



Optimization of Photo-Fenton Treatment of Mature Landfill Leachate

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ABSTRACT

Photo-Fenton treatment of a mature landfill leachate was optimized by using the response surface methodology (RSM). The optimum operating variables to achieve 70% removal of COD, 80% removal of colour and 80% removal of $\text{NH}_3\text{-N}$ were: $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 3.75, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 10.5 and irradiation time 1.5 h. There was good agreement (< 2% error) between experimental removal efficiency and model prediction. The characteristics of the photo-Fenton treated leachate were: $\text{NH}_3\text{-N}$ 112 mg/L, colour 108 Pt-Co Unit, COD 350 mg/L, BOD_5 116 mg/L and BOD_5/COD ratio 0.33, indicating that the treated leachate was amenable to biological treatment. The study has revealed that RSM is an effective tool to optimize the treatment process and photo-Fenton is an effective pretreatment of mature landfill leachate for biological treatment.

INTRODUCTION

Landfill leachates have been identified as potential sources of ground and surface water contamination as they may percolate through soil and subsoil or cause extensive pollution of streams and lakes if they are not properly collected, treated and disposed off. Landfill leachate contains a number of contaminants, which are measured in terms of chemical oxygen demand (COD), biochemical oxygen demand (BOD), ammonia, halogenated hydrocarbons, suspended solids, heavy metals and inorganic salts (Trebouet et al. 2001, Bagchi 2004). Leachates present considerable variations in both volumetric flow and chemical composition (Tatsi et al. 2003). As a landfill becomes older, there is shift from a relatively shorter initial aerobic period to a longer anaerobic decomposition period, which has two distinct sub-phases: an acidic phase, followed by a methanogenic phase, and the specific composition of the mature leachate determines its relative treatability (Tatsi et al. 2003). Organic compounds present in mature landfill leachate are mainly humic and fulvic acids which are not readily biodegradable (Tchobanoglous et al. 1993). Biological processes are commonly used to degrade organic compounds and are not effective in treating mature landfill leachate with low biodegradability (BOD_5/COD ratio).

Advanced oxidation processes have proved to be highly effective in the degradation of most pollutants in wastewater (Pera-Titus et al. 2004). Oxidation (degradation) of organic compounds with Fenton reagent is based on hydroxyl radicals ($\cdot\text{OH}$) produced by catalytic decomposition of hydrogen peroxide (H_2O_2) in reaction with ferrous ion. In the

photo-Fenton process, additional reactions occur in the presence of light that produce $\cdot\text{OH}$ radicals or increase the production rate of $\cdot\text{OH}$ radicals (Pignatello et al. 1999). The photo-Fenton reaction combines ultraviolet (and some visible) light, Fe(III) and hydrogen peroxide, and facilitates the production of $\cdot\text{OH}$ radicals by a photochemical route followed by the Fenton reaction (Hislop & Bolton 1999). More importantly, iron is cycled between the +2 and +3 oxidation states, so Fe(II) is not depleted, and $\cdot\text{OH}$ radical production is limited only by the availability of light and hydrogen peroxide. An essential characteristic of the photo-Fenton process is that pH in the acidic range strongly favours oxidation. At pH around 3, highly soluble $\text{Fe}(\text{OH})^{2+}$ is the predominant ferric hydroxide complex as opposed to free Fe^{3+} , $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_2^{4+}$, which are less photoreactive (Faust & Hoigne 1990). However, amorphous iron oxyhydroxide sludge that may accumulate at pH above 5 prevents the transmission of UV light through the reactor (Kim et al. 1997, Kim & Vogelpohl 1998). Application of the photo-Fenton process for the treatment of mature landfill leachate has been reported (Kim et al. 2001, de Morais & Zamora 2005, Primo et al. 2008, Hermosilla et al. 2009, Rocha et al. 2011). Optimum pH for photo-Fenton treatment of mature landfill leachate was found to be 3.0-4.5 (Kim et al. 2001), 2.8 (de Morais & Zamora 2005), 3.0 (Primo et al. 2008) and 2.5 (Hermosilla et al. 2009).

Appropriate implementation of the photo-Fenton treatment depends mainly on the operating variables - $\text{H}_2\text{O}_2/\text{COD}$ molar ratio, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and irradiation time. Conventional method is to optimize the operating variables by changing one factor at a time method, i.e. a single factor is

varied while all other factors are kept unchanged for a particular set of experiment. Likewise, other variables are individually optimized through single-dimensional searches, which are time consuming and incapable of reaching the actual optimum as interaction among variables is not taken into consideration (Mason et al. 2003). de Morais & Zamora (2005) optimized the experimental variables (Fe^{2+} , H_2O_2 and pH) of the photo-Fenton treatment of a mature landfill leachate by using a 2^3 factorial design.

Response surface methodology (RSM) is a collection of mathematical and statistical techniques for analysing the interactive effects of several independent process variables on the response (Montgomery 2001, Bas & Boyaci 2007). RSM has been used to optimize the photo-Fenton treatment of used tires leachate (Sarasa et al. 2006) and ampicillin solutions (Rozas et al. 2010), and electro-Fenton treatment of mature landfill leachate (Mohajeri et al. 2010).

In the present study, photo-Fenton treatment of a mature landfill leachate was optimized by using RSM, for the removal of chemical oxygen demand (COD), colour and ammonia-nitrogen ($\text{NH}_3\text{-N}$).

MATERIALS AND METHODS

Leachate: Samples of mature leachate were collected from the influent end of the detention pond of the Pulau Burung Landfill (PBL) in Nibong Tebal, Penang, Malaysia. The samples were stored in a cold room at 4°C to minimize 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 of the raw, settled (2 h) and preliminary treated leachate are presented in Table 1.

Analytical methods: 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 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 Method No. 8000 (Hach 2002). 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 (Talinli & Anderson 1992, Kang et al. 1999). Turbidity was measured by a turbidity meter and reported in nephelometric turbidity unit (NTU). Solids (total solids, total suspended solids (TSS) and total dissolved solids) were measured according to the Standard Methods (APHA 2005). Colour, total phosphorus and $\text{NH}_3\text{-N}$ were measured accord-

ing to Hach (2002).

Photo-Fenton process: Batch photo-Fenton treatment was performed in a 600-mL Pyrex reactor with 250 mL of the preliminary treated leachate. Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) and hydrogen peroxide (H_2O_2) were added simultaneously according to the selected $\text{H}_2\text{O}_2/\text{COD}$ and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratios. The mixture was kept stirred to ensure complete homogeneity during reaction and irradiated with a UV lamp (Spectroline Model EA-160/FE, 230 volts, 0.17 amps, 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 selection of this type of UV lamp (365 nm) was based on economic point of view since this type is cheap compared with the expensive types such as medium pressure mercury lamps (254 nm) (Olmez 2009). Aliquots were taken at selected irradiation time for measurement of COD, colour and $\text{NH}_3\text{-N}$.

Experimental design and data analysis: Design expert software (version 6.0) was used for statistical design of experiments and data analysis. Central composite design (CCD) and response surface methodology (RSM) were applied to optimize the three most important operating variables - $\text{H}_2\text{O}_2/\text{COD}$ molar ratio, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and irradiation time. The coded values for $\text{H}_2\text{O}_2/\text{COD}$ molar ratio (A), $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (B) and irradiation time (C) were set at five levels: $-\alpha$ (minimum), -1, 0 (central), +1 and $+\alpha$ (maximum). The operating variables were chosen as $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 1.32-4.68, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 1.59-18.41 and irradiation time 0.66-2.34 h. Range and levels of the operating variables are given in Table 2.

In order to obtain the optimum $\text{H}_2\text{O}_2/\text{COD}$ molar ratio, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and irradiation time, three main parameters were analysed as response: COD, colour and $\text{NH}_3\text{-N}$ 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 an overlay plot. The following response equation was used to assess the predicted result (Y) as a function of the operating variables $\text{H}_2\text{O}_2/\text{COD}$ molar ratio (A), $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (B) and irradiation 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 effects (AB, AC and BC).

$$Y = \beta_0 + \beta_1A + \beta_2B + \beta_3C + \beta_{11}A^2 + \beta_{22}B^2 + \beta_{33}C^2 + \beta_{12}AB + \beta_{13}AC + \beta_{23}BC \quad \dots(1)$$

RESULTS AND DISCUSSION

Statistical analysis: $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 1.32-4.68, $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 1.59-18.41 and irradiation time 0.66-2.34 h

Table 1: Characteristics of PBL leachate.

Parameter	Raw	Settled	Preliminarily treated
pH	8.4-8.7	8.0-8.8	2.9-3.1
Colour (Pt-Co Units)	2160-2560	1950-2180	520-560
Turbidity (NTU)	308-314	208-256	86-105
BO₅ (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

Table 2: Range and levels of operating variables.

Operating variable	Code	Range and levels				
		-1.68	-1	0	1	1.68
H ₂ O ₂ /COD molar ratio	A	1.32	2	3	4	4.68
H ₂ O ₂ /Fe ²⁺ molar ratio	B	1.59	5	10	15	18.41
Irradiation time (h)	C	0.66	1	1.5	2	2.34

were chosen as the study range of the operating variables. The results obtained were analysed by ANOVA to assess the “goodness of fit”. The models for COD, colour and NH₃-N removal (Y₁, Y₂ and Y₃) 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 H₂O₂/COD molar ratio (A), H₂O₂/Fe²⁺ molar ratio (B) and irradiation time (C) on the photo-Fenton process performance.

$$\text{COD removal: } Y_1 = 66.48 + 8.90A - 8.44B + 0.83C - 4.48A^2 + 0.019B^2 - 2.23C^2 + 1.14AB - 0.23AC + 1.59BC \quad \dots(2)$$

$$\text{Colour removal: } Y_2 = 69.44 + 8.64A + 15.76B + 2.25C + 6.85A^2 - 14.170B^2 + 4.70C^2 - 6.14AB - 1.76AC + 0.96BC \quad \dots(3)$$

$$\text{NH}_3\text{-N removal: } Y_3 = 84.81 + 5.41A - 13.90B - 0.27C - 3.04A^2 - 13.69B^2 + 1.72C^2 + 3.44AB - 0.72AC + 0.61BC \quad \dots(4)$$

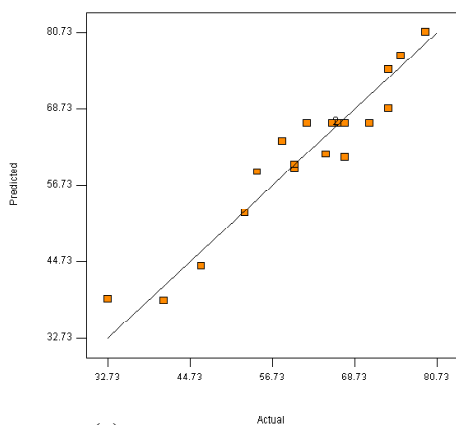
In equations 2, 3 and 4, the values of the sum of a constant, 66.48, 69.44 and 84.81 represent the predicted percentage removal of COD, colour and NH₃-N, respectively at “level 0”. The positive sign indicates that the parameter (variable) is directly proportional to the responses COD removal, colour removal and NH₃-N removal; on the other hand, the negative sign indicates that the parameter is inversely proportional to the responses. For example, the decrease of H₂O₂/Fe²⁺ molar ratio (B) increases the COD and NH₃-N removal. It is to be noted that relatively lower values were found for irradiation time (C), indicating that variation of irradiation

time had less effect on the photo-Fenton process compared to H₂O₂/COD and H₂O₂/Fe²⁺ molar ratio.

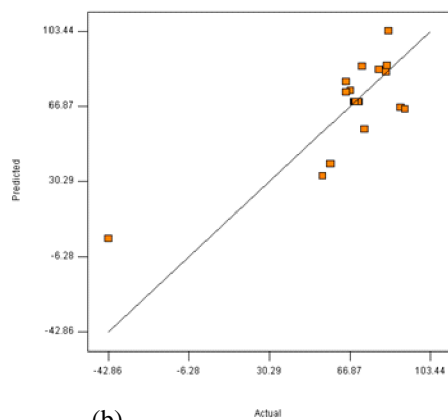
Table 3 shows the central composite design (CCD) in the form of a 2³ full factorial design with five additional experimental trials (run number 4, 5, 9, 14 and 15) as replicates of the central point and observed (actual) experimental results and predicted results from the model at each assay. The replication 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 H₂O₂/COD and H₂O₂/Fe²⁺, h for irradiation time and the coded levels 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 was 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 normally can be considered reproducible if its CV is not greater than 10% (Beg et al. 2003). A CV of 22.91 indicates colour removal fell short in the model in terms of reproducibility.

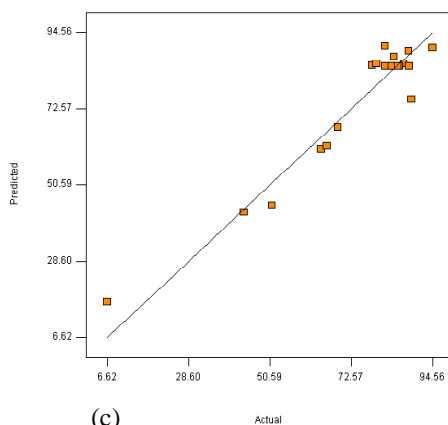
Diagnostic plot (Fig. 1) of the predicted versus actual values can judge the model satisfactoriness by indicating an agreement between the actual data and the one obtained from the model. The R² value gives the proportion of the total variation in the response predicted by the model and a value close to 1 is desirable and ensures a satisfactory adjustment of the quadratic model to the experimental data. The R² value was found to be close to 1 (0.9177 and 0.9719 for COD and NH₃-N removal, respectively), indicating that the regression



(a)



(b)

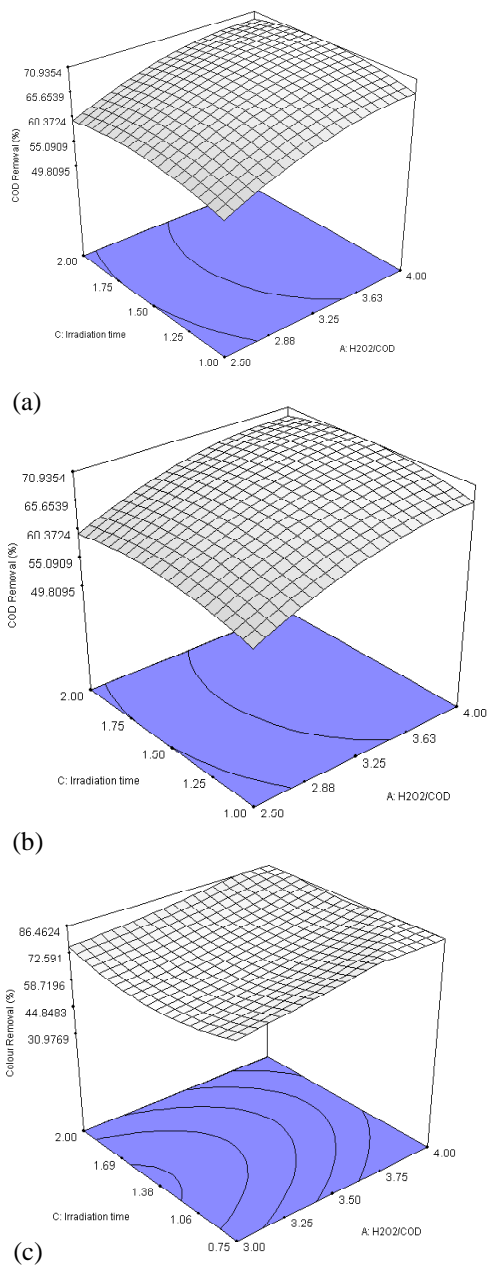


(c)

Fig. 1: Diagnostic plot of (a) COD, (b) colour, and (c) $\text{NH}_3\text{-N}$ removal.

model explained the prediction well (Olmez 2009). The R^2 value for colour removal was low (0.8573), but acceptable.

Process analysis: Figs. 2, 3 and 4 show the response surface plots for COD, colour and $\text{NH}_3\text{-N}$ removal in the form of two-dimensional contour plots. The two-dimensional contour plots represent the responses (COD, colour and $\text{NH}_3\text{-N}$



(a)

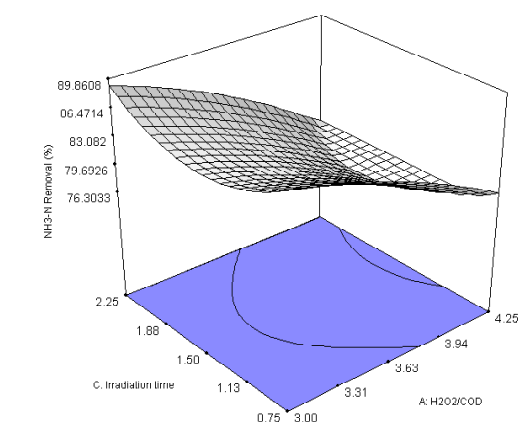
(b)

(c)

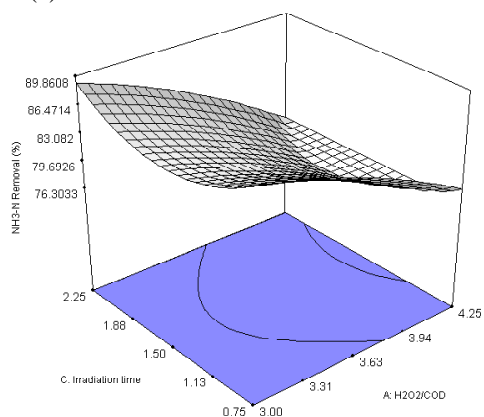
Fig. 2: Response surface plot of (a) COD, (b) colour and (c) $\text{NH}_3\text{-N}$ removal as a function of $\text{H}_2\text{O}_2/\text{COD}$ molar ratio and irradiation time at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 10.

removal) on the $\text{H}_2\text{O}_2/\text{COD}$ molar ratio and irradiation time (Fig. 2), $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and irradiation time (Fig. 3) and $\text{H}_2\text{O}_2/\text{COD}$ molar ratio and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio (Fig. 4). The centre of the plots indicates the range of optimum operating variables.

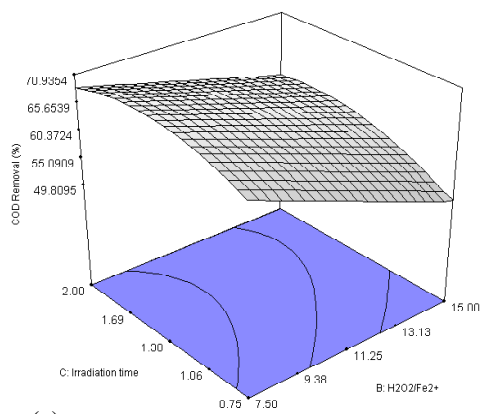
Effect of $\text{H}_2\text{O}_2/\text{COD}$ molar ratio: Figs. 2 (a), (b) and (c) show that the maximum COD, colour and $\text{NH}_3\text{-N}$ removal are 70.9,



(a)



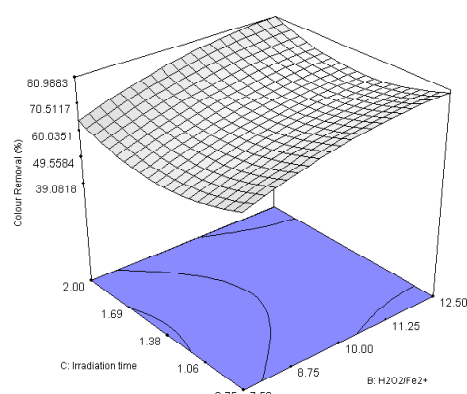
(b)



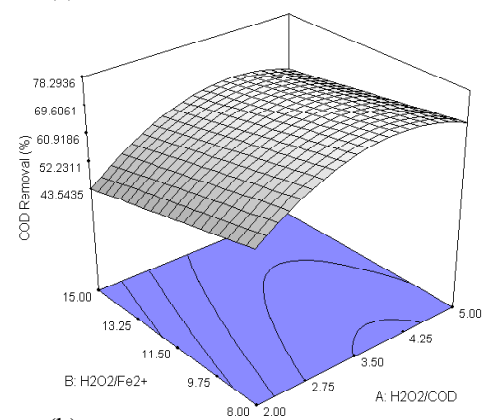
(c)

Fig. 3: Response surface plot of (a) COD, (b) colour and (c) $\text{NH}_3\text{-N}$ removal as a function of $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio and irradiation time at $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 3.0.

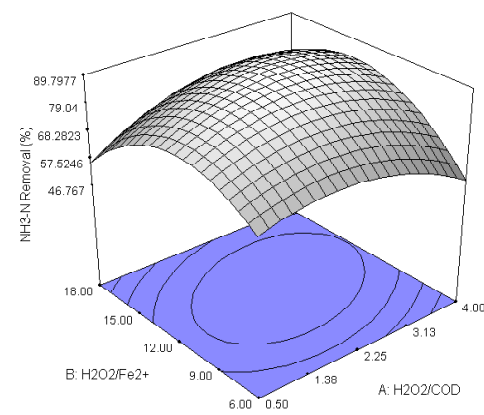
86.5 and 89.9% at about $\text{H}_2\text{O}_2/\text{COD}$ molar ratio 3.5-4.0 at $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio 10. COD and colour removal increases when the H_2O_2 dose increases. This may be due to the fact that increased H_2O_2 dosage produces more $\cdot\text{OH}$ radicals leading to higher substrate degradation (Deng & Englehardt 2006). Fur-



(a)



(b)



(c)

Fig. 4: Response surface plot of (a) COD, (b) colour and (c) $\text{NH}_3\text{-N}$ removal as a function of $\text{H}_2\text{O}_2/\text{COD}$ molar ratio and $\text{H}_2\text{O}_2/\text{Fe}^{2+}$ molar ratio at irradiation time 1.5 h.

ther increase of H_2O_2 dose does not improve the removal. This may be due to scavenging of $\cdot\text{OH}$ radicals by H_2O_2 as in the following reaction (Andreozzi et al. 2005).

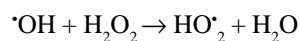


Table 3: CCD for the study of operating variables of the photo-Fenton process.

No.	Experimental design			Removal (%)					
	A:H ₂ O ₂ /COD (Coded level)	B:H ₂ O ₂ /Fe ²⁺ (Coded level)	C:Irradiation time (Coded level)	Observed			Predicted		
				COD	Colour	NH ₃ -N	COD	Colour	NH ₃ -N
1	3.00 (0)	1.59 (-1.68)	1.50 (0)	79.1	-42.9	25.9	80.7	-14.1	27.4
2	3.00 (0)	18.41 (1.68)	1.50 (0)	52.7	73.6	80.3	52.3	60.2	74.2
3	4.68 (1.68)	10.00 (0)	1.50 (0)	73.6	90.4	69.0	68.8	100.0	66.5
4	3.00 (0)	10.00 (0)	1.50 (0)	61.8	69.1	88.2	66.5	69.4	84.8
5	3.00 (0)	10.00 (0)	1.50 (0)	70.9	70.7	85.1	66.5	69.4	84.8
6	4.00 (1)	5.00 (-1)	2.00 (1)	73.6	68.6	43.5	75.0	51.8	45.8
7	3.00 (0)	10.00 (0)	1.50 (0)	67.3	71.1	85.6	66.5	69.4	84.8
8	2.00 (-1)	5.00 (-1)	2.00 (1)	60.0	42.1	66.0	59.9	29.4	65.0
9	3.00 (0)	10.00 (0)	1.50 (0)	65.5	70.4	81.8	66.5	69.4	84.8
10	4.00 (1)	5.00 (-1)	1.00 (-1)	75.5	66.3	51.2	77.0	52.8	49.1
11	3.00 (0)	10.00 (0)	0.66 (-1.68)	54.5	65.2	88.1	58.8	71.7	87.2
12	2.00 (-1)	15.00 (1)	1.00 (-1)	40.9	67.1	84.1	38.7	73.1	85.1
13	2.00 (-1)	15.00 (1)	2.00 (1)	46.4	82.9	81.8	44.0	85.4	87.1
14	3.00 (0)	10.00 (0)	1.50 (0)	67.3	69.3	83.5	66.5	69.4	84.8
15	3.00 (0)	10.00 (0)	1.50 (0)	66.4	68.8	83.8	66.5	69.4	84.8
16	2.00 (-1)	5.00 (-1)	1.00 (-1)	67.3	36.4	64.4	61.0	22.3	65.3
17	1.32 (-1.68)	10.00 (0)	1.50 (0)	32.7	65.2	86.8	38.8	70.9	84.7
18	4.00 (1)	15.00 (1)	1.00 (-1)	60.0	83.4	78.2	59.2	85.3	82.5
19	3.00 (0)	10.00 (0)	2.34 (1.68)	64.5	72.3	90.0	61.6	81.2	86.3
20	4.00 (1)	15.00 (1)	2.00 (1)	58.2	86.1	79.4	63.6	89.4	81.7

Table 4: ANOVA for response surface quadratic model.

Response	R ²	AP	PLOF	CV
COD	0.9177	12.728	0.0771	7.55
Colour	0.8573	11.041	<0.0001	22.91
NH ₃ -N	0.9719	21.527	0.0443	5.25

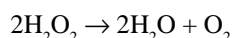
AP: adequate precision; PLOF: probability of lack of fit; CV: coefficient of variance

Table 5: Experimental removal efficiency and model prediction.

Response	Model prediction	Experimental	Error
COD removal (%)	70.0	65.8-73.4 (68.2)	-1.8
Colour removal (%)	80.0	79.2-82.0 (80.7)	0.7
NH ₃ -N removal (%)	80.0	78.9-81.2 (80.1)	0.1

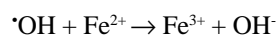
This reaction leads to the production of hydroperoxyl radical (HO₂[•]), a species with much weaker oxidizing power compared to [•]OH radical (Ting et al. 2008).

Besides, an excess amount of H₂O₂ can cause the auto decomposition of H₂O₂ to water and oxygen, and the recombination of [•]OH radicals as in the following reactions (Mandal et al. 2010), thereby decreasing the concentration of [•]OH radicals and reducing degradation efficiency.



Effect of H₂O₂/Fe²⁺ molar ratio: According to Figs. 3 (a), (b) and (c), the maximum COD, colour and NH₃-N removal

are 70.9, 81.0 and 92.6% at about H₂O₂/Fe²⁺ molar ratio 7.5-15.0 at H₂O₂/COD molar ratio 3.0. COD removal increases with increasing Fe²⁺ dose and the results show increase in COD removal with decrease in H₂O₂/Fe²⁺ ratio up to about 7.5-10.0. Further decrease in H₂O₂/Fe²⁺ molar ratio does not improve the removal due to direct reaction of [•]OH radicals with metal ions at high concentration of Fe²⁺ as in the following reaction (Joseph et al. 2000).



On the other hand, colour removal decreases when the H₂O₂/Fe²⁺ molar ratio decreases. This may due to interference with colour measurement when there is excess Fe²⁺. Figs. 4 (a), (b) and (c) show interaction between H₂O₂/COD and H₂O₂/Fe²⁺ molar ratios on COD, colour and NH₃-N removal. Maximum COD, colour and NH₃-N removal are 78.3, 88.4 and 89.8% at about H₂O₂/COD molar ratio 3.5-4.0 and H₂O₂/Fe²⁺ molar ratio 8.0-13.0 at irradiation time of 1.5 h.

Effect of irradiation time: According to Figs. 2(a), (b) and (c) and 3(a), (b) and (c), the maximum COD, colour and NH₃-N removal are achieved at about irradiation time of 1.4-1.5 h at H₂O₂/Fe²⁺ molar ratio 10 and H₂O₂/COD molar ratio 3.0. The results show that COD, colour and NH₃-N removal increase with increasing irradiation time. However, further increase of irradiation time above 1.5 h does not improve the process significantly. This may be due to the fact that organics are rapidly degraded by the Fenton reagent and most organics removal occurred within 1.5 h.

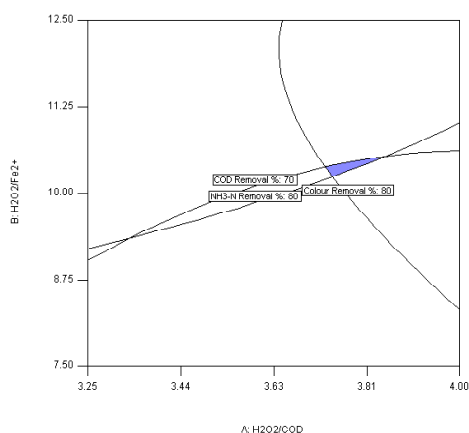


Fig. 5: Overlay plot for optimal region at irradiation time 1.5 h.

Response surface plots indicate the optimum points in the range of H_2O_2/COD molar ratio 3.0-4.0, H_2O_2/Fe^{2+} molar ratio 7.5-15.0 and irradiation time 1.5 h with maximum removal of COD 78.3%, colour 88.4% and NH_3-N 92.6%, respectively.

Process optimization: With multiple responses, the optimum operating conditions where all parameters simultaneously meet the desired 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 variable close to their acquired removal efficiency – COD 70%, colour 80% and NH_3-N 80% (Fig. 5). The shaded region shows the optimum variables – H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.5 and irradiation time 1.5 h, and constitute the optimum operating variables.

Model verification: Three additional experiments were conducted under the optimum operating variables (H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.5 and irradiation time 1.5 h) to verify the model prediction. As shown in Table 5, experimental removal efficiency and model prediction were in close agreement with less than 2% error.

The characteristics of the photo-Fenton treated leachate were: NH_3-N 112 mg/L, colour 108 Pt-Co Units, COD 350 mg/L, BOD_5 116 mg/L and BOD_5/COD ratio 0.33, indicating that the treated leachate was amenable to biological treatment.

CONCLUSIONS

Central composite design (CCD) and response surface methodology (RSM) were used with three operating variables viz.

H_2O_2/COD molar ratio, H_2O_2/Fe^{2+} molar ratio and irradiation time to investigate their interactive effects on the removal of COD, colour and NH_3-N from a mature landfill leachate by the photo-Fenton process. Satisfactory prediction equations were derived by using RSM. The optimum operating variables to achieve 70% removal of COD, 80% removal of colour and 80% removal of NH_3-N were at H_2O_2/COD molar ratio 3.75, H_2O_2/Fe^{2+} molar ratio 10.5 and irradiation time 1.5 h. There was good agreement (<2% error) between experimental removal efficiency and model prediction. The characteristics of the photo-Fenton treated leachate were: NH_3-N 112 mg/L, colour 108 Pt-Co Units, COD 350 mg/L, BOD_5 116 mg/L and BOD_5/COD ratio 0.33, indicating that the treated leachate was amenable to biological treatment. The study has revealed that RSM is a useful tool to optimize the treatment process and photo-Fenton is an effective pretreatment of mature landfill leachate for biological treatment.

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