Therefore, initial pH 3, $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 3, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 10 reagent additions yielded highest oxidation and coagulation of the Fenton process.

CONCLUSIONS

Fenton process is effective in the treatment of an aqueous solution of chlorpyrifos, cypermethrin and chlorothalonil. Under the optimum operating conditions, complete degradation of the pesticides occurred in 1 min. Biodegradability increased from zero to 0.35 in 60 min and COD and TOC removal were 69.03 and 55.61%, respectively. Mineralization of organic carbon led to ammonia-nitrogen decrease from 22 to 6.1 mg L^{-1} and increase in nitrate from 0.7 to 15.2 mg L^{-1} . Fenton process can be used for pretreatment of combined chlorpyrifos, cypermethrin and chlorothalonil aqueous solution or wastewater for further biological treatment. Based on the results, oxidation and coagulation in Fenton treatment of the chosen pesticide under the above mentioned operating conditions is feasible in removal of COD being one of the most important organic compound parameter to monitor in wastewater treatment before discharge.

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REFERENCES

- APHA, AWWA and WPCF, 2005. Standard Methods for the Examination of Water and Wastewater. 21st Edn., American Public Health Association, Washington, DC., USA.
- Abdel-Nasser, G., A.M. Al-Turki, M.I. Al-Wabel and M.H. El-Saeid, 2011. Behavior of atrazine and malathion pesticides in soil: Simulation of transport process using numerical and analytical models. *Res. J. Environ. Sci.*, 5: 221-235.
- Al-Masri M.G., M. Rasheed and M. Alawi, 2009. Degradation of organochlorine pesticides in carbonate sediments from Aqaba Gulf, Red Sea. *Res. J. Environ. Toxicol.*, 3: 147-158.
- Al-Momani, F., Touraud, J.R. Degorce-Dumas, J. Roussy and O. Thomas, 2002. Biodegradability enhancement of textile dyes and textile wastewater by UV photocatalysis. *J. Photochem. Photobiol. Chem.*, 153: 191-197.
- Al-Wabel, M.I., M.H. El-Saeid, A.M. Al-Turki and G. Abdel-Nasser, 2011. Monitoring of pesticide residues in Saudi Arabia agricultural soils. *Res. J. Environ. Sci.*, 5: 269-278.

- Ambali, S.F., A.T. Abubakar, M. Shittu, L.S. Yaqub, S.B. Anafi and A. Abdullahi, 2010. Chlorpyrifos-induced alteration of hematological parameters in Wistar rats: Ameliorative effect of zinc. *Res. J. Environ. Toxicol.*, 4: 55-66.
- Armenta, S., G. Quintas, S. Garrigues and M. de la Guardia, 2005. A validated and fast procedure for FTIR determination of Cypermethrin and Chlorpyrifos. *Talanta*, 67: 634-639.
- Arnold, S.M., W.J. Hickey and R.F. Harris, 1995. Degradation of atrazine by Fentons reagent: Condition optimization and product quantification. *Environ. Sci. Technol.*, 29: 2083-2089.
- Badawy, M.I., M.Y. Ghaly and T.A. Gad-Allah, 2006. Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater. *Desalination*, 194: 166-175.
- Bhattacharyya, S. and D.K. Bhattacharya, 2006. Pest control through viral disease: Mathematical modeling and analysis. *J. Theor. Biol.*, 238: 177-197.
- Binswanger, H., P. Hazell and A. McCalla, 1998. Agriculture and the environment: Perspectives on sustainable rural development. International Bank for Reconstruction and Development, World Bank, Washington DC.
- Brillas, E., I. Sires and M.A. Oturan, 2009. Electro-Fenton process and related electrochemical technologies based on Fenton's reaction chemistry. *Chemical Rev.*, 109: 6570-6631.
- Casero, I., D. Sicilia, S. Rubio and D.F. Bendito, 1997. Chemical degradation of aromatic amines by Fenton reagent. *Water Res.*, 31: 1985-1995.
- Chamarro, E., A. Marco and S. Esplugas, 2001. Use of Fenton reagent to improve organic chemical biodegradability. *Water Res.*, 35: 1047-1051.
- Chen, F., L. Zeng, Y. Zhang, X. Liao, Y. Ge, X. Hua and L. Jiang, 2009. Degradation behaviour of methamidophos and chlorpyrifos in apple juice treated with pulsed electric fields. *Food Chem.*, 112: 956-961.
- Cox, C., 1997. Fungicide fact sheet: Chlorothalonil. *J. Pesticide Reform*, 17: 14-20.
- De Laat, J., H. Gallard, S. Ancelin and B. Legube, 1999. Comparative study of the oxidation of Atrazine and acetone by H_2O_2/UV , $Fe(3)/UV$, $Fe(3)/H_2O_2/UV$ and $Fe(2)$ or $Fe(3)/H_2O_2$. *Chemosphere*, 39: 2693-2706.
- Dhas, D.A., I. H. Joea, S.D.D. Roy and T.H. Freed, 2010. DFT computations and spectroscopic analysis of a pesticide: Chlorothalonil. *Spectrochimica Acta Part A: Mol. Biomol. Spectroscopy Spectrochimica Acta Part A*, 77: 36-44.
- Eneh, O.C., 2011. Enhancing Africas environmental management: Integrated pest management for minimization of agricultural pesticides pollution. *Res. J. Environ. Sci.*, 5: 521-529.
- Foo, K.Y. and B.H. Hameed, 2010. Detoxification of pesticide waste via activated carbon adsorption process: Review. *J. Hazardous Mater.*, 175: 1-11.
- Gareth, O.T., M. Wilkinson, S. Hodson and K.C. Jones, 2006. Organohalogen chemicals in human blood from the United Kingdom. *Environ. Pollution*, 141: 30-41.
- Gentz, M.C., 2009. A review of chemical control options for invasive social insects in island ecosystems. *J. Applied Entomol.*, 133: 229-235.
- Ghauch, A. and A. Tuqan, 2008. Catalytic degradation of chlorothalonil in water using bimetallic iron-based systems. *Chemosphere*, 73: 751-759.
- Gonzalez, O., C. Sans and S. Esplugas, 2007. Sulfamethoxazole abatement by photo-Fenton: Toxicity, inhibition and biodegradability assessment of intermediates. *J. Hazardous Mater.*, 146: 459-464.
- Gromboni, C.F., M.Y. Kamogawa, A.G. Ferreira, J.A. Nobrega and A.R.A. Nogueira, 2007. Microwave-assisted photo-Fenton decomposition of chlorfenvinphos and cypermethrin in residual water. *J. Photochem. Photobiol. A: Chemistry*, 185: 32-37.

- Gulkaya, I., G.A. Surucu and F.B. Dilek, 2006. Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater. *J. Hazardous Mater.*, 136: 763-769.
- Hua, F, Y. Yunlong, C. Xiaoqiang, W. Xiuguo, Y. Xiaoe and Y. Jingquan, 2009. Degradation of chlorpyrifos in laboratory soil and its impact on soil microbial functional diversity. *J. Environ. Sci.*, 21: 380-386.
- Joseph, J.M., H. Destailats, H.M. Hung and M.R. Hoffmann, 2000. The sonochemical degradation of azobenzene and related azo dyes: Rate enhancements via Fenton's reactions. *J. Phys. Chem. A*, 104: 301-307.
- Kandil, M.A., E.S. Swelam, M.M. Abu-Zahw and M.A. Shalby, 2011. Effect of light and temperature on chlorfenapyr and identification of its main degradation products. *Res. J. Environ. Toxicol.*, 5: 316-322.
- Kang, Y.W., M.J. Cho and K.Y. Hwang, 1999. Correction of hydrogen peroxide interference on standard chemical oxygen demand test. *Water Res.*, 33: 1247-1251.
- Kavitha, V. and K. Palanivelu, 2005. Destruction of cresols by Fenton oxidation process. *Water Res.*, 39: 3062-3072.
- Leong, K.H., L.L. Benjamin Tan and A.M. Mustafa, 2007. Contamination levels of selected organochlorine and organophosphate pesticides in the Selangor River, Malaysia between 2002 and 2003. *Chemosphere*, 66: 1153-1159.
- Lin, S.H. and C.D. Jiang, 2003. Fenton oxidation and Sequencing Batch Reactor (SBR) treatments of high strength semiconductor wastewater. *Desalination*, 154: 107-116.
- Lodha, B. and S. Chaudhari, 2007. Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions. *J. Hazard. Mater.*, 148: 459-466.
- Loftin, K.A., C.D. Adams, M.T. Meyer and R. Surampalli, 2008. Effects of ionic strength, temperature and pH on degradation of selected antibiotics. *J. Environ. Qual.*, 37: 378-386.
- Pera-Titus, M., V. Garcia-Molina, M.A. Banos, J. Gimenez, and S. Esplugas, 2004. Degradation of Chlorophenols by means of advanced oxidation processes: a general review. *Applied Catalysis B Environ.*, 47: 219-256.
- Pignatello, J.J., 1992. Dark and photo-assisted Fe^{3+} catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environ. Sci. Technol.*, 26: 944-951.
- Reichenberger, S, M. Bach, A. Skitschak and H.G. Frede, 2007. Mitigation strategies to reduce pesticide inputs into ground and surface water and their effectiveness: A review. *Sci. Total Environ.*, 384: 1-35.
- Rongxi, L., Y. Chunping, C. Hong, Z. Guangming, Y. Guanlong and G. Junyuan, 2009. Removal of triazophos pesticide from wastewater with Fenton reagent. *J. Hazardous Mater.*, 167: 1028-1032.
- Samadi, M.T., M. Khodadai and A.R. Rahmani, 2011. The comparison of advanced oxidation process and chemical coagulation for the removal of residual pesticides from water. *Res. J. Environ. Sci.*, 5: 817-826.
- Samet, Y., L. Agengui and R. Abdelhedi, 2010a. Anodic oxidation of chlorpyrifos in aqueous solution at lead dioxide electrodes. *J. Electroanalytical Chem.*, 650: 152-158.
- Samet, Y., L. Agengui and R. Abdelhedi, 2010b. Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes. *Chem. Eng. J.*, 161: 167-172.
- Sharbidre, A.A., V. Metkari and P. Patode, 2011. Effect of diazinon on acetylcholinesterase activity and lipid peroxidation of *Poecilia reticulata*. *Res. J. Environ. Toxicol.*, 5: 152-161.

- Sherrarda, R.M, J.S. Bearrb, C.L. Murray-Guldec, J.H. Rodgers Jr. and Y.T. Shahd, 2004. Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures. *Environ. Pollution*, 127: 385-394.
- Sinnaraprasat S. and P. Fongsatitkul, 2011. Optimal condition of Fenton`s reagent to enhance the alcohol production from palm oil mill effluent (POME). *Int. J. Thai Soc. Higher Edu. Inst. Environ.*, 4: 9-16.
- Somchit, N., M.N. Somchit, S.A. Hadi and M.P. Zakaria, 2009. Persistent organic chemicals in Malaysian waters a review. *Res. J. Environ. Toxicol.*, 3: 101-112.
- Talinli, I. and G.K. Anderson, 1992. Interference of hydrogen peroxide on the standard COD test. *Water Res.*, 26: 107-110.
- Tamimi, M., S. Qourzal, N. Barka, A. Assabbane and Y. Ait-Ichou, 2008. Methomyl degradation in aqueous solutions by Fenton`s reagent and the photo-Fenton system. *Separation Purif. Technol.*, 61: 103-108.
- Tang, W. and S. Tassos, 1997. Oxidation kinetics and mechanisms of trihalomethanes by fentones reagent. *War. Res.*, 31: 1117-1125.
- Tang, W.Z. and P. Huang, 1997. Stoichiometry of Fenton`s reagent in the oxidation of chlorinated aliphatic pollutants. *Environ. Technol.*, 18: 13-23.
- Tariq, M.I., S. Afzal and I. Hussain, 2006. Degradation and persistence of cotton pesticides in sandy loam soils from Punjab. *Pak. Environ. Res.*, 100: 184-196.
- Tengrui, L., A. Al-Harbawi, Z. Jun and L.M. Bo, 2007. The effect and its influence factors of the fenton process on the old landfill leachate. *J. Applied Sci.*, 7: 724-727.
- Xiaoqiang, C., F. Hua, P. Xuedong, W. Xiao, S. Min, F. Bo and Y. Yunlong, 2008. Degradation of chlorpyrifos alone and in combination with chlorothalonil and their effects on soil microbial populations. *J. Environ. Sci.*, 20: 464-469.
- Zhang, Y., J. Lu, L. Wu, A. Chang and W.T. Frankenberger Jr., 2007. Simultaneous removal of chlorothalonil and nitrate by *Bacillus cereus* strain NS1. *Sci. Total Environ.*, 382: 383-387.
- Zhenglong, X., C. Xiang and S. Dezhi, 2011. Pretreatment of heterocyclic pesticide wastewater using ultrasonic/ozone combined process. *J. Environ. Sci.*, 23: 725-730.