Combined UV/Fenton and SBR Treatment
of a Semi-aerobic Landfill Leachate
(Penggabungan Rawatan UV/Fenton dan SBR untuk Larut Resapan dari Tapak Pelupusan Semi-aerobik)

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ABSTRACT

This study examined the combined UV/Fenton and sequencing batch biological reactor (SBR) treatment of a semi-aerobic landfill leachate. Fenton pretreatment of the leachate was optimized by the response surface methodology (RSM). UV/Fenton pretreatment of the leachate was performed under the optimum operating conditions of the Fenton pretreatment (H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0 and reaction/irradiation time 1.5 h). The characteristics of the UV/Fenton pretreated leachate were: COD 390 mg/L, sCOD 330 mg/L, BOD_5 136 mg/L, BOD_5/COD ratio 0.35, NH_3-N 112 mg/L, TKN 157 mg/L, NO_3^--N 6.8 mg/L and colour 99 Pt-Co Unit. SBR treatment of the UV/Fenton pretreated leachate resulted in sCOD, BOD_5 and NH_3-N removal of 78%, 81% and 88%, respectively. The final effluent characteristics were: COD 92 mg/L, sCOD 71 mg/L, BOD_5 26 mg/L, NH_3-N 7 mg/L, NO_3^--N 27 mg/L, TKN 13 mg/L and TSS 38 mg/L. The effluent met the Malaysian discharge standard (B) – COD 100 mg/L, BOD_5 50 mg/L and TSS 100 mg/L. Combined UV/Fenton and SBR is an effective treatment for mature leachate from semi-aerobic landfill.

Keywords: Mature landfill leachate; response surface methodology (RSM); sequencing batch biological reactor (SBR); UV/Fenton

ABSTRAK

Kajian ini adalah untuk menyelidik tentang penggabungan rawatan UV/Fenton dan reaktor biologi kumpulan jujukan (SBR) untuk larut resapan dari tapak pelupusan yang semi-aerobik. Rawatan awalan dengan Fenton dioptimumkan oleh kaedah sambutan permukaan (RSM) terhadap larut resapan. Rawatan awalan untuk larut resapan dengan UV/Fenton dilaksanakan di bawah keadaan optimum daripada rawatan awalan dengan Fenton (H_2O_2/COD 2.25, nisbah molar H_2O_2/Fe^{2+} 10.0 dan masa tindak balas selama 1.5 jam). Ciri-ciri larut resapan selepas rawatan UV/Fenton adalah: COD 390 mg/L, sCOD 330 mg/L, BOD_5 136 mg/L, nisbah BOD_5/COD 0.35, NH_3-N 112 mg/L, TKN 157 mg/L, NO_3^--N 6.8 mg/L dan warna 99 Pt-Co Unit. Rawatan SBR untuk larut resapan selepas UV/Fenton memberi keputusan dalam sCOD, BOD_5 dan NH_3-N dengan penyingkiran 78%, 81% dan 88% masing-masing. Ciri-ciri efluen akhir adalah: COD 92 mg/L, sCOD 71 mg/L, BOD_5 26 mg/L, NH_3-N 7 mg/L, NO_3^--N 27 mg/L, TKN 13 mg/L dan TSS 38 mg/L. Efluen tersebut memenuhi syarat-syarat dalam Akta Kualiti Alam Sekitar – COD 100 mg/L, BOD_5 50 mg/L dan TSS 100 mg/L. Penggabungan rawatan UV/Fenton dan SBR merupakan satu rawatan yang efektif untuk larut resapan dari tapak pelupusan yang semi-aerobik.

Kata kunci: Kaedah sambutan permukaan (RSM); larut resapan yang lama; reaktor biologi kumpulan jujukan (SBR); UV/Fenton

INTRODUCTION

Municipal landfill leachate is considered as heavily polluted wastewater with significant temporal and spatial variations in characteristics and a potential source of ground and surface water contamination as it may percolate through soil and subsoil, causing extensive pollution of streams, creeks and water wells (Tatsi et al. 2003). The leachate characteristics are influenced by the type and quality of the deposited solid waste, hydrogeological factors and age of the landfill. The specific characteristics of the leachate determine its relative treatability (Tatsi et al. 2003). Biological processes are quite effective when applied to relatively younger (i.e. recently produced) leachate containing mainly volatile fatty acids, but they are less efficient for the treatment of older (i.e.

mature or stabilized) leachate (Amokrane et al. 1997). Recalcitrant organics, contained in mature landfill leachates, are not amenable to conventional biological treatment and high ammonia content might also be inhibitory to microorganisms (Li et al. 1999). Combining advanced oxidation process (AOP) with biological process has received attention in recent years as a promising alternative treatment for recalcitrant wastewater. Using advanced oxidation process as pretreatment for recalcitrant wastewater is important to improve the biodegradability (BOD_5/COD ratio) and produce a new effluent that can be treated biologically (Sarria et al. 2002).

Fenton and combination of UV radiation with Fenton reagent (UV/Fenton or photo-Fenton) have evolved as

promising AOPs for pretreatment of mature landfill leachate for subsequent biological treatment (Cortez et al. 2011; de Morais & Zamora 2005; Kim et al. 2001; Lopez et al. 2004). Oxidation (degradation) of organic compounds with Fenton's reagent is based on ferrous (Fe^{2+}) ion, hydrogen peroxide (H_2O_2) and hydroxyl radical ($\cdot OH$) produced by the catalytic decomposition of H_2O_2 in acidic solution (Chamarro et al. 2001). In the UV/Fenton or photo-Fenton process, additional reactions occur in the presence of light that produce $\cdot OH$ radicals or increase the production rate of $\cdot OH$ radicals (Pignatello et al. 1999), thus increase the efficiency of the process. Sequencing batch biological reactor (SBR) is a wastewater treatment process based on the principles of the activated sludge process. SBR has been successfully employed in the biodegradation of both municipal and industrial wastewater (Mace & Mata-Alvarez 2002). Combined Fenton-SBR and photo-Fenton-SBR treatment of mature municipal landfill leachate have been conducted in Brazil (de Morais & Zamora 2005) and China (Guo et al. 2010; Liu et al. 2010).

The objective of this study was to examine combined UV/Fenton and sequencing batch biological reactor (SBR) treatment of a semi-aerobic landfill leachate. Fenton pretreatment of the leachate was optimised by the response surface methodology (Bezerra et al. 2008; Khuri & Cornell 1996). UV/Fenton pretreatment of the mature leachate was conducted under the optimum operating conditions and the new effluent was subjected to biological treatment by SBR.

MATERIALS & METHODS

LEACHATE

Leachate sample was collected from the Pulau Burung Landfill (PBL), Nibong Tebal, Penang and stored in a cold room at 4°C to minimise biological and chemical reactions. Before experiment, the sample was mixed and settled for 2 h and subjected to preliminary treatment by pH adjustment to 3 and 1 h settling (Heng et al. 2009). The characteristics (range from triplicate samples) of the raw, settled (2 h) and preliminary treated leachate are presented in Table 1.

ANALYTICAL MEASUREMENT

The pH measurement was performed using a pH meter (Hach sension 4) and a pH probe (Hach platinum series pH electrode model 51910, Hach Company). Five-day biochemical oxygen demand (BOD_5) was measured according to method 5210 B of the Standard Methods (APHA 2005). DO was measured using a YSI 5000 dissolved oxygen meter. The bacterial seed for BOD_5 test was obtained from a municipal wastewater treatment plant. Chemical oxygen demand (COD) was measured by the Reactor Digestion Hach method No. 8000 (Hach 2003). For soluble COD (sCOD), the sample was filtered through 0.45 μm membrane filter before COD measurement. If the sample contained hydrogen peroxide (H_2O_2), to reduce interference in COD determination pH was increased to above 10 to decompose H_2O_2 to oxygen and water (Kang et al. 1999; Talinli & Anderson 1992). Turbidity was measured by a turbidity meter and reported in nephelometric turbidity unit (NTU). Solids (total solids, total suspended solids, mixed liquor suspended solids (MLSS) and total dissolved solids were measured according to methods 2540 B C D of the Standard Methods (APHA 2005). Colour, total phosphorus (TP), ammonia-nitrogen (NH_3-N) and nitrate-nitrogen (NO_3^--N) were measured according to Hach Handbook (Hach 2003). Method 4500-N_{org} C of the Standard Methods (APHA 2005) was used to measure total Kjeldahl nitrogen (TKN).

FENTON & UV/FENTON PRETREATMENT

Batch experiments were performed in a 600 mL Pyrex reactor with 250 mL of preliminary treated leachate sample at pH3. The optimum pH for Fenton treatment of mature leachate has been found to be pH3 (Kim et al. 2001; Kim & Huh 1997; Kim & Hwang 2000). Ferrous sulfate ($FeSO_4.7H_2O$) and hydrogen peroxide (H_2O_2) were added simultaneously according to the selected H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio. The mixture was magnetically stirred to ensure complete homogeneity during reaction. Aliquots were taken at selected reaction time and adjusted to pH above 10 with sodium hydroxide for measurement of COD, colour and NH_3-N. For UV/Fenton pretreatment, the mixture was irradiated with an UV lamp (Spectroline Model EA-160/FE, 230 volts, 0.17 amps,

TABLE 1. Characteristics of PBL leachate

Parameter	Raw	Settled	Preliminary treated
pH	8.4-8.7	8.0-8.8	2.9-3.1
Colour (PtCo)	2160-2560	1950-2180	520-560
Turbidity (NTU)	308-314	208-256	86-105
BOD_5 (mg/L)	83-144	-	40-44
COD (mg/L)	1960-2880	1350-2740	990-1100
Total solids (mg/L)	6410-6625	-	-
Total suspended solids (mg/L)	175-198	98-122	19-25
Total dissolved solids (mg/L)	6232-6427	-	-
Total phosphorus (mg/L)	143-168	-	-
Ammonia-nitrogen (mg/L)	730-980	630-878	555-680

Spectronics Corporation, New York, USA) with nominal power of 6 W, emitting radiations at wavelength ≈ 365 nm, and placed 5 cm above the reactor.

SEQUENCING BATCH BIOLOGICAL REACTOR (SBR) TREATMENT

Figure 1 shows a schematic diagram of the experimental setup. The SBR total volume was 2 L with operating volume of 1.5 L. The operating volume was divided into 1.0 L decanting volume and 0.5 L sludge volume. The SBR was equipped with an air pump and air diffuser to keep dissolved oxygen above 3 mg/L and a magnetic stirrer for mixing purpose. Feeding and decanting were performed using two peristaltic pumps. The cycle period was divided into five phases: filling (0.25 h), aeration-reaction (21.75 h), settling (1.5 h), decant (0.25 h) and idle (0.25 h). Cycle phases were controlled by an electric control panel. Pretreated leachate was used to feed the SBR after pH adjustment to 6.9-7.1. For start up, the SBR was inoculated with 300 mL of aerobic sludge from the aeration tank of a municipal wastewater treatment plant. In order to acclimate the sludge, hydraulic retention time (HRT) was chosen to be 2 days and the pretreated leachate was mixed with domestic wastewater, with mixing ratio 25%:75%, 50%:50%, 75%:25% and 100%:0% and the acclimation period was extended to 8 days. Daily analyses of soluble COD (sCOD), ammonia-nitrogen (NH_3-N) and nitrate-nitrogen (NO_3^--N) for both influent and effluent were carried out.

EXPERIMENTAL DESIGN AND DATA ANALYSIS

Design expert software (version 6.0.7) was used for statistical design of experiment and data analysis. Central composite design (CCD) and response surface methodology (RSM) were applied to optimise the three important operating variables (conditions) of the Fenton process: H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction time. The coded values for H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction time (C) were set at five levels: -α (minimum), -1, 0 (central), +1 and +α (maximum). The study ranges were chosen as H_2O_2/COD molar ratio 1.16-2.84, H_2O_2/Fe^{2+} molar ratio 3.18-36.82 and reaction time 0.66-2.34 h as shown in Table 2. It is to be noted that optimum H_2O_2/COD molar ratio in the range 1.1-3.0 (Cortez et al. 2011; Kim et al. 2001) and optimum H_2O_2/Fe^{2+} molar ratio in the range 1.2-19.7 (Cortez et al. 2011; Deng 2007; Kim et al. 2001; Lopez et al. 2004) have been observed for Fenton treatment of mature leachate.

In order to obtain the optimum H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and reaction time, three parameters were analyzed as responses: COD removal, colour removal and NH_3-N removal. The regression analyses, graphical analyses and analyses of variance (ANOVA) were carried out using the design expert software. The optimum region was identified based on the main parameters in the overlay plot (Table 2).
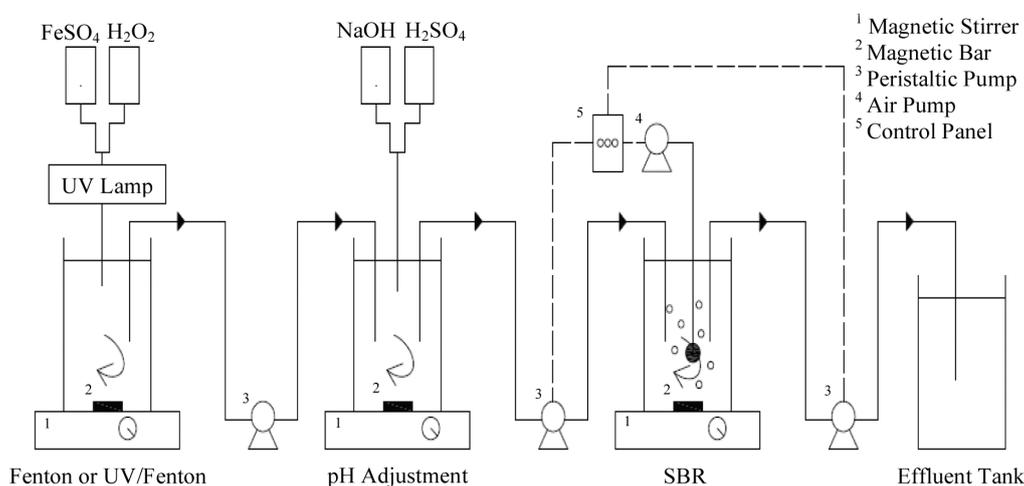
FIGURE 1. Schematic diagram of experimental setup

TABLE 2. Range of levels of operating variables

Independent variables	Codes	Range and levels (coded)				
		-1.68	-1	0	1	1.68
H_2O_2/COD molar ratio	A	1.16	1.5	2	2.5	2.84
H_2O_2/Fe^{2+} molar ratio	B	3.18	10	20	30	36.82
Reaction Time (h)	C	0.66	1	1.5	2	2.34

The following response equation,

$$Y = \beta_0 + \beta_1 A + \beta_2 B + \beta_3 C + \beta_{11} A^2 + \beta_{22} B^2$$
$$+ \beta_{33} C^2 + \beta_{12} AB + \beta_{13} AC + \beta_{23} BC, \qquad (1)$$

was used to assess the predicted result (Y) as a function of the operating variables H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction time (C), and calculated as the sum of a constant (β_0), three first-order effects (A, B and C), three second-order effects (A^2, B^2 and C^2) and three interaction effect (AB, AC and BC).

RESULTS & DISCUSSION

STATISTICAL ANALYSIS

The results obtained were analyzed by ANOVA to assess the 'goodness of fit'. The models for COD, colour and NH_3-N removal (Y_1, Y_2 and Y_3) were significant by the F-test at the 5% confidence level if Prob>F<0.05. The following fitted regression models (equation in terms of coded values for the regressors) were obtained to quantitatively investigate the effects of H_2O_2/COD molar ratio (A), H_2O_2/Fe^{2+} molar ratio (B) and reaction time (C) on the Fenton process performance.

COD removal:
$$Y_1 = 47.63 + 3.03A - 6.73B + 1.69C - 1.26A^2 + 2.60B^2$$
$$- 0.93C^2 - 1.70AB + 0.34AC - 0.11BC. \qquad (2)$$

Colour removal:
$$Y_2 = 75.64 + 6.71A - 7.33B + 2.59C - 6.75A^2 - 3.92B^2$$
$$- 3.24C^2 + 0.70AB - 0.46AC - 3.15BC. \qquad (3)$$

NH_3-N removal:
$$Y_3 = 74.79 + 5.57A - 3.66B + 0.34C - 2.30A^2 + 0.37B^2$$
$$- 0.84C^2 - 1.79AB + 0.53AC + 0.26BC. \qquad (4)$$

In (2), (3) and (4), the values of the sum of a constant (β_0), 47.63, 75.64 and 74.79 represent the predicted percentage removal of COD, colour and NH_3-N, respectively at 'level 0'. The positive sign indicates that the parameter (variable) is directly proportional to the responses COD removal, colour removal and NH_3-N removal; on the other hand, the negative sign indicates that the parameter is inversely proportional to the responses. For example, the decrease of H_2O_2/Fe^{2+} molar ratio (B) increases the removal. It is to be noted that relatively lower values were found for reaction time (C), indicating that variation of reaction time has less effect on the Fenton process compared to H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio.

Table 3 shows the central composite design (CCD) in the form of a 2^3 full factorial design with five additional experimental trials (run number 4, 5, 9, 14 and 15) as

replicates of the central point and observed (actual) experimental results and predicted results from the model at each assay. The R^2 coefficient was found to be close to 1 (0.9392 and 0.9103 for COD and NH_3-N removal, respectively), indicating that the regression models explained the prediction well (Olmez 2009). The R^2 coefficient of colour removal was low (0.8124) but the value is acceptable. The R^2 values indicate adequate agreement between the data predicted by the model and the observed data. The replication of the central points was to get a good estimation of the experimental error. In this table, the parameter levels are presented in terms of molar ratio for H_2O_2/COD and H_2O_2/Fe^{2+}, and h for reaction time and the coded level in parentheses.

The ANOVA for response surface quadratic model is shown in Table 4. Adequate precision (AP) compares the range of the predicted values at the design points to the average prediction error. Ratios greater than 4 indicate adequate model discrimination and can be used to navigate the design space defined by the CCD. The AP for all the responses were greater than 4 in the present study. The probability of lack of fit (PLOF) describes the variation of the data around the fitted model. If the model does not fit the data well, this will be significant (PLOF<0.05). In this case, COD removal fits the data well. The coefficient of variance (CV) is the ratio of the standard error of estimate to the mean value of the observed response and defines reproducibility of the model. A model is considered reproducible if its CV is not greater than 10% (Beg et al. 2003). A CV of 11.28 indicates colour removal falls short in the model in terms of reproducibility.

PROCESS ANALYSIS

Figures 2, 3 and 4 show the response surface plots for COD, colour and NH_3-N removal in the form of two-dimensional contour plots. The two-dimensional contour plots represent the responses (COD, colour and NH_3-N removal) on the H_2O_2/COD molar ratio and reaction time (Figure 2), H_2O_2/Fe^{2+} molar ratio and reaction time (Figure 3) and H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio (Figure 4). The center of the plots indicates the range of optimum operating variables.

Figures 2(a), 2(b) and 2(c), shows that maximum COD, colour and NH_3-N removal were 50.5, 77.7 and 78.3% at about H_2O_2/COD molar ratio 2.0-2.7 at H_2O_2/Fe^{2+} molar ratio 20 and reaction time in the range of 1.5-2.0 h (Table 5). Figures 2 and 4 show that COD, colour and NH_3-N removal increased when the H_2O_2 dose was increased. This was presumably due to the fact that increased H_2O_2 dose produced more hydroxyl radicals leading to higher substrate degradation (Deng & Englehardt 2006). Further increase of H_2O_2 dose either did not improve the removal efficiency. This was due to scavenging of $\cdot$OH radicals by H_2O_2 as in Reaction 1 (Andreozzi et al. 2005). This reaction leads to the production of hydroperoxyl radical, a species with much weaker oxidising power compared to $\cdot$OH radical (Ting et al. 2008).

TABLE 3. CCD for the study of operating variables of the Fenton process

Run no.	A:H_2O_2/COD (Code)	B:H_2O_2/Fe^{2+} (Code)	C:Reaction Time* (Code)	COD	Observed Colour	NH$_3$-N	COD	Predicted Colour	NH$_3$-N
1	2.00 (0)	3.18 (-1.68)	1.50 (0)	70.0	85.4	85.2	66.3	76.9	82.0
2	2.00 (0)	36.82 (1.68)	1.50 (0)	41.8	56.2	70.1	43.7	52.2	69.7
3	2.84 (1.68)	20.00 (0)	1.50 (0)	50.0	79.8	81.8	49.2	67.9	77.6
4	2.00 (0)	20.00 (0)	1.50 (0)	49.1	76.5	75.9	47.6	75.6	74.8
5	2.00 (0)	20.00 (0)	1.50 (0)	48.2	77.9	74.2	47.6	75.6	74.8
6	2.50 (1)	10.00 (-1)	2.00 (1)	59.1	72.1	80.5	61.7	80.4	83.7
7	2.00 (0)	20.00 (0)	1.50 (0)	45.5	74.0	75.7	47.6	75.6	74.8
8	1.50 (-1)	10.00 (-1)	2.00 (1)	50.9	64.6	66.0	51.5	69.3	67.9
9	2.00 (0)	20.00 (0)	1.50 (0)	45.5	75.4	74.4	47.6	75.6	74.8
10	2.50 (1)	10.00 (-1)	1.00 (-1)	56.4	62.5	79.8	57.4	69.8	82.4
11	2.00 (0)	20.00 (0)	0.66 (-1.68)	43.6	65.8	72.3	42.1	62.1	71.9
12	1.50 (-1)	30.00 (1)	1.00 (-1)	40.0	46.5	65.1	38.8	47.1	64.5
13	1.50 (-1)	30.00 (1)	2.00 (1)	40.9	45.4	64.7	41.2	46.9	64.6
14	2.00 (0)	20.00 (0)	1.50 (0)	50.0	73.7	73.2	47.6	75.6	74.8
15	2.00 (0)	20.00 (0)	1.50 (0)	47.3	74.2	74.8	47.6	75.6	74.8
16	1.50 (-1)	10.00 (-1)	1.00 (-1)	45.5	55.6	68.8	48.6	56.9	68.8
17	1.16 (-1.68)	20.00 (0)	1.50 (0)	40.0	45.8	58.4	39.0	45.3	58.9
18	2.50 (1)	30.00 (1)	1.00 (-1)	40.0	58.7	70.3	40.7	62.3	71.0
19	2.00 (0)	20.00 (0)	2.34 (1.68)	48.2	79.6	76.2	47.8	70.8	73.0
20	2.50 (1)	30.00 (1)	2.00 (1)	46.4	53.3	70.6	44.6	60.1	73.3

* Unit of reaction time: h

TABLE 4. ANOVA for response surface quadratic model

Response	AP	PLOF	CV
COD	15.672	0.1678	5.19
Colour	6.649	0.0005	11.28
NH$_3$-N	13.093	0.0065	3.67

AP: adequate precision; PLOF: probability of lack of fit; CV: coefficient of variance

(a)　　　　　　　　(b)　　　　　　　　(c)
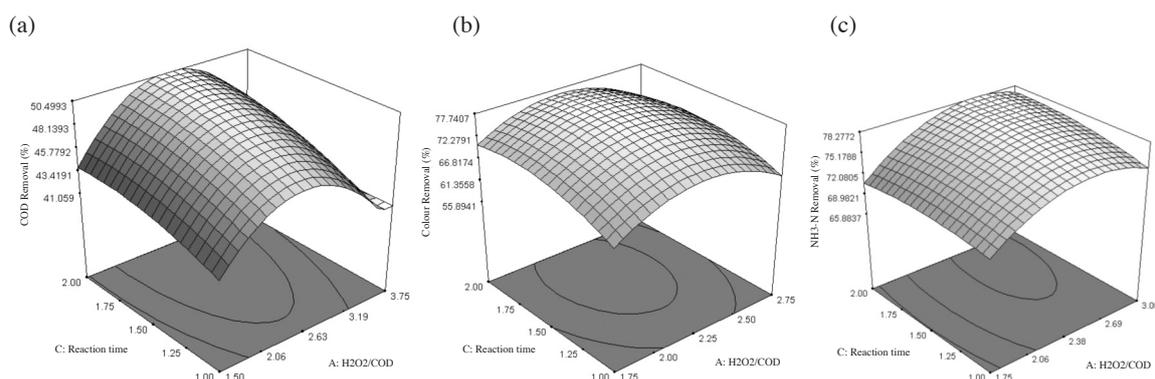
FIGURE 2. Response surface plot of (a) COD, (b) colour & (c) NH$_3$-N removal as function of H_2O_2/COD molar ratio and reaction time at H_2O_2/Fe^{2+} molar ratio 20

$$^\bullet OH + H_2O_2 \longrightarrow HO_2^\bullet + H_2O \qquad \text{(Reaction 1)}$$
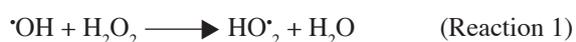
Besides, an excess amount of H_2O_2 can cause the auto decomposition of H_2O_2 to water and oxygen (Reaction 2) and the recombination of $^\bullet OH$ radicals (Reaction 3) (Mandal et al. 2010), thereby decreasing the concentration of $^\bullet OH$ radicals and reducing degradation efficiency.

$$2H_2O_2 \longrightarrow 2H_2O + O_2 \qquad \text{(Reaction 2)}$$

$$\bullet OH + \bullet OH \longrightarrow H_2O_2 \qquad \text{(Reaction 3)}$$
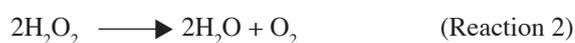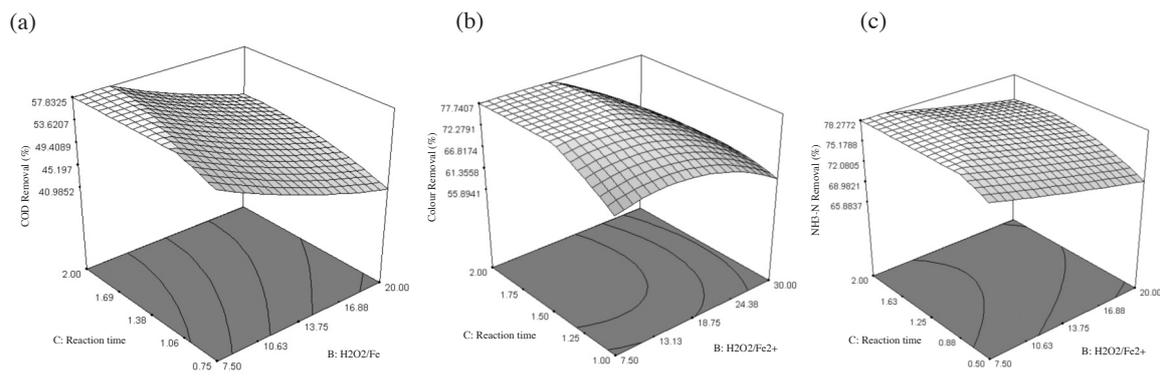
FIGURE 3. Response surface plot of (a) COD, (b) colour & (c) NH_3-N removal as function of H_2O_2/Fe^{2+} molar ratio and reaction time at H_2O_2/COD molar ratio 2.0
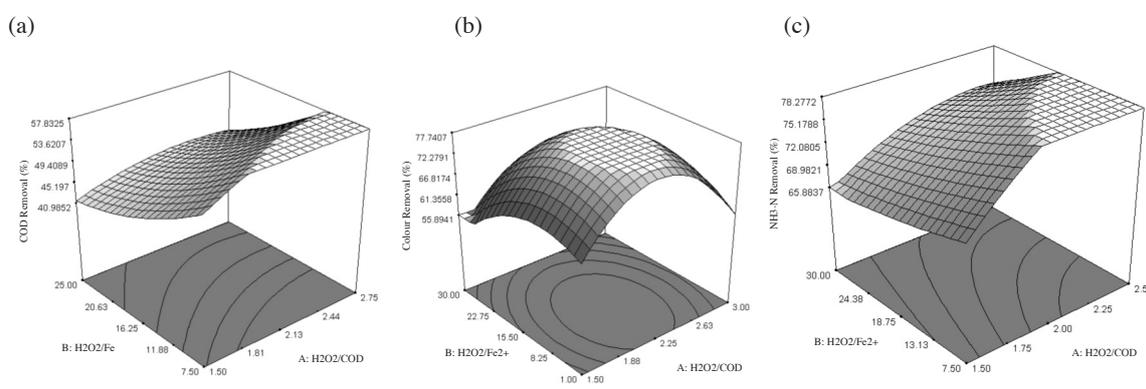
FIGURE 4. Response surface plot of (a) COD, (b) Colour & (c) NH_3-N removal as function of H_2O_2/COD molar ratio and H_2O_2/Fe^{2+} molar ratio at reaction time 1.5 h

According to Figures 3(a), 3(b) and 3(c), the maximum COD, colour and NH_3-N removal were 57.8%, 77.7% and 78.3% at about H_2O_2/Fe^{2+} molar ratio 7.5-13.0 at H_2O_2/COD molar ratio 2.0 and reaction time in the range 1.5-2.0 h (Table 5). Figures 3 and 4 show that COD, colour and NH_3-N removal increased with increasing Fe^{2+} dose and with decrease in H_2O_2/Fe^{2+} molar ratio up to about 7.5. Further decrease in H_2O_2/Fe^{2+} ratio did not improve the removal due to direct reaction of ·OH radicals with metal ions at high concentration of Fe^{2+} as in Reaction 4 (Joseph et al. 2000).

$$·OH + Fe^{2+} \longrightarrow Fe^{3+} + OH^- \qquad (Reaction\ 4)$$
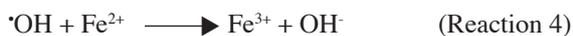
Interaction between H_2O_2/COD and H_2O_2/Fe^{2+} molar ratio on COD, colour and NH_3-N removal are shown in Figure 4 (a), 4(b) and 4(c). Maximum COD, colour and NH_3-N removal were 60.4%, 80.4% and 83.9% at about H_2O_2/COD molar ratio 2.0-2.7 and H_2O_2/Fe^{2+} molar ratio 7.5-13.0 at reaction time 1.5 h (Table 5).

Figures 2(a), 2(b), 2(c), 3(a), 3(b) and 3(c) show that maximum COD, colour and NH_3-N removal were achieved at about reaction time 1.5-2.0 h at H_2O_2/Fe^{2+} molar ratio 20 and H_2O_2/COD molar ratio 2.0. The results showed COD, colour and NH_3-N removal increased when the reaction time increased. However, further increase in reaction time above 1.5 h did not significantly improve the removal. This

TABLE 5. A summary of response surface plots of COD, colour and NH_3-N removal

Operating variables			COD removal (%)	Colour removal (%)	NH_3-N removal (%)
H_2O_2/COD molar ratio 2.0-2.7	Reaction time 1.5-2.0 h	H_2O_2/Fe^{2+} molar ratio 20	41.1-50.5	55.9-77.7	65.9-78.3
H_2O_2/Fe^{2+} molar ratio 7.5-13.0	Reaction time 1.5-2.0 h	H_2O_2/COD molar ratio 2.0	41.0-57.8	55.9-77.7	65.9-78.3
H_2O_2/COD molar ratio 2.0-2.7	H_2O_2/Fe^{2+} molar ratio 7.5-13.0	Reaction time 1.5	41.0-60.4	55.9-80.4	65.9-83.9

was due to the fact that organics were rapidly degraded by the Fenton reagent and most organics removal occurred in 1.5 h.

Response surface plots indicate the optimum points in the range of H_2O_2/COD molar ratio 2.0-2.7, H_2O_2/Fe^{2+} molar ratio 7.5-13.0 and 1.5-2.0 h reaction time with maximum removal of COD 60.4%, colour 80.4% and NH_3-N 83.9%, respectively. In Fenton treatment of mature leachate, 46, 45-50, 60, 61 and 65% COD removal was observed at H_2O_2/Fe^{2+} molar ratio 3, 1.2, 19.7, 3 and 3, respectively (Cortez et al. 2011; Deng 2007; Hermosilla et al. 2009; Kim et al. 2001; Lopez et al. 2004).

PROCESS OPTIMISATION

With multiple responses, the optimum operating variables where all parameters simultaneously meet the desirable removal criteria could be visualized graphically by superimposing the contours of the response surfaces in an overlay plot. Graphical optimization displays the area of feasible response value in the factor space and the regions that do fit the optimization criteria would be shaded (Mason et al. 2003). In order to obtain a moderately precise optimum zone, response limits as the minimum permissible values were chosen for each parameter close to their acquired removal efficiencies - COD 55%, colour 80% and NH_3-N 80% (Figure 5). The shaded region shows the optimum parameters - H_2O_2/
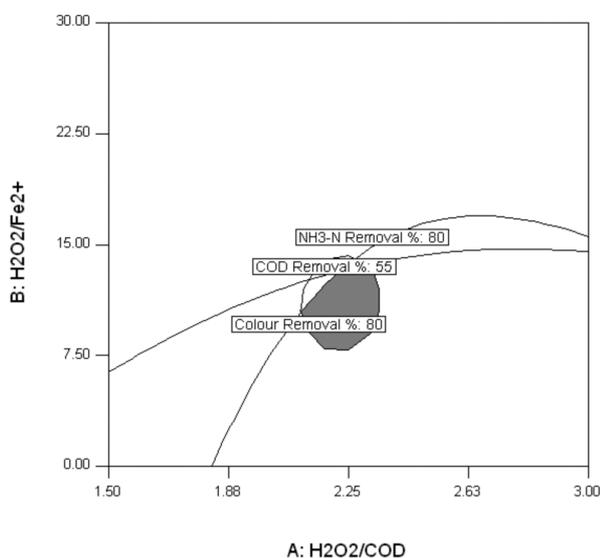
FIGURE 5. Overlay plot for optimal region at reaction time 1.5 h

COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.00 and reaction time 1.5 h and constitute the optimum operating variables (conditions). The results agreed well optimum H_2O_2/COD molar ratio in the range 1.1-3.0 (Cortez et al. 2011; Kim et al. 2001) and optimum H_2O_2/Fe^{2+} molar ratio in the range 1.2-19.7 (Cortez et al. 2011; Deng 2007; Kim et al. 2001; Lopez et al. 2004) reported for Fenton treatment of mature leachate.

Three additional experiments were conducted under the optimum operating conditions (H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.00 and reaction time 1.5 h) to verify the model prediction. As shown in Table 6, the experimental removal efficiency and model prediction were in close agreement with less than 5% error.

The characteristics of the Fenton pretreated leachate were: COD 545 mg/L, BOD_5 114.5 mg/L, biodegradability (BOD_5/COD ratio) 0.21, NH_3-N 90.5 mg/L and colour 120 Pt-Co Unit. The residual COD was high and the biodegradability was low after Fenton pretreatment.

UV/Fenton pretreatment was conducted under the optimum operating conditions of the Fenton pretreatment (H_2O_2/COD molar ratio 2.25, H_2O_2/Fe^{2+} molar ratio 10.0) and irradiation time 1.5 h. The characteristics of the UV/Fenton pretreated leachate were: COD 390 mg/L, sCOD 330 mg/L, BOD_5 136 mg/L, BOD_5/COD ratio 0.35, NH_3-N 112 mg/L, TKN 157 mg/L, NO_3^--N 6.8 mg/L and colour 99 Pt-Co Unit. UV/Fenton was selected as pretreatment of the landfill leachate for biological treatment.

SEQUENCING BATCH BIOLOGICAL REACTOR
(SBR) TREATMENT

The feeding pattern for acclimation appeared to be successful and the sCOD removal of 65% was achieved after 8 d acclimation. The effluent characteristics were: sCOD 114 mg/L, NH_3-N 48 mg/L, NO_3^--N 17 mg/L and TKN 72 mg/L. Following acclimation, the SBR was operated for 30 d.

Figure 6 shows the effluent sCOD and mixed liquor suspended solids (MLSS) in SBR during 30 d operation. Monitoring of MLSS was necessary to ensure that sufficient biomass was maintained in the reactor for biodegradation. The sCOD of the SBR effluent was 71 mg/L (COD 92 mg/L) with the removal percentage of 78%. It is to be noted that the degradation of organics occurred rapidly in the first 6 h (Figure 7). Effluent BOD_5 after 30-d treatment was 26 mg/L with removal percentage of 81%. Guo et al. (2010) reported up to 83.1% COD removal in SBR treatment (20 h aeration) of a Fenton pretreated mature leachate. de Morais and Zamora (2005) reported more than 90% COD

TABLE 6. Experimental removal efficiency and model prediction

Response	Model response	Experimental values	Error
COD removal (%)	55.0	46.3-52.1 (50.5)	-4.5
Colour removal (%)	80.0	72.8-78.4 (76.9)	-3.1
NH_3-N removal (%)	80.0	82.2-84.5 (83.7)	3.7
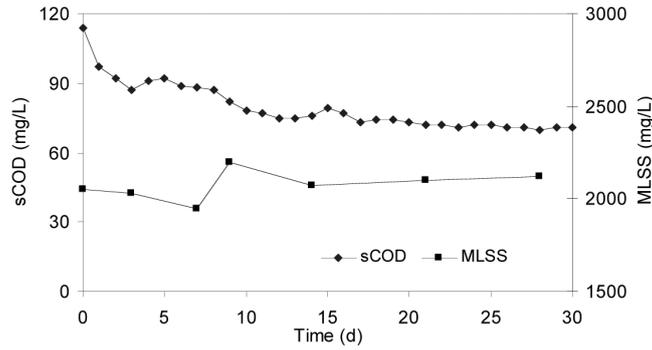
FIGURE 6. Effluent soluble COD (sCOD) & MLSS in SBR
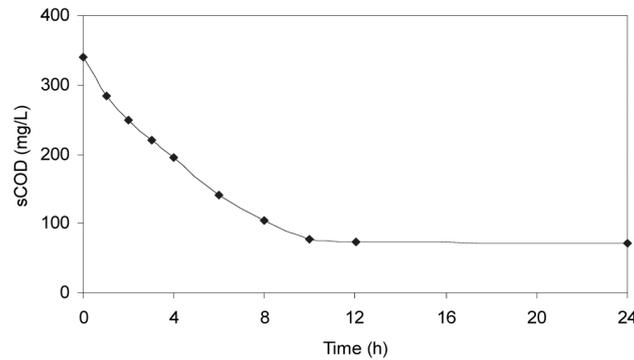
FIGURE 7. Effluent soluble COD (sCOD) in SBR during 24 h cycle

removal by SBR treatment (72 h cycle) of a photo-Fenton pretreated mature leachate.

Figure 8 shows the effluent ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) and total Kjeldahl nitrogen (TKN) in SBR during 30 d operation. The NH_3-N and TKN gradually reduced from 112 to 7 mg/L and from 157 to 13 mg/L, respectively during treatment, whereas NO_3^--N increased from 6.8 mg/L to 27 mg/L, indicating nitrification. Figure 9 shows the concentration of ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) and total Kjeldahl nitrogen (TKN) during a 24 h cycle.

Nitrification occurred rapidly with about 75% conversion for both NH_3-N and TKN in the first 4 h.

Aerobic sequencing batch biological reactor (SBR) treatment of the UV/Fenton pretreated mature leachate resulted in sCOD, BOD_5 and NH_3-N removal of 78, 81 and 88%, respectively. The final effluent characteristics were COD 92 mg/L, sCOD 71 mg/L, BOD_5 26 mg/L, NH_3-N 7 mg/L, NO_3^--N 27 mg/L, TKN 13 mg/L and TSS 38 mg/L. The effluent met the Malaysian discharge standard (B) – COD 100 mg/L, BOD_5 50 mg/L and TSS 100 mg/L (EQA 2007).
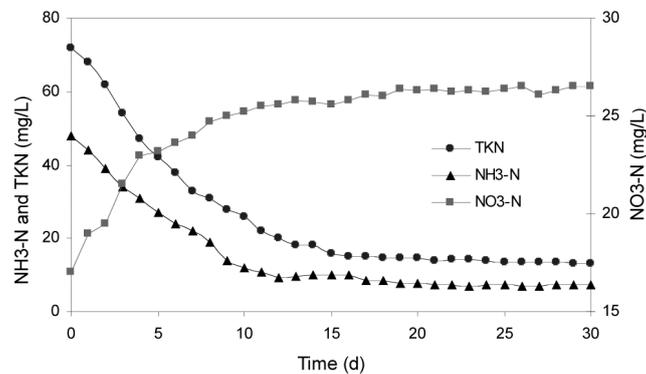
FIGURE 8. Effluent ammonia-nitrogen (NH_3-N), nitrate-nitrogen (NO_3^--N) & total Kjeldahl nitrogen (TKN) in SBR
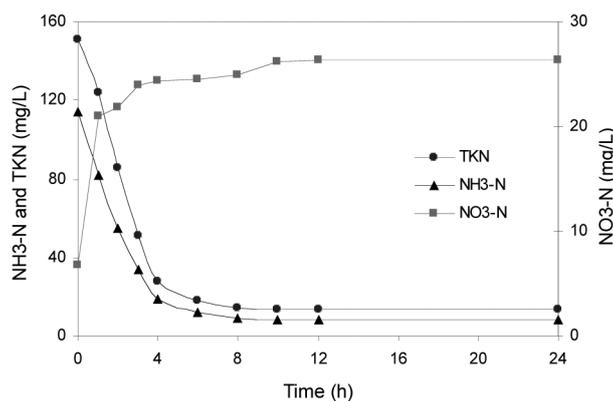
FIGURE 9. Ammonia-nitrogen (NH$_3$-N), nitrate-nitrogen (NO$_3^-$-N) & total
Kjeldahl nitrogen (TKN) in SBR during 24 h cycle

CONCLUSION

UV/Fenton is an effective pretreatment for biological treatment of mature leachate from a semi-aerobic landfill. The characteristics of the UV/Fenton pretreated leachate are: COD 390 mg/L, sCOD 330 mg/L, BOD$_5$ 136 mg/L, BOD$_5$/COD ratio 0.35, NH$_3$-N 112 mg/L, TKN 157 mg/L, NO$_3^-$-N 6.8 mg/L and colour 99 Pt-Co Unit.

Combined UV/Fenton and SBR is an effective treatment for mature leachate from semi-aerobic landfill. The characteristics of combined UV/Fenton and SBR treated effluent are: COD 92 mg/L, sCOD 71 mg/L, BOD$_5$ 26 mg/L, NH$_3$-N 7 mg/L, NO$_3^-$-N 27 mg/L, TKN 13 mg/L and TSS 38 mg/L. The effluent meets the Malaysian discharge standard (B) – COD 100 mg/L, BOD$_5$ 50 mg/L and TSS 100 mg/L.

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