Desalination and Water Treatment
www.deswater.com

doi: 10.1080/19443994.2014.1001441

57 (2016) 5146–5154
March

Taylor & Francis
Taylor & Francis Group

Degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution by FeGAC/H_2O_2 process

Augustine Chioma Affam[a,b,*], Malay Chaudhuri[a], Shamsul Rahman M. Kutty[a], Khalida Muda[b]

[a]*Department of Civil Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia, Tel. +6 010 3849 701; emails: acaffam@utm.my, affamskii@yahoo.com (A.C. Affam), Tel. +6 012 5103 547; email: malaychaudhuri@yahoo.com (M. Chaudhuri), Tel. +6017 5724 633; email: shamsulrahman@petronas.com.my (S.R.M. Kutty)*
[b]*Faculty of Civil Engineering, Universiti Teknologi Malaysia, 81310 Skudai, Johor, Malaysia, Tel. +6 013 7774 774; email: khalida@utm.my (K. Muda)*

Received 23 April 2014; Accepted 17 December 2014

ABSTRACT

This study examined the degradation of pesticide aqueous solution containing chlorpyrifos, cypermethrin and chlorothalonil by the FeGAC/H_2O_2 process. Under the operating conditions (FeGAC 5 g/L, H_2O_2 concentration 100 mg/L and pH 3), chemical oxygen demand (COD) and total organic carbon removal were 96.2 and 79.2%, respectively, and biodegradability (BOD_5/COD ratio) increased from 0 to 0.40 after 60 min reaction. Complete degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides active ingredients occurred in 1 min. Kinetic models such as pseudo-first-order, pseudo-second-order and intraparticle diffusion were evaluated. The Fourier transform infrared spectra (treated and untreated pesticide aqueous solutions) also indicated modification and/or degradation of the pesticide organic bonds. The study showed that FeGAC/H_2O_2 process can be used for the pretreatment of pesticide aqueous solution containing chlorpyrifos, cypermethrin and chlorothalonil before further treatment by biological process.

Keywords: Pesticide; Aqueous solution; Degradation; FeGAC/H_2O_2 process; Kinetics

---

1. Introduction

The presence of highly recalcitrant organic contaminants in the hydrosphere due to industrial and intensive agricultural activity is of particular concern for the freshwater, coastal and marine environment. It is, therefore, important to develop and promote low-cost and/or easy-to-handle treatment processes that will assist in degradation of these contaminants [1]. Wastewater from agricultural pesticide manufacturing plants, rinsing and washing of pesticide spray equipment are major sources of pesticides in surface water. The pesticide concentrations from these sources are reported to be as high as 500 mg/L [2]. Removal of pesticide by conventional wastewater treatment plant especially at low pesticide concentration (sub-ppb to ppb level) is a serious concern [2,3].

Advanced oxidation process (AOP) produces hydroxyl radicals ($OH^•$) which oxidizes organic contaminants in water/wastewater under mild experimental condition [4]. Oxidation with Fenton's reagent is based on the reaction between ferrous ions and

---

*Corresponding author.

hydrogen peroxide (H_2O_2) which produces $OH^•$ for the degradation of contaminants in wastewater [5]. Fenton's reagent has been reported to be effective in the treatment of recalcitrant wastewater [6–11].

When ferrous/ferric ions and H_2O_2 are used to generate $OH^•$, production of iron sludge is inevitable. This may cause additional cost in terms of handling and disposal of the sludge produced. To circumvent this problem in homogeneous Fenton process and to comply with environmental regulations [12], alternative oxidation processes were required. Thus, a modified Fenton process—Fe-granular-activated carbon/hydrogen peroxide (FeGAC/H_2O_2) process has been proposed [13]. FeGAC has both catalytic and adsorption properties due to GAC surface and the coating of iron oxides. Also, the oxidation strength of the process is enhanced by the addition of H_2O_2. The application of FeGAC/H_2O_2 process for decolourization of Acid Black 24 at pH 2 was 76% [13], the removal of humic substances (humic and fulvic acids) in municipal landfill leachate at pH 6 was 70% [14] and the degradation of crystal violet at pH 3 was 71% [15]. The following reaction mechanism has been suggested for the FeGAC/H_2O_2 process (Eqs. (1)–(7)) [16].

$$AC + Fe^{3-+} \rightarrow AC^{+} + Fe^{2+} \tag{1}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2^{•} + H^{+} \tag{2}$$

$$AC^{+} + H_2O_2 \rightarrow AC + HOO^{•} + H^{+} \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^{•} + OH^{-} \tag{4}$$

$$Fe^{2+} + OH^{•} \rightarrow Fe^{3+} + OH^{-} \tag{5}$$

$$H_2O_2 + OH^{•} \rightarrow HOO^{•} + H_2O \tag{6}$$

$$HOO^{•} + OH^{•} \rightarrow H_2O + O_2 \tag{7}$$

The characteristics of activated carbon (AC) which makes it a very resourceful material have been described elsewhere [16,17]. AC as an electron donor reduces the ferric ion to ferrous ion in Eq. (1). The competing reaction during the formation of ferrous ion is shown in Eqs. (1) and (2), and its consumption is seen in Eqs. (4) and (5). The production of hydroxyl radical ($OH^•$) is shown in Eqs. (6) and (7). Fenton mechanism and GAC adsorption is basic for the degradation of contaminants in a typical wastewater [12,14].

Chlorothalonil and chlorpyrifos were removed by constructed wetland [18], chlorothalonil was degraded by the use of endemic bacterial strains [19], anodic oxidation at lead dioxide and boron-doped diamond electrodes were used to degrade chlorpyrifos [20,21], chlorothalonil was degraded by catalytic bimetallic-based doped electrode methods [22] and cypermethrin was degraded by microwave irradiated photo-Fenton reaction [23]. There has been no study on degradation of combined chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution by the FeGAC/H_2O_2 process.

In our previous study [24], TiO_2 photocatalytic process required a long duration for almost complete mineralization and degradation of the pesticide active ingredients. In this study, we investigated the operating conditions of FeGAC/H_2O_2 process for degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution. In addition, chemical oxygen demand (COD) and total organic carbon (TOC) removal and biodegradability (BOD_5/COD ratio) improvement were monitored. Fourier transform infrared (FTIR) spectroscopy was used to measure modification and/or degradation of the pesticide organic bonds. Kinetic models including pseudo-first-order, pseudo-second-order and intraparticle diffusion were evaluated. The optimum time required for the pesticide active ingredients to be degraded was also monitored.

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (30%, w/w) and ferric nitrate ($Fe(NO_3)_3·9H_2O$) were purchased from R&M Marketing, Essex, UK. Analytical grade of cypermethrin and chlorothalonil were obtained from Sigma–Aldrich, while chlorpyrifos was obtained from Dr Ehrenstorfer, GmbH (Augsburg, Germany). They were used for analytical determination of pesticide concentrations by HPLC. The pesticides used were obtained from a commercial source.

2.2. Fe-granular-activated carbon (FeGAC)

Granular-activated carbon (GAC) was obtained from the Calgon Corporation, Pittsburgh, PA and ground to a size of 425 μm. FeGAC was prepared by mixing GAC in a solution of $Fe(NO_3)_3·9H_2O$ for 12 h at 50 mg ferric nitrate/g GAC. This was followed by drying at 105℃ for 3 d. The resulting FeGAC was washed several times with distilled water, dried at 105℃ for another 3 d and stored in stopper glass bottle [13].

2.3. Analytical methods

COD was determined according to the standard methods [25]. To reduce interference in COD determination, pH was increased to above 10 so as to decompose hydrogen peroxide to oxygen and water [26,27]. TOC analyser (Model 1010, O&I analytical) was used for determining 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 using five d biochemical oxygen demand (BOD_5) test according to the standard methods [25]. DO was measured using YSI 5000 dissolved oxygen meter. The seed for the BOD_5 test was obtained from a municipal wastewater treatment plant. 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% acentonitrile. Standard chlorpyrifos, cypermethrin and chlorothalonil pesticides were used to prepare stock solutions. About 5 mL of sample (treated/untreated) was placed inside a 50 mL screw top vial, followed by the addition of 5 mL of a premixed solution of 25% buffer solution (0.001 M KH_2PO_4 in double distilled water) and 75% acentonitrile. The sample was mixed gently by hand, vortex mixed for 5 min, then centrifuged at 2,000 rpm for 10 min, and the supernatant was removed and transferred to a 20 mL beaker. Thereafter, an aliquot of the extract was filtered through a 0.20 μm membrane filter and placed in the HPLC vial for measurement of chlorpyrifos, cypermethrin and chlorothalonil pesticides' concentration. The GAC and FeGAC were analysed by the Brunauer, Emmet and Teller (BET) method (Micrometrics ASAP 2010). The morphology of GAC and FeGAC was done by a scanning electron microscope (Leo Model 1430–VP).

2.4. Pesticide aqueous solution

Pesticide aqueous solution was 400 mg/L of the pesticides (100 mg/L of chlorpyrifos, 50 mg/L of cypermethrin and 250 mg/L of chlorothalonil). It was prepared in distilled water weekly and stored in a cold room at 4˚C. The pesticide aqueous solution COD, TOC, NH_3-N and NO_3^--N concentrations were 1,130, 274.4, 22 and 0.7 mg/L, respectively. Biodegradability index (BOD_5/COD ratio) was zero.

2.5. Experimental procedure

Batch FeGAC/H_2O_2 treatment was performed using 250 mL Pyrex flasks with 200 mL of the pesticide aqueous solution. The pH was adjusted as required using 1 M NaOH or 1 M H_2SO_4. Thereafter, FeGAC and H_2O_2 were added and the flask was placed on an orbital shaker. At selected reaction time, the flask was removed from the orbital shaker, and an aliquot of the supernatant was filtered through 0.45 μm membrane filter for the measurement of COD, TOC, BOD_5, and NH_3-N and NO_3^--N concentrations as required. It was also filtered through 0.20 μm membrane filter for HPLC and FTIR measurement.

3. Results and discussion

3.1. SEM of GAC and FeGAC and characteristics of GAC

The SEM morphology at magnification 5.00 K for GAC and FeGAC is shown in Fig. 1. The characteristics of GAC and FeGAC are shown in Table 1.

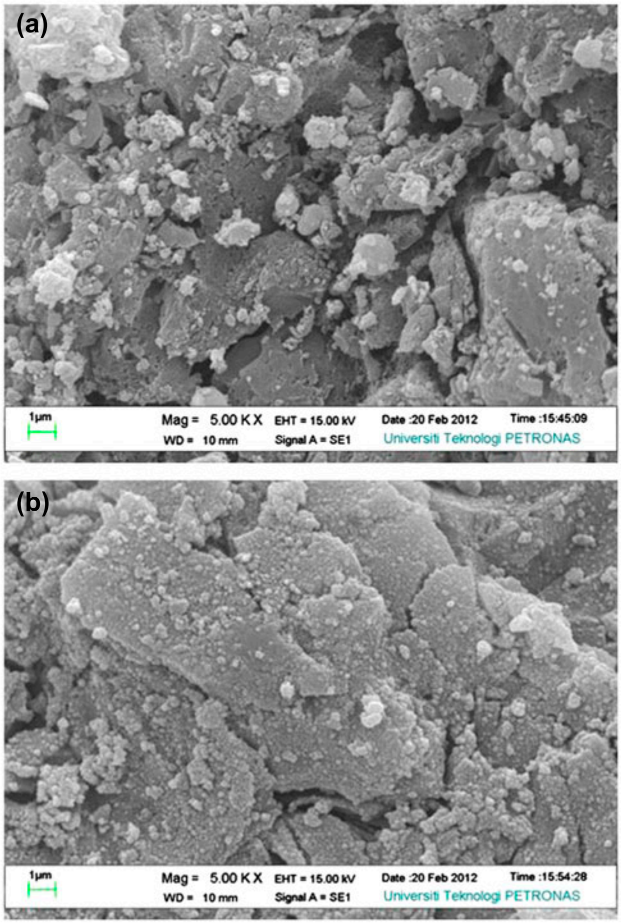

Fig. 1. SEM of (a) GAC and (b) FeGAC.

Table 1
Characteristics of GAC and FeGAC

Parameter	GAC	FeGAC
Surface area (m^2/g)	626	745
Micropore area (m^2/g)	509	729
Micropore volume (mL/g)	0.23	0.20
Average pore diameter (Å)	15.35	23.79
Bulk density (g/mL)	0.52	0.81
Conductivity (μS/cm)	4.00	5.20
pH	5.65	4.80
pH_{ZPC}	6.20	5.60

3.2. *Effect of FeGAC*

The effect of FeGAC concentration on the adsorption of the pesticide aqueous solution was studied. The FeGAC concentration varied from 1 to 5 g/L. COD and TOC removal were 56.9 and 38.2% after 60 min reaction time (Fig. 2). The results indicate that an increase in FeGAC concentration yielded higher removal efficiency. This may be attributed to high granular structure and increase in number of sites available for adsorption of contaminants [16].

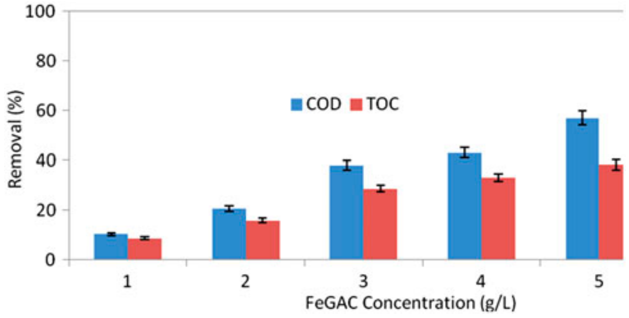

Fig. 2. Effect of FeGAC concentration in terms of COD and TOC removal. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

3.3. *Effect of FeGAC and H_2O_2 addition*

The effect of FeGAC concentration and H_2O_2 addition was studied. In heterogeneous Fenton or Fenton-like processes, the reaction between ferrous/ferric ions and H_2O_2 would occur at the surface of the catalyst and this depends on the specific area of the catalyst [16]. On the other hand, FeGAC has been reported to enhance the oxidation strength of H_2O_2 [13–15]. To study the effect of H_2O_2 addition, the concentration of H_2O_2 varied from 10 to 300 mg/L. The COD and TOC removal efficiency and BOD_5/COD ratio increased with increase in H_2O_2 concentration (Fig. 3). However, above 100 mg/L, there was no significant degradation of the pesticide aqueous solution. The decrease in the process efficiency was probably due to competing reaction of GAC, $OH^\bullet$ and ferrous/ferric ions upon H_2O_2 degradation. In addition, scavenging of $OH^\bullet$ by excess H_2O_2 decreases the efficiency of the process [13]. The COD and TOC removals were 96.2 and 79.2%, respectively, and the biodegradability (BOD_5/COD ratio) was 0.40 after 60-min reaction The BOD_5/COD ratio of 0.40 indicates that the solution is amenable to biological treatment [28].

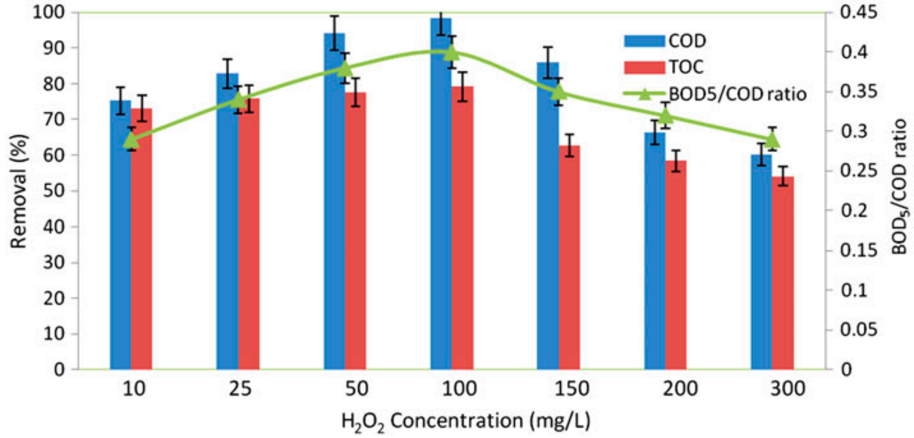

Fig. 3. Effect of FeGAC and H_2O_2 addition in terms of COD and TOC removal and BOD_5/COD ratio after 60 min reaction time. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

3.4. Effect of pH

The pH is an important parameter in heterogeneous Fenton process. Several studies have shown that pH 3 is usually optimum for Fenton and/or heterogeneous Fenton oxidation [23]. The pH of a solution influences adsorption and dissociation of the substrate. Other factors include catalyst surface charge, oxidation potential of the valence band and the physico-chemical properties of the system [11,29,30]. To determine the optimum pH, experiments were conducted by varying the pH in the range 2–8. The effect of pH on COD and TOC removal and BOD_5/COD ratio is shown in Fig. 4. After 60-min reaction time, COD removal was 84.1, 96.2, 87.9, 76.0 and 71.3%; TOC removal was 73.3, 79.2, 75.2, 69.2 and 64.1%; and BOD_5/COD ratio was 0.36, 0.40, 0.38, 0.33 and 0.31 at pH 2, 3, 4, 5, 6 and 8, respectively. The study indicated that pH 3 was optimum for the process.

3.5. Effect of initial pesticide concentration

The effect of initial pesticide concentration on degradation of the pesticide aqueous solution was studied. Pesticide concentration varied from 400 to 1,200 mg/L. After 60-min reaction time, COD removal was 96.2, 93.1 and 90.8%; TOC removal was 79.2, 77.3 and 74.9%; and BOD_5/COD ratio was 0.40, 0.37 and 0.35 at 400, 800 and 1,200 mg/L, respectively (figure not shown). Decrease in the degradation efficiency was observed with increase in the initial pesticide concentration. The presumed reason is that when the initial concentration of the pesticide increased, the $OH^{\bullet}$ concentration remains constant for the pesticide molecules [31]. The efficiency of the FeGAC/H_2O_2 process depends on the formation of $OH^{\bullet}$ and less scavenging of $OH^{\bullet}$ [32]. Therefore, the concentration of FeGAC and H_2O_2 are important factors that should be considered when applying FeGAC/H_2O_2 process to the treatment of different pesticide wastewater COD loadings.

3.6. Degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides

To determine the time required for degradation of the pesticide active ingredients during the treatment process, an aliquot of the solution being treated was withdrawn every 1 min and measured by HPLC. The degradation of chlorpyrifos, cypermethrin and

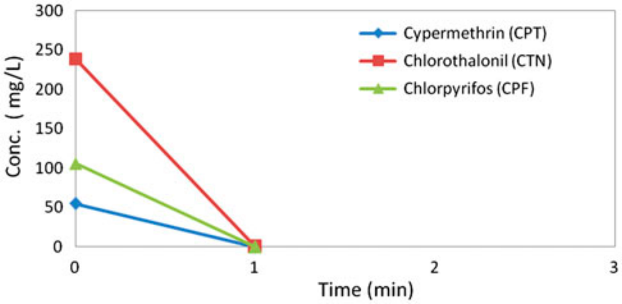

Fig. 5. Degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticides. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

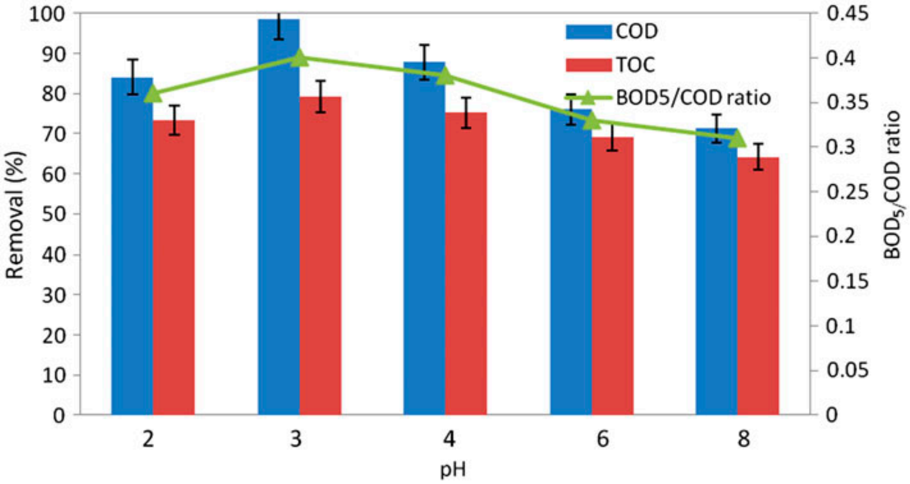

Fig. 4. Effect of pH in terms of COD and TOC removal and BOD_5/COD ratio after 60 min reaction time. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

chlorothalonil pesticide active ingredients under the optimum operating conditions (chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and TOC 274.4 mg/L, FeGAC 5 g/L, H_2O_2 concentration 100 mg/L and pH 3) is shown in Fig. 5. Complete degradation of the pesticide active ingredients occurred in 1 min. This result is similar to our previous finding in classical Fenton process [33].

3.7. Mineralization of degraded pesticides under optimum operating conditions

Under similar conditions as in section 3.6, mineralization of the degraded pesticides intermediates was monitored. Ammonia-nitrogen (NH_3-N) concentration decreased from 22 to 2.1 mg/L and nitrate (NO_3^--N) concentration increased from 0.7 to 21.1 mg/L after 60 min reaction time (Fig. 6(a)). Maximum COD and TOC removals were 96.2 and 79.2%, respectively, and the corresponding BOD_5/COD ratio was 0.40 after 60 min reaction time. Wastewater is considered as biodegradable if BOD_5/COD ratio is 0.40 [28] (Fig. 6(b)).

3.8. FTIR study

The FTIR spectra of the untreated and treated pesticide aqueous solutions are shown in Fig. 7. Cross reactivity or interference from a mixture of pesticides in aqueous solution may lead to disappearance of individual peaks of each compound [34]. The band which occurred at 3,458.13 cm^{-1} shifted to 3,365.55 cm^{-1} in the treated pesticide aqueous solution. This may indicate the vibration of the hydrogen-bonded hydroxyl groups and/or absorbed H_2O molecules [35,36]. The stretching vibration of the carbonyl peak in the untreated solution at band 1,650.95 cm^{-1} broadened in the treated solution at band 1,634.16 cm^{-1}. This may suggest the formation of different carbonyl groups such as aldehydes and carboxylic acids. The band at 1,523.66 cm^{-1} modified and shifted to 1,389.21 cm^{-1} indicating the weakening of C=C stretching in the chloroalkenes, C–C stretching of phenyl ring and the C=N stretching due to the pesticide molecule vibration [37]. The band at 1,027.99 cm^{-1} shifted to 969.04 cm^{-1} in the treated pesticide aqueous solutions. This may indicate isomerization of the pesticide as well as modification of the Cl–C, P=S stretching and the (C=O)–O– stretching [37,38]. The difference in FTIR spectrum (untreated and treated pesticide aqueous solutions) indicates degradation of the pesticides organic bonds.

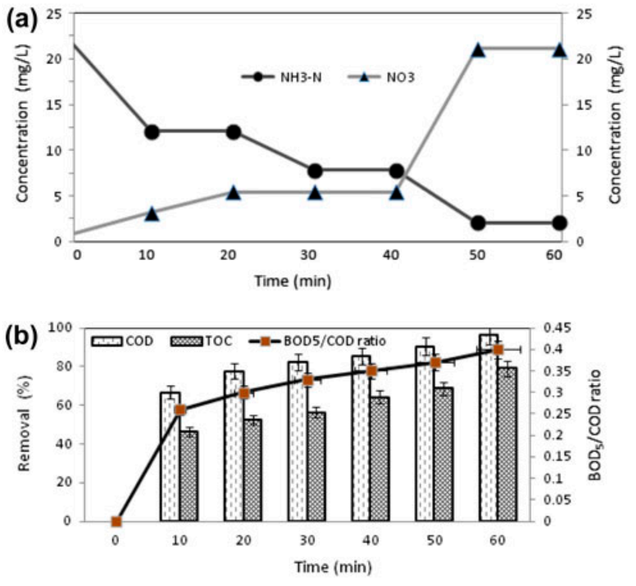

Fig. 6. Degradation under optimum operating conditions (a) NH_3-N reduction and NO_3^--N formation, and (b) COD and TOC removal and BOD_5/COD ratio after 60 min reaction time. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

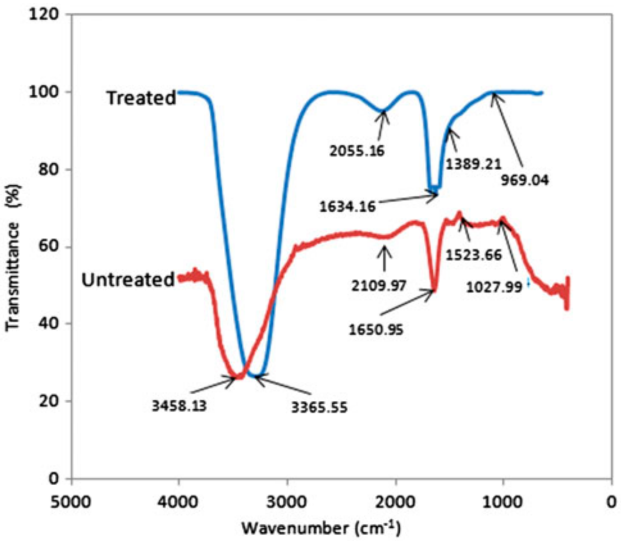

Fig. 7. FTIR Spectra of untreated and treated pesticide aqueous solutions. Chlorpyrifos–100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

3.9. Kinetics

To understand the kinetics of degradation of the pesticide aqueous solution, different kinetic models including pseudo-first-order, pseudo-second-order and intraparticle diffusion were evaluated.

3.9.1. Pseudo-first-order

A general pseudo-first-order reaction rate expression for kinetics of pesticide aqueous solution degradation has been reported [29]. The presence of GAC in the FeGAC/H_2O_2 process acted as an additional catalyst together with the iron oxide. This accelerated the formation rate of ferrous irons, which is known to be the rate-limiting constituent in $OH^{\bullet}$ production in Fenton-like processes. The pseudo-first-order kinetics is given according to Eq. (8) [16].

$$\ln\left(\frac{C_t}{C_o}\right) = -k_1 \times t \tag{8}$$

where C_t and C_o are the TOC concentrations at time t and zero, respectively, k_1 (min^{-1}) is the rate constant. If the kinetics follows the pseudo-first-order, a plot of ln (C_t/C_o) vs. time is shown in Fig. 8.

3.9.2. Pseudo-second-order

The pseudo-second-order equation is shown in Eq. (9) [39].

$$\frac{1}{C_t} = \frac{1}{C_o} + k_2 t \tag{9}$$

where C_t and C_o are the TOC concentrations at time t and zero and k_2 (min^{-1}) is the calculated pseudo-second-order rate constant. If the kinetics follows the pseudo-second-order, a plot of $1/C_t$ vs. time should be linear (Fig. 9).

3.9.3. Intraparticle diffusion model

The linearized form of intraparticle diffusion equation is shown in Eq. (10) [40].

$$q_t = k_{id} t^{0.5} + C_i \tag{10}$$

where k_{id} (mg/g $\text{min}^{0.5}$) is a measure of the diffusion coefficient and C_i is the intraparticle diffusion constant (mg/g). If intraparticle diffusion is the rate-limiting step, a plot of fraction of organics adsorbed q_t against the square root of time ($t^{0.5}$) should be linear, passing through the origin. k_{id} and C_i are obtained from the slope and intercept of the graph, respectively (Fig. 10). C_i is directly proportional to the boundary layer thickness.

The kinetic constants and correlation coefficients of the three kinetic models are shown in Table 2. A high correlation coefficient indicates how well a model describes the data obtained from an experiment. The correlation coefficient from highest to lowest was in the following order; pseudo–first-order > intraparticle diffusion model > pseudo-second-order. The pseudo-first-order model was found to describe the reaction kinetics most effectively.

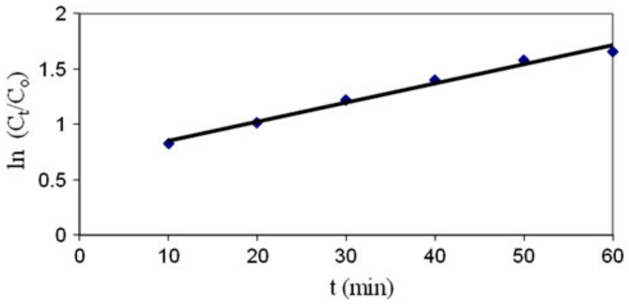

Fig. 8. Pseudo-first-order kinetics. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

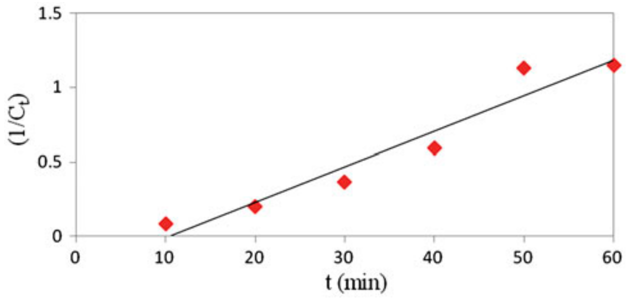

Fig. 9. Pseudo-second-order kinetics. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

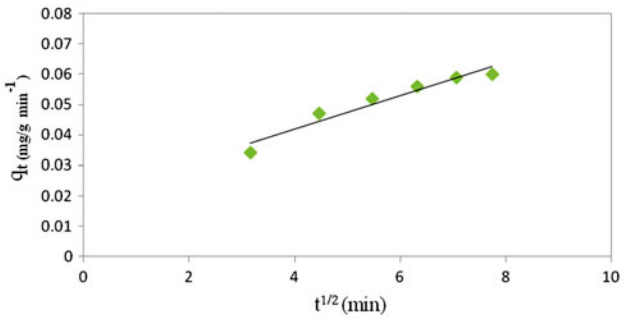

Fig. 10. Intraparticle diffusion model. Chlorpyrifos—100 mg/L, cypermethrin—50 mg/L, chlorothalonil—250 mg/L. Initial COD 1,130 mg/L and initial TOC 274.4 mg/L.

Table 2
Summary of correlation coefficients and rate constants

Pseudo first order		Pseudo second order		Intra particle diffusion model		
k_1 (min^{-1})	R^2	k_2 (min^{-1})	R^2	kid (mg/g min$^{0.5}$)	C_i (mg/g)	R^2
0.017	0.987	0.024	0.937	0.0056	0.0196	0.939

4. Conclusions

FeGAC/H_2O_2 process has been applied in the treatment of pesticide aqueous solution containing chlorpyrifos, cypermethrin and chlorothalonil. Increasing the FeGAC beyond a certain point may cause the production of iron sludge. The chosen operating conditions were sufficient to ensure that no sludge was produced at the end of the treatment. Under the optimum operating conditions (FeGAC 5 g/L, H_2O_2 100 pH 3 and 60 min reaction time), complete degradation of chlorpyrifos, cypermethrin and chlorothalonil pesticide active ingredients occurred in 1 min, COD and TOC removals were 96.2 and 79.2%, respectively. Biodegradability (BOD_5/COD ratio) increased from 0 to 0.40. Kinetics of degradation of the pesticide aqueous solution was obtained and fitted to different kinetics models. The pseudo-first-order model was found to describe the reaction kinetics most effectively. The FeGAC/H_2O_2 process can be used for pretreatment of pesticide aqueous solution containing chlorpyrifos, cypermethrin and chlorothalonil before biological treatment may be applied.

Acknowledgement

The authors are thankful to the management and authorities of the Universiti Teknologi PETRONAS, Malaysia for providing facilities for this research.

References

[1] M.Y. Farré, M.I. Franch, S. Malato, J.A. Ayllón, J. Peral, X. Doménech, Degradation of some biorecalcitrant pesticides by homogeneous and heterogeneous photocatalytic ozonation, Chemosphere 58 (2005) 1127–1133.

[2] S. Malato, J. Blanco, M.I. Maldonado, P. Fernández-Ibáñez, A. Campos, Optimising solar photocatalytic mineralisation of pesticides by adding inorganic oxidising species—Application to the recycling of pesticide containers, Appl. Catal., B 28 (2000) 163–174.

[3] S. Chiron, A. Fernandez-Alba, A. Rodrguez, E. Garcia-Calvo, Pesticide chemical oxidation: State-of-the-art, Water Res. 34 (2000) 366–377.

[4] H. Zhou, D.W. Smith, Advanced technologies in water and wastewater treatment, J. Environ. Eng. Sci. 1 (2002) 247–264.

[5] E. Chamarro, A. Marco, S. Esplugas, Use of fenton reagent to improve organic chemical biodegradability, Water Res. 35 (2001) 1047–1051.

[6] B. Lodha, S. Chaudhari, Optimization of Fenton-biological treatment scheme for the treatment of aqueous dye solutions, J. Hazard. Mater. 148 (2007) 459–466.

[7] S.H. Lin, C.D. Jiang, Fenton oxidation and sequencing batch reactor (SBR) treatments of high strength semiconductor wastewater, Desalination 154 (2003) 107–116.

[8] I. Gulkaya, G.A. Surucu, F.B. Dilek, Importance of H_2O_2/Fe^{2+} ratio in Fenton's treatment of a carpet dyeing wastewater, J. Hazard. Mater. 136 (2006) 763–769.

[9] L. Rongxi, Y. Chunping, C. Hong, Z. Guangming, Y. Guanlong, G. Junyuan, Removal of triazophos pesticide from wastewater with Fenton reagent, J. Hazard. Mater. 167 (2009) 1028–1032.

[10] M. Tamimi, S. Qourzal, N. Barka, N. Assabbane, Y. Aitichou, Methomyl degradation in aqueous solutions by Fenton's reagent and the photo-Fenton system, Sep. Purif. Technol. 61 (2008) 103–108.

[11] M.I. Badawy, M.Y. Ghaly, T.A. Gad-Allah, Advanced oxidation processes for the removal of organophosphorus pesticides from wastewater, Desalination 194 (2006) 166–175.

[12] H. Hassan, B.H. Hameed, Fe–clay as effective heterogeneous Fenton catalyst for the decolorization of reactive blue 4, Chem. Eng. J. 171 (2011) 912–918.

[13] H. Fan, H. Shu, T. Tajima, Decolorization of acid black 24 by the FeGAC/H_2O_2 process, J. Hazard. Mater. 128 (2006) 192–200.

[14] H. Fan, C. Chen, L. Ming-Hsien, C. Tzuchen, Using FeGAC/H_2O_2 process for landfill leachate treatment, Chemosphere 67 (2007) 1647–1652.

[15] C.C. Chen, C. Wen-Ching, C. Mei-Rung, C. Sheng-Wei, C.Y. Yin, H. Fan, Degradation of crystal violet by an FeGAC/H_2O_2 process, J. Hazard. Mater. 196 (2011) 420–425.

[16] A. Bach, R. Semiat, The role of activated carbon as a catalyst in GAC/iron oxide/H_2O_2 oxidation process, Desalination 273 (2011) 57–63.

[17] S. Ji, Y. Ren, A. Buekens, T. Chen, S. Lu, K. Cen, X. Li, Treating PCDD/Fs by combined catalysis and activated carbon adsorption, Chemosphere 102 (2014) 31–36.

[18] R.M. Sherrard, J.S. Bearr, C.L. Murray-Gulde, J.H. Rodgers Jr., Y.T. Shah, Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures, Environ. Pollut. 127 (2004) 385–394.

[19] Y. Zhang, J. Lu, L. Wu, A. Chang, W.T. Frankenberger, Simultaneous removal of chlorothalonil and nitrate by *Bacillus cereus* strain NS1, Sci. Total Environ. 382 (2007) 383–387.

[20] Y. Samet, L. Agengui, R. Abdelhédi, Anodic oxidation of chlorpyrifos in aqueous solution at lead dioxide electrodes, J. Electroanal. Chem. 650 (2007) 152–158.

[21] Y. Samet, L. Agengui, R. Abdelhédi, Electrochemical degradation of chlorpyrifos pesticide in aqueous solutions by anodic oxidation at boron-doped diamond electrodes, Chem. Eng. J. 161 (2010) 167–172.

[22] A. Ghauch, A. Tuqan, Catalytic degradation of chlorothalonil in water using bimetallic iron-based systems, Chemosphere 73 (2008) 751–759.

[23] C.F. Gromboni, M.Y. Kamogawa, A.G. Ferreira, J.A. N´Obrega, A.R.A Nogueira, Microwave-assisted photo-Fenton decomposition of chlorfenvinphos and cypermethrin in residual water, J. Photochem. Photobiol., A 185 (2007) 32–37.

[24] A.C. Affam, M. Chaudhuri, Degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil in aqueous solution by TiO_2 photocatalysis, J. Environ. Manage. 130 (2013) 160–165.

[25] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, twenty-first ed., American Public Health Association, Washington, DC, 2005.

[26] I. Talinli, G.K. Anderson, Interference of hydrogen peroxide on the standard COD test, Water Res. 26 (1992) 107–110.

[27] Y.W. Kang, M.J. Cho, K.Y. Hwang, Correction of hydrogen peroxide interference on standard chemical oxygen demand test, Water Res. 33 (1999) 1247–1251.

[28] F. Al-Momani, E. Touraud, J.R. Degorce-Dumas, J. Roussy, O. Thomas, Biodegradability enhancement of textile dyes and textile wastewater by UV photolysis, J. Photoch. Photobiol. A 153 (2003) 191–197.

[29] M.V. Shankar, S. Anandan, N. Venkatachalam, B. Arabindoo, V. Murugesan, Novel thin-film reactor for photocatalytic degradation of pesticides in an aqueous solution, J. Chem. Technol. Biotechnol. 79 (2004) 1279–1285.

[30] E. Elmolla, M. Chaudhuri, Optimization of Fenton process for treatment of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution, J. Hazard. Mater. 170 (2009) 666–672.

[31] E. Neyens, J. Baeyens, A review of classic Fenton's peroxidation as an advanced oxidation technique, J. Hazard. Mater. 98 (2003) 33–50.

[32] N. Modirshahla, M.A. Behnajady, F. Ghanbary, Decolorization and mineralization of C.I. acid yellow 23 by Fenton and photo-Fenton processes, Dyes Pigm. 73 (2007) 305–310.

[33] A.C. Affam, M. Chaudhuri, S.R.M. M. Kutty, Fenton treatment of chlorpyrifos, cypermethrin and chlorothalonil pesticides in aqueous solution, J. Environ. Sci. Technol. 5 (2012) 407–418.

[34] F. Regan, M. Meaney, J.G. Vos, B.D. MacCraith, J.E. Walsh, Determination of pesticides in water using ATR-FTIR spectroscopy on PVC/chloroparaffin coatings, Anal. Chim. Acta 334 (1996) 85–92.

[35] Y. You, H. Zhao, G.F. Vance, Adsorption of dicamba (3, 6-dichloro-2-methoxy benzoic acid) in aqueous solution by calcined–layered double hydroxide, Appl. Clay Sci. 21 (2002) 217–226.

[36] D.A. Dhas, I.H. Joe, S.D.D. Roy, T.H. Freeda, DFT computations and spectroscopic analysis of a pesticide: Chlorothalonil, Spectrochim. Acta, Part A 77 (2010) 36–44.

[37] M. Segal-Rosenheimer, Y. Dubowski, Heterogeneous ozonolysis of cypermethrin using real-time monitoring ftir techniques, J. Phys. Chem. C 111 (2007) 11682–11691.

[38] S. Armenta, G. Quintas, S. Garrigues, M. Delaguardia, A validated and fast procedure for FTIR determination of cypermethrin and chlorpyrifos, Talanta 67 (2005) 634–639.

[39] J. He, X. Yang, B. Men, Z. Bi, Y. Pu, D. Wang, Heterogeneous Fenton oxidation of catechol and 4-chlorocatechol catalyzed by nano-Fe_3O_4: Role of the interface, Chem. Eng. J. 258 (2014) 433–441.

[40] W. Morris, W. Weber, Kinetics of adsorption on carbon from solution, J. Sanit. Eng. Div. 89 (1963) 31–60.