Journal of Hazardous Materials 192 (2011) 1418–1426

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat

Combined photo-Fenton–SBR process for antibiotic wastewater treatment

Emad S. Elmolla[a,*], Malay Chaudhuri[b]

[a] Department of Civil Engineering, Faculty of Engineering, Al-Azhar University, Cairo, Egypt
[b] Department of Civil Engineering, Universiti Teknologi PETRONAS, Bandar Seri Iskandar, 31750 Tronoh, Perak, Malaysia

ARTICLE INFO

Article history:
Received 30 October 2010
Received in revised form 20 June 2011
Accepted 21 June 2011
Available online 28 June 2011

Keywords:
Antibiotic wastewater
Amoxicillin
Cloxacillin
Photo-Fenton–SBR

ABSTRACT

The study examined combined photo-Fenton–SBR treatment of an antibiotic wastewater containing amoxicillin and cloxacillin. Optimum H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio of the photo-Fenton pretreatment were observed to be 2.5 and 20, respectively. Complete degradation of the antibiotics occurred in one min. The sequencing batch reactor (SBR) was operated at different hydraulic retention times (HRTs) with the wastewater treated under different photo-Fenton operating conditions (H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio). The SBR performance was found to be very sensitive to BOD_5/COD ratio of the photo-Fenton treated wastewater. Statistical analysis of the results indicated that it was possible to reduce the Fe^{2+} dose and increase the irradiation time of the photo-Fenton pretreatment. The best operating conditions of the combined photo-Fenton–SBR treatment were observed to be H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 150, irradiation time 90 min and HRT of 12 h. Under the best operating conditions, 89% removal of sCOD with complete nitrification was achieved and the SBR effluent met the discharge standards.

1. Introduction

Among all the pharmaceutical drugs that contaminate the environment, antibiotics occupy an important place due to their high consumption rates in both veterinary and human medicine. Problem that may be created by the presence of antibiotics at low concentration in the environment is the development of antibiotic resistant bacteria [1]. In recent years, incidence of antibiotic resistant bacteria has increased and it is believed that the increase is due to the use of antibiotics [2]. Furthermore, presence of antibiotics in wastewaters has increased in the past years and their abatement is a challenge.

Advanced oxidation processes (AOPs) are effective in the degradation of most pollutants in wastewater [3], and the photo-Fenton process has proved to be highly effective [4]. Oxidation with Fenton's reagent is based on ferrous ion, hydrogen peroxide and hydroxyl radical produced by the catalytic decomposition of H_2O_2 in acidic solution [5]. In the photo-Fenton process, additional reactions occur in the presence of light that produce hydroxyl radicals or increase the production rate of hydroxyl radicals [4], thus increase the efficiency of the process.

Coupling AOP with biological process has received attention in recent years as a promising alternative treatment of recalcitrant wastewater. Using AOP pretreatment is important to improve the biodegradability and produce an effluent that can be treated biologically [6]. However, some practical aspects should be considered for combined AOP and biological process. Chemical oxidant and bioculture cannot be mixed because the oxidant can cause damaging effects on the microorganisms. Adjustment of pH to approximately 7 before the biological process is necessary because of generation of acid species in the oxidation process and the required acid pH condition of some AOPs. Also, the required chemical dosage and how long the reaction should be continued for the effluent to be biodegradable must be known [7]. Assessment of the biodegradability and toxicity during the oxidation process is necessary to determine an optimum pretreatment time that guarantees the success of the combined process. Methods for measuring biodegradability have been proposed by a number of authors, and BOD_5 value and BOD_5/COD ratio are commonly used [8,9]. Other biodegradability measures such as by-product identification, oxygen uptake and toxicity measurement have also been used [7,10].

Sequencing batch reactor (SBR) is a wastewater treatment process based on the principles of the activated sludge process. SBR has been successfully employed in the treatment of both municipal and industrial wastewater [11]. Combined photo-Fenton–SBR process has been reported to be effective in treatment of recalcitrant wastewater such as Cibacron Red FN-R and Procion Red H-E7B dyes [12,13], Diuron and Linuron herbicides [14], Laition, Metasystox, Sevnol and Ultracid pesticides [15] and sulfamethoxazole antibiotic aqueous solution [16]. In our previous work, degradation of antibiotics using Fenton [17], photo-Fenton [18,19], TiO_2 photocatalysis [20] and ZnO photocatalysis [21] was studied. In addition,

---

* Corresponding author. Tel.: +20 11 3301 981.
E-mail addresses: em_civil@yahoo.com, emadsoliman3@gmail.com, emadelmolla@azhar.edu.eg (E.S. Elmolla).

0304-3894/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.jhazmat.2011.06.057

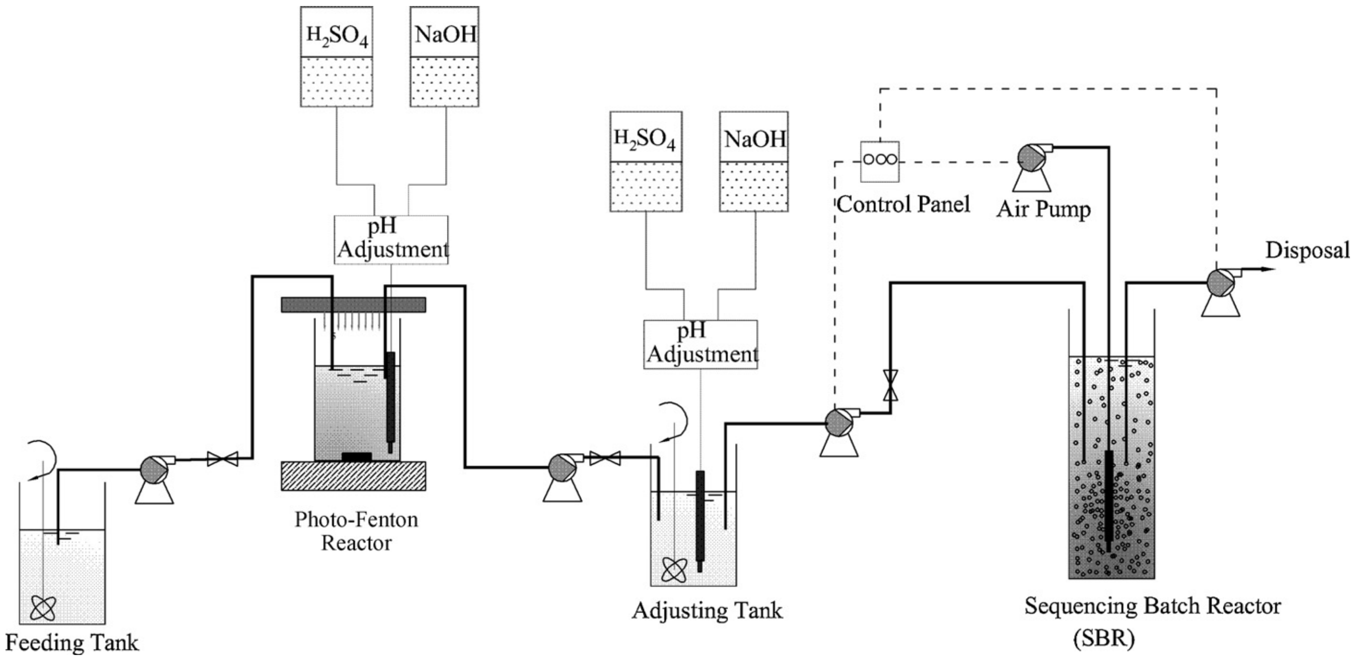

Fig. 1. Schematic of combined photo-Fenton–SBR process.

technical and economic comparisons among different AOPs as well as simulation of the Fenton process for treatment of an antibiotic aqueous solution were made [22,23]. Recently, limited feasibility of using combined UV/H_2O_2/TiO_2–SBR process for antibiotic wastewater treatment has been reported [24].

First part of this study examined the effect of operating conditions (H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio) of the photo-Fenton pretreatment of an antibiotic wastewater containing amoxicillin and cloxacillin. Second part of the study examined combined photo-Fenton–SBR treatment of the antibiotic wastewater. Effects of photo-Fenton treated wastewater characteristics under different photo-Fenton operating conditions and SBR hydraulic retention time (HRT) on SBR and combined process efficiency were also evaluated.

2. Materials and methods

2.1. Antibiotics and chemicals

Analytical grade of amoxicillin (AMX) and ampicillin (AMP) was purchased from Sigma and cloxacillin (CLX) from Fluka, and were used to construct HPLC analytical curves for determination of antibiotic concentration. Potassium dihydrogen phosphate (KH_2PO_4) was purchased from Fluka and acentonitrile HPLC grade from Sigma. Hydrogen peroxide (30%, w/w) and ferrous sulphate ($FeSO_4{\cdot}7H_2O$) were purchased from R&M Marketing, Essex, U.K.

2.2. Antibiotic wastewater

Antibiotic wastewater used in this study was obtained from a local antibiotic industry producing amoxicillin and cloxacillin. The antibiotic wastewater characteristics are summarized in Table 1.

2.3. Analytical methods

Antibiotic 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) (Agilent 1100 Series), at wavelength 204 nm. The data were recorded by a chemistation software. The column was ZORBAX SB-C18 (4.6 mm × 150 mm, 5 μm) and the column temperature was set at 60 °C. Mobile phase was made up of 55% buffer solution (0.025 M KH_2PO_4 in ultra purified water) and 45% acentonitrile, and flow rate of 0.5 mL/min. Ions present in raw wastewater such as SO_4^{2-} and Cl^- were determined by a Metrohm ion chromatograph. The eluent phase consisted of 3.2 mM Na_2CO_3 and 1.0 mM $NaHCO_3$. The analytical column was METROSEP A SUPP 5-150 (4.0 mm × 150 mm, 5 μm). The flow rate was 0.7 mL/min and the temperature was 20 °C. Chemical oxygen demand (COD) was determined according to the Standard Methods [25]. The sample was filtered through 0.45 μm membrane filter for determination of soluble chemical oxygen demand (sCOD). When 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 [26]. The pH was measured using a pH meter (HACH sension 4) and a pH probe (HACH platinum series pH electrode model 51910, HACH Company, USA). Biodegradability was measured by 5-day biochemical oxygen demand (BOD_5) test according to the Standard Methods [25]. Dissolved oxygen (DO) was measured by a YSI 5000 dissolved oxygen meter. The seed for BOD_5 test was obtained from a municipal wastewater treatment plant. TOC analyzer (Model 1010; O&I Analytical) was used for determining dissolved organic carbon (DOC). Determination of total suspended solids (TSS) and volatile suspended solids (VSS) was carried out according to the Standard Methods [25].

Table 1
Antibiotic wastewater characteristics.

Parameter	Value	Parameter	Value
Amoxicillin (mg/L)	138 ± 5	TP (mg/L)	7.5
Cloxacillin (mg/L)	84 ± 4	NO_3^-–N (mg/L)	5.1
COD (mg/L)	670 ± 20	NH_3–N (mg/L)	11.1
sCOD (mg/L)	575 ± 20	SO_4^{2-} (mg/L)	0.7
DOC (mg/L)	145 ± 5	Cl^- (mg/L)	5.92
BOD_5 (mg/L)	70 ± 10	Turbidity (NTU)	45
pH	6.8	Conductivity (μS/cm)	125
TSS (mg/L)	70 ± 5		

2.4. Experimental setup and procedure

Fig. 1 shows a schematic of the combined photo-Fenton–SBR process. The treatment was accomplished in two stages, photo-Fenton process as stage 1 and aerobic sequencing batch reactor (SBR) as stage 2.

2.4.1. Stage 1: photo-Fenton process

Batch experiments were conducted using a 2.2-L Pyrex reactor with 2000 mL of the antibiotic wastewater. The required amount of iron ($FeSO_4 \cdot 7H_2O$) was added to the wastewater and mixed by a magnetic stirrer to ensure complete homogeneity during reaction. Thereafter, necessary amount of hydrogen peroxide was added to the mixture with simultaneous adjustment to the required pH value by H_2SO_4. The mixture was subjected to UV irradiation by an UV lamp (Spectroline Model EA-160/FE, 230 V, 0.17 A, Spectronics Corporation, New York, USA) with nominal power of 6 W, emitting radiations at wavelength ≈365 nm and it was placed 5 cm above the reactor. The time at which hydrogen peroxide was added to the mixture was considered the beginning of the experiment. The reaction was allowed to continue for the required time. Thereafter, pH was increased to above 10 for iron precipitation and decomposing residual H_2O_2 [26]. Precipitated iron was separated from the reactor and the supernatant was used to feed the SBR after pH adjustment to 6.8–7.2. Samples were taken and filtered through a 0.45 μm membrane syringe filter for determination of soluble chemical oxygen demand (sCOD), biochemical oxygen demand (BOD_5) and dissolved organic carbon (DOC), and filtered through a 0.20 μm membrane syringe filter for measurement of antibiotic concentration by HPLC.

2.4.2. Stage 2: aerobic sequencing batch reactor (SBR)

The operating liquid volume of the 2-L SBR was 1.5 L and depth 20 cm. The reactor was equipped with an aquarium pump and air diffuser to keep DO above 3 mg/L, and stirring plate and stirrer bar (200 rpm) for mixing. Feeding and decanting were performed using two peristaltic pumps. The cycle period was divided into five phases: filling (0.25 h), aeration (variable), settling (1.25 h), decant (0.25 h) and idle (0.25 h). The cycle was repeated 6–9 times as necessary to allow cell acclimation and/or to obtain repetitive results. Daily analysis of sCOD and DOC of influent and effluent were carried out. Concentration of mixed liquor suspended solids (MLSS) and mixed liquor volatile suspended solids (MLVSS) were monitored throughout the operation.

2.4.3. Start up of SBR

The SBR was inoculated with 200 mL of sludge from the aeration tank of a wastewater treatment plant. Concentration of MLSS in the reactor after inoculation was 2300 mg/L. In order to acclimate the biomass, a HRT of 2 days and acclimation period of 8 days were used and the photo-Fenton treated antibiotic wastewater was mixed with domestic wastewater at ratio of 25:75, 50:50, 75:25 and 100:0.

3. Results and discussion

3.1. Photo-Fenton pretreatment

3.1.1. Effect of H_2O_2/COD molar ratio

Expectantly, higher H_2O_2/COD molar ratio would generate more hydroxyl radicals ($OH^\bullet$) for substrate degradation. To study the effect of H_2O_2/COD molar ratio on biodegradability improvement and mineralization of the antibiotic wastewater (sCOD 575 mg/L (17.97 mM) and DOC 145 mg/L), initial H_2O_2 concentration was varied in the range 17.97–53.9 mM. The corresponding H_2O_2/COD and COD/H_2O_2/Fe^{2+} molar ratios were 1, 1.5, 2, 2.5 and 3, and 1.0/1.0/0.02, 1.0/1.5/0.03, 1.0/2.0/0.04, 1.0/2.5/0.05 and 1.0/3.0/0.06, respectively. The other operating conditions were pH 3, irradiation time 30 min and H_2O_2/Fe^{2+} molar ratio 50. Effect of H_2O_2/COD molar ratio on sCOD and DOC removal and biodegradability (BOD_5/COD ratio) improvement is shown in Fig. 2. The sCOD removal was 45 ± 1, 51 ± 1, 57 ± 1, 59 ± 1 and 58 ± 1% at H_2O_2/COD molar ratio 1, 1.5, 2.0, 2.5 and 3.0, respectively. The BOD_5/COD ratio was 0.34 ± 0.01, 0.41 ± 0.02, 0.43 ± 0.01, 0.44 ± 0.01 and 0.42 ± 0.01 at H_2O_2/COD molar ratio 1, 1.5, 2.0, 2.5 and 3.0, respectively. It may be noted that a wastewater is considered biodegradable if the BOD_5/COD ratio is 0.40 [27]. The DOC removal was 32 ± 3, 34 ± 1, 36 ± 1, 49 ± 1 and 48 ± 1% at H_2O_2/COD molar ratio 1, 1.5, 2.0, 2.5 and 3.0, respectively. The results show that sCOD and DOC removal, and biodegradability (BOD_5/COD ratio) improved with increasing H_2O_2/COD molar ratio. Addition of H_2O_2 in excess of H_2O_2/COD molar ratio 2.5 did not improve removal and biodegradability. This was presumably due to scavenging of $OH^\bullet$ by H_2O_2 as in Reaction (1) [28].

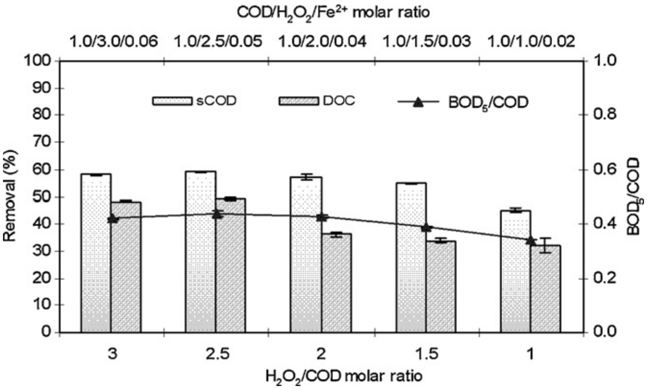

Fig. 2. Effect of H_2O_2/COD molar ratio on sCOD and DOC removal, and BOD_5/COD ratio.

$$OH^\bullet + H_2O_2 \rightarrow H_2O + HO_2^\bullet \tag{1}$$

Based on the results, the optimum H_2O_2/COD molar ratio was 2.5 for biodegradability improvement, sCOD removal and mineralization. The optimum H_2O_2/COD molar ratio in this case was higher than that observed in our previous study [18] on degradation of antibiotics in aqueous solution by the photo-Fenton process. This was ascribed to decreasing light penetration and presence of inorganic ions in the wastewater. A H_2O_2/COD molar ratio of 2.5 was used in all subsequent experiments.

3.1.2. Effect of H_2O_2/Fe^{2+} molar ratio

In the photo-Fenton process, Fe^{2+} and H_2O_2 are two major chemicals determining the operation cost as well as efficiency. To study the effect of H_2O_2/Fe^{2+} molar ratio on biodegradability improvement and mineralization of the antibiotic wastewater (sCOD 575 mg/L (17.97 mM) and DOC 165 mg/L), experiments were conducted at constant H_2O_2 dose (44.9 mM) and varying Fe^{2+} dose in the range 0.3–4.5 mM. The corresponding H_2O_2/Fe^{2+} and COD/H_2O_2/Fe^{2+} molar ratios were 10, 20, 50, 100 and 150, and 1.0/2.5/0.25, 1.0/2.5/0.125, 1.0/2.5/0.05, 1.0/2.5/0.025 and 1.0/2.5/0.017, respectively. The other operating conditions were pH 3, irradiation time 30 min and H_2O_2/COD molar ratio 2.5. The results (Fig. 3) show that sCOD and DOC removal and BOD_5/COD ratio increased with decrease of H_2O_2/Fe^{2+} molar ratio up to 20. This may be explained by the fact that higher Fe^{2+} dose generated more $OH^\bullet$ radicals resulting in improved sCOD removal. Decrease of H_2O_2/Fe^{2+} molar ratio below 20 did not improve sCOD and DOC removal and BOD_5/COD ratio. This was presumably due to direct reaction of $OH^\bullet$ radicals with metal ions at high concentration of

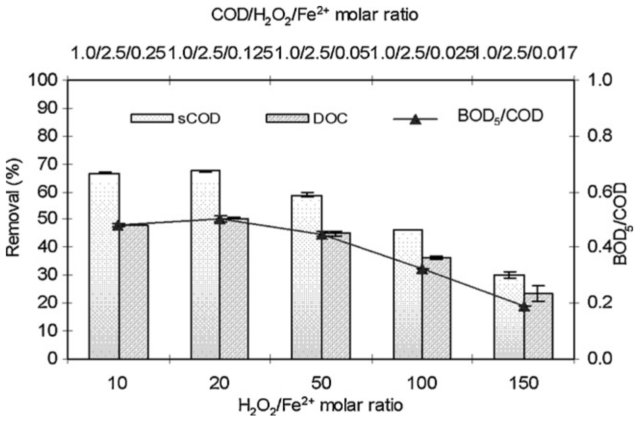

Fig. 3. Effect of H_2O_2/Fe^{2+} molar ratio on sCOD and DOC removal, and BOD_5/COD ratio.

Fe^{2+} as in Reaction (2) [29] or due to recombination of $OH^\bullet$ radicals or increase of turbidity that hindered the absorption of the UV light.

$$Fe^{2+} + OH^\bullet \rightarrow Fe^{3+} + OH^- \qquad (2)$$

Based on the results, the optimum H_2O_2/Fe^{2+} molar ratio was 20 for biodegradability improvement, sCOD removal and mineralization.

3.1.3. Degradation of antibiotics

To confirm degradation of the antibiotics in the antibiotic wastewater and study the matrix effect, an experiment was conducted under the following operating conditions: H_2O_2/COD molar ratio 2.5, H_2O_2/Fe^{+2} molar ratio 20 and pH 3. As shown in Fig. 4, complete degradation of amoxicillin (AMX) and cloxacillin (CLX) occurred in 1 min. This agreed well with our previous study [18] on degradation of antibiotics in aqueous solution by the photo-Fenton process and thus, the effect of water matrix could be neglected. It also agreed well with the results reported by Trovó et al. [30] on degradation of amoxicillin, bezafibrate and paracetamol by the Fenton process. They observed 90 and 89% amoxicillin degradation in 1 min in distilled water and in sewage treatment plant effluent, respectively.

3.2. Combined photo-Fenton–SBR treatment

3.2.1. Effect of photo-Fenton operating conditions on SBR and combined process efficiency

To study the effect of photo-Fenton operating conditions and photo-Fenton-treated wastewater characteristics on SBR and com-

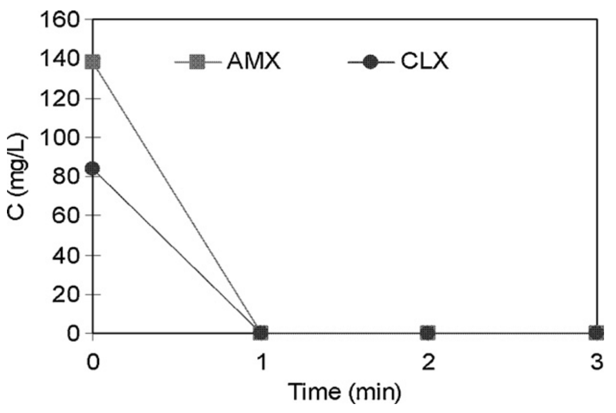

Fig. 4. Degradation of AMX and CLX in antibiotic wastewater.

Table 2
Photo-Fenton-treated wastewater and SBR effluent characteristics, and combined process efficiency at different H_2O_2/COD molar ratio.

Case	Photo-Fenton-treated wastewater							SBR effluent						Combined efficiency	
	H_2O_2/COD (MR)	sCOD		DOC		BOD_5	BOD_5/COD	sCOD		DOC		MLSS	*F*/*M*	sCOD	DOC
		mg/L	*R*%	mg/L	*R*%	mg/L		mg/L	*R*%	mg/L	*R*%	mg/L	day^{-1}	%	%
PF1	3	238 ± 2	58 ± 1	85 ± 2	48 ± 1	100 ± 2	0.42 ± 0.1	79 ± 4	67 ± 2	28 ± 2	68 ± 2	2560	0.062	86	83
PF2	2.5	222 ± 2	59 ± 1	83 ± 2	49 ± 1	97 ± 3	0.44 ± 0.02	76 ± 2	66 ± 1	29 ± 1	66 ± 2	2520	0.058	86	83
PF3	2	232 ± 5	57 ± 1	95 ± 2	36 ± 1	99 ± 1	0.43 ± 0.01	82 ± 1	65 ± 1	34 ± 1	64 ± 2	2500	0.061	85	77
PF4	1.5	245 ± 2	55 ± 1	98 ± 6	34 ± 4	158 ± 1	0.39 ± 0.01	158 ± 1	41 ± 1	41 ± 1	58 ± 1	2500	0.065	81	72
PF5	1	300 ± 2	45 ± 12	245 ± 1	32 ± 3	132 ± 31	0.34 ± 0.01	151 ± 2	50 ± 1	51 ± 3	51 ± 3	2480	0.080	72	67

Table 3
Photo-Fenton-treated wastewater and SBR effluent characteristics, and combined process efficiency at different H_2O_2/Fe^{2+} molar ratio.

Case	Photo-Fenton-treated wastewater							SBR effluent						Combined efficiency	
	H_2O_2/Fe^{2+} (MR)	sCOD		DOC		BOD_5	BOD_5/COD	sCOD		DOC		MLSS	*F/M*	sCOD	DOC
		mg/L	*R*%	mg/L	*R*%	mg/L		mg/L	*R*%	mg/L	*R*%	mg/L	day^{-1}	%	%
PF6	10	183 ± 2	67 ± 1	80 ± 2	48 ± 2	80 ± 2	0.48 ± 0.01	56 ± 1	69 ± 1	24 ± 1	70 ± 2	2460	0.049	90	84
PF7	20	179 ± 2	67 ± 1	76 ± 3	51 ± 3	90 ± 1	0.50 ± 0.02	56 ± 2	69 ± 1	24 ± 1	69 ± 1	2400	0.049	90	85
PF8	50	225 ± 3	59 ± 1	84 ± 1	45 ± 2	165 ± 1	0.45 ± 0.01	130 ± 1	63 ± 1	30 ± 1	65 ± 1	2360	0.063	85	81
PF9	100	300 ± 4	46 ± 1	105 ± 1	46 ± 1	52 ± 1	0.32 ± 0.01	151 ± 1	36 ± 1	52 ± 1	51 ± 1	2160	0.092	77	69
PF10	150	391 ± 2	30 ± 1	126 ± 3	24 ± 2	74 ± 8	0.19 ± 0.02	220 ± 4	44 ± 1	45 ± 1	45 ± 1	2080	0.124	61	58

bined process efficiency, antibiotic wastewater treated under different H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios (cases PF1–PF10, Tables 2 and 3) were used to feed the SBR. The SBR was operated for 71 days at cycle period of 24 h. The cycle was repeated 6–9 times to allow cell acclimation and to obtain repetitive results. Cases PF1–PF5 examined the effect of decreasing H_2O_2 dose (decreasing H_2O_2/COD molar ratio) and PF6–PF10 the effect of decreasing Fe^{2+} dose (increasing H_2O_2/Fe^{2+} molar ratio).

Table 2 shows photo-Fenton-treated wastewater and SBR effluent characteristics, and combined process efficiency under H_2O_2/COD molar ratios 3, 2.5, 2, 1.5 and 1 (cases PF1–PF5). The other operating conditions of the photo-Fenton process were H_2O_2/Fe^{2+} molar ratio 50, irradiation time 30 min and pH 3. The H_2O_2/COD molar ratio 3 (H_2O_2 1832 mg/L) was considered as the starting point. The SBR efficiency (*R*%) was 67 ± 2 and 68 ± 2 for sCOD and DOC removal, respectively. Under H_2O_2/COD molar ratio 2.5 (H_2O_2 1527 mg/L), the characteristics of the photo-Fenton-treated wastewater were sCOD 222 ± 2 mg/L, DOC 83 ± 2 mg/L and BOD_5/COD ratio 0.44 ± 0.03, and the SBR efficiency (*R*%) was 66 ± 1 and 66 ± 2 for sCOD and DOC removal, respectively. Comparing SBR performance of case PF3 with that of PF2 and PF1, it is observed that increasing H_2O_2/COD molar ratio to more than 2 did not significantly improve the SBR efficiency. This was presumably due to the fact that biodegradability (BOD_5/COD ratio) of the photo-Fenton-treated wastewater was more than 0.40 in all cases, which is considered biodegradable [27]. Reduced SBR efficiency under H_2O_2/COD molar ratio below 2 (cases PF4 and PF5) was ascribed to decrease of biodegradability below 0.4, indicating inhibition of aerobic oxidation by the antibiotic intermediates. The mixed liquor suspended solids (MLSS) in the SBR varied from 2560 mg/L at BOD_5/COD ratio 0.42 ± 0.01 (case PF1) to 2480 mg/L at BOD_5/COD ratio 0.34 ± 0.01 (case PF5). The reduction in MLSS concentration was considered small and it was presumably due to biomass growth on the SBR wall as well as inhibition of aerobic oxidation by antibiotic intermediates. The *F*/*M* ratio varied in the range 0.065–0.080 day^{-1} and this was mainly due to variation in sCOD of the photo-Fenton-treated wastewater.

Table 3 shows photo-Fenton-treated wastewater and SBR effluent characteristics, and combined process efficiency under H_2O_2/Fe^{2+} molar ratios 10, 20, 50, 100 and 150 (cases PF6–PF10). The other operating conditions of the photo-Fenton process were H_2O_2/COD molar ratio 2.0, irradiation time 30 min and pH 3. The H_2O_2/Fe^{2+} molar ratio 10 (Fe^{2+} 250 mg/L) was considered as the starting point. The SBR efficiency (*R*%) was 69 ± 1 and 70 ± 2 for sCOD and DOC removal, respectively. Under H_2O_2/Fe^{2+} molar ratio 20 (Fe^{2+} 125 mg/L), the characteristics of the photo-Fenton-treated wastewater were sCOD 179 ± 2 mg/L, DOC 76 ± 3 mg/L and BOD_5/COD ratio 0.50 ± 0.02, and SBR efficiency (*R*%) was 69 ± 1 and 69 ± 1 for sCOD and DOC removal, respectively. The photo-Fenton-treated wastewater characteristics were similar in cases PF6 and PF7 and hence the SBR efficiency. Both photo-Fenton-treated wastewater were biodegradable since the BOD_5/COD ratio was more than 0.4. Decreasing SBR efficiency with increase of H_2O_2/Fe^{2+} molar ratio (cases PF9 and PF10) was presumably due to decrease of biodegradability (BOD_5/COD ratio) below 0.4 and this indicated inhibition of biological oxidation by the antibiotic intermediates. It is noteworthy that SBR efficiency in terms of sCOD and DOC was very sensitive to BOD_5/COD ratio below 0.40. SBR efficiency (*R*%) in terms of sCOD removal decreased from 69 ± 1 at BOD_5/COD ratio 0.48 ± 0.01 to 44 ± 1 at BOD_5/COD ratio 0.19 ± 0.02 (cases PF6 and PF10). A marked decline in MLSS concentration was observed at higher influent sCOD and low BOD_5/COD ratio (case PF10). This reduction in MLSS concentration was ascribed to wall growth [14] and inhibition of biological oxidation by the antibiotic intermediates. The *F*/*M* ratio varied in the range 0.049–0.124 day^{-1} and this was mainly due to variation in sCOD of

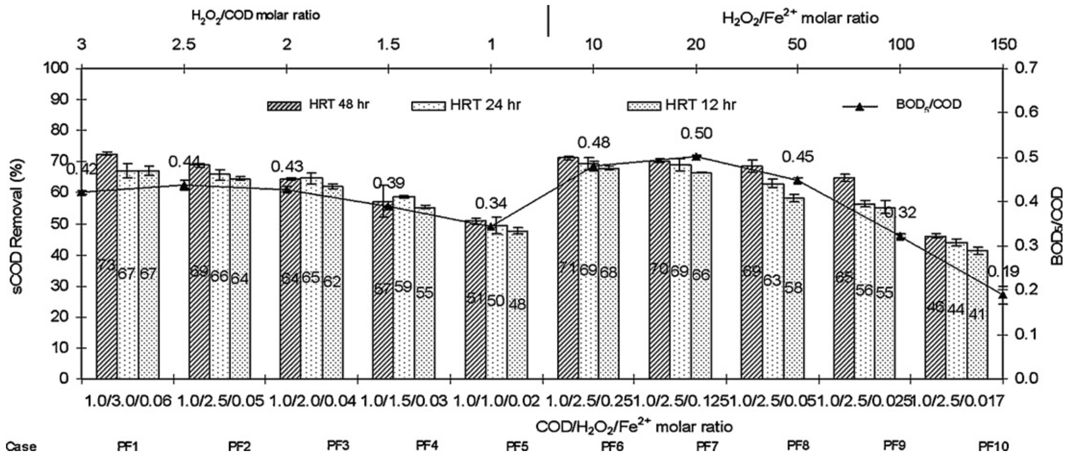

Fig. 5. SBR efficiency in terms of sCOD removal at HRT 48, 24 and 12 h.

the photo-Fenton-treated wastewater as well as change in biomass concentration.

Combined photo-Fenton–SBR process efficiency achieved was similar to those observed in the reported studies. Farré et al. [14] reported 80% DOC removal in combined photo-Fenton and biological treatment of Diuron and Linuron pesticide water at H_2O_2/Fe^{2+} molar ratio ~12.7, HRT of 2 days and VSS 0.60 ± 0.03 g/L. García-Montaño et al. [12] reported 80% DOC removal in combined photo-Fenton–SBR treatment of a synthetic textile effluent containing a hetero-bioreactive dye (Cibacron Red FN-R, 250 mg/L) at H_2O_2/Fe^{2+} molar ratio 12.5, of HRT 1 day, irradiation time 90 min and VSS 0.56 ± 0.03 g/L. González et al. [16] reported 75.7% TOC removal by photo-Fenton-sequencing batch biofilm reactor treatment of a synthetic wastewater containing 200 mg/L sulfamethoxazole. The treatment conditions were 300 mg/L H_2O_2 and 10 mg/L Fe^{2+}, and HRT of 8 h.

It should be noted that the Malaysian standard for discharge of treated industrial wastewater into receiving water bodies (lakes and rivers) is COD 100 mg/L [31]. Assuming that COD contribution by suspended solids is ~30 mg/L, minimum sCOD of the final effluent should be ~70 mg/L. Table 3 shows that combined photo-Fenton–SBR treatment of the antibiotic wastewater (cases PF6 and PF7) met the discharge standard.

3.2.2. *Effect of cycle period on performance of SBR*

In order to examine the effect of cycle period on SBR performance, HRT was varied in the range 12–48 h. The SBR was operated for 203 days at HRT of 48, 24 and 12 h, and was fed with antibiotic wastewater treated under different H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios (cases PF1–PF10). Fig. 5 shows the SBR efficiency in terms of sCOD at HRT of 48, 24 and 12 h. No remarkable improvement in SBR efficiency was observed due to HRT increase from 12 to 48 h. This indicated that most substrate degradation occurred during the first 12 h and a smaller portion was degraded in rest of the retention time. In order to confirm this, a statistical analysis (one-way ANOVA) was made on the results at a 5% level of significance. As shown in Table 4, the statistical analysis indicated that increase of HRT from 24 to 48 h did not significantly improve sCOD removal (P-value $0.132 > 0.05$) or DOC removal (P-value $0.198 > 0.05$). HRT decrease from 24 to 12 h also did not significantly reduce sCOD removal (P-value $0.201 > 0.05$) or DOC removal (P-value $0.096 > 0.05$). García-Montaño et al. [12,13] observed no remarkable increase in DOC removal due to increase of HRT from 1 to 2 and 4 days in the treatment of dye solution of commercial hetero-bioreactive dye Cibacron Red FN-R and reactive dye Procion Red H-E7B by combined photo-Fenton SBR treatment. It was decided to operate the SBR at HRT of 12 h in subsequent experiments.

3.2.3. *Optimization of combined photo-Fenton–SBR treatment*

In Sections 3.2.1 and 3.2.2, it was observed that both H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios significantly affected the SBR performance, whereas HRT increase did not significantly improve the SBR performance, and H_2O_2/COD molar ratio 2 and HRT of 12 h were suitable for the combined photo-Fenton–SBR treatment. The next step was to study the effect of increasing irradiation time and H_2O_2/Fe^{2+} molar ratio (decreasing Fe^{2+} dose) on combined process efficiency. The experimental design consisted of nine photo-Fenton-treated wastewater (cases PF11–PF19, Table 5). The SBR was operated from day 204 to 239 (36 days) at HRT of 12 h and the cycle was repeated 8 times to obtain repetitive results.

Table 5 shows photo-Fenton-treated wastewater and SBR effluent characteristics, and combined process efficiency under different irradiation time and H_2O_2/Fe^{2+} molar ratio. The other operating conditions of the photo-Fenton process were H_2O_2/COD molar ratio 2.0 and pH 3. H_2O_2/Fe^{2+} molar ratio 50 (Fe^{2+} 200 mg/L) was considered as the starting point since it did not meet the discharge standards (Table 3). When irradiation time was increased from 30 to 60 min (case PF11), the SBR efficiency (R%) was 71 ± 1 and 76 ± 1 for sCOD and DOC removal, respectively, and the SBR effluent (sCOD 52 ± 1 mg/L) met the discharge standards. When irradiation time was increased to 90 min (case PF12) and 120 min (case PF13), SBR

Table 4
One-way ANOVA for SBR efficiency in terms of sCOD and DOC removal at different HRTs.

One-way ANOVA	Parameter	No. of groups	*F*	*P*-value	*F*-crit
24 h vs. 48 h	sCOD	2	2.3	0.132	3.9
12 h vs. 24 h	sCOD	2	1.7	0.201	3.9
12 h vs. 24 h vs. 48 h	sCOD	3	3.9	0.023	3.1
24 h vs. 48 h	DOC	2	1.7	0.198	3.9
12 h vs. 24 h	DOC	2	2.8	0.096	3.9
12 h vs. 24 h vs. 48 h	DOC	3	4.4	0.014	3.1

Table 5
Photo-Fenton-treated wastewater and SBR effluent characteristics, and combined process efficiency at different irradiation time and H_2O_2/Fe^{2+} molar ratio.

Case	Photo-Fenton-treated wastewater								SBR effluent						Combined efficiency	
	Irradiation time (min)	H_2O_2/Fe^{2+} (MR)	sCOD		DOC		BOD_5	BOD_5/COD	sCOD		DOC		MLSS	*F*/*M*	sCOD	DOC
			mg/L	*R*%	mg/L	*R*%	mg/L		mg/L	*R*%	mg/L	*R*%	mg/L	day^{-1}	%	%
PF11	60	50	180 ± 1	67 ± 1	65 ± 1	61 ± 1	84 ± 1	0.47 ± 0.01	52 ± 1	71 ± 1	16 ± 1	76 ± 1	2380	0.050	91	90
PF12	90	50	109 ± 1	81 ± 1	50 ± 1	70 ± 1	71 ± 1	0.65 ± 0.01	30 ± 1	73 ± 1	12 ± 1	76 ± 2	2260	0.032	95	93
PF13	120	50	83 ± 1	86 ± 1	33 ± 1	80 ± 1	57 ± 2	0.68 ± 0.01	23 ± 3	73 ± 1	9 ± 1	73 ± 3	2300	0.024	96	95
PF14	60	100	210 ± 1	64 ± 1	84 ± 2	49 ± 1	80 ± 2	0.38 ± 0.01	65 ± 1	69 ± 1	26 ± 1	69 ± 1	2260	0.061	90	88
PF15	90	100	159 ± 1	72 ± 1	68 ± 1	59 ± 1	88 ± 1	0.55 ± 0.01	43 ± 2	16 ± 1	16 ± 1	74 ± 1	2240	0.047	93	91
PF16	120	100	139 ± 1	77 ± 1	57 ± 1	66 ± 1	91 ± 2	0.66 ± 0.01	33 ± 2	14 ± 1	14 ± 1	75 ± 1	2310	0.040	95	92
PF17	60	150	259 ± 2	56 ± 1	103 ± 5	39 ± 1	94 ± 1	0.36 ± 0.01	84 ± 1	68 ± 1	31 ± 1	70 ± 1	2200	0.078	86	82
PF18	90	150	232 ± 2	60 ± 1	81 ± 2	52 ± 1	97 ± 1	0.42 ± 0.01	66 ± 2	72 ± 1	24 ± 1	71 ± 1	2160	0.071	89	86
PF19	120	150	170 ± 1	71 ± 1	64 ± 1	62 ± 1	17 ± 2	0.45 ± 0.01	39 ± 1	71 ± 1	18 ± 1	72 ± 1	2150	0.052	93	89

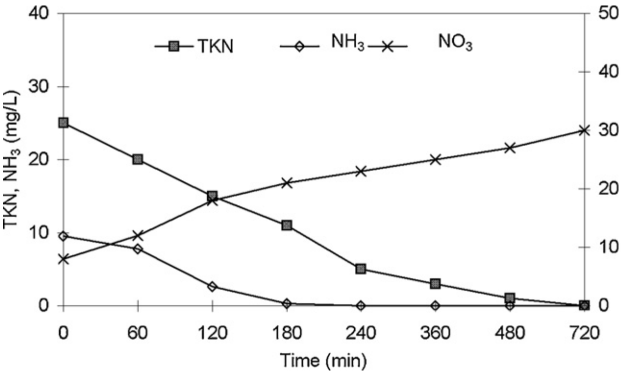

Fig. 6. Nitrification in SBR (case PF18).

efficiency (*R*%) did not improve significantly. The SBR effluent (cases PF11, PF12 and PF13) amply met the discharge standards of less than 100 mg/L COD (70 mg/L sCOD), and based on these results it was decided to increase H_2O_2/Fe^{2+} molar ratio (decrease Fe^{2+} dose) by 50% to 100 (Fe^{2+} 100 mg/L). The irradiation time was 60 min (case PF14), 90 min (case PF15) and 120 min (case PF16). The SBR efficiency (*R*%) (case F14) was 69 ± 1 and 69 ± 1 for sCOD and DOC removal, respectively, and the SBR effluent (sCOD 65 ± 1 mg/L) met the discharge standard. When irradiation time was increased to 90 min (case PF15) and 120 min (case PF16), SBR efficiency (*R*%) improved further (73 ± 1 and 76 ± 1) and the SBR effluent sCOD was 43 ± 2 and 33 ± 2 mg/L, respectively.

The SBR effluent of the combined photo-Fenton–SBR treatment at H_2O_2/Fe^{2+} molar ratio 100 and irradiation time 60, 90 and 120 min (cases PF14–F16) amply met the discharge standards. In order to assess the effect of further increasing H_2O_2/Fe^{2+} molar ratio (reducing Fe^{2+} concentration) on SBR and combined process performance, H_2O_2/Fe^{2+} molar ratio 150 (Fe^{2+} 66.6 mg/L) was used with irradiation time 60, 90 and 120 min (cases PF17–F19). The SBR efficiency (*R*%) was 68 ± 1 and 70 ± 1 for sCOD and DOC removal, respectively and the SBR effluent (sCOD 84 ± 1 mg/L) did not meet the discharge standards (case PF17). When irradiation time was increased from 60 min to 90 min (case PF18), SBR efficiency (*R*%) was 72 ± 1 and 71 ± 1 for sCOD and DOC removal, respectively, and the SBR effluent (sCOD 66 ± 2 mg/L) met the discharge standards. When irradiation time was increased further to 120 min (case F19), SBR efficiency (*R*%) for sCOD removal improved to 77 ± 1 and the SBR effluent sCOD was 39 ± 1 mg/L.

Since the objective was to minimize the Fe^{2+} dose, it was important to know if increasing irradiation time and reducing Fe^{2+} dose significantly affected the SBR performance. A two-way analysis of variance (ANOVA) was conducted using the SPSS statistical software. Table 6 shows the significance of the difference between the two means for sCOD removal in the SBR at H_2O_2/Fe^{2+} molar ratio 50, 100 and 150 and irradiation time 60, 90 and 120 min using Tukey HSD method. When the value of significance was less than 0.05, it indicated that COD removal in SBR was significantly different and was not significantly different if the value of significance was more than 0.05 (the highlighted values in Table 6). There was no difference between the SBR efficiency at H_2O_2/Fe^{2+} molar ratio 100 and irradiation time 90 min (100 MR – 90 min), and SBR efficiency at H_2O_2/Fe^{2+} molar ratio 150 and irradiation time 90 min (150 MR – 90 min). Since the SBR effluent in both cases (PF15 and PF18, Table 5) met the discharge standard, it would be more economical to select H_2O_2/Fe^{2+} molar ratio 150 and irradiation time 90 min as the best operating conditions (case PF18, Table 5).

To study nitrification in SBR, NH_3, TKN and NO_3^- were measured during the cycle period (12 h) for case PF18 and shown in Fig. 6. Oxidation of NH_3 was complete in 6 h, oxidation of TKN was complete

Table 6
Significance of the difference between two means for sCOD removal in SBR using Tukey HSD method.

H_2O_2/Fe^{2+} (MR) and irradiation time (min)	50 MR – 60 min (PF11)	50 MR – 90 min (PF12)	50 MR – 120 min (PF13)	100 MR – 60 min (PF14)	100 MR – 90 min (PF15)	100 MR – 120 min (PF16)	150 MR – 60 min (PF17)	150 MR – 90 min (PF18)	150 MR – 120 min (PF19)
50 MR – 60 min (PF11)									
50 MR – 90 min (PF12)	0.14								
50 MR – 120 min (PF13)	0.15	1							
100 MR – 60 min (PF14)	0.01	0	0						
100 MR – 90 min (PF15)	0.05	1	1	0					
100 MR – 120 min (PF16)	0	0	0	0	0				
150 MR – 60 min (PF17)	0	0	0	0.09	0	0			
150 MR – 90 min (PF18)	0	0.26	0.28	0	0.11	0	0		
150 MR – 120 min (PF19)	1	0	0	0	0	0.97	0	0	

in 12 h and NO_3^- concentration was 30 mg/L in 12 h, indicating complete nitrification. Discharge of the SBR effluent to Malaysian receiving waters presents no problem. Either there is sufficient dilution of the nitrate (e.g. release into the ocean) or there is sufficient flow (a river with strong currents) to prevent accumulation of the nitrates. It is also to be noted that the Malaysian discharge standards for nitrate is 20 mg/L (upstream of water supply source) and 50 mg/L (downstream of water supply source) [32].

4. Conclusions

- The optimum H_2O_2/COD and H_2O_2/Fe^{2+} molar ratios of photo-Fenton pretreatment of an antibiotic wastewater containing amoxicillin and cloxacillin were 2.5 and 20, respectively.
- Complete degradation of the antibiotics occurred in one min.
- The best operating conditions for combined photo-Fenton–SBR treatment of the antibiotic wastewater were H_2O_2/COD molar ratio 2, H_2O_2/Fe^{2+} molar ratio 150, irradiation time 90 min and HRT of 12 h. Under these conditions, the combined process efficiency was 89% for sCOD removal with complete nitrification and the SBR effluent met the discharge standards.
- SBR performance was found to be very sensitive to BOD_5/COD ratio below 0.40 of the photo-Fenton treated wastewater.
- Combined photo-Fenton–SBR is an effective process for treatment of antibiotic wastewater.

Acknowledgement

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

References

[1] M.V. Walter, J.W. Vennes, Occurrence of multiple-antibiotic resistant enteric bacteria in domestic sewage and oxidative lagoons, Appl. Environ. Microbiol. 50 (1985) 930–933.
[2] R. Alexy, T. Kümpel, D.K. Kummerer, Assessment of degradation of 18 antibiotics in the closed bottle test, Chemosphere 57 (2004) 505–512.
[3] M. Pera-Titus, V. Garcıa-Molina, M.A. Banos, J. Gimĭenez, S. Esplugas, Degradation of chlorophenols by means of advanced oxidation processes: a general review, Appl. Catal. B 47 (2004) 219–256.
[4] J.J. Pignatello, D. Liu, P. Huston, Evidence for an additional oxidant in the photo assisted Fenton reaction, Environ. Sci. Technol. 33 (1999) 1832–1839.
[5] E. Chamarro, A. Marco, S. Esplugas, Use of Fenton reagent to improve organic chemical biodegradability, Water Res. 35 (2001) 1047–1051.
[6] V. Sarria, S. Parra, N. Adler, P. Péringer, N. Benítez, C. Pulgarín, Recent developments in the coupling of photoassisted and aerobic biological processes for the treatment of biorecalcitrant compounds, Catal. Today 76 (2002) 301–315.
[7] J.P. Scott, O.F. Oills, Integration of chemical and biological oxidation processes for water treatment: review and recommendations, Environmental Progress 14 (1995) 88–103.
[8] A. Marco, S. Esplugas, G. Saum, How and why to combine chemical and biological processes for wastewater treatment, Water Science &Technology 35 (1997) 321–327.
[9] Y. Yu, S. Hu, Preoxidation of chlorophenolic wastewaters for their subsequent biological treatment, Water Science and Technology 29 (1994) 313–320.
[10] C. Pulgarin, M. Invernizzi, S. Parra, V. Sarria, R. Polania, P. Peringer, Strategy for the coupling of photochemical and biological flow reactors useful in mineralization of biorecalcitrant industrial pollutants, Catalysis Today 54 (1999) 341–352.
[11] S. Mace, J. Mata-Alvarez, Review of SBR technology for wastewater treatment: an overview, Ind. Eng. Chem. Res. 41 (2002) 5539–5553.
[12] J. García-Montaño, F. Torrades, J.A. García-Hortal, X. Doménech, J. Peral, Combining photo-Fenton process with aerobic sequencing batch reactor for commercial hetero-bireactive dye removal, Applied Catalysis B: Environmental 67 (2006) 86–92.
[13] J. García-Montaño, F. Torrades, J.A. García-Hortal, X. Doménech, J. Peral, Degradation of Procion Red H-E7B reactive dye by coupling a photo-Fenton system with a sequencing batch reactor, J. Hazard. Mater 134 (2006) 220–229.
[14] M.J. Farré, X. Doménech, J. Peral, Combined photo-Fenton and biological treatment for Diuron and Linuron removal from water containing humic acid, J. Hazard. Mater. 147 (2007) 167–174.

[15] M.M.B. Martín, J.A.S. Pèrez, J.L.C. López, I. Oller, S.M. Rodríguez, Degradation of a four-pesticide mixture by combined photo-Fenton and biological oxidation, Water Res. 43 (2009) 653–660.

[16] O. González, M. Esplugas, C. Sans, A. Torres, S. Esplugas, Performance of a sequencing batch biofilm reactor for the treatment of pre-oxidation sulfamethoxazole solutions, Water Res. 43 (2009) 2149–2158.

[17] 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.

[18] E.S. Elmolla, M. Chaudhuri, Degradation of the antibiotics amoxicillin, ampicillin and cloxacillin in aqueous solution by the photo-Fenton process, J. Hazard. Mater. 172 (2009) 1476–1481.

[19] E.S. Elmolla, M. Chaudhuri, Effect of photo-Fenton operating conditions on the performance of photo-Fenton–SBR process for recalcitrant wastewater treatment, Journal of Applied Sciences 10 (2010) 3236–3242.

[20] E.S. Elmolla, M. Chaudhuri, Photocatalytic degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution using UV/TiO_2 and UV/H_2O_2/TiO_2 photocatalysis, Desalination 252 (2010) 46–52.

[21] E.S Elmolla, M. Chaudhuri, Degradation of amoxicillin, ampicillin and cloxacillin antibiotics in aqueous solution by the UV/ZnO photocatalytic process, J. Hazard. Mater 173 (2010) 445–449.

[22] E.S. Elmolla, M. Chaudhuri, Comparison of different advanced oxidation processes for treatment of antibiotic aqueous solution, Desalination 256 (2010) 43–47.

[23] E.S. Elmolla, M. Chaudhuri, M.M. Eltoukhy, The use of artificial neural network (ANN) for modeling of COD removal from antibiotics aqueous solution by Fenton process, J. Hazard. Mater. 179 (2010) 127–134.

[24] E.S. Elmolla, M. Chaudhuri, The feasibility of using combined TiO_2 photocatalysis–SBR process for antibiotic wastewater treatment, Desalination 272 (2011) 218–224.

[25] APHA, AWWA, WPCF, Standard Methods for the Examination of Water and Wastewater, 18th ed., American Public Health Association, American Water Works Association, Water Pollution Control Federation, Washington, DC, USA, 1992.

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

[27] 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. Photochem. Photobiol. A: Chem. 153 (2002) 191–197.

[28] V. Kavitha, K. Palanivelu, Destruction of cresols by Fenton oxidation process, Water Res. 39 (2005) 3062–3072.

[29] J.M. Joseph, H. Destaillats, H.M. Hung, M.R. Hoffmann, The sonochemical degradation of azobenzene and related azo dyes: rate enhancements via Fenton's reactions, J. Phys. Chem. A 104 (2000) 301–307.

[30] A.G. Trovó, S.A.S. Melo, R.F.P. Nogueira, Photodegradation of the pharmaceuticals amoxicillin, bezafibrate and paracetamol by the photo-Fenton process: application to sewage treatment plant effluent, J. Photochem. Photobiol. A: Chem. 198 (2008) 215–220.

[31] Environmental Quality Act 1974 [Act 127], Environmental Quality (Sewage and Industrial Effluents) Regulations 1979, Ministry of Health, Malaysia.

[32] Akta Kualiti Alam Sekeliling 1974, Peraturan-Peraturan Kualiti Alam Sekeliling (Kumbahan) 2009, Ministry of Health, Malaysia.