

# Application of the central composite design for condition optimization for semi-aerobic landfill leachate treatment using electrochemical oxidation

Soraya Mohajeri, Hamidi Abdul Aziz, Mohamed Hasnain Isa, Mohammad Ali Zahed, Mohammed J. K. Bashir and Mohd. Nordin Adlan

## ABSTRACT

In the present study, Electrochemical Oxidation was used to remove COD and color from semi-aerobic landfill leachate collected from Pulau Burung Landfill Site (PBLs), Penang, Malaysia. Experiments were conducted in a batch laboratory-scale system in the presence of NaCl as electrolyte and aluminum electrodes. Central composite design (CCD) under Response surface methodology (RSM) was applied to optimize the electrochemical oxidation process conditions using chemical oxygen demand (COD) and color removals as responses, and the electrolyte concentrations, current density and reaction time as control factors. Analysis of variance (ANOVA) showed good coefficient of determination ( $R^2$ ) values of  $>0.98$ , thus ensuring satisfactory fitting of the second-order regression model with the experimental data. In un-optimized condition, maximum removals for COD (48.77%) and color (58.21%) were achieved at current density 80 mA/cm<sup>2</sup>, electrolyte concentration 3,000 mg/L and reaction time 240 min. While after optimization at current density 75 mA/cm<sup>2</sup>, electrolyte concentration 2,000 mg/L and reaction time 218 min a maximum of 49.33 and 59.24% removals were observed for COD and color respectively.

**Key words** | COD, color, electrochemical oxidation, response surface methodology, semi-aerobic leachate

**Soraya Mohajeri**  
**Hamidi Abdul Aziz** (corresponding author)  
**Mohammad Ali Zahed**  
**Mohammed J. K. Bashir**  
**Mohd. Nordin Adlan**  
School of Civil Engineering,  
Universiti Sains Malaysia,  
14300 Nibong Tebal,  
Penang,  
Malaysia  
E-mail: [cehamidi@eng.usm.my](mailto:cehamidi@eng.usm.my)

**Mohamed Hasnain Isa**  
Civil Engineering Department,  
Universiti Teknologi PETRONAS,  
31750 Tronoh,  
Perak,  
Malaysia

## INTRODUCTION

Safe disposal of municipal landfill leachate is one of the most important problems of modern society. Leachate generated from municipal landfills is a complicated wastewater that often contains organic substances, heavy metals, chlorinated organic compounds, inorganic salts and many other soluble compounds (Knox & Jones 1979; Wang *et al.* 2002).

Landfill leachate is considered a potential source of contamination of groundwater and if it is not properly collected, treated and safely disposed could harm the environment (Read *et al.* 2001). The composition and concentration of contaminants in leachate are influenced

by the type of waste and the age of the landfill (Cabeza *et al.* 2007a).

Advanced oxidation processes (AOPs) have recently attracted increasing attention. They can improve the biodegradability of organic compounds through the use of reactive radicals (Benatti *et al.* 2006). The free radicals react quickly with most organic compounds and produce organic radicals which then react with oxygen to initiate a series of oxidation reactions leading to mineralization of the organics to produce CO<sub>2</sub> and H<sub>2</sub>O.

Electrochemical oxidation is becoming an alternative wastewater treatment method and is replacing the

conventional processes. In this study, the electrochemical treatment of leachate was investigated using NaCl as electrolyte and aluminium electrodes.

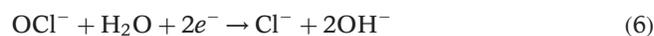
The technique removes organic pollutants through two different means: indirect oxidation, where a mediator is electrochemically generated to carry out the oxidation, and direct anodic oxidation, where pollutants are destroyed on the anode surface by the anodic electron-transfer reaction (Grimm *et al.* 1998). Hydroxyl radicals can also be generated on the anode surface to enhance the rate of oxidation (Cabeza *et al.* 2007b). Hydroxyl radical (OH) is a very powerful, non-selective, oxidizing agent that reacts rapidly with organic compounds via hydroxylation with addition of a hydroxyl group to a non saturated bond or dehydrogenation with the loss of a hydrogen atom, following a radical mechanism until their overall mineralization, i.e. the transformation of initial pollutants into carbon dioxide, water and inorganic ions (Boye *et al.* 2003). Organic pollutants can also be oxidized electrochemically by active chlorine compounds generated by the oxidation of chloride either present in the wastewater or added to it. The oxidation of organic compounds is strongly assisted by the presence of Cl<sup>-</sup>, which is oxidized to Cl<sub>2</sub>, hypochlorite, chlorate, and perchlorate due to electrolysis, and also other oxidants such as O<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, and peroxides may be present due to the oxidation of the electrolyte support (Szyrkowicz *et al.* 2001; Chen 2004; Arevalo & Calmano 2007; Panizza *et al.* 2007; Un *et al.* 2008).

In the presence of chloride ions, the possible electrochemical reactions are shown as follows:



Hypochlorous acid, HOCl, is also a strong oxidant, which can oxidize organic compounds.

These anodic reactions occur simultaneously with the following primary cathodic reactions:



Hypochlorite ion (OCl<sup>-</sup>) generated in solution is a strong oxidant that can oxidize aqueous organic compounds.



Advantages of electrochemical oxidation over other oxidizing treatment methods include high efficiency, simplicity in destroying the contaminants, leaving no residue, suitability to treat a wide range of substances, no requirement of special equipment, relatively inexpensive, etc. (Martinez-Huitle & Ferro 2006; Andrade *et al.* 2009; Nasr *et al.* 2009).

Response surface methodology is a technique used for modeling, designing experiments, evaluating the effects of variables and their interactions, and searching optimum conditions of variables to predict goal responses (Montgomery 2008). In the present study, we investigated the feasibility of electrochemical oxidation (EC) to treat organic pollutants in leachate. Central composite design (CCD) was used as a design framework for second-order response surface modeling to evaluate the influence of the key process variables: electrolyte dosage, reaction time and current density, on the efficiency of COD and color removals from landfill leachate. Response surface optimization techniques were applied to maximize COD and color removals.

## MATERIALS AND METHODS

### Sampling

Leachate samples were collected from Pulau Burung Landfill Site (PBLs) in Nibong Tebal, Penang, Malaysia. It has been developed semi-aerobically employing a controlled tipping technique and leachate recirculation system (Aziz *et al.* 2004). The semi-aerobic landfill leachate characteristics are given in Table 1. The parameters were analyzed according to (APHA 2005). Collected samples

**Table 1** | Characteristics of leachate collected from PBLs, Penang, Malaysia

Parameters	Range	Average	Standard deviation
pH	7.9–8.3	8.0	0.14
COD (mg/L)	2,550–2,710	2,600	58.65
BOD (mg/L)	175–310	237	52.32
COD/ BOD ratio	0.06–0.11	0.09	0.02
NH <sub>3</sub> -N	910–1030	978	50.37
Color (Pt.Co.)	3,120–3,360	3,250	76.71
Turbidity (FAU)	245–270	261	8.81
TSS (mg/L)	135–160	152	9.61
Temperature	28–31	29	1.10
Fe (mg/L)	6.3–6.6	6.4	0.10

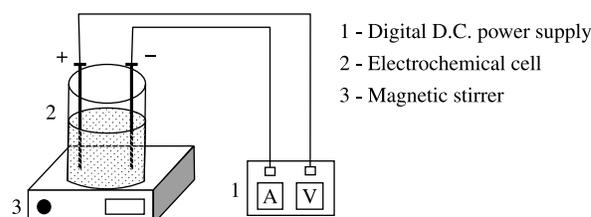
were immediately moved to a cold room and stored at 4°C until use in the experiments.

### Electrochemical oxidation experiments

Batch experiments were conducted in this study. In each run, 500 ml leachate was placed in the electrochemical cell. EC oxidation was carried out at pre-decided current densities. The current required during the electrolysis experiments was provided by a laboratory DC power supply (DAZHENG, PS-305D) with maximum output of 3 A–30 V.

A pair of aluminum electrodes was used as anode and cathode. The electrodes had a surface area of 15 cm<sup>2</sup> each and were placed vertically and parallel to each other in the electrolytic cell. Their separation distance was 3 cm. The electrolytic cell was equipped with a magnetic stirrer maintained at 400 rpm to keep the solution well mixed. The electrodes were replaced when more than 10% of electrode material was lost. The experimental set-up used for the present study is shown in Figure 1.

Analytical grade NaCl (Merck, Germany) was added as electrolyte and source of chloride for the EC process. In this set of experiments different amounts of NaCl (1,000–3,000 mg Cl<sup>-</sup>) were added to the leachate in order to investigate the effect of chloride concentration on the efficiency of COD and color removals. At the end of each run, the solution was allowed to settle for 30 min and the supernatant was drawn for analysis. In this study, three important parameters (initial NaCl dosage, reaction time

**Figure 1** | Experimental set-up.

and current density) were varied to determine the optimum condition of the treatment process for degradation of leachate. Meanwhile, the initial pH of the influent (pH 8), temperature (28°C), and distance between electrodes (3 cm) were kept constant to reduce the number of factors and to simplify the experimental design.

### Chemical analysis

COD concentration was measured colorimetrically using a DR/2010 spectrophotometer (HACH Company, USA). Color was measured using Hach color method (HACH, DR/2010) at 465 nm wavelength (APHA 2005). Experiments were conducted in triplicate and analytical measurements (COD and color) were made in triplicate as well. All the runs were performed at room temperature and atmospheric pressure.

### Data analysis

Design Expert 6.0.7 software (Stat-Ease Inc., Minneapolis, USA) was employed for design, mathematical modeling and optimization. The number of experiments in this study was 15 plus another 5 replicates at the centre point. Thus, a total of 20 experiments were conducted as presented in Table 2. For the statistical calculations, the selected independent variables were coded according to Equation (8):

$$X_i = \frac{X_i - X_0}{\Delta X} \quad i = 1, 2, \dots, k \quad (8)$$

where  $X_i$  is the dimensionless coded value of the  $i$ th independent variable ( $i = 1, 2, \dots, k$ ),  $X_0$  is the value of  $X_i$  at the center point and  $\Delta X$  is the step change value (Montgomery 2008).

**Table 2** | Experimental matrix for central composite design (CCD)

Run No.	Point type	Factors		
		Electrolyte dosage, mg/L	Current density, mA/cm <sup>2</sup>	Reaction time, min
1	Fact	1,000	20	60
2	Fact	1,000	80	60
3	Fact	1,000	20	240
4	Fact	1,000	80	240
5	Fact	3,000	20	60
6	Fact	3,000	80	60
7	Fact	3,000	20	240
8	Fact	3,000	80	240
9	Axial	2,000	20	150
10	Axial	2,000	80	150
11	Axial	2,000	50	60
12	Axial	2,000	50	240
13	Axial	1,000	50	150
14	Axial	3,000	50	150
15	Center	2,000	50	150
16	Center	2,000	50	150
17	Center	2,000	50	150
18	Center	2,000	50	150
19	Center	2,000	50	150
20	Center	2,000	50	150

The three independent variables were set at low, center and high levels, designated as  $-1$ ,  $0$ , and  $+1$ , respectively (Table 3).

The ranges of selected parameters were determined from available literature (Wang *et al.* 2001; Chen 2004; Shao *et al.* 2006; Cabeza *et al.* 2007a; Deng & Englehardt 2007; Andrade *et al.* 2009; Bashir *et al.* 2009). Furthermore preliminary studies were performed in order to estimate

**Table 3** | Coded and actual values of variables of the design of experiments for overall electrochemical optimization

Code	Factor	Unit	Coded levels of variables		
			$-1.00$	$0$	$1.00$
A	Electrolyte concentration	mg/L	1,000	2,000	3,000
B	Current density	mA/cm <sup>2</sup>	20	50	80
C	Reaction time	Min	60	150	240

narrower ranges of the process variables before conducting the factorial design experiments as presented in Table 3.

## RESULTS AND DISCUSSION

### Results and response surface modeling

In optimizing a response surface, model should fit adequately to avoid poor or ambiguous results. In order to determine the optimal conditions for the operational variables (electrolyte concentrations, current density and reaction time), the experimental response chosen to analyze the results was the percent of COD and color removals.

The quadratic model used is shown in Equation (9):

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{i=1}^k \sum_{j=1, j \neq i}^k \beta_{ij} x_i x_j + \varepsilon \quad (9)$$

where  $Y$  is the predicted response (COD and color removal efficiencies, %) used as the dependent variables,  $x_i$  and  $x_j$  are variables or independent factors,  $\beta_0$  is the constant coefficient,  $\beta_i$ ,  $\beta_{ij}$  and  $\beta_{ii}$  are interaction coefficients of linear, quadratic and the second-order terms, respectively,  $k$  is the number of independent parameters ( $= 3$ ) and  $\varepsilon$  is the error (Montgomery 2008).

Empirical relationships between COD and color removal efficiencies and the variables after neglecting statistically non-significant terms are expressed by the following second-order polynomial equations:

$$\begin{aligned} \text{COD Removal} = & 40.02 + 5.87 A + 8.91 B + 4.08 C \\ & - 8.84 C^2 - 0.85 AC \end{aligned} \quad (10)$$

$$\begin{aligned} \text{Color Removal} = & 50.68 + 8.59 A + 9.55 B + 4.84 C \\ & - 11.65 C^2 - 3.50 AC \end{aligned} \quad (11)$$

where  $A$ ,  $B$  and  $C$  are model terms that represent the operating factors electrolyte concentration, current density and reaction time, respectively.

Table 4 shows the results of the electrochemical experiments as average of the triplicate tests conducted for each operating condition.

Analysis of variance (ANOVA) of regression parameters of the response surface quadratic model for COD and color

**Table 4** | Observed and predicted percent removals for the response functions

Run No.	COD removal%			Color removal %		
	Observed	Predicted	StD*	Observed	Predicted	StD*
1	11.24	11.48	0.17	13.89	12.54	0.95
2	25.58	24.92	0.47	36.59	36.73	0.10
3	29.79	29.29	0.35	31.05	31.65	0.42
4	42.34	42.73	0.28	56.86	55.84	0.72
5	21.35	21.33	0.01	28.25	29.23	0.69
6	31.38	31.38	0.00	38.95	39.41	0.32
7	38.68	39.14	0.33	48.43	48.34	0.07
8	48.77	49.20	0.30	58.21	58.51	0.21
9	33.43	34.15	0.51	41.55	42.09	0.38
10	45.15	45.90	0.53	58.47	59.27	0.57
11	29.80	31.12	0.94	39.16	41.13	1.39
12	48.83	48.93	0.07	57.82	60.23	1.71
13	26.58	27.11	0.37	32.57	34.19	1.15
14	36.14	35.26	0.62	45.52	43.87	1.17
15	40.87	40.03	0.60	53.33	50.68	1.87
16	40.85	40.03	0.58	52.21	50.68	1.08
17	40.11	40.03	0.06	52.48	50.68	1.27
18	41.02	40.03	0.70	51.36	50.68	0.48
19	40.53	40.03	0.36	51.08	50.68	0.28
20	39.67	40.03	0.25	49.34	50.68	0.95

\*Standard deviation.

removals by EC process are presented in **Tables 5 and 6** respectively. The models for the COD and color removals were found to be significant using the *t*-test at 5% significance level ( $\text{Prob} < 0.05$ ). The models *F*-values of 597.91 and 209.94 and low probability values indicate that the models are significant for COD and color removals.

For the COD removal model the Lack of Fit *F*-value of 2.67 implies the Lack of Fit is not significant relative to the pure error. There is a 14.58% chance that a Lack of Fit *F*-value this large could occur due to noise. For color removal the Lack of Fit *F*-value of 1.51 also implies the Lack of Fit is not significant relative to the pure error. There is a 33.99% chance that a Lack of Fit *F*-value this large could occur due to noise.

The analysis of variance show a reliable confidence in the estimation of COD and color removal efficiencies respectively ( $R^2 = 0.9953$  and  $R^2 = 0.9868$ ).

**Table 5** | Analysis of variance for COD removal

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> Value	Prob > <i>F</i>
Model	1,701.11	5	340.22	597.91	<0.0001
<i>A</i>	344.92	1	344.92	606.17	<0.0001
<i>B</i>	793.35	1	793.35	1,394.25	<0.0001
<i>C</i>	166.38	1	166.38	292.40	<0.0001
<i>C</i> <sup>2</sup>	390.73	1	390.73	686.68	<0.0001
<i>AC</i>	5.73	1	5.73	10.07	0.0068
Residual	7.97	14	0.57		
Lack of fit	6.59	9	0.73	2.67	0.1458
Pure error	1.37	5	0.27		
Cor total	1,709.07	19			

**Table 6** | Analysis of variance for color removal

Source	Sum of squares	Degree of freedom	Mean square	<i>F</i> Value	Prob > <i>F</i>
Model	2,661.50	5	532.30	209.94	<0.0001
<i>A</i>	738.05	1	738.05	291.09	<0.0001
<i>B</i>	912.60	1	912.60	359.93	<0.0001
<i>C</i>	234.26	1	234.26	92.39	<0.0001
<i>C</i> <sup>2</sup>	678.38	1	678.38	267.55	<0.0001
<i>AC</i>	98.21	1	98.21	38.73	<0.0001
Residual	35.50	14	2.54		
Lack of fit	25.93	9	2.88	1.51	0.3399
Pure error	9.57	5	1.91		
Cor total	2,696.99	19			

The Predicted *R*-Squared of 0.9911 and 0.9765 are in reasonable agreement with the Adjusted *R* – Squared of 0.9937 and 0.9821, respectively. A high  $R^2$  coefficient indicates a satisfactory adjustment of the quadratic model to the experimental data.

PRESS refers to Predicted Residual Sum of Squares and the adequate precision (AP) is a measure of the signal to noise ratio and was found to be in the range of 54–92, which indicates an adequate signal (**Table 7**). AP values higher than four are desirable and confirm that the predicted models can be used to navigate the space defined by the CCD. Therefore, the response surface model developed in this study for predicting COD and color removal efficiencies were considered to be satisfactory.

**Table 7** | Model validation for COD and color removals

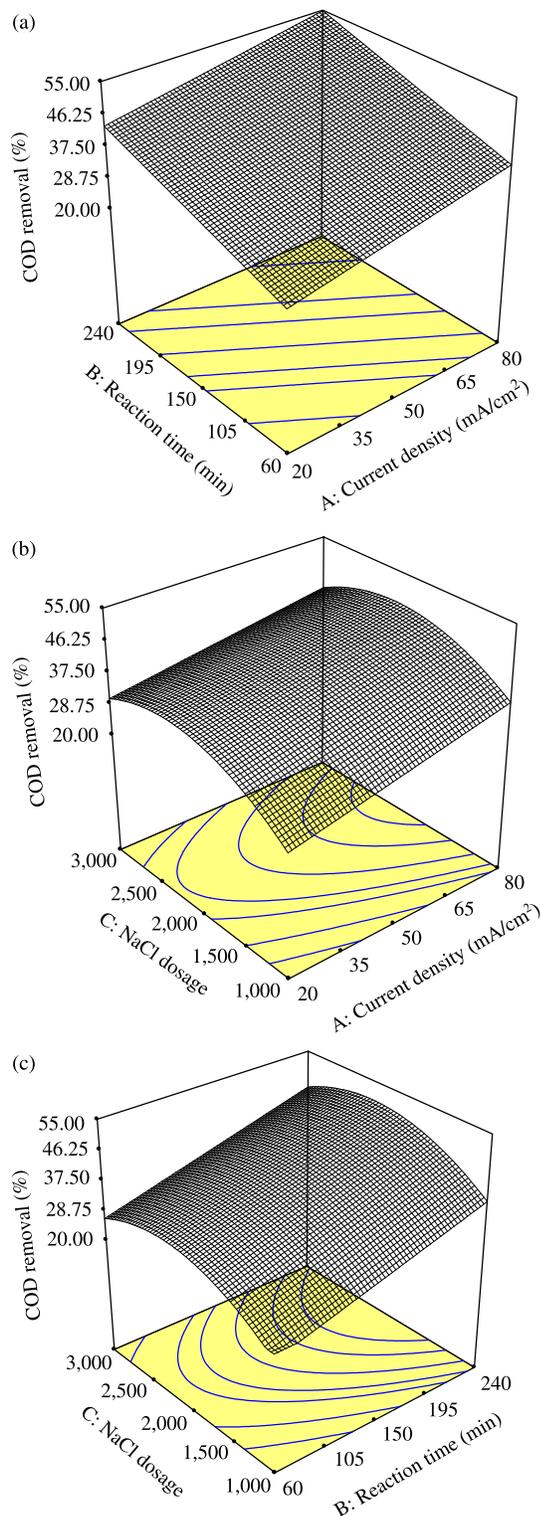
Variable	COD removal	Color removal
Standard deviation	0.75	1.59
Mean	35.61	44.86
$R^2$	0.9953	0.9868
$R^2$ adjusted	0.9937	0.9821
$R^2$ predicted	0.9911	0.9765
Coefficient of variance	2.12	3.55
PRESS	15.25	63.46
Adequate precision	91.291	54.680

### Interactions between variables

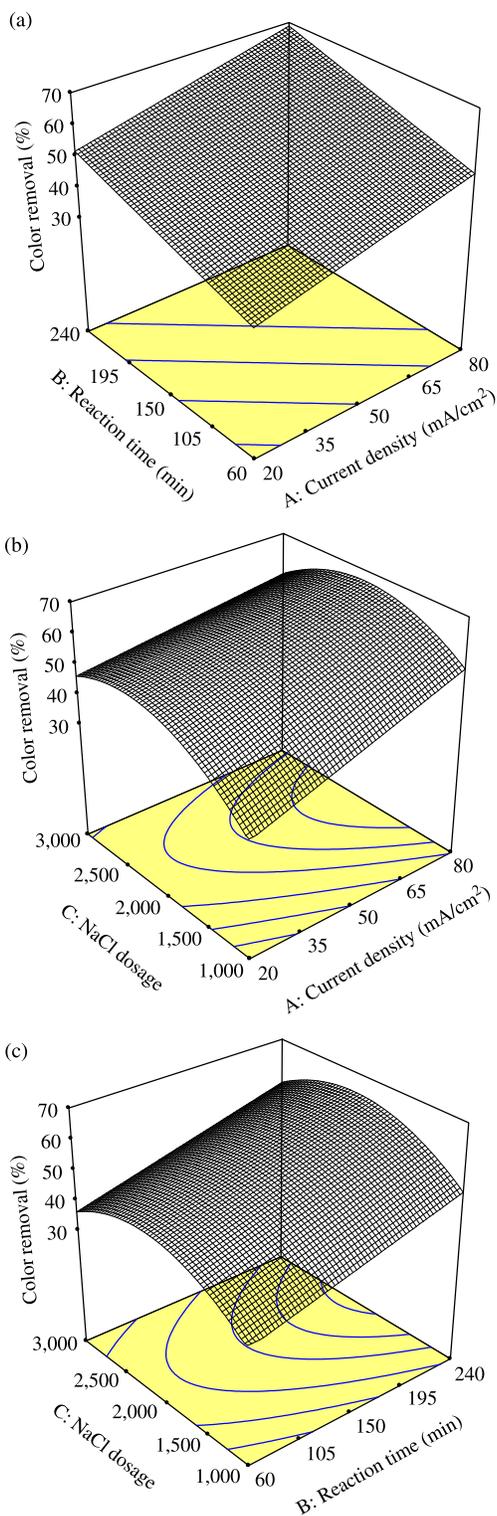
Equations 10 and 11 were used to visualize the effects of experimental factors (i.e. NaCl concentration, current density and reaction time) on COD and color removals; presented in Figures 2 a–c and 3 a–c. Some interactions between/among variables were significant so that the curvature of three-dimensional surfaces was obvious.

Figure 2 gives three dimensional surface graphs of COD removal as a function of: (a) current density and reaction time, (b) current density and NaCl concentration, (c) NaCl concentration and reaction time. Figure 3 shows three dimensional surface graphs of color removal as a function of: (a) current density and reaction time, (b) current density and NaCl concentration, (c) NaCl concentration and reaction time.

Pollutants can be destroyed by direct anodic oxidation, or indirect oxidation processes during electrochemical treatment, but it seems indirect oxidation plays an important role in the electrochemical treatment of leachate (Polcaro & Palmas 1997; Deng & Englehardt 2007; Panizza *et al.* 2007). Current density, the current per unit area of electrode, is one of the most important parameters in the success of electrochemical removal of pollutants because it controls the reaction rate. As shown in Figures 2 and 3, both COD and color removals of samples exhibited a positive correlation with the applied current density. By increasing the current density from 20 mA/cm<sup>2</sup> to 80 mA/cm<sup>2</sup>, the COD and color removal efficiencies increased from 22% to 45% and 38% to 60%, respectively. The results showed that an increase in the current density increased the COD and color removal efficiencies.



**Figure 2** | Contour plots of COD removal as a function of: (a) current density and reaction time, (b) current density and NaCl concentration, (c) NaCl concentration and reaction time.



**Figure 3** | Contour plots of color removal as a function of: (a) current density and reaction time, (b) current density and NaCl concentration, (c) NaCl concentration and reaction time.

The anodic oxidation of water due to high current density increases the formation of hydroxyl radicals which would facilitate the indirect electrochemical oxidation of organic compounds (Polcaro & Palmas 1997; Un *et al.* 2008; Yi *et al.* 2008). Another explanation is that an increased current density during electrochemical oxidation enhances active chlorine generation, which is also responsible for the removal of pollutants (Chiang *et al.* 1995; Li *et al.* 2001).

Another important issue in the application of electrochemical treatment of wastewater is the use of electrolyte. The conductivity of raw leachate can influence the treatment since it facilitates the passage of current. The removal efficiencies were found to increase with increasing  $\text{Cl}^-$  concentration. As can be seen in Figures 2 and 3, as the  $\text{Cl}^-$  concentration was increased from 1,000 to 3,000 mg/L, the COD and color removal efficiencies increased to 48.77% and 58.21% respectively. It shows high concentrations of supporting NaCl electrolyte is required to achieve high COD and color removal efficiencies.

The phenomenon may be attributed to the indirect electro-oxidation of organic compounds by active chlorine (chlorine/hypochlorite), generated from  $\text{Cl}^-$  at the anode. The increased electrolyte concentration directly increased the concentration of these chemicals in the medium enabling faster destruction of organic molecules, and improving the treatment efficiency (Comninellis & Nerini 1995; Israilides *et al.* 1997; Körbahti *et al.* 2007). These results revealed that the addition of chloride had an enhancing effect on the treatment of leachate by electrochemical oxidation. The addition of NaCl will also lead to the decrease in power consumption due to increase in conductivity. Moreover, the electrochemically generated chlorine will also be effective in water disinfection (Chen 2004; Avsar *et al.* 2007).

Since the field application of EC method is not documented yet, there is a lack of knowledge regarding final effluent generated by this method. Moreover the level of electrolyte used is one of the challenges faced by researchers. Though addition of extra  $\text{Cl}^-$  can enhance oxidation efficiency, concern about the formation of toxic chloro-organic compounds during treatment may hinder wide application of electrochemical oxidation (Stucki *et al.* 1991; Naumczyk *et al.* 1996). However, investigation on formation of chlorinated organic compounds during

electro-chemical oxidation of leachate is rare (Deng & Englehardt 2007).

The combined influence of current density and electrolyte concentration on the COD and color removal efficiencies showed that the response surface was much more sensitive to combined effect than to each one alone.

### Current efficiency

Current efficiency was investigated to evaluate effectiveness; owing to the action of direct oxidation by means of hydroxyl radicals and indirect oxidation via electro-generated active chlorine. The average current efficiency (ACE) percentage was calculated from the values of COD using the following general expression: (Montanaro & Petrucci 2009)

$$\text{ACE} = \frac{(\text{COD}_0 - \text{COD}_t)FV}{8It} \times 100 \quad (12)$$

where  $\text{COD}_0$  ( $\text{g O}_2 \text{L}^{-1}$ ) donates the initial chemical oxygen demand,  $\text{COD}_t$  ( $\text{g O}_2 \text{L}^{-1}$ ) is the chemical oxygen demands at a given time  $t$  (s),  $F$  is the Faraday constant ( $96,487 \text{ C mol}^{-1}$ ),  $V$  is the volume of the treated solution (L),  $I$  is the current applied (A), 8 is the oxygen equivalent mass ( $\text{g eq}^{-1}$ ). The highest ACE of 87.34% was observed for current density of  $20 \text{ mA/cm}^2$  in 150 min of the experiment. In general, an increase in current density would lead to the decrease in current efficiency. At high current density ( $80 \text{ mA cm}^{-2}$ ) the efficiency decreased presumably due to an increase in the undesired reaction of oxygen evolution as shown in Equation (13):



### Optimization of experimental conditions and validation experiment

The results were optimized by Design-Expert software. In numerical optimization current density were goaled to be in range, electrolyte concentration was targeted to be  $2,000 \text{ mg/L}$ , COD and color removals were goaled to be maximized. Considering the additional costs for the higher NaCl concentrations, an initial dosage of  $2,000 \text{ mg/L}$  could

be regarded as an optimal selection to achieve good COD and color removals while minimizing electrolyte addition.

At the optimized conditions, current density of  $75 \text{ mA/cm}^2$ , electrolyte concentration of  $2,000 \text{ mg/L}$  and reaction time of 218 minute, 51.61% COD and 64.99% color removals were predicted based on desirability function of 1.00.

To confirm the accuracy of the predicted model and the reliability of the optimum combination, a further degradation test was performed under optimal conditions based on the results from the model. Table 8 summarizes the degradation and decolorization efficiencies for leachate treatment. The results demonstrated that the model predictions for the COD and color removal efficiencies were very close to the actual experimental results. These results confirm that RSM is a powerful tool for optimizing the operational conditions of EC for COD and color removals.

Compared to literature data, reasonably successful results were obtained in this study under specific conditions for electrochemical treatment of a highly polluted leachate, indicating that electrochemical degradation could be used as a step of a joint treatment. The results from this study suggest that further treatment of leachate is needed in order to achieve higher COD and color removals to meet the required environmental regulations.

Electrochemical oxidation method for treatment of landfill leachate was used by other researchers (Shao *et al.* 2006; Aloui *et al.* 2009; Bashir *et al.* 2009). Shao *et al.* (2006) reported that COD removal was 56% in case of using a  $\text{Ti/TiO}_2\text{-IrO}_2\text{-RuO}_2$  anode and stainless steel cathode within 1.5 h and electrolysis time at a current density of  $100 \text{ mA/cm}^2$ . In a study performed by Aloui and co-authors, they found that at a pH value of 9, current density of  $4 \text{ A dm}^{-2}$  and electrolysis time of 60 minutes, COD was reduced to  $1,000 \text{ mg L}^{-1}$ . Bashir *et al.* (2009) also applied

**Table 8** | Verification experiments at optimum conditions (electrolyte dosage  $2,000 \text{ mg/L}$ , current density  $75 \text{ mA/cm}^2$  and reaction time 218 min)

	COD	Color
Experimental value	49.33	59.24
Model response	51.61	64.99
Error	2.28	5.75
Standard deviation	1.61	4.06

electrochemical treatment for landfill leachate using graphite carbon electrodes and sodium sulfate as electrolyte. The highest COD removal of 68% was achieved under operating conditions of 4 h reaction time and 79.9 mA/cm<sup>2</sup> current density while the initial COD was 1,414 mg/L.

## CONCLUSIONS

Electrochemical oxidation process for treatment of landfill leachate was studied using CCD and RSM. Optimum conditions for this form of advanced oxidation process could be achieved by setting the experiment with NaCl dose of 2,000 mg/L, current density of 75 mA/cm<sup>2</sup> and reaction time of 218 min. The quadratic model fitted well with the experimental data. RSM yielded a significant model for optimization of electrochemical treatment. Analysis of variance showed a good coefficient of determination value ( $R^2 = 0.9953$  for COD and 0.9868 for color removal). Under optimal experimental conditions, removal of COD and color were 49.33% and 59.24%, respectively.

As a conclusion, electrochemical oxidation process is recommended for pretreatment as it will not be able to economically treat leachate to meet effluent discharge standards on its own.

## REFERENCES

- Aloui, F., Fki, F., Loukil, S. & Sayadi, S. 2009 Application of combined membrane biological reactor and electro-oxidation processes for the treatment of landfill leachates. *Water Sci. Technol.* **60**(3), 605–614.
- Andrade, L. S., Tasso, T. T., da Silva, D. L., Rocha-Filho, R. C., Bocchi, N. & Biaggio, S. R. 2009 On the performances of lead dioxide and boron-doped diamond electrodes in the anodic oxidation of simulated wastewater containing the Reactive Orange 16 dye. *Electrochim. Acta* **54**(7), 2024–2030.
- APHA 2005 *Standard Methods for the Examination of Water and Wastewater*, 21st edition. American public health association, Washington, DC, USA.
- Arevalo, E. & Calmano, W. 2007 Studies on electrochemical treatment of wastewater contaminated with organotin compounds. *J. Hazard. Mater.* **146**(3), 540–545.
- Avsar, Y., Kurt, U. & Gonullu, T. 2007 Comparison of classical chemical and electrochemical processes for treating rose processing wastewater. *J. Hazard. Mater.* **148**(1–2), 340–345.
- Aziz, H. A., Adlan, M. N., Zahari, M. S. M. & Alias, S. 2004 Removal of ammoniacal nitrogen (NH<sub>4</sub>-N) from municipal solid waste leachate by using activated carbon and limestone. *Waste Manage. Res.* **22**(5), 371–375.
- Bashir, M. J. K., Isa, M. H., Kutty, S. R. M., Awang, Z. B., Aziz, H. A., Mohajeri, S. & Farooqi, I. H. 2009 Landfill leachate treatment by electrochemical oxidation. *Waste Manage.* **29**(9), 2534–2541.
- Benatti, C. T., Tavares, C. R. G. & Guedes, T. A. 2006 Optimization of Fenton's oxidation of chemical laboratory wastewaters using the response surface methodology. *J. Environ. Manage.* **80**(1), 66–74.
- Boye, B., Dieng, M. M. & Brillas, E. 2003 Anodic oxidation, electro-Fenton and photoelectro-Fenton treatments of 2, 4, 5-trichlorophenoxyacetic acid. *J. Electroanal. Chem.* **557**, 135–146.
- Cabeza, A., Urtiaga, A. M. & Ortiz, I. 2007a Electrochemical treatment of landfill leachates using a boron-doped diamond anode. *Ind. Eng. Chem. Res.* **46**(5), 1439–1446.
- Cabeza, A., Urtiaga, A., Rivero, M.-J. & Ortiz, I. 2007b Ammonium removal from landfill leachate by anodic oxidation. *J. Hazard. Mater.* **144**(3), 715–719.
- Chen, G. 2004 Electrochemical technologies in wastewater treatment. *Sep. Purif. Technol.* **38**(1), 11–41.
- Chiang, L.-C., Chang, J.-E. & Wen, T.-C. 1995 Indirect oxidation effect in electrochemical oxidation treatment of landfill leachate. *Water Res.* **29**(2), 671–678.
- Comminellis, Ch. & Nerini, A. 1995 Anodic oxidation of phenol in the presence of NaCl for wastewater treatment. *J. Appl. Electrochem.* **25**(1), 25–28.
- Deng, Y. & Englehardt, J. D. 2007 Electrochemical oxidation for landfill leachate treatment. *Waste Manage.* **27**(3), 380–388.
- Grimm, J., Bessarabov, D. & Sanderson, R. 1998 Review of electro-assisted methods for water purification. *Desalination* **115**(3), 285–294.
- Israilides, C. J., Vlyssides, A. G., Mourafeti, V. N. & Karvouni, G. 1997 Olive oil wastewater treatment with the use of an electrolysis system. *Bioresour. Technol.* **61**(2), 163–170.
- Knox, K. & Jones, P. H. 1979 Complexation characteristics of sanitary landfill leachates. *Water Res.* **13**(9), 839–846.
- Körbahti, B. K., Aktaş, N. & Tanyolaç, A. 2007 Optimization of electrochemical treatment of industrial paint wastewater with response surface methodology. *J. Hazard. Mater.* **148**(1–2), 83–90.
- Li, X. M., Wang, M., Jiao, Z. K. & Chen, Z. Y. 2001 Study on electrolytic oxidation for landfill leachate treatment. *China Water Wastewater* **17**(8), 14–17.
- Martínez-Huitle, C. A. & Ferro, S. 2006 Electrochemical oxidation of organic pollutants for the wastewater treatment: direct and indirect processes. *Chem. Soc. Rev.* **35**(12), 1324–1340.
- Montanaro, D. & Petrucci, E. 2009 Electrochemical treatment of Remazol Brilliant Blue on a boron-doped diamond electrode. *Chem. Eng. J.* **153**(1–3), 138–144.
- Montgomery, D. C. 2008 *Design and Analysis of Experiments*, 7th edition. Wiley, New York.

- Nasr, B., Hsen, T. & Abdellatif, G. 2009 Electrochemical treatment of aqueous wastes containing pyrogallol by BDD-anodic oxidation. *J. Environ. Manage.* **90**(1), 523–530.
- Naumczyk, J., Szpyrkowicz, L., De Faveri, M. D. & Zilio-Grandi, F. 1996 Electrochemical treatment of tannery wastewater containing high strength pollutants. *Process Saf. Environ. Prot.* **74**(1), 59–68.
- Panizza, M., Barbucci, A., Ricotti, R. & Cerisola, G. 2007 Electrochemical degradation of methylene blue. *Sep. Purif. Technol.* **54**(3), 382–387.
- Polcaro, A. M. & Palmas, S. 1997 Electrochemical oxidation of chlorophenols. *Ind. Eng. Chem. Res.* **36**(5), 1791–1798.
- Read, A. D., Hudgins, M., Harper, S., Phillips, P. & Morris, J. 2001 The successful demonstration of aerobic landfilling: the potential for a more sustainable solid waste management approach? *Resour. Conserv. Recycling* **32**(2), 115–146.
- Shao, L., He, P., Xue, J. & Li, G. 2006 Electrolytic degradation of biorefractory organics and ammonia in leachate from bioreactor landfill. *Water Sci. Technol.* **53**(11), 143–150.
- Stucki, S., Kotz, R., Carcer, B. & Suter, W. 1991 Electrochemical waste water treatment using high overvoltage anodes, part II: anode performance and applications. *J. Appl. Electrochem.* **21**(2), 99–104.
- Szpyrkowicz, L., Kelsall, G. H., Kaul, S. N., De Faveri, M. & Satyanarayan, S. 2001 Performance of electrochemical reactor for treatment of tannery wastewaters. *Chem. Eng. Sci.* **56**(4), 1579–1586.
- Un, U. T., Altay, U., Koparal, A. S. & Ogutveren, U. B. 2008 Complete treatment of olive mill wastewaters by electrooxidation. *Chem. Eng. J.* **139**(3), 445–452.
- Wang, P., Lau Ivan, W. C. & Fang Herbert, H. P. 2001 Landfill leachate treatment by anaerobic process and electrochemical oxidation. *Environ. Sci.* **22**(5), 70–73.
- Wang, Z.-P., Zhang, Z., Lin, Y.-J., Deng, N.-S., Tao, T. & Zhuo, K. 2002 Landfill leachate treatment by a coagulation-photooxidation process. *J. Hazard. Mater.* **95**(1–2), 153–159.
- Yi, F., Chen, S. & Yuan, C. 2008 Effect of activated carbon fiber anode structure and electrolysis conditions on electrochemical degradation of dye wastewater. *J. Hazard. Mater.* **157**(1), 79–87.