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UV Fenton and sequencing batch reactor treatment of chlorpyrifos, cypermethrin and chlorothalonil pesticide wastewater

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ABSTRACT

This study examined the effect of operating conditions of UV Fenton pretreatment combined with aerobic sequencing batch reactor on degradation and biodegradability (BOD_5/COD ratio) improvement of chlorpyrifos, cypermethrin and chlorothalonil pesticide wastewater. The optimum operating conditions in the pretreatment phase were H_2O_2/COD molar ratio 2.0, H_2O_2/Fe^{2+} molar ratio 25, pH 3 and reaction time 60 min and achieved COD and TOC removal were 64.8 and 45.9% for COD and TOC removal, respectively and biodegradabilty (BOD_5/COD ratio) improved from 0.02 to 0.31. In the aerobic SBR phase, five different UV Fenton operating conditions were investigated and UV F-SBR 1 appeared to be the most significant ($p < 0.05$). Increasing UV Fenton pretreatment time and combining the pretreated pesticide wastewater and municipal treatment plant wastewater enabled sustenance of the SBR operation. The UV Fenton-SBR (C) achieved COD and TOC removal efficiency of 96.2 and 97.4%, respectively after 40 d operation at 12 hr HRT. Effluent COD, TOC and BOD_5 were 24, 19 and 18 mg L^{-1}, respectively and BOD_5/COD ratio was 0.75. Applying the Monod model, values of the biological first order kinetic constant (K_{ob}), cell yield ($Y_{x/s}$) and decay coefficients (k_d) were 0.1332 hr^{-1}, 0.5301 (mg COD mg^{-1} MLSS) and 0.0072 hr^{-1}, respectively. The UV Fenton-SBR (C) process is effective in treatment of pesticide wastewater containing chlorpyrifos, cypermethrin and chlorothalonil to meet Malaysian industrial effluent discharge standard.

1. Introduction

Compliance with stringent discharge standard is required for toxic substances that are non-biodegradable or inhibitory to biological degradation. Among these substances, pesticides are considered to be significant surface and groundwater pollutant introduced through crop disinfection and pesticide wastewater discharge (Shawaqfeh and Al Momani, 2010). The concentration of pesticides in wastewater may not be less than 500 mg L^{-1} (Malato et al., 2000). Due to potentially adverse health effects associated with pesticides even at very small concentrations (pg $L^{-1}$to ng L^{-1}), satisfactory treatment including degradation of the active pesticide ingredient in wastewater is recommended. Incompletely treated wastewater is one of the main sources of pesticides in the aquatic environment (Cahill et al., 2011). Pesticide active ingredients have been detected in inland waterways and rivers in Malaysia. For example in Krian river basin Perak, Tanjong Karang and Selangor rivers, Penang marine fish, Sabah sediments and major rivers in West Malaysia (Abdullah, 1995). In the Cameron highlands area and Johor agro-ecosystems, traces of organochlorine (aldrin, dieldrin, DDT, endosulfan and lindane) and organophosphorus (chlorpyrifos diazinon, dimethoate, fenthion, malathion, paration ethyl and parathion methyl) pesticides were found (Cheah, 1996). In particular, analysis of water sample from the Kial river in Tringkap, Cameron highlands found 0.810 mg L^{-1} of 4,4'DDD, 0.140 mg L^{-1} of 4,4'DDE and 0.970 mg L^{-1} of 4,4'DDT pesticides (IPOPs, 2005). Another study detected organophosphate pesticides (chlorpyrifos and diazinon) and organochlorine pesticides (lindane, heptachlor, endosulfan, dieldrin, endosulfan sulfate, DDT and DDE) in the Selangor river (Leong et al., 2007). Recovery of alkylphenols and other pesticide compounds were in the range of 50–120% in selected rivers in the state of Selangor (Tan and Mustafa, 2004). Pesticides used in a tobacco farm in Kelantan have been found to

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have effect on the central and peripheral nervous system of eighty local farmers (Kimura et al., 2005). Organochlorine pesticides such as heptachlor, dieldrin and pp-DDT (52–159 mg kg^{-1}) have been detected in sewage sludge in three locations in South Johore, Johor State (Ahmad et al., 2004). Sewage sludge may contain pesticides and other toxic substances that could be incorporated into agricultural lands during application (Tadeo et al., 2010). Besides, formation of dioxins during exposure of pesticide formulations to sunlight has also been reported (Holt et al., 2012).

Several treatments have been reported forremoval and/or degradation of pesticides chlorpyrifos, cypermethrin and chlorothalonil; however, they have targeted pesticide removal by wet lands (Xiaoqiang et al., 2008; Hua et al., 2009) bimetallic iron and nitrogen spurge (Ghauch and Tuqan, 2008), electrochemical oxidation (Samet et al., 2010a and 2010b), ozone (Wu et al., 2007), and *Bacillus cereus* and sentinel species (Sherrard et al., 2004; Zhang et al., 2009) and mostly in residual water or aqueous solution (Gromboni et al., 2007). There is a need to study the treatment of a pesticide wastewater containing pesticides and their formulation agents with a higher total organic carbon (TOC) concentration over 500 mg L^{-1} by combined AOP and biological treatment (Zapata et al., 2009; Oller et al., 2011).

There is no report on combined UV Fenton and SBR treatment for degradation and biodegradability (BOD_5/COD ratio) improvement of chlorpyrifos, cypermethrin and chlorothalonil pesticide wastewater to meet the Malaysian industrial effluent discharge standard. The first phase of this study examined the effect of H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios on the UV Fenton pretreatment. The second phase examined various operating conditions of the UV Fenton pretreatment combined with SBR treatment of the pesticide wastewater. In addition, assessment of NH_3–N, TKN, COD and TOC removal efficiencies, and nitrification study were done. The biological first order kinetic constant (K_{ob}), cell yield ($Y_{x/s}$) and decay coefficients (k_d) during the steady state of the UV Fenton-SBR (C) process were also studied.

2. Materials and methods

2.1. Chemicals

Hydrogen peroxide (H_2O_2) (30%, w/w) and ferrous sulphate ($FeSO_4{\cdot}7H_2O$) 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 gas chromatography mass spectroscopy (GC/MS).

2.2. Analytical methods

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 so as to decompose hydrogen peroxide to oxygen and water (Talinli and Anderson, 1992; Kang et al., 1999), 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). Ammonia-nitrogen (NH_3–N) was measured by the Nessler Method (Method 8038) (HACH, 2002), Nitrate (NO_3^--N) was measured by the Cadmium Reduction Method (High Range) (HACH, 2002) and Total Kjeldahl Nitrogen (TKN) was measured according to the Standard Methods Section 4500-Norg B Macro-Kjeldahl Method (APHA, 2005). Biodegradability was measured by 5-day biochemical oxygen demand (BOD_5) test according to the Standard Methods (APHA, 2005). DO was measured using YSI 5000 dissolved oxygen meter. Other parameters such as MLSS and MLVSS were measured according to the Standard Methods (APHA, 2005). The seed for BOD_5 test was obtained from a municipal wastewater treatment plant. Pesticide concentration in untreated and treated samples was determined by Gas Chromatograph–Mass Spectrometer (GC/MS). The analysis was carried-out on a GCMS-QP5050A equipped with a column of dimension 30 m × 0.25 mm, 0.25 μm. The mass spectrometer employed was an ion trap (20 μA) with 0.82 s of scan time and mass spectra between 35 and 500 nm. The injector was maintained at 300 °C and operated in the splitless mode with the split closed for 0.75 min. Helium (>99.999% pure) was used as the carrier gas at a flow rate of 1.0 ml min^{-1}. The column oven was initially set at 50 °C for 1 min, programmed to 190 °C at 20 °C min^{-1} rate for 5 min, and finally to 280 °C at 3.5 °C min^{-1} rate. The column flow was 2.4 ml min^{-1} and injected volume of 1 μl. The interface temperature was set at 300 °C and the detector voltage at 4 V. A 35 min time was allowed for all analysis. The base peak ion and two other significant ions of each analyte were chosen as the quantifying ions. Prior to quantification, the identification of all target compounds was based on their mass spectra and GC retention times (Cortada et al., 2009).

2.3. Pesticide wastewater

Pesticide wastewater contained chlorpyrifos, cypermethrin and chlorothalonil and had a COD of 3350 mg L^{-1} and TOC of 2960 mg L^{-1}. Other characteristics of the pesticide wastewater are presented in Table 1. It was collected from a pesticide formulation and production company located in Klang, Malaysia and was stored in a cold room at 4 °C until it was used.

2.4. Experimental procedure

2.4.1. UV Fenton pretreatment (phase 1)

In the UV Fenton pretreatment phase, batch experiments were carried out in a 6000 mL reactor with 5000 mL of the pesticide wastewater. The required amount of ferrous sulphate ($FeSO_4{\cdot}7H_2O$) was added to the aqueous solution and the pH was adjusted to the required value using 1 M sulfuric acid (H_2SO_4) or 1 M sodium hydroxide (NaOH) and mixed by a magnetic stirrer to ensure complete homogeneity. Thereafter, the necessary amount of H_2O_2 was added to the mixture and was subjected to UV irradiation at room

Table 1
Characteristics of pesticide wastewater.

Parameter	Unit	Range
Chlorpyrifos	mg/L	805.56 ± 10.0
Cypermethrin	mg/L	105.75 ± 10.0
Chlorothalonil	mg/L	692.08 ± 10.0
Chemical oxygen demand (COD)	mg/L	3350.0 ± 100
Total organic carbon (TOC)	mg/L	2960.0 ± 100
Biochemical oxygen demand (BOD_5)	mg/L	63.0 ± 5.0
BOD_5/COD ratio		0.02 ± 0.01
Ammonia-nitrogen (NH_3–N)	mg/L	57.4 ± 2.0
Nitrate (NO_3^--N)	mg/L	13.1 ± 0.5
Total phosphate (TP)	mg/L	79.0 ± 0.5
Chloride (Cl^-)	mg/L	1280 ± 0.5
Fluoride (F^-)	mg/L	5.0 ± 0.5
Sulfate (SO_4^{2-})	mg/L	500.0 ± 10
Conductivity	(μS/cm)	680.0 ± 10
Total suspended solids (TSS)	mg/L	130.0 ± 5.0
Total volatile suspended solids (TVSS)	mg/L	105.0 ± 5.0
Total nitrogen	mg/L	114.8 ± 2.0
pH		5.08 ± 0.5