Optimization of composite coagulant made from polyferric chloride and tapioca starch in landfill leachate treatment

M Z N Shaylinda1*, A A Hamidi1, N A Mohd3, A Ariffin3, D Irvan3, Z A M Hazreek1 and Z M Nizam1
1Faculty of Civil and Environmental Engineering, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat Johor, MALAYSIA
2Micropollutant Research Centre, Universiti Tun Hussein Onn Malaysia, 86400 Batu Pahat Johor, MALAYSIA
3School of Civil Engineering, Universiti Sains Malaysia, 14300 Nibong Tebal Penang, MALAYSIA

E-mail: nursha@uthm.edu.my

Abstract. In this research, the performance of polyferric chloride and tapioca flour as composite coagulants for partially stabilized leachate was investigated. Response surface methodology (RSM) was used to optimize the coagulation and flocculation process of partially stabilized leachate. Central composite design a standard design tool in RSM was applied to evaluate the interactions and effects of dose and pH. Dose 0.2 g/L Fe and pH 4.71 were the optimum value suggested by RSM. Experimental test based on the optimum condition, resulted in 95.9%, 94.6% and 50.4% of SS, color and COD removals, respectively. The percentage difference recorded between experimental and model responses was <5%. Therefore, it can be concluded that RSM was an appropriate optimization tool for coagulation and flocculation process.

1. Introduction
Application of landfill as a disposal method for solid waste is a common approach in Malaysia due to its simplicity. However, the negative drawback of this treatment approach is the production of polluted leachate. Leachate is a liquid that contain mix of various hazardous elements originated from decomposition processes of solid waste. Thus, direct discharge of leachate into any receiving water bodies must be prohibited to ensure safety of the environment. Treatment of leachate up to permissible discharge standard is crucial. Generally, treatment of leachate is depending on the characteristics of the leachate [1]. Leachate changed its characteristics as its ageing. Biological treatment is suitable for young leachate. While for partially stabilized and stabilized leachate, physical-chemical treatment is effective. Coagulation-flocculation is one of the physical-chemical treatment method that can be applied for leachate treatment [2].

The application of coagulation-flocculation in reducing pollutant from leachate was proven to be effective especially for stabilized leachate. Chemical coagulant is commonly used in leachate treatment. However the use of chemical coagulant will indirectly affect the health and quite costly, thus to reduce the effect and cost, substituting the chemical coagulant with natural material (tapioca starch (TF)) can be adapted. A combination of chemical and natural coagulant as a composite
Coagulant is able to simplify the process and offer many benefits. Instead of using ferric chloride (IC), prehydrolyzed of ferric chloride (PHI) was chosen as it offers more advantages than those offered by iron chloride alone [3][4]. Moreover, the application of this type of composite coagulant in leachate is unusual.

Generally, finding the optimum condition is the main objective for coagulation-flocculation study. To fulfil this objective, one-factor-at-one-time (OFOT) is the conventional method used. Basically, this approach is simple and easy to follow. However, OFOT required more time, more energy, limited statistical analysis and inability to cover empty value between the values tested. The application of optimization of coagulation-floculation by using statistical tool (Respond Surface Methodology (RSM)) offers better utilization of the experimental data through the statistical analysis in the development of mathematical modelling, interactive influence of factors, prediction of operating condition and etc. [5].

Hence, the aims of this study, was to demonstrate the optimization of coagulation-flocculation for composite coagulant made from polyferric chloride and tapioca starch in the removals of colour, suspended solid and COD from partially stabilized leachate. Consequently, RSM was used for experimental designs, mathematical models development and optimization of coagulation-flocculation condition.

2. Materials and Methods

2.1 Sampling and characterization

Leachate samples were obtained from Matang Landfill (ML) site located in Taiping, Perak. ML site size is 12 ha and received 300 ton/day of solid waste. ML site applied improved anaerobic leachate treatment system. The characterization of the ML leachate was obtained from previous publish data of this study and is presented in Table 1 (Zin et al., 2012). Based on the characterization of ML leachate (Table 1), ML is categories as partially stabilized leachate (Zin et al., 2012).

| No. | Parameter       | Min  | Max  | Average |
|-----|-----------------|------|------|---------|
| 1   | Temperature (°C) | 28   | 31   | 29      |
| 2   | pH              | 7.96 | 8.17 | 8.1     |
| 3   | BODs (mg/L)     | 60   | 184  | 109     |
| 4   | COD (mg/L)      | 470  | 1261 | 770     |
| 5   | Suspended solid (mg/L) | 222 | 303 | 271 |
| 6   | Ammonia-N (mg/L NH₃-N) | 311 | 693 | 500 |
| 7   | Total phosphorus (mg/L) | 22 | 54 | 42 |
| 8   | Ferum (mg/L)    | 2.3  | 3.1  | 2.7     |
| 9   | Turbidity (NTU) | 15   | 41   | 28      |
| 10  | True color (ptCo) | 885 | 6680 | 3199 |
| 11  | BOD/COD         | 0.12 | 0.16 | 0.14    |

*Samples were collected from December 2011 –Mac 2012

2.2 Materials and chemicals

The composite coagulant (PHITF) used in this study was prepared in laboratory based on method described by Zin et al. [7]. A solution of PHI (Basicity=0.1) was prepared and newly made to prevent aging. PHITF was prepared by injecting heated TF solution into PHI (Basicity=0.1) at 0.3 mL/min under strong mixing intensities (700-800 rpm) at 50°C water bath. PHITF mixture was allowed to age at room temperature for 24 h before used. Sulfuric acid (H₂SO₄) and sodium hydroxide (NaOH) were used to adjust pH of leachate sample.
2.3 Experimental procedure

A six-beaker standard jar test apparatus (SW6 Stuart, Bibby Scientific Limited, UK) was used for this study. Each beaker was filled with 500 mL of ML leachate. The constant operating coagulation parameters involved in the coagulation/flocculation is listed in Table 2. Sample of treated ML leachate was collected 3 cm below the surface and analyse for colour, suspended solid, and COD. Percentage of removal was calculated based on the following equation:

\[
\text{Percentage removal} = \left(\frac{C_i - C_f}{C_i}\right) \times 100
\]

where \( C_i \) and \( C_f \) are the initial and final concentration of the removal parameter.

| Parameter                                     | Value  |
|-----------------------------------------------|--------|
| Rapid mixing speed (rpm)                      | 200    |
| Rapid mixing duration (minutes)               | 4      |
| Slow mixing speed (rpm)                       | 30     |
| Rapid mixing duration (minutes)               | 15     |
| Settling duration (minutes)                   | 30     |

2.4 Experimental design and data analysis

Central composite design (CCD) was used for the experimental design of RSM. CCD very useful for development of mathematical model. In this experiment, the relationship between independent variables (pH and dose) and response (suspended solid (SS), colour, and COD were investigated. The coded of experimental levels and range of independent variables were shown in Table 3 and 4. The four response parameters in term percent removal were used to evaluate the effectiveness of PHITF as a composite coagulant.

A total of 13 experimental runs were listed by CCD (Table 5). The four response parameters in term percent removal were used to evaluate the effectiveness of PHITF as a composite coagulant. A quadratic mathematical equation model was proposed to predict the optimum value of pH and dose for composite coagulant. Adequacy of the mathematical model developed is then revealed using ANOVA analysis. The P-value (probability) or significance level with 95% confidence level was used in the evaluation of model terms. The quality of fit polynomial was measured through coefficient of \( R^2 \). Finally, the optimum values and interaction between variables and responses of pH and dose were evaluated through the mathematical model, perturbation plot and 3D-plots.

| Table 2. Constant operating coagulation parameters. (Zin et al., 2015) |
|---------------------------------------------------------------|
| Parameter                                    | Value  |
| Rapid mixing speed (rpm)            | 200    |
| Rapid mixing duration (minutes)     | 4      |
| Slow mixing speed (rpm)             | 30     |
| Rapid mixing duration (minutes)     | 15     |
| Settling duration (minutes)         | 30     |

| Factor (symbol) | Coded value |
|-----------------|-------------|
|                 | -1.414      | -1  | 0  | +1   | +1.414 |
| pH (A)          | High        | Low | Center | High | Higher |
|                 | 3.59        | 4   | 5     | 6    | 6.41   |
| Dose (B) (g/L Fe) | 0.05    | 0.1 | 0.25  | 0.35  | 0.4    |
Table 4. PHI range of factors for RSM [8]

| Factor     | range   |
|------------|---------|
| Dose (g/L Fe) | 0.1-0.35 |
| pH         | 4-6     |

Table 5. CCD of the two experimental variables for PHI.

| Run No. | Experimental design | Percent removal |
|---------|---------------------|-----------------|
|         | Factor 1 | Factor 2 | Response 1 | Response 2 | Response 3 |
|         | A:pH     | B:dose   | SS (mg/L) | Colour (mg/L) | COD (mg/L) |
| 1       | 3.59     | 0.23     | 93.50     | 85.15       | 42.86      |
| 2       | 6.00     | 0.10     | 39.41     | 20.15       | 1.90       |
| 3       | 5.00     | 0.23     | 96.02     | 94.06       | 49.05      |
| 4       | 5.00     | 0.23     | 95.18     | 94.64       | 51.33      |
| 5       | 4.00     | 0.35     | 90.36     | 80.91       | 41.39      |
| 6       | 5.00     | 0.23     | 96.23     | 94.31       | 50.68      |
| 7       | 6.41     | 0.23     | 45.28     | 27.11       | 3.97       |
| 8       | 5.00     | 0.23     | 95.18     | 94.64       | 51.33      |
| 9       | 5.00     | 0.23     | 96.23     | 94.31       | 50.68      |
| 10      | 5.00     | 0.05     | 41.93     | 22.14       | 5.27       |
| 11      | 4.00     | 0.10     | 88.47     | 81.13       | 34.06      |
| 12      | 6.00     | 0.35     | 59.33     | 67.42       | 21.94      |
| 13      | 5.00     | 0.40     | 92.66     | 85.43       | 50.24      |

3. Results and Discussions

3.1 Development of mathematical model equation and validation of the model. Development of model equation was obtained after run the 13 experiments suggested by CCD. The data of the responses were used to develop the regression model. Table 6 shows the reduced regression model and ANOVA analysis. The positive sign in front of the terms expressed the synergistic effects and the negative sign expressed antagonistic effect [9]. As shown in Table 6, all the regression models were highly significant (P<0.05) and fitted to the experimental results well. An RSM analysis by Ghafari et al. [2], also used p<0.05 as the acceptable significance value. The large F- values indicated significance correlation between variables and removal parameter. R² value for all mathematical model obtained were closed to 1 and this indicates a satisfactory adjustment of the regression model to the experimental data. Furthermore, a closed value between adjusted-R² and R² for SS, colour and COD regression model, conform the accuracy of the model obtained.

For a model to be reliable, others than ANOVA analysis, a plot between actual and predicted values is used and it should shows a reasonable accuracy. According to Ghafari et al. [2], others than actual and predicted value plot analysis, the value of AP should be more then 4 to ensure the reliability of the predicted model. This analysis is able to further strengthen the judgement of model satisfactoriness [10]. Figure 1 presented the actual verses predicted values for SS, colour and COD.
Based on Figure 1, an adequate agreement between real data and models were obtained. Thus, SS, colour and COD mathematical models developed is statistically satisfied.

Table 6. PHITF regression model and ANOVA.

| Response parameters | Final equation in terms of coded factors | p-value | F-value | R² | Adjusted R² | A.P |
|---------------------|----------------------------------------|---------|---------|----|-------------|----|
| SS                  | +94.13-25.70A+16.28B-17.92A²-19.37B²+6.25AB | 0.0002  | 25.88   | 0.9487 | 0.9127 | 13.233 |
| colour              | +94.39-19.57A+17.07B-17.27A²-18.44B²+11.87AB | <0.0001 | 40.28   | 0.9664 | 0.9424 | 17.693 |
| COD                 | +50.61-13.33A+11.37B-13.79A²-11.62B²+3.18AB | <0.0001 | 37.04   | 0.9639 | 0.9376 | 15.509 |

Figure 1. Design-expert plot; predicted vs. actual values plot for (a) SS removal, (b) colour removal, (c) COD removal using PHITF
3.2 Response surface and perturbation plot
Figure 2, illustrated the obtained data in 3D response surface plot that showed the interaction of the factors. Figure 2, exhibited a clear peak, which indicated the optimum removal is within the design boundary. Hundred percent removal was achieved by SS and color. While for COD, 55% removal is the highest calculated by the model. The decrement of pH influenced the charge value of hydrolysis products and precipitation of metal oxides produced by the coagulant [9]. As shown in Figure 2, a decrement of pH decreased efficiency of PHITF in removing SS, color and COD. The best removal was recorded at low pH and at dose approximately 0.2 g/L Fe. At low pH, protonation of leachate might be occurred and resulted in self-aggregation of leachate and reducing the dose required to destabilize leachate compared at higher pH value [9].

The comparative effects of pH and dose on SS, color and COD removals were illustrated by perturbation plots (Figure 3). According to Figure 3, a sharp curvature was portrays by each of the perturbation plot. This indicates pH and dose values have a great influence on the removals of SS, color and COD [11].

![Figure 2](image_url)

**Figure 2.** Design-expert plot; response surface plot for (a) SS removal, (b) colour removal and (c) COD removal

3.3 Optimization of PHITF
Optimization of PHITF was determined through the numerical optimization method. The optimization goal for each respond was selected as maximum, while pH as in range and dose as in minimum. Based on the numerical optimization method, pH 4.71 and dose 0.2 g/L Fe was suggested as the optimum condition of PHITF (Table 7). The optimum condition suggested was further validated by performing the actual experiment. The difference between actual removal and model response was <5%. Thus, a good agreements between RSM prediction and actual experiment was achieved. In terms of removals performance, the ability of PHITF at optimum condition by RSM was not far from the removal recorded by Ghafari et al. [2], Adlan et al.[12], and Liu et al. [13].
Figure 3. PHITF perturbation plot for (a) SS, (b) colour and (c) COD

Table 7. Confirmatory experiments at optimum conditions of PHITF

| RSM optimum condition | Removal efficiency (%) |
|-----------------------|------------------------|
|                       | SS            | colour | COD    |
| pH 4.71               | experimental value | 94.7   | 91.3   | 48.7   |
| dose 0.2 g/L Fe       | model response   | 95.9   | 94.6   | 50.4   |
| % difference          | 1.25           | 3.5    | 3.4    |

4. Conclusion

In this research, application of composite coagulant made from polyferic chloride and tapioca flour was studied to remove SS, color and COD from partially stabilized leachate through coagulation and flocculation method. A statistical optimization tool (response surface methodology) were used to overcome the weakness of OFOT method. RSM was successfully employed to obtain optimum conditions and interactions between factors. The analysis, clearly shown that the removals of SS, color and COD from partially stabilized leachate was highly influenced by pH and dose. The optimum condition, suggested by the model (pH 4.71 and dose 0.2 g/L Fe) is in good agreements with the experimental values obtained. Based on the mathematical model, at optimum condition, 95%, 94.6%
and 50.4% of SS, color and COD can be achieved by PHITF respectively. Therefore, RSM has demonstrated to be a suitable statistical tool for optimization of coagulation and flocculation process of PHITF. Furthermore, PHITF can be a good alternative coagulant for leachate coagulation and flocculation process.

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