

## Multiple responses analysis and modeling of Fenton process for treatment of high strength landfill leachate

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### ABSTRACT

Landfill leachate is one of the most recalcitrant wastes for biotreatment and can be considered a potential source of contamination to surface and groundwater ecosystems. In the present study, Fenton oxidation was employed for degradation of stabilized landfill leachate. Response surface methodology was applied to analyze, model and optimize the process parameters, i.e. pH and reaction time as well as the initial concentrations of hydrogen peroxide and ferrous ion. Analysis of variance showed that good coefficients of determination were obtained ( $R^2 > 0.99$ ), thus ensuring satisfactory agreement of the second-order regression model with the experimental data. The results indicated that, pH and its quadratic effects were the main factors influencing Fenton oxidation. Furthermore, antagonistic effects between pH and other variables were observed. The optimum  $H_2O_2$  concentration, Fe(II) concentration, pH and reaction time were 0.033 mol/L, 0.011 mol/L, 3 and 145 min, respectively, with 58.3% COD, 79.0% color and 82.1% iron removals.

**Key words** | advanced oxidation processes, fenton, response surface methodology, semi-aerobic landfill leachate

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### INTRODUCTION

Landfill leachate is generally considered a potential source of contamination to surface and groundwater due to its organic and inorganic contents. Leachate characteristics are strongly dependent on the age of landfill and composition of the wastes (Lopez *et al.* 2004). Although biological treatments are universally used for the treatment of landfill leachates, they are usually insufficient in degrading high molecular weight fractions. Mature leachates with their low BOD/COD ratio (low biodegradability) are particularly difficult to treat by biological process. Therefore additional physico-chemical processes are needed for pre- or post-treatment of leachate (Tauchert *et al.* 2006). Recently, advanced oxidation processes (AOPs), have received great attention as an alternative method for reducing the organic load of landfill leachate. These methods are capable of transforming non-biodegradable pollutants into non toxic substances (Catalkaya & Kargi 2007).

AOPs use hydroxyl radicals ( $OH^\bullet$ ) as the oxidizing agent to non-selectively oxidize a wide range of biorefractory organic pollutants (Lucas *et al.* 2007). Amongst the AOPs, Fenton reagent has been increasingly used for the treatment of landfill leachate and recalcitrant compounds (Deng & Englehardt 2006; Kochany & Lipczynska-Kochany 2009).

Fenton oxidation can be described as a process that is based on the hydrogen peroxide decomposition in acid medium, catalyzed by ferrous ion to produce hydroxyl radicals (Mohajeri *et al.* 2010a). The process is complicated, with numerous parallel reactions, but could be briefly represented by the following reaction:



Hydroxyl radicals produced during Fenton's reactions react with the pollutants to oxidize and break organic molecules, leading to mineralization of the organics to produce

CO<sub>2</sub> and H<sub>2</sub>O (Kang & Hwang 2000; Neyens & Baeyens 2003). Therefore, Fenton oxidation is a promising alternative for the removal of recalcitrant organic compounds.

The use of H<sub>2</sub>O<sub>2</sub>/Fe(II) as an oxidant for leachate treatment is attractive due to: (1) iron is highly abundant, inexpensive and non-toxic element, and (2) hydrogen peroxide could be handled easily and environmentally benign (Sudarjanto *et al.* 2006).

The present study investigates the feasibility of using Fenton's reagent to treat organic pollutants from leachate generated at the Pulau Burung landfill site (PBLs), Penang, Malaysia. The process variables were H<sub>2</sub>O<sub>2</sub> and Fe (II) concentration, initial pH and reaction time; and the responses were COD and color removals. The data were analyzed and the optimum treatment conditions were determined using central composite design (CCD) and response surface methodology (RSM). The synergistic and antagonistic effects of variables were particularly evaluated. The selected parameters are considered the most important elements in the overall impact of Fenton oxidation process.

## MATERIALS AND METHODS

### Sampling

Semi aerobic landfill leachate samples were collected in a polyethylene sampler from PBLs and stored at 4 °C in a cool room prior to the treatability study. The main parameters of the PBLs leachate are illustrated in Table 1.

The PBLs leachate has a very low BOD<sub>5</sub>/COD ratio (0.11) and is therefore not amenable to biological treatment. This type of leachate is characteristically categorized as strong and old (stabilized) leachate with low biodegradability (Bashir *et al.* 2010; Ghafari *et al.* 2010).

**Table 1** | The main parameters of leachate collected from PBLs

Parameters	Range	Average	SD <sup>a</sup>
pH	8.3–8.8	8.5	0.2
COD (mg/L)	2,320–2,480	2,360	59.9
BOD <sub>5</sub>	180–345	287	64.6
BOD <sub>5</sub> /COD	0.07–0.19	0.11	0.05
Color (PtCo.)	3,900–4,250	4,200	122.3
TSS (mg/L)	135–160	151	9.9
Ammonia-N (mg/L)	815–1,115	950	125.7
Fe (mg/L)	6.2–6.9	6.6	0.3

<sup>a</sup>SD: Standard deviation.

### Chemicals and instruments

Analytical grade ferrous sulfate, hydrogen peroxide, sodium hydroxide and sulfuric acid were obtained from Merck (Darmstadt, Germany). COD and color were determined using spectrophotometer (spectrophotometer DR/2010, HACH, Loveland, CO) according to APHA (2005). Experiments were carried out in triplicate in order to ensure the principle of replication is observed (APHA 2005).

### Treatment experiments

Landfill leachate oxidation experiments were performed in 500 mL beakers at room temperature (28 ± 3 °C) under atmospheric pressure with constant stirring using a magnetic stirrer. Appropriate volumes of 5M H<sub>2</sub>SO<sub>4</sub> or NaOH were added until the target pH was achieved. The pH adjustments were performed before adding each reagent and then the required amount of reagents was added according to the statistical experimental design. Finally, when the desired reaction time has reached, the reaction was suppressed with NaOH by increasing the pH to above 8. At such high pH the removal efficiency of organics via oxidation would stop (Papadopoulos *et al.* 2007). At the end of each run, the solution was allowed to settle for 30 min before the supernatant was taken for analysis.

### Experimental design and statistical analysis

Design Expert<sup>®</sup> 6.0.7 (Stat-Ease Inc., Minneapolis, USA), is employed for optimization of the Fenton oxidation process. Reaction time, pH, initial concentrations of ferrous ion (Fe(II)) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) were chosen as the control factors to be optimized. CCD was used for the experimental design, in which the four independent variables were converted to dimensionless ones (A, B, C, D). The low, center and high levels of each variable are designated as -1, 0 and +1, respectively. The variable levels were selected based on the results obtained from preliminary experiments as well as from literature (Zhang *et al.* 2006; Yetilmezsoy & Sakar 2008; Mohajeri *et al.* 2010b).

The ranges for independent variables were: pH, 2–6; reaction time, 60–180 min; Fe(II) concentration 0.005–0.015 mol/L and H<sub>2</sub>O<sub>2</sub> concentration 0.015–0.045 mol/L. The dependent variables (or objective functions) were the COD (Y<sub>1</sub>) and color (Y<sub>2</sub>) removals.

## RESULTS AND DISCUSSION

### Regression model and results statistics

The behavior of the system is described by Equation (2), an empirical second-order polynomial model (Montgomery 2008):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{i \neq j=1}^k \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

where  $Y$  is the response variable (i.e. COD or color removal),  $\beta_0$  the constant coefficient,  $\beta_i$ ,  $\beta_{ii}$  and  $\beta_{ij}$  the coefficients for the linear, quadratic and interaction effect,  $x_i$  and  $x_j$  the factors (i.e. pH, reaction time, Fe(II) concentration and  $\text{H}_2\text{O}_2$  concentration) and  $\varepsilon$  is the error.

Analysis of variance (ANOVA) was used for graphical analyses of the data to obtain the interaction between the process variables and the responses. The quality of the fit polynomial model was expressed by the coefficient of determination  $R^2$ , and its statistical significance was checked by the student  $t$ -test in the same program.

Model terms were evaluated by the  $P$ -value (probability) with 95% confidence level. Three-dimensional plots and their respective contour plots were obtained based on effects of the four factors (pH, reaction time, Fe(II) concentration and  $\text{H}_2\text{O}_2$  concentration) at three levels.

Equations (3) and (4) represent COD and color removals, where the insignificant coefficients were excluded from the model:

$$\begin{aligned} \% \text{ COD removal} = & 56.84 - 7.64 A + 5.65 B + 3.14 C + 3.97 D \\ & - 16.38 A^2 - 6.26 B^2 - 7.12 C^2 - 8.23 D^2 \\ & - 0.98 AB - 0.99 AC - 1.15 AD \end{aligned} \quad (3)$$

$$\begin{aligned} \% \text{ Color removal} = & 77.76 - 9.64 A + 7.27 B + 4.43 C + 5.45 D \\ & - 24.41 A^2 - 7.83 B^2 - 9.63 C^2 - 9.02 D^2 \\ & - 1.05 AB - 2.13 AD + 1.72 BC \end{aligned} \quad (4)$$

where A, B, C and D are pH, reaction time, Fe(II) concentration and  $\text{H}_2\text{O}_2$  concentration, respectively.

The measured and predicted response data obtained from Equations (3) and (4) are shown in Table 2. It shows that the proposed empirical model is suitable for predicting COD and color removals, revealing a reasonably good agreement. On the basis of the coefficients in Equations (3) and (4) it can be concluded that the variables and

interactions that significantly affect the COD and color removals are all variables viz. pH, reaction time, Fe(II) concentration and  $\text{H}_2\text{O}_2$  concentration and their squares. Moreover, pH (A) is the major regressor variable influencing the responses (greatest coefficients) while this variable has a considerable interaction with other variables. A significant effect of the interactions among the variables pH and  $\text{H}_2\text{O}_2$  concentration (AC), pH and Fe(II) concentration (AD) and pH and reaction time (AB) is observed. For color removal, Equation (4) suggests that there is a slight effect of the interaction among the variables Fe(II) concentration and reaction time (BC).

$F$ -values of 400.72 and 1138.24 imply that the models are significant for COD and color removals and there is only 0.01% chance for this model to be due to noise. For the COD removal model the 'Lack of Fit  $F$ -value' of 3.03 implies the Lack of Fit is not significant relative to the pure error. For color removal the 'Lack of Fit  $F$ -value' of 2.14 also implies the Lack of Fit is not significant. A high  $R^2$  coefficient ensures a satisfactory adjustment of the quadratic model to the experimental data.  $R^2$  was 0.9959 and 0.9986 for COD and color removal efficiencies, respectively. In optimizing a response surface, an adequate fit of the model should be achieved to keep away from poor outcome. It also demonstrates that response surface quadratic models for our parameters were significant at the 5% confidence level since  $P$ -values were  $<0.05$ . The Predicted  $R^2$  of 0.9861 and 0.9956 are reasonably in agreement with the Adjusted  $R^2$  of 0.9934 and 0.9977, respectively.

### Interactions among variables

The response surface plots (Figures 1 and 2) obtained from the software provide a three-dimensional view of the COD and color removals surface over different combinations of independent variables. Some interactions among variables were significant so the curvature of three-dimensional surfaces was obvious, as shown in Figures 1 and 2.

All response plots have clear peaks, which suggest that the optimum conditions for maximum values of the responses are attributed to all four variables, i.e. pH; reaction time; Fe(II) concentration and  $\text{H}_2\text{O}_2$  concentration in the design space. Response surface plots in Figures 1 and 2 indicate optimum points are at about pH 3, reaction time 120 min, Fe(II) concentration 0.01 mol/L and  $\text{H}_2\text{O}_2$  concentration 0.03 mol/L.

The COD and color removals under these conditions were 57.81 and 78.15%, respectively. Moving away from

**Table 2** | Experimental matrix and results for COD and color removal

Run No.	Factors				COD removal %		Color removal %	
	pH	RT	Fe	H <sub>2</sub> O <sub>2</sub>	Observed	Predicted	Observed	Predicted
1	2	60	0.005	0.015	11.38	10.60	17.06	17.89
2	6	60	0.005	0.015	3.57	1.56	5.33	4.98
3	2	180	0.005	0.015	23.23	23.87	31.13	31.12
4	6	180	0.005	0.015	11.20	10.91	14.78	13.99
5	2	60	0.015	0.015	18.18	18.87	24.10	23.32
6	6	60	0.015	0.015	5.54	5.87	9.72	10.41
7	2	180	0.015	0.015	31.18	32.14	42.33	43.41
8	6	180	0.015	0.015	14.21	15.21	26.06	26.28
9	2	60	0.005	0.045	20.45	20.83	31.90	33.04
10	6	60	0.005	0.045	7.94	7.21	13.24	11.62
11	2	180	0.005	0.045	33.57	34.10	46.72	46.27
12	6	180	0.005	0.045	15.23	16.55	19.13	20.63
13	2	60	0.015	0.045	29.15	29.10	38.76	38.47
14	6	60	0.015	0.045	11.33	11.51	16.23	17.05
15	2	180	0.015	0.045	42.31	42.37	58.04	58.56
16	6	180	0.015	0.045	23.18	20.85	34.07	32.92
17	2	120	0.01	0.03	50.55	48.10	65.02	62.99
18	6	120	0.01	0.03	30.30	32.82	43.01	43.72
19	4	60	0.01	0.03	42.94	44.92	63.08	62.66
20	4	180	0.01	0.03	58.14	56.23	78.11	77.21
21	4	120	0.005	0.03	45.65	46.57	63.93	63.70
22	4	120	0.015	0.03	53.71	52.86	73.65	72.56
23	4	120	0.01	0.015	45.20	44.64	64.17	63.29
24	4	120	0.01	0.045	51.95	52.58	74.63	74.19
25	4	120	0.01	0.03	56.62	56.84	77.72	77.76
26	4	120	0.01	0.03	57.81	56.84	78.15	77.76
27	4	120	0.01	0.03	57.47	56.84	77.54	77.76
28	4	120	0.01	0.03	57.82	56.84	75.89	77.76
29	4	120	0.01	0.03	55.50	56.84	76.12	77.76
30	4	120	0.01	0.03	56.01	56.84	77.19	77.76

these points shows reduction in removal efficiencies, suggesting that neither increase nor decrease in any of the tested variables is desired. The plots show that pH, Fe(II) and H<sub>2</sub>O<sub>2</sub> concentrations are the major determining factors for COD and color removals.

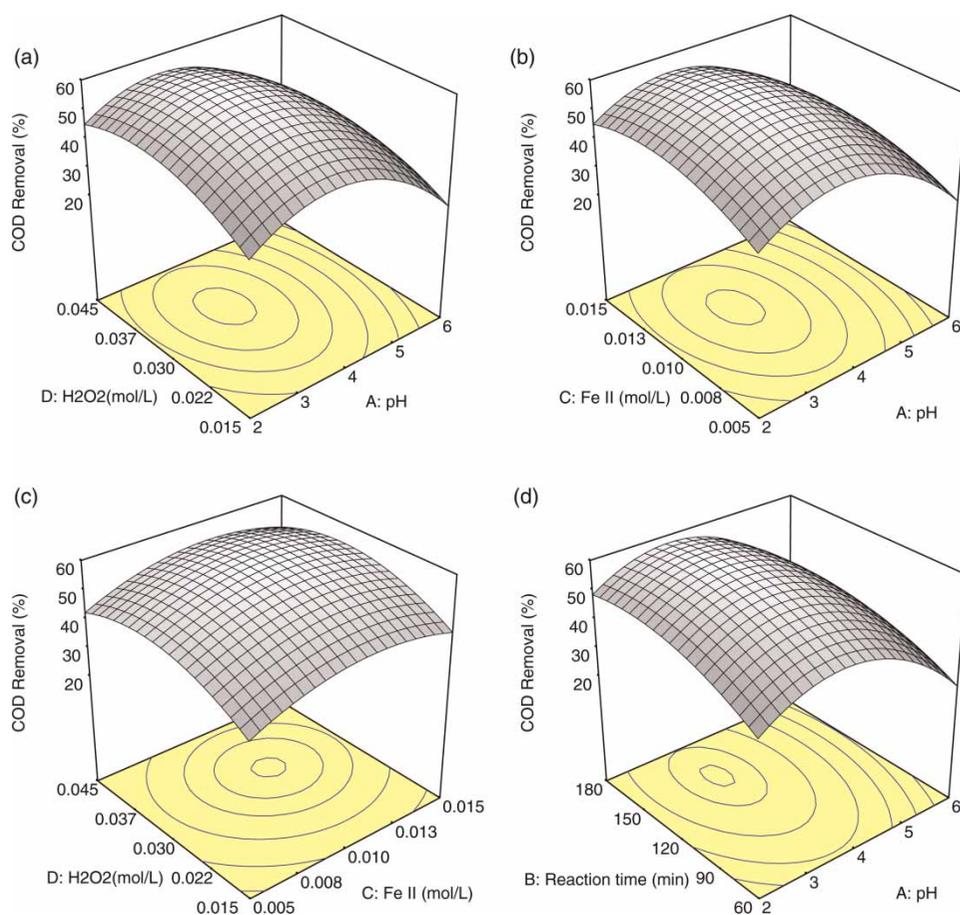
As shown in Figures 1 and 2, the influence of Fenton reagent dosage and pH on COD and color removal efficiencies were more significant than with reaction time, which had limited effects on COD and color removals.

Generally, removal of organics increases with increasing concentration of iron salt and hydrogen peroxide (Deng &

Englehardt 2006). However, the incremental removal may be limited by extra concentration. Thus particular attention must be paid to Fe<sup>2+</sup> and H<sub>2</sub>O<sub>2</sub> dosages in order to avoid the undesired OH<sup>•</sup> radicals scavenging reactions occurring in the presence of an excess of each of the two reagents.

Relationship between dosages of Fenton reagents and COD and color removal efficiencies for Fenton treatment of leachate are shown in Figures 1 and 2.

Concentration of hydrogen peroxide plays a more crucial role in Fenton process, because it directly affects the degradation efficiency.



**Figure 1** | Three-dimensional surface plots of COD removal as a function of: (a) H<sub>2</sub>O<sub>2</sub> concentration and pH, (b) Fe<sup>2+</sup> concentration and pH, (c) concentration of [H<sub>2</sub>O<sub>2</sub>] and [Fe<sup>2+</sup>] and (d) pH and reaction time.

Figures 1(a) and 1(c) indicate that higher H<sub>2</sub>O<sub>2</sub> doses produced more hydroxyl radicals that improved the COD removal efficiency. With an increase of H<sub>2</sub>O<sub>2</sub> doses from 0.015 to 0.03 mol/L, at constant Fe<sup>2+</sup> dosage, average COD removal efficiency increased. From this figure, the H<sub>2</sub>O<sub>2</sub> dosage that yielded COD removals higher than 50% was 0.03 mol/L.

Further increase in the H<sub>2</sub>O<sub>2</sub> concentration beyond optimum value did not improve the degradation efficiency. This may be attributed to auto decomposition of H<sub>2</sub>O<sub>2</sub> to oxygen and water, and the recombination of OH<sup>•</sup> radicals. Moreover, higher concentrations of hydrogen peroxide act as free-radical scavenger itself, thereby decreasing the concentration of hydroxyl radicals and reducing compound elimination efficiency. These effects can be explained by Equations (5), (6), and (7):

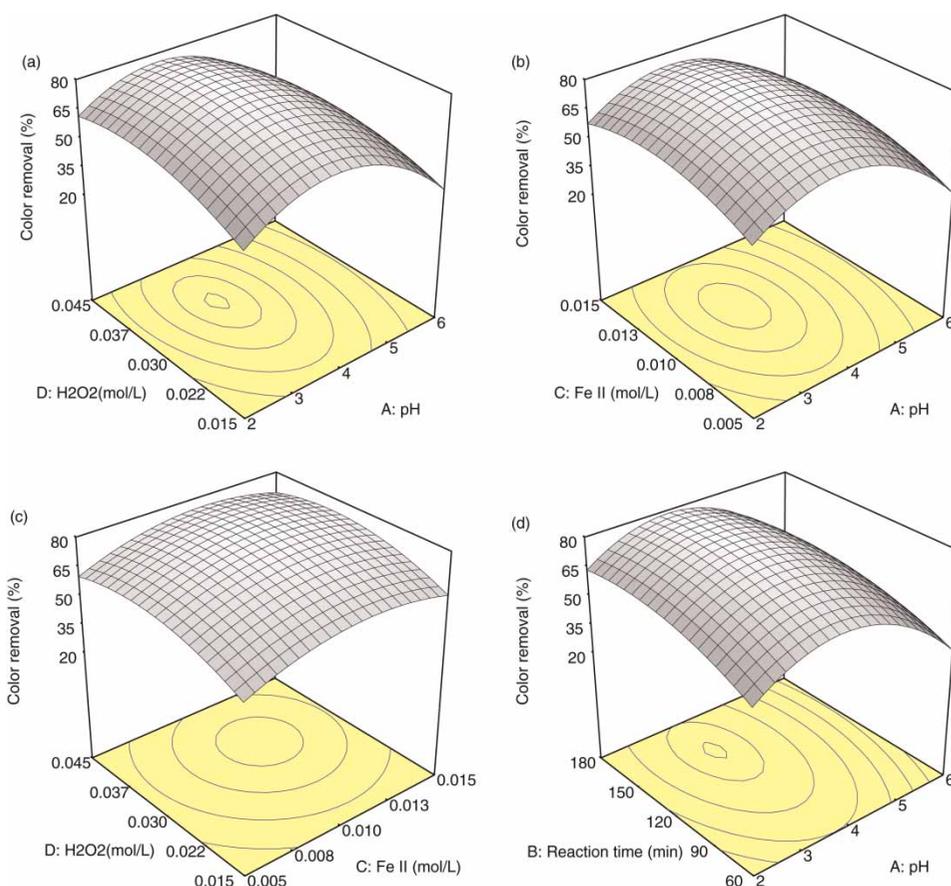


This phenomenon was also observed by (Deng & Englehardt 2006; Mohajeri *et al.* 2010a). The same decrease in color removal after 0.03 mol/L of H<sub>2</sub>O<sub>2</sub> can be explained due to the scavenging effect of over dose of H<sub>2</sub>O<sub>2</sub> on OH radicals. Therefore, H<sub>2</sub>O<sub>2</sub> should be added at an optimum concentration to achieve the best degradation and decolorization. It is important to optimize the amount of H<sub>2</sub>O<sub>2</sub> in the Fenton method because the main cost of the method is the price of H<sub>2</sub>O<sub>2</sub> and excessive doses of H<sub>2</sub>O<sub>2</sub> trigger side effects.

Based on Figures 1(b) and 1(c), COD removal decreased with increasing in Fe<sup>2+</sup> dosage. The inhibition of the mineralization process for Fe<sup>2+</sup> dosage higher than 0.01 mol/L can be explained by the rapid consumption of OH<sup>•</sup> with the greater amount of regenerated Fe<sup>2+</sup> as follows:



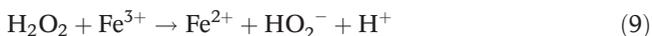
It means excess Fe<sup>2+</sup> has a scavenging effect on



**Figure 2** | Three-dimensional surface plots of color removal as a function of: (a) H<sub>2</sub>O<sub>2</sub> concentration and pH, (b) Fe<sup>2+</sup> concentration and pH, (c) concentration of [H<sub>2</sub>O<sub>2</sub>] and [Fe<sup>2+</sup>] and (d) pH and reaction time.

hydroxyl radicals. This phenomenon was also reported by other researchers (Ramirez *et al.* 2005; Lee & Shoda 2008).

In addition, the Fe<sup>3+</sup> formed can react with H<sub>2</sub>O<sub>2</sub> (Equation (9)) to generate Fe<sup>2+</sup> and hydroperoxyl radicals (HO<sub>2</sub><sup>·</sup>) in solution:



Additionally, excess iron salt contributes to an increase in the amount of iron sludge that requires extra treatment.

The results obtained from Figures 1 and 2 demonstrated that there is an optimum H<sub>2</sub>O<sub>2</sub> and Fe(II) concentration for COD and color removals, so that the consumption of hydroxyl radical by ferrous ion or hydrogen peroxide would be minimum via reaction (5) or (8). Moreover, the optimal amount of Fenton reagents is related to pH and decreased with pH (Figures 1(a) and 1(b)).

The efficiency of the Fenton process in terms of increased COD removal is influenced by the pH and the initial pH adjustment is important.

According to optimization study, maximum removals of COD and color were obtained at pH 3. The maximum COD and color removals were 57.81 and 78.15%, respectively.

Thus, pH has to be in the acidic range to generate maximum amount of hydroxyl radicals to oxidize organic compounds. A similar phenomenon was observed by previous researchers (Zhang *et al.* 2007; Mohajeri *et al.* 2010b).

However, pH should not be too low since at very low pH values (<2.0) the reaction will be slow down due to the formation of complex iron species and formation of oxonium ion [H<sub>3</sub>O<sub>2</sub>]<sup>+</sup> (Kwon *et al.* 1999).

On the other hand, at high pH (pH > 4), the iron ions especially the Fe<sup>3+</sup> precipitate; which inhibit the regeneration of ferrous ions. Therefore, the amount of catalyst available for Fenton's reaction decreases. Hydrogen peroxide is also unstable in basic solution and may decompose to oxygen and water and lose its oxidation ability (Badawy & Ali 2006; Zhang *et al.* 2007).

The interaction implies that the effect produced by changing the H<sub>2</sub>O<sub>2</sub> and Fe(II) concentrations, as two regressor

variables depends on the level of pH as the other regressor variable. For a constant H<sub>2</sub>O<sub>2</sub> and Fe(II) concentrations, the COD removal decreased with the increase in initial pH from 4.0 to 6.0. In other words, COD decreases as the pH increases toward its high level, i.e. pH > 4 and stronger influence of pH occurred when the pH was at its center level (acidic media). Therefore, the Fenton system is pH sensitive, and acidic condition is necessary for iron solubility; because the dissolved fraction of iron species decreases at pH above 4. It is demonstrated that there is an obvious interaction between the initial pH and the Fenton reagents concentration on degradation and decolorization of leachate.

These results are in agreement with other studies on the oxidation of organic compounds in landfill leachate (Kang & Hwang 2000; Zhao *et al.* 2007).

Figures 1(d) and 2(d) show that reaction time has a positive effect on mineralization and decolorization of leachate. It is noted that the maximum COD and color removals are obtained with a reaction time of about two hours. After that the removal efficiencies did not change considerably. It means that the supplied H<sub>2</sub>O<sub>2</sub> was probably almost completely consumed as shown in Figure 1.

### Optimization and method verification

Numerical optimization was used to determine the optimum process parameters for maximum leachate mineralization and decolorization. Based on response surface and desirability functions, the optimum conditions for COD and color removals were obtained. In this case, all variables were targeted to be in range in DoE software, COD and color removals were goaled to be maximized with highest importance. Optimized conditions under specified constraints were obtained for highest desirability (1.000) at pH 3, Fe(II) concentration 0.011 mol/L and H<sub>2</sub>O<sub>2</sub> concentration 0.033 mol/L, after 145 min of reaction time. Under these optimized conditions, 60.03% COD and 81.92% color removals were predicted.

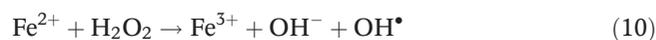
In order to confirm the accuracy of the predicted model and the reliability of the optimum combination, one additional experiment was carried out at optimum conditions. The experimental values were found to agree well with the predicted ones, with a mean COD and color removal efficiencies of 58.33 and 79.02%, respectively. Previously, Fenton method for treatment of landfill leachate was employed by other researchers. Hermosilla *et al.* (2009) observed that under the optimal conditions, the conventional Fenton process was able to achieve slightly over 80% COD removal from a 'young' leachate; while the COD removal

from the 'old' and 'mixed' leachates resulted <70%. In a study performed by Lopez *et al.* (2004), they found that Fenton process achieved maximum 60% COD removal using reagent dosages as high as 10,000 mg/L of H<sub>2</sub>O<sub>2</sub> and 830 mg/L of Fe<sup>2+</sup> within 2 h. Kochany & Lipczynska-Kochany (2009) reported that 66% of COD was removed at pH 3.5 and 650 mg/L of H<sub>2</sub>O<sub>2</sub> using Fenton catalyst. In another landfill leachate treatment study (Barnes *et al.* 2007), COD was lowered by 76% using Fenton oxidation at optimized conditions of H<sub>2</sub>O<sub>2</sub> dosage of 3,500 mg/L, Fe<sup>2+</sup> dosage of 437.5 mg/L, pH 4, a mass ratio of 8 for H<sub>2</sub>O<sub>2</sub>:Fe<sup>2+</sup> dosage and reaction time of 30 min.

### Iron removal

Fenton's reaction is widely applied for the removal of organic substances. However, the capability of the technique to remove iron from landfill leachate is not documented. In order to investigate the effect of Fenton process on Fe<sup>2+</sup> removal, residual Fe<sup>2+</sup> concentration in the final effluent were determined. Under the optimum condition, partial removal efficiency of 82.1% was obtained. The suggested mechanism could be relevant to the following reactions:

The ferrous iron (Fe<sup>2+</sup>) initiates and catalyses the decomposition of H<sub>2</sub>O<sub>2</sub>, resulting in the production of hydroxyl radicals and Fe<sup>3+</sup> in the solution by reaction 10:



Ferrous ions can also be rapidly destroyed by hydroxyl radicals:



Therefore, most of the iron in the effluent leachate is in the form of Fe<sup>3+</sup>.

On the other hand, since all iron species precipitate as ferric hydroxide at pH above 8 (Eren & Acar 2006), in neutralization stage (pH adjustment), residual ferrous ions can be hydrolyzed to form iron hydroxide precipitates, resulting in complete removal of ferrous ions (Fe<sup>2+</sup>).

### Process competency and drawbacks

As declared in advance, owing to its age (>10 years) and low biodegradability (BOD<sub>5</sub>/COD = 0.11), PBLs leachate was classified as stabilized leachate. In the present study,

Fenton oxidation has been employed for PBLs stabilized leachate treatment. This resulted in 79.0% COD and 82.1% color removals, respectively. Due to its renowned stabilized characteristics, aged leachates generated from different landfills will probably have same treatment tendency. Thus, the performance efficiency of using Fenton oxidation technique in treatment of PBLs leachate can be generalized particularly for leachate with identical properties. Compared with other techniques used in stabilized landfill leachate treatment, the efficiency of Fenton oxidation has been found to be appropriate. For instance, the implementation of electrochemical oxidation process was resulted in 59% color and 49% COD removals (Mohajeri et al. 2010c); Less than 15% of COD was eliminated via air stripping (Calli et al. 2005); About 50–65% COD removal from stabilized leachate can be obtained by applying coagulation technique (Amokrane et al. 1997). Adsorption process has achieved 70 and 85% removal of COD and color from PBLs stabilized leachate (Daud et al. 2009).

In spite of all the foregoing-mentioned advantages, Fenton oxidation technique has some drawbacks, i.e. (i) inadequacy in ammonia elimination; (ii) although Fenton oxidation leads to a considerable elimination, but it's not capable to diminish the COD and color below the discharge limits allowed by Malaysian laws (i.e. 400 mg/L for COD and 100 Pt-Co/L), as stipulated by the Environmental Quality (2009). With Fenton oxidation it is understandable that a complementary treatment should be employed to purify the effluent; additional treatment leads to additional cost. Hence, Fenton oxidation technology should not be used as a final treatment but is better suited as a post or pre-treatment process; and (iii) the conventional Fenton process is costly because it requires chemicals, related with higher hydrogen peroxide utilization levels.

## CONCLUSIONS

The effectiveness of Fenton catalyst for the treatment of landfill leachate was studied using CCD and RSM. Optimum conditions for this advanced oxidation process were found at H<sub>2</sub>O<sub>2</sub> concentration 0.033 mol/L, Fe(II) concentration 0.011 mol/L, pH 3, and reaction time 145 min. Agreement of the quadratic models with the experimental data was satisfactory. ANOVA had given good values for the coefficient of determination ( $R^2 > 0.99$ ). Within the tested operating conditions, maximum COD, color and Fe<sup>2+</sup> removals were 58.3, 79.0, and 82.1%, respectively. RSM was demonstrated to be an effective technique for optimization of Fenton

process. From the results of this study it is concluded that Fenton oxidation can be used as post or pre-treatment for mature landfill leachate.

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