Optimization of electrocoagulation process for the treatment of landfill leachate

N. Huda¹, A. A. Raman¹*, and S. Ramesh²

¹Chemical Engineering Department, Faculty of Engineering, University Malaya, 50603 Kuala Lumpur, Malaysia.
²Centre of Advanced Manufacturing & Material Processing (AMMP), Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.

E-mail: azizraman@um.edu.my

Abstract. The main problem of landfill leachate is its diverse composition comprising of persistent organic pollutants (POPs) which must be removed before being discharge into the environment. In this study, the treatment of leachate using electrocoagulation (EC) was investigated. Iron was used as both the anode and cathode. Response surface methodology was used for experimental design and to study the effects of operational parameters. Central Composite Design was used to study the effects of initial pH, inter-electrode distance, and electrolyte concentration on color, and COD removals. The process could remove up to 84 % color and 49.5 % COD. The experimental data was fitted onto second order polynomial equations. All three factors were found to be significantly affect the color removal. On the other hand, electrolyte concentration was the most significant parameter affecting the COD removal. Numerical optimization was conducted to obtain the optimum process performance. Further work will be conducted towards integrating EC with other wastewater treatment processes such as electro-Fenton.

1. Introduction

Waste generation increases yearly due to the exponential population growth and urbanization [1]. Being the lowest ranking waste management option in the waste hierarchy, landfilling still remains as the dominant method used in many countries. At present, landfilling contributes 80% of the main waste disposal method in many countries including Malaysia and has become ubiquitous in modern society [2]. Leachates generated during the landfilling operation varies according to the nature of the landfill material, and poses hazard to the environment since it is difficult to be treated for its complex mixture [3] of biodegradable or non-biodegradable, organic or inorganic and toxic or non-toxic waste [4]. Sustainable management of leachate appears to be an enduring problem for landfill operators and regulators as landfill can continue to generate leachate for several hundred years after they have ceased to operate. Thus, it is necessary to purify the leachate before its discharge into the environment.

Usage of conventional leachate treatment methods such as aerobic, anaerobic, flotation, coagulation–flocculation, chemical precipitation, adsorption, and air stripping are declining in recent years [5,6] even though they are economical and easy to maintain, due to its incapability to eliminate the recalcitrant pollutants efficiently from the wastewater [7], while chemical oxidation produces intermediate products which remain in the solution and may entail a similar or even higher toxicity than initial compounds [8]. Advanced Oxidation Processes (AOPs) were identified to treat the wastewater, where oxidation processes using highly reactive hydroxyl radicals (•OH) are used to remove the recalcitrant organic pollutants that are difficult to treat by conventional methods [9]. However, AOPs can result in high chemical consumption, high demand of electrical energy for devices and produce secondary waste, which increases the treatment costs [9].

Electrocoagulation (EC) is an evolving alternative technology which can be used to remove various pollutants from wastewater [10] through in-situ generation of coagulants by electro-oxidation of the sacrificial anode, constructed mainly from iron (Fe) or aluminium (Al) metals [11]. EC has been applied...
in broad range successfully for treatment of textile dyes [12], biodiesel wastewater [13], pharmaceutical wastewater [14], oil tanning effluent [15], industrial wastewater [16], pretreated coke wastewater [17], and heavy metals in groundwater [18]. EC has gained significant attention from many researchers, owing to its advantages like reduced sludge production, no requirement for chemical use, ease of operation [19], short operating time, and low capital and operating costs [11]. Thus, the main objective of the present study is to investigate the decolorisation and degradation of a landfill leachate using iron as non-toxic and readily available electrode material. Several parameters, namely initial pH, conductivity, and inter-electrode distance were investigated for their effects on the color and COD removal efficiency. Central Composite Design (CCD) was employed to obtain optimal parameters for efficient removal of pollutants with a limited number of experiments.

2. Methodology

2.1 Chemicals
Sulfuric Acid (H$_2$SO$_4$) (96% purity, AR Grade, Fisher Scientific) and Sodium Hydroxide, NaOH (R & M Chemicals) were used for pH alteration. Hydrochloric acid, HCl (37% purity, AR Grade, Eriendem Schmidt) was used to clean the electrodes. Sodium chloride, NaCl (R & M Chemicals) was used as electrolyte. COD Cell Test (300 – 3500 mg/l, Spectroquant-Merck) was used to measure COD of the leachate.

2.2 Effluent Preparation and Characteristic
Raw landfill leachate was collected from Jeram Municipal Solid Waste Sanitary Landfill, Selangor and used without pretreatment. Effluent dilution was done using distilled water. COD and color removal of treated effluent was measured using Spectrophotometer (Spectroquant Pharo 300). The pH of the effluent was measured using a pH meter (CyberScan pH 300, EUTECH Instruments).

2.3 Electrochemical system setup
The basic electrochemical setup was developed using iron sheet as anode and cathode (42 cm$^2$ effective surface area), dipped into 500 mL leachate solution in a 600-mL beaker (Figure 1). The reaction mixture was stirred using magnetic stirrer (WiseStir MS-20D) and magnetic stirring bar at 100 rpm. DC regulated power supply (EXTECH-382213) was used to supply 1.0 A of current to the electrochemical system for 60 minutes.

2.4 Electrochemical design
The experimental design and mathematical modelling were performed using Design-Expert 8.0 software. Central Composite Design (CCD) was used for optimization of operating parameters for the removal of pollutants by EC. Three important operating parameters that were optimized in this study are initial pH, inter-electrode distance and electrolyte concentration. The levels and range of factors chosen for this study is presented in Table 1. Responses included in the model were removal efficiency of color and COD.
Figure 1. Schematic diagram of EC setup: (1) DC power supply, (2) anode, (3) cathode, (4) EC cell, (5) effluent, (6) magnetic stirrer and (7) magnetic stirrer.

| Variable                     | Coded levels |
|------------------------------|--------------|
| A, Initial pH                | -1  0  +1    |
| B, Inter-electrode distance  | 3.00 6.00 9.00 |
| C, NaCl concentration        | 1.00 1.50 2.00 |

Table 1. The level and range of factors chosen in EC study.

3. Results & Discussion

3.1 RSM Modal Development
Total 20 runs with 8 factorials, 6 axial, and 6 center points were suggested by Design Expert to optimize responses. All the results for color and COD removal from RSM model are presented in Table 2. Based on the experimental results, empirical second order polynomial equations showing the interaction between the proposed independent factors are presented in Table 3 as equation (1) and (2). The observed color and COD removal varied between 15.7 - 84.1 and 20.0 - 49.5, respectively.

Table 4 provides the analysis of variance for color and COD removal efficiency. For color removal, the Model F-value of 375.51 implies the model is significant. There is only a 0.01% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case A, AB, AC, BC, A², ABC, A²C, AB² are significant model terms. The "Lack of Fit F-value" of 0.87 implies the Lack of Fit is not significant relative to the pure error. There is a 47.43% chance that a "Lack of Fit F-value" this large could occur due to noise. Non-significant lack of fit is good since we want the model to fit. "Adequate precision" measures the signal to noise ratio. A ratio greater than 4 is desirable. In this case, the ratio of 69.671 indicates an adequate signal. This model can be used to navigate the design space, since the R-squared value is very close to 1.0000. Besides, for COD removal, the Model F-value of 3.40 implies the model is significant. There is only a 4.78% chance that a "Model F-Value" this large could occur due to noise. Values of "Prob > F" less than 0.0500 indicate model terms are significant. In this case C and BC are significant model terms. The "Lack of Fit F-value" of 1.01 implies the Lack of Fit is not significant relative to the pure error. There is a 46.30% chance that a "Lack of Fit F-value" this large could occur due to noise. A ratio of 7.648 indicates an adequate signal. This model can be used to navigate the design space.
Table 2. Factors and response of CCD

| Run | pH | Electrode distance (cm) | NaCl (g) | Removal efficiency (%) |
|-----|----|-------------------------|----------|------------------------|
| 1   | 6  | 1.5                     | 2.34     | 23.6                   |
| 2   | 3  | 1                       | 2        | 40.2                   |
| 3   | 0.95 | 1.5                    | 1.5      | 20.0                   |
| 4   | 6  | 0.66                    | 1.5      | 44.1                   |
| 5   | 9  | 2                       | 2        | 20.8                   |
| 6   | 3  | 2                       | 1        | 42.9                   |
| 7   | 9  | 2                       | 1        | 49.1                   |
| 8   | 6  | 1.5                     | 1.5      | 29.8                   |
| 9   | 9  | 1                       | 1        | 48.6                   |
| 10  | 6  | 1.5                     | 1.5      | 41.6                   |
| 11  | 6  | 1.5                     | 1.5      | 43.7                   |
| 12  | 9  | 1                       | 2        | 49.5                   |
| 13  | 3  | 1                       | 1        | 42.4                   |
| 14  | 6  | 1.5                     | 0.66     | 49.3                   |
| 15  | 3  | 2                       | 2        | 35.1                   |
| 16  | 6  | 1.5                     | 1.5      | 43.3                   |
| 17  | 6  | 1.5                     | 1.5      | 40.4                   |
| 18  | 6  | 1.5                     | 1.5      | 42.9                   |
| 19  | 11.05 | 1.5                   | 1.5      | 40.6                   |
| 20  | 6  | 2.34                    | 1.5      | 43.3                   |

Table 3. Quadratic equations color and COD removal

| Response          | Equation                                                                 |
|-------------------|--------------------------------------------------------------------------|
| Color removal (%) | 82.60 + 27.33*A - 0.58*B + 0.30*C - 1.04*A*B + 3.53*A*C + 8.29*B*C - 21.43*A^2 - 0.12*B^2 - 9.53*A*B*C - 5.25*A^2*C - 11.62*A*B^2 (1) |
| COD removal (%)   | 40.24 + 0.67*A - 2.51*B - 5.90*C - 2.94*A*B - 2.15*A*C - 4.35*B*C + 0.13*A^2 + 1.43*B^2 - 1.13*C^2 - 2.94*A*B*C (2) |

Table 4: ANOVA output

| Source            | Sum of squares | df | Mean square | F value | Prob>F  | Remarks        |
|-------------------|----------------|----|-------------|---------|---------|----------------|
| For color         |                |    |             |         |         |                |
| Model             | 5636.02        | 11 | 512.37      | 375.51  | < 0.0001 | significant    |
| Lack of Fit       | 2.46           | 2  | 1.23        | 0.87    | 0.4743   | not significant|
| R-Square          | 0.9983         |    |             |         |         |                |
| Adeq. Precision   | 69.671         |    |             |         |         |                |
| For COD           |                |    |             |         |         |                |
| Model             | 946.76         | 10 | 94.68       | 3.40    | 0.0478   | significant    |
| Lack of Fit       | 83.72          | 3  | 27.91       | 1.01    | 0.4630   | not significant|
| R-Square          | 0.8997         |    |             |         |         |                |
| Adeq. Precision   | 7.648          |    |             |         |         |                |
3.2 Effects of operating parameters

3.2.1 Color removal.
The response surface 3D plots to estimate the color removal over independent variables initial pH and inter-electrode distance are shown in Figure 2. All three factors were found to be the significant parameter affecting the color removals. Decolorization of leachate using EC process is tightly bounded by the pH of the reaction. Decolourization of effluent is very high at neutral and alkaline pH, but very low at acidic medium. This could be related to the reactions taking place at anode and cathode during EC process: Eq (3-5). When iron electrode is used as anode and cathode, the generated Fe$^{2+}$ ions will further oxidize and react to produce corresponding hydroxides and/or polyhydroxides [17], and the formation of these complexes depends strongly on the pH of the effluent [20]. At alkaline pH, iron hydroxides formed remains in the aqueous streams as a gelatinous suspension, thus remove the pollutants from effluent by coagulation, adsorption, co-precipitation and sweep flocculation [21].

Anode:
Fe (s) $\rightarrow$ Fe$^{2+}$ (aq) + 2e$^{-}$

Cathode:
2H$^+$ (aq) + 2e$^{-}$ $\rightarrow$ H$_2$ (g) (acidic medium) (4)
2H$_2$O + 2e$^{-}$ $\rightarrow$ H$_2$ (g) + 2OH$^-$ (aq) (neutral or alkaline medium) (5)

Moreover, it is also observed that decolorization of effluent increases as the inter-electrode distance decreases, due to increasing conductivity. Closer inter-electrode distance enhances the electrode dissolution process due to enhancement of electrode pore size [22]. This phenomenon would indirectly reduce the power consumption and operating cost.

![Figure 2](image)

**Figure 2:** Effect of a) initial pH and inter-electrode distance, and b) initial pH and electrolyte concentration on color removal (%); 3D surface plots.

3.2.2 COD removal. The response surface 3D plots to estimate the COD removal over independent variables electrolyte concentration and inter-electrode distance are shown in Figure 3. Electrolyte concentration was the most significant parameter affecting the COD removal. The addition of the supporting electrolyte which allows the color and COD removal efficiency increases occurs due to the participation of active chlorine anion roles in EC reaction [23]. Sodium chloride added to the EC system increase the conductivity and generates hypochlorite ions, which act as an oxidizing agent in the pollutant degradation.
3.3 Optimization using response surface methodology

In this study of RSM, optimization of the experimental results is keeping all factors within the range and all responses as maximum. From the analysis, the optimum conditions for initial pH, inter-electrode distance and electrolyte concentration are 7.73, 1.16 cm and 1.00 g respectively. Experiments were conducted to validate the optimized conditions and predicted results as presented in Table 5. The actual results obtained for color and COD removal are 89.01% and 46.05%, respectively which is very close to the predicted result. This indicates a good agreement of the experimental and predicted results under optimized conditions.

Table 5: Predicted and actual responses at optimized operating parameter

| pH   | Electrode distance (cm) | NaCl (g) | Removal Efficiency (%) | Desirability |
|------|-------------------------|----------|------------------------|--------------|
| Predicted | 7.73              | 1.16     | 90.23                  | 0.92         |
| Actual   | 89.01              | 46.05    |                        |              |

4. Conclusion

In this study, the efficiency of EC process applied to the treatment of landfill leachate effluent was investigated. It was shown that EC treatment achieves an effective removal of color and COD. The treatment efficiency was found to be function of the initial pH, inter-electrode distance and electrolyte concentration. The quadratic model developed in this study shows the presence of a high correlation between experimental and predicted values. Analysis of variance showed a high coefficient of determination value ($R^2 = 0.9983$ for color removal and 0.946 for COD removal), thus ensuring a satisfactory adjustment of the second-order regression model with the experimental data. Under optimal values of process parameters (initial pH: 7.73, inter-electrode distance: 1.16 cm, and electrolyte concentration: 1.00g), 89.01% of color removal and 46.05% of COD removal were obtained. Since the COD removal of leachate using EC is very low, further work will be conducted towards integrating EC with other wastewater treatment processes such as electro-Fenton.

Acknowledgment: This work was financially supported by the University of Malaya Postgraduate Research Fund (IPPP) Number PG093-2016A.
References

[1] Azni, I. (2009). What is the choice: Land disposal or Biofuel? In Waste management (pp. 1–65). Universiti Putra Malaysia.

[2] Norkhadijah, S. S. I., & Latifah A. M. 2013 *Journal of Toxicology and Environmental Health Sciences* **5** 86–96.

[3] Labanowski, J., Pallier, V., & Feuillade-Cathilinaud, G. 2010 *Journal of Hazardous Materials* **179** 166–172.

[4] Brennan, R. B., Healy, M. G., Morrison, L., Hynes, S., Norton, D., & Clifford, E. 2016 *Waste Management* **55** 355–363.

[5] Thompson, G., Swain, J., Kay, M., Forster, C. F. 2001 *Bioresource Technology* **77** 275–286.

[6] Renou, S., Givaudan, J. G., Poulain, S., Dirassouyan, F., & Moulin, P. 2008 *Journal of Hazardous Materials* **150** 468–493.

[7] Jeworski M, Heinzle, E. 2000 *Biotechnology Annual Review* **6** 163-196.

[8] Sirés, I., Brillas, E., Oturan, M. A., Rodrigo, M. A., & Panizza, M. 2014 *Environmental Science and Pollution Research* **21** 1491–1496.

[9] Chavalparit, O., & Ongwandee, M. 2009 *Journal of Environmental Science* **21** 1491–1496.

[10] Farhadi, S., Aminzadeh, B., Torabian, A., Khatibiakmal, V., & Alizadeh Fard, M. 2012 *Journal of Hazardous Materials* **219–220** 35–42.

[11] Emamjomeh, M. M., & Sivakumar, M. 2009 *Journal of Environmental Management* **90** 1663–1679.

[12] García-garcía, A., Martínez-miranda, V., Martínez-cienfuegos, I. G., Almazán-sánchez, P. T., Castañeda-juárez, M., & Linares-hernández, I. 2015 *Fuel* **149** 46–54.

[13] Ozyonar, F., & Karagözoglu, B. 2015 *Separation and Purification Technology* **150** 268–277.

[14] You, H. J., & Han, I. S. 2016 *Journal of Environmental Chemical Engineering* **4** 1008–1016.

[15] Susree, M., Asaithambi, P., Saravanathamizhan, R., & Matheswaran, M. 2013 *Journal of Environmental Chemical Engineering* **1** 552–558.