

PAPER • OPEN ACCESS

The use of factorial design in screening of factors influencing hexavalent chromium extraction by continuous green emulsion liquid membrane

To cite this article: N F M Noah *et al* 2018 *IOP Conf. Ser.: Mater. Sci. Eng.* **458** 012032

View the [article online](#) for updates and enhancements.

The use of factorial design in screening of factors influencing hexavalent chromium extraction by continuous green emulsion liquid membrane

N F M Noah¹, N Othman^{1,2*} and N Jusoh¹

¹Department of Chemical Engineering, Faculty of Chemical and Energy Engineering, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

²Centre of Lipids Engineering & Applied Research (CLEAR), Ibnu Sina Institute for Scientific and Industrial Research (Ibnu Sina ISIR), Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia.

*norasikin@cheme.utm.my

Abstract. Recently, increasing concerns on hexavalent chromium as an environmental pollutant can be observed due to its build-up to toxic levels in the environment, resulting from various industrial and agricultural activities such as electroplating, stainless steel production, leather tanning and textile manufacturing. This work screens the significant factors that largely affect the efficiency of hexavalent chromium (Cr(VI)) removal from electroplating wastewater in continuous green emulsion liquid membrane using fractional factorial design. There are six factors investigated for affecting the removal of chromium which are residence time (t), TOMAC concentration (M), stripping agent concentration (M), rotational speed (rpm), treat ratio, and modifier concentration (w/v). The response variable of the chromium removal was identified using the two-level fractional factorial (two level) design and the results were analyzed statistically. Five factors were identified to have significant influence on chromium removal which are retention time, rotational speed, treat ratio, modifier concentration and carrier concentration. Regression models for chromium extraction were developed and the adequacy of the model was examined. The results of this study indicate that fractional factorial design is capable to predict the significant factors affecting hexavalent chromium extraction by using continuous green emulsion liquid membrane.

1. Introduction

Chromium is a transition metal with a number of industrial uses due to its toughness and resistance to heat and corrosion. It is widely used for manufacturing stainless steel such as chromate manufacturing, chrome plating, ferrochrome production, and stainless steel welding. Nevertheless, these applications increase the concentrations of chromium that is known to be a toxic and mutagenic substance in wastewater. Chromium exposures in both occupational and environmental settings have the ability to trigger human carcinogen. Several restrictions have been imposed on the use of chromium compounds in many parts of the world due to these health and environmental issues.



Previously, various techniques have been investigated in order to choose the best technique to remove the economically hazardous metals of hexavalent chromium from manufacturing wastewater such as chemical precipitation [1], reverse osmosis[2], adsorption[3], ion exchange[4], solvent extraction processes [5], and so forth. On top of that, emulsion liquid membrane (ELM) is regarded as one of the potential and promising technologies for the extraction of chromium ions from industrial wastewater. This is due to the pronounced advantages of ELM which are low capital and operating costs, low energy and reagent consumption, high concentration factors, and high mass fluxes [6]. Even though the two substantial problems of the ELMs which are membrane fouling and extractant leakage are still in need of a solution, the research proposed in this paper was proceeded in order to investigate the commercial applicability of chromium extraction in large scale industrial application using continuous green emulsion liquid membrane (CGELM).

In CGELM, various factors such as residence time (t), TOMAC concentration (M), stripping agent concentration (M), rotational speed (rpm), treat ratio, and modifier concentration (w/v) affect the removal of chromium. Generally, the optimum condition of these factors was preceded by screening experiments that were carried out by one-factor at a time (OFAT) method where the effect of one factor is assessed by varying the value of only one factor while all other independent variables remain constant [7][8][9]. However, this traditional approach was reported to be very costly and time consuming due to many kinds of high materials expense and large number of experiments [10]. Furthermore, this method can only be used to study one factor at a time thus cannot capture the interactions between the factors[11].

Experimental designs, such as the full factorial designs are useful for studying systems with a small number of factors as these experimental designs provide information concerning interactions between factors [12]. A frequently stated advantage of fractional factorial (FF) designs over OFAT designs is their high relative efficiency. However, as the number of factors become larger, the total number of experimental runs required often becomes impractical, if not impossible[13]. In order to save on costly runs, experimenters usually perform only a fractional factorial design, which can overcome this problem as it usually requires fewer experimental running which is just a partial number of a full factorial design. Thus, its relatively inexpensive and efficient way to improve a process has become its major attractiveness. A fractional factorial design is a modified standard factorial that permits gaining information on main effects and low-order interactions without having to run the full design. It consists of confounding the factorial into blocks, and run only one of them [10]. This method has been used in various fields such as in studying the role of eight parameters in both stability and thermal conductivity of carbon nanotubes/water nanofluids [14], in investigating the main competitive factors in the adsorption of arsenic(V) onto reclaimed iron-oxide coated sands [15] as well as in identifying the key factors influencing the extraction efficiency of Cu(II) from aqueous solutions using soybean oil-based organic solvents[16].

Nevertheless, so far there is no work reported on the usage of fractional factorial design in screening the effect of several controllable factors on the extraction efficiency of chromium from real industrial effluent in continuous green emulsion liquid membrane in vegetable oil-based organic solvents which is more renewable, environmental-friendly and economic than the petroleum-based ones. In this work, six parameters were screened in order to evaluate their effects on a response using a two-level fractional factorial design. Furthermore, analysis of variance (ANOVA) and predicted chromium removal from the model at 95% confidence interval against the experimental result is used to examine the adequacy of the developed empirical relationship regression model.

2. Materials, equipment and methods

2.1 Materials

Diluents used were palm oil (Buruh) which is refined cooking oils obtained from Lam Soon Edible Oils. Extractant tricaprilmethylammonium Chloride (Aliquat 336/TOMAC) was obtained from Fluka. Sorbitan monooleate (Span 80) as a nonionic surfactant and 1-octanol were used as surfactant and

modifier, respectively were purchased from Fluka. Thiourea and Sulphuric acid (H_2SO_4) solution were used as stripping agents and were purchased from Merck. Real rinse electroplating process wastewater sample was obtained from the Electroplating Company at Masai, Johor. All chemicals and reagents used were of analytical reagent grade.

2.2 Preparation of Water in Oil (W/O) Emulsion

The primary W/O emulsion was produced by mixing equal volume of (50mL) organic membrane solution (Span 80, 1-octanol and extractant with diluent) with stripping liquid solution (Thiourea acidic) using the Heidolph Silent Crusher-M Homogenizer. The homogenizer speed was set to be 7000 rpm in order to produce a stable emulsion with 1 minute of emulsification time. Then, the white milky emulsion was ready for extraction process. The emulsion needs to be freshly prepared before each step of the experiment.

2.3 CGELM Chromium Extraction

2.3.1 Rig set up for CGELM. Figure 1 shows the schematic diagram of the single-stage, continuous-flow mixer settler apparatus used in this work. The rig consists of 1.5 L extraction vessel with 4 baffled, which is about 12cm in diameter and 15cm height. There are two peristaltic pumps (Cole-Parmer, Masterflex Models) equipped with quick-load heads used to pump the emulsion and feed solutions through two inlet lines mounted on the upper wall of the vessel. Digital drives were used to control the pump speed variations within 1%. The pumps were calibrated before running the experiment. An outlet port mounted at the extractor bottom was controlled for the liquid level to be constant along the experiment (1000 mL). An outlet port mounted on the separator bottom wall was used to take the samples.

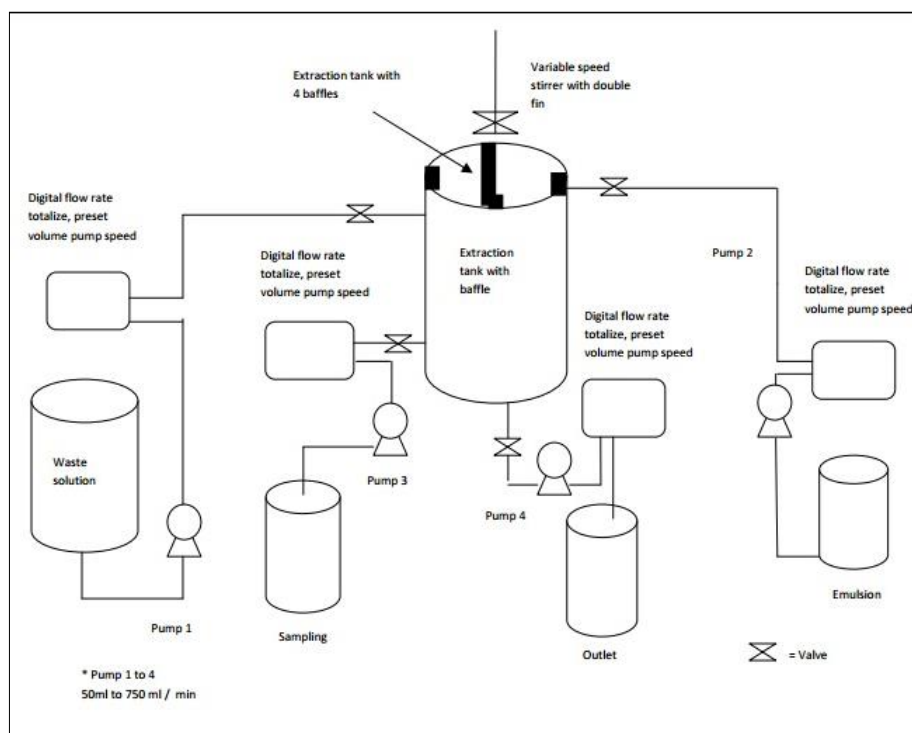


Figure 1. Schematic diagram of continuous ELM extraction system

2.3.2 Chromium removal in CGELM. A series of 100 mL W/O emulsion of optimized condition was prepared using 120 mL beaker and continuously supplied into the emulsion vessel. The emulsion need

to be freshly prepared before each step of experiment. Then, the prepared emulsion and rinsed electroplating solution were combined continuously in the extractor using a digital mixer system (IKA RW 20 Digital Dual Range Mixers) at agitation speed of 350 rpm for 3 minutes retention time. Pump controller 1 and pump controller 2 were adjusted to control the flow rate of feed phase and emulsion solution, respectively into the extraction vessel to maintain the treat ratio. The experiment started with low flow rate of 20ml/min and 180ml/min for emulsion and feed phase, respectively.

Along the process, the sample was taken out every five minutes of extraction process. Sample taken from the screening process undergoes phase separation using separating funnel within 10 minutes. The aqueous phase is the treated chromium solution that was analysed using AAS to determine the efficiency of extraction as well as the removal percentage of chromium in the liquid solution. Steady state was indicated as the chromium concentrations did not change over a period of two or three samples. After achieving the steady state concentration, the pumps and mixer were stopped to separate the emulsion and the aqueous phase. The separation of emulsion was conducted in a separating funnel within 15 minutes, where the three-phase dispersion was settled into the emulsion and the external phase. The treated chromium solution (external feed phase) at the bottom of the separating funnel was taken for concentration measurement. Then, the internal of the liquid membrane was separated to recover the chromium ions. The emulsion was demulsified using high voltage electrostatic coalescer.

The efficiency of chromium removal from the feed and the percentage of swelling/breakage occurred during the process were calculated using Equations 1 and 5, respectively.

$$\% \text{ chromium removal} = \frac{c_i - c_f}{c_i} \times 100 \quad (1)$$

where C_i is the initial concentration of chromium in feed phase and C_f is the final concentration of chromium in feed phase after ELM process.

2.4 Design of experiment

2.4.1 Two-level fractional factorial design. A 2^{6-3} fractional factorial design with resolution III was applied to screen the effects in chromium removal with variations in residence time (t), TOMAC concentration (M), stripping agent concentration (M), rotational speed (rpm), treat ratio, and modifier concentration (w/v). Resolution III was chosen due to the expensive runs and plentiful factors. The variables of interest and their real values at the specified levels in the design are exhibited in table 1. The delimitation of experimental region for each factor was determined from the preliminary experiments. Each independent variable was set to a high (+1) and a low (-1) level. Other factors such ratio aqueous to organic (1:1), Span 80 concentration (3%), initial feed concentration (40 mg/L) and operating temperature (25°C) were fixed. In the design matrix, the effects of six variables on the removal efficiency of chromium were evaluated. A total of 8 experimental runs were randomized for statistical purposes. The statistical significance of each individual factor and their combinations at 5% significance level were evaluated using the Statistica 7 software.

Table 1. The high and low levels of the different factors applied in 2^{6-3} fractional factorial design

| Factors | Symbols | Units | Levels | |
|-------------------------------|----------------|---------------|-----------|----------|
| | | | High (+1) | Low (-1) |
| Residence time | X ₁ | min | 5 | 1 |
| TOMAC concentration | X ₂ | M | 0.04 | 0.004 |
| Stripping agent concentration | X ₃ | M | 1.0 | 0.1 |
| Rotational speed | X ₄ | Rpm | 450 | 150 |
| Treat ratio | X ₅ | Emulsion:Feed | 0.25 | 0.1 |
| Modifier concentration | X ₆ | % (w/v) | 5 | 1 |

2.4.2 Regression analysis. A multiple regression analysis was performed on a regression model which corresponds to the following first-order response function:

$$y = \beta_o + \sum_{i=1}^k \beta_i x_i + \sum \sum_{j<i} \beta_{ij} x_i x_j + \varepsilon \quad (2)$$

Where β_o , β_i and β_{ij} are the regression coefficients for the intercept, linear and interaction coefficients, respectively, y is the dependent variable or the response, x_i and x_j are the independent variables in coded units, and ε is the error term. Estimation of the regression coefficients that caused the model to best fit a set of collected response variable data was carried out by the least squares method [10]. All analysis was performed using the Statistica 7 software.

2.4.3. Model adequacy checking. The adequacy of regression models obtained in fitting the observed data was examined by the analysis of variance (ANOVA), coefficient of determination (R^2) and the absolute average deviation (AAD). ANOVA evaluates the significance of regression by determining whether there is a relationship between the response variable and a subset of the regression variables via the Fisher's statistical test (F-test). R^2 , which has a value from 0 to 1, measures the global fit of a model and is calculated by equation (3):

$$R^2 = \frac{SST - SSE}{SST} = 1 - \left(\frac{SSE}{SST} \right) \quad (3)$$

where SST and SSE are the total sum of squares and error sum of squares, respectively. However, adding a variable to a model will always increase its R^2 value regardless of whether the additional variable is statistically significant or not [10]. Therefore, Pilkington *et al* [17] suggested the analysis of average absolute deviation (or mean absolute deviation) (AAD) as a method to describe the magnitude of deviation present in equation (4):

$$AAD = \left[\frac{\sum_{i=1}^N \left(\frac{|y_{i,exp} - y_{i,pre}|}{y_{i,exp}} \right)}{N} \right] \times 100 \quad (4)$$

where $y_{i,exp}$ and $y_{i,pre}$ are the experimental and predicted responses, respectively, and N is the total number of experimental points. Evaluation of the R^2 and AAD values together would give a better judgment about the adequacy of the model.

3. Results and discussions

3.1 Screening of factors affecting chromium removal

The design matrix used in the 2^{6-3} fractional factorial design to screen the factors affecting the removal percentage is shown in table 2. In this study, a total of 8 runs of experiment were conducted under consistent conditions in one block of measurements and the experimental sequence (standard order) was randomized so that the effects of uncontrollable factors are minimized. The results showed that the removal efficiency was found to be in the range of 81 to 100%. This indicates that continuous green emulsion liquid membrane is applicable to remove chromium from electroplating wastewater.

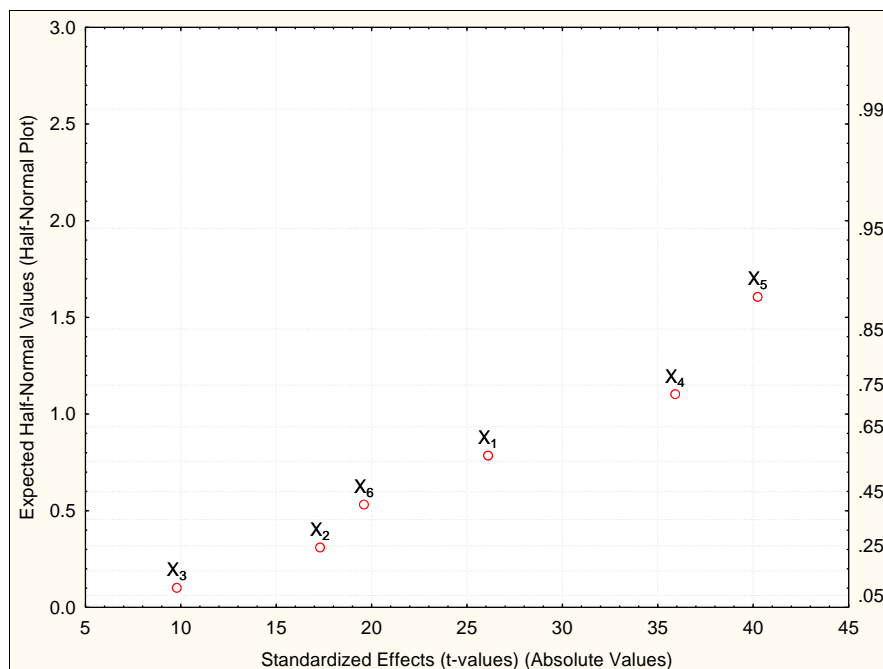
Next, all important factors that significantly affect the chromium removal was evaluated based on a half-normal probability plot of standardized effects, t-value and p-value, a Pareto chart, main effects and interaction plots at 5% significance level using the Statistica 7 software.

Table 2. Design Matrix for 2^{6-3} fractional factorial design and chromium removal performance

| Std Order | Run Order | Blocks | Variables | | | | | | % Removal |
|-----------|-----------|--------|----------------|----------------|----------------|----------------|----------------|----------------|-----------|
| | | | X ₁ | X ₂ | X ₃ | X ₄ | X ₅ | X ₆ | |
| 4 | 1 | 1 | 5 | 0.040 | 0.1 | 450 | 0.10 | 1 | 97.84 |
| 2 | 2 | 1 | 5 | 0.004 | 0.1 | 150 | 0.10 | 5 | 91.05 |
| 7 | 3 | 1 | 1 | 0.040 | 1.0 | 150 | 0.10 | 5 | 81.16 |
| 1 | 4 | 1 | 1 | 0.004 | 0.1 | 450 | 0.25 | 5 | 100.00 |
| 3 | 5 | 1 | 1 | 0.040 | 0.1 | 150 | 0.25 | 1 | 94.05 |
| 5 | 6 | 1 | 1 | 0.004 | 1.0 | 450 | 0.10 | 1 | 94.63 |
| 8 | 7 | 1 | 5 | 0.040 | 1.0 | 450 | 0.25 | 5 | 100.00 |
| 6 | 8 | 1 | 5 | 0.004 | 1.0 | 150 | 0.25 | 1 | 100.00 |

X₁: t(min), X₂: [TOMAC] (M), X₃: [Tu Acidic], X₄: Rotational speed (rpm), X₅: treat ratio (Emulsion:Feed), and X₆: [Octanol] (% w/v); All variables are in uncoded units.

3.1.1 Half-Normal probability plot of standardized effects. The half normal probability plot of the effects in figure 2 shows the absolute values of the estimated effects from the largest effect to the smallest effect. Generally, the estimated effects of an unimportant variable will typically manifest themselves as being near zero and tend to be on or close to a near-zero line in the plot, while the estimated effects of an important factor will typically manifest themselves by being off the line and well-displaced from zero. Hence, the larger the important effects, the further they are from the zero line in the plot.

**Figure 2.** Half-normal probability plot of standardized effects on chromium removal

From this analysis, it could be observed that the largest effect on chromium recovery that is well-displaced in the plot is the X_5 (treat ratio) followed by X_4 (rotational speed), X_1 (residence times), X_6 (modifier concentration) and X_2 (extractant concentration). The sequence of the significant main effects with respect to decreasing influence on chromium removal is found to be $X_5 > X_4 > X_1 > X_6 > X_2$. The analysis indicates the results as consistent to the CGELM system principles and is explained below.

According to the plot, treat ratio is the most significance effect on the chromium removal efficiency due to treat ratio controlled the interfacial mass transfer across an ELM. Treat ratio is the volume ratio of emulsion to the aqueous external phase solution (volume feed solution). Basically, its increment will increase the volume of emulsion as a whole. Therefore, the surface area for mass transfer is increased owing to the formation of a larger number of emulsion globules. As a result, a higher degree of chromium removal is obtained. This finding is supported by Sulaiman *et al.* [18] and Noah *et al.* [6], who observed that high treat ratio significantly increased the emulsion phase hold up in the feed phase, which then increased the removal capacity of the solutes.

Meanwhile, the second and third most significant process variables were rotational speed and retention time, respectively. Generally, in order for the extraction to be effective in the continuous extractor, fluid circulated by the impeller (rotational speed) must be swept into the entire vessel in a reasonable time (residence time) [7][8]. This implies that the effective mixing of fluids in the extractor depend to that the rotational speed and retention time of the operation system.

On the other hand, modifier concentration gives a significance effect in stabilizing the ELM resulting to an increment in the removal efficiency. Lastly, as the removal of chromium in CGELM system is a facilitated transport mechanism, an extractant is needed to promote solute transportation through the membrane. The TOMAC was reacted with chromium to form a TOMAC-chromium complex and diffused through the liquid membrane. This means that the more carrier compound existed in the liquid membrane phase, the more chromium was removed within the retention time. However, increasing the amount of extractant will increase the viscosity of the membrane phase, which limits the removal rate. This finding is in line with our previous study which change in TOMAC concentration will change the rate of chromium transport as well as viscosity of the liquid membrane significantly [19].

It should be noted that the aliased of the main factors with interaction of the 2 factor and higher is negligible due to the use of resolution III in the experimental design. Moreover, the 3-way interactions are usually not significant [10]. Therefore, it can be assured that X_5 , X_4 , X_1 , X_6 and X_2 are the subset of important factors. On the contrary, the linear individual terms (X_3) is found to be insignificant or less significant. This indicates that thiourea acidic concentration in the internal phase did not affect chromium removal in the CGELM system.

3.1.2 Pareto chart. Another quick way to screen the significant factors is by analysing the pareto chart of the estimated effects. In order to validate the results obtained from the half-normal probability plot of effects in figure 2, a Pareto chart was generated and tabulated as shown in figure 3. The p-value serves as a tool for checking the significance of each coefficient and can be used to indicate the strength of interaction between variables. Low values of $p < 0.05$ indicate high significance of the corresponding coefficients. Pareto chart analyses revealed that there are 5 factors that are statistically significant, and clearly have much larger effect than the other factor. The 5 factors are X_1 which is the retention time, X_2 which is the extractant concentration, X_4 which is the rotational speed, X_5 which is the treat ratio, and X_6 which is the modifier concentration. Compared to figure 2, the sequence of the significant main and interaction effects with respect to decreasing influence on chromium removal is parallel with that obtained from the half-normal probability plot of standardized effects, that is $X_5 > X_4 > X_1 > X_6 > X_2$.

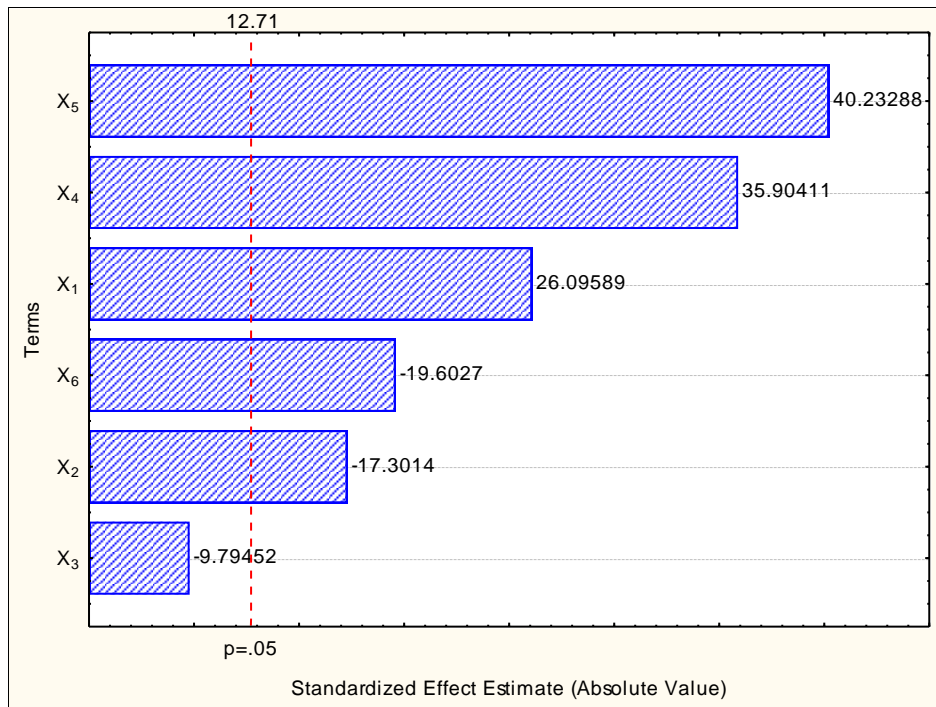


Figure 3. Pareto chart of each parameter coefficient for chromium extraction

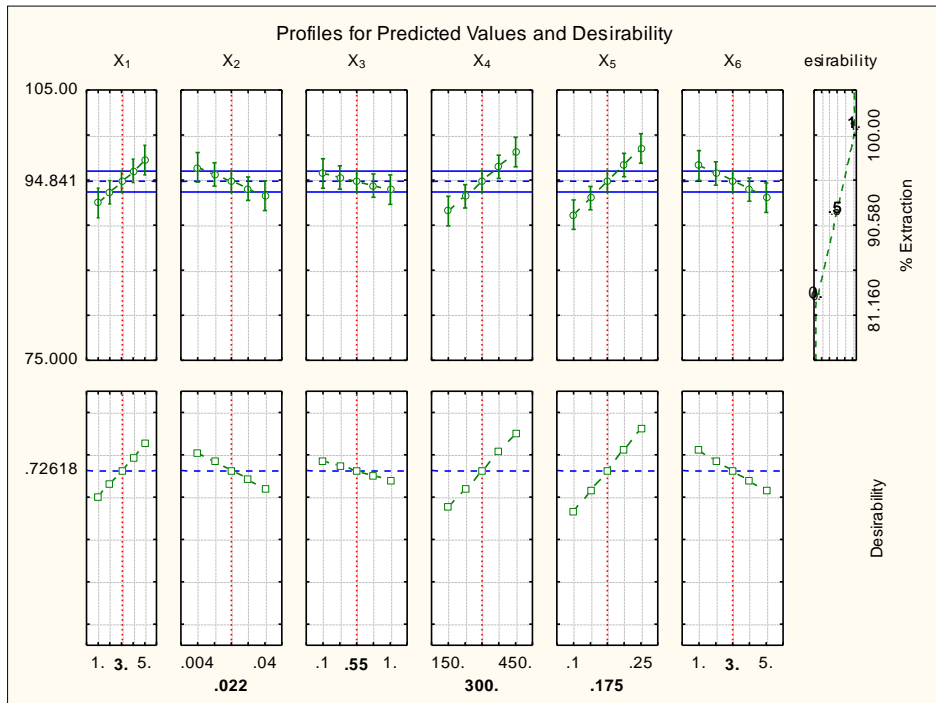


Figure 4. Prediction profiler and desirability plot in fractional factorial design

3.1.3 Main effects and interactions plots. The standardised main effects of the main factors were also observed and shown in figure 4. Based on the specified goals for each response, the value of each factor is obtained as $X_1=3$, $X_2=0.22$, $X_3=0.55$, $X_4=300$, $X_5=0.175$, $X_6=3$, in the screening design. According to the graph, the main effects of X_1 , X_2 , X_4 , X_5 , and X_6 obtained are shown as the steep lines indicating their significant effects toward chromium removal. Meanwhile, the nearly flat effect lines attained for the main effects of X_3 reveals their unimportant effects on chromium removal. As the main factor X_3 has no significant effects on the chromium removal, the value of 0.5M of thiourea acidic can be used as fixed conditions in future study.

3.2 Regression Model and Analysis of Variance (ANOVA) for Response

Table 3 shows the estimated effects and regression coefficients (Coef) together with the corresponding standard deviation (SD_{coef}), t-value (T) and probability (P) values for the main effects terms attained from the linear least square method using the Statistica 7 software. Generally, greater magnitude of T, F and lower value of P value indicate that the corresponding coefficient terms are more significant. The linear regression model of the response (chromium removal) with six independent variables (X_1 , X_2 , X_3 , X_4 , X_5 and X_6) was given with their first order model in coded units as illustrated in equation (5):

$$Y = 94.84 + 2.38X_1 - 1.57X_2 - 0.89X_3 + 3.27X_4 + 3.67X_5 - 1.78X_6 \quad (5)$$

where each regression coefficient was computed according to the linear least square method and the results produced are as tabulated in table 3. In equation (5), a positive relationship with residence time (X_1), rotational speed (X_4) and treat ratio (X_5) can be seen, whereas, a negative relationship with extractant concentration (X_2) and modifier concentration (X_6) can be observed for chromium removal. This is in agreement with work conducted by [20] stated that the positive sign in the equation represents synergistic effects and the negative sign denotes antagonistic effects on the dependent variable, denoted as Y. This suggests that longer retention time, higher rotational speed and treat ratio will enhance chromium removal. Meanwhile, an increase in the amount of extractant and modifier concentration tends to reduce the chromium removal efficiency. In addition, the size of regression coefficients in equation (5) denotes the degree of significance of each independent variable. The order of decreasing significance with respect to the influence on chromium removal, is $X_5 > X_4 > X_1 > X_6 > X_2$. This is in good agreement with the findings attained earlier.

Table 3. Estimated effects and coefficients of the regression models for chromium removal

| Term | Effect | Coef | SD_{coef} | T | P |
|----------|----------|----------|-------------|----------|----------|
| Constant | 94.84125 | 94.84125 | 0.091250 | 1039.356 | 0.000613 |
| X_1 | 4.76250 | 2.38125 | 0.091250 | 26.096 | 0.024383 |
| X_2 | -3.15750 | -1.57875 | 0.091250 | -17.301 | 0.036755 |
| X_3 | -1.78750 | -0.89375 | 0.091250 | -9.795 | 0.064773 |
| X_4 | 6.55250 | 3.27625 | 0.091250 | 35.904 | 0.017727 |
| X_5 | 7.34250 | 3.67125 | 0.091250 | 40.233 | 0.015820 |
| X_6 | -3.57750 | -1.78875 | 0.091250 | -19.603 | 0.032448 |

3.3 Model adequacy checking

The adequacy or goodness of fitted model of the regression model for chromium removal is checked by analysis of variance (ANOVA) using Fisher F-test at 5% significance level. Table 4 shows the analysis of variance (ANOVA) model for the percentage of chromium removal at high confidence level (95%) to obtain a good prediction model. According to table 4, the F-value calculated for response is 713.31 which is higher than the F-value tabulated ($F_{0.05,9,5} = 233.99$) indicating that the model contributes significantly to the response and rejects the null hypothesis at the 0.05 level of significance. Null hypothesis will comply if all variables do not give significant outcome with the response. This is in agreement with the result obtained by Ooi *et al.* [21] which stated that the calculated F-value must be greater than the tabulated F-value in order to ensure the model to accurately predict the experimental result.

On the other hand, the value of R^2 in the model obtained is 0.9998 (99.98%) which is closer to 1 denoting that only 0.02% of the total varians is not explained by the regressors in the model. Therefore, it can be concluded that the predicted values calculated from Equation 5 are in good agreement with the experimental values. This is strongly supported by Wan Omar and Saidina Amin [22] who reported that if R^2 value is more than 0.75 it is considered as acceptable value, however, R^2 value of more than 0.8 is much better.

As there is only small differences between the R-squared ($R^2 = 0.9998$) and the adjusted R-squared (Adjusted $R^2 = 0.9984$) values which is 0.14%, this implies that the model is in good reliability to produce good estimation of the response [10]. This finding is in agreement with Nam *et al.* [19] who observed that smaller gap between R^2 and the adjusted R^2 is desirable for the judgement of the goodness of the model. This can be explained by the fact that the addition of input (independent) variables which are significant to a dependent variable will increase the value of adjusted R^2 , whereas if non-significant variables being added into the model, the value of adjusted R^2 will decrease, while the R^2 value will continuously increase with the addition of more variables, regardless of the input variables' significance to the model.

The predicted chromium removal from the model at 95% confidence interval against the experimental result using the Statistica 8.0 is plotted in figure 5 with its AAD of 0.00041%, which was computed from equation (5). The high R^2 and small AAD values signify the model as able to give a reasonably good estimate of response (chromium removal) for the system in the range studied. Meanwhile, the observed experimental values are evenly distributed close to the straight line, lending support to that the model was accurately predict the experimental result. Hence, the regression model (equation (5)) can be used as a predictive tool to obtain chromium removal over the entire uncertainty range of significant effects studied.

Table 4. Analysis of variance (ANOVA) for first order model chromium removal by CGELM

| | SS | DF | Mean Square | F-value | F-tabulated ($\alpha=0.05$) |
|------------|--------|----|-------------|---------|-------------------------------|
| Regression | 291.03 | 6 | 48.51 | 713.31 | 233.99 |
| Residual | 0.06 | 1 | 0.067 | | |
| Total SS | 291.09 | 7 | | | |

ANOVA; Var.:% Extraction; R-sqr=.99977; Adj:.9984 (Spreadsheet6) 2**(6-3) design; MS Residual=.0666125 DV: % Extraction.

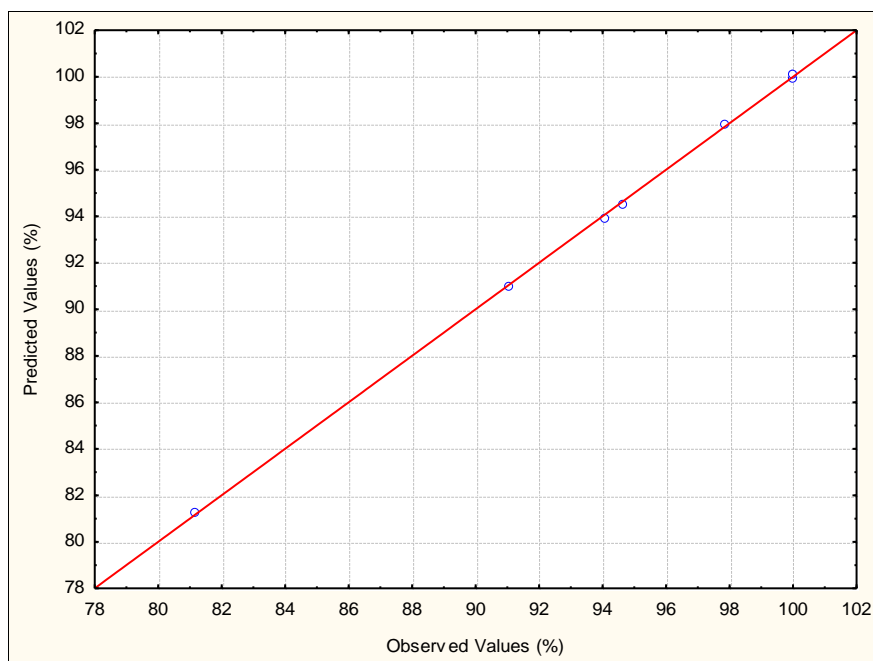


Figure 5. Comparison of predicted and experimental value on chromium removal

3.4 Hexavalent chromium removal using CGELM

One of the important parts is whether the screened condition gives high efficiency of chromium removal using the continuous green emulsion liquid membrane system. Based on the specified goals for each response, the value of each factor is obtained as $X_1=3$, $X_2=0.22$, $X_3=0.55$, $X_4=300$, $X_5=0.175$, $X_6=3$, in the screening design with 95% chromium removal. In order to confirm the prediction, further experiment was carried out at the screening condition for the chromium removal and the result shows that 99% of chromium was recovered with less only 4% deviation with predicted values as tabulated in table 5. This result indicates that continuous green emulsion liquid membrane is applicable to remove chromium from electroplating wastewater.

Table 5. Best Stability Conditions for Chromium Extraction by ELM

| Factors | Symbols | Screened value | Chromium extraction (%) | | Error (%) |
|---------------------|---------|----------------|-------------------------|-----------------|-----------|
| | | | Observed value | Predicted value | |
| Residence time | X_1 | 3 | | | |
| TOMAC concentration | X_2 | 0.22 | | | |
| Thiourea acidic | X_3 | 0.55 | | | |
| Rotational speed | X_4 | 300 | 99 | 95 | 4 |
| Treat ratio | X_5 | 0.175 | | | |
| 1-octanol | X_6 | 3 | | | |

4. Conclusion

A systematic experimental design approach has been applied to screen six factors which is residence time (t), TOMAC concentration (M), stripping agent concentration (M), rotational speed (rpm), treat ratio, and modifier concentration (% w/v) that affects the chromium removal in continuous green emulsion liquid membrane using a 1/8 fraction of 2^{6-3} full factorial design. The results reveal that the degree of significance of each independent variable in the order of decreasing significance with respect to the influence on chromium removal is $X_5 > X_4 > X_1 > X_6 > X_2$. A regression model for chromium removal was developed and its R^2 (99.98%), R^2 (adj) (99.84%) and AAD (0.00041%) values were determined. The high R^2 and small AAD values signify that the model obtained is able to give a reasonably good estimate of chromium removal for the system in the range studied.

Reference

- [1] F Fu, L Xie, B Tang, Q Wang and S Jiang 2012 Application of a novel strategy-Advanced Fenton-chemical precipitation to the treatment of strong stability chelated heavy metal containing wastewater *Chem. Eng. J.* **189-190** 283–287.
- [2] A Tripathi and A K Dwivedi 2012 Studies on recovery of chromium from tannery wastewater by Reverse Osmosis *J. Ind. Pollut. Control.* **28** 29–34.
- [3] K S Padmavathy, G Madhu and P V Haseena 2016 A study on Effects of pH, Adsorbent Dosage, Time, Initial Concentration and Adsorption Isotherm Study for the Removal of Hexavalent Chromium (Cr (VI)) from Wastewater by Magnetite Nanoparticles *Procedia Technol.* **24** 585–594.
- [4] A S Dharnaik and P K Ghosh 2014 Hexavalent chromium [Cr(VI)] removal by the electrochemical ion-exchange process *Environ. Technol.* **35** 2272–2279.
- [5] M Kul and K O Oskay 2015 Separation and recovery of valuable metals from real mix electroplating wastewater by solvent extraction *Hydrometallurgy* **155** 153–160.
- [6] N F M Noah, N Othman and N Jusoh 2016 Highly selective transport of palladium from electroplating wastewater using emulsion liquid membrane process *J. Taiwan Inst. Chem. Eng.* **64** 134–141.
- [7] A Bhowal, G Bhattacharyya, B Inturu and S Datta 2012 Continuous removal of hexavalent chromium by emulsion liquid membrane in a modified spray column *Sep. Purif. Technol.* **99** 69–76.
- [8] S C Lee 2000 Continuous extraction of penicillin G by emulsion liquid membranes with optimal surfactant compositions *Chem. Eng. J.* **79** 61–67.
- [9] S C Lee, K H Lee, G H Hyun and W K Lee 1997 Continuous extraction of penicillin G by an emulsion liquid membrane in a countercurrent extraction column *J. Memb. Sci.* **124** 43–51.
- [10] R H Myers, D C Montgomery and C Anderson-Cook 2009 Response Surface Methodology: Process and Product Optimization Using Designed Experiments *Wiley Ser. Probab. Stat.* **704**.
- [11] M A Bezerra, R E Santelli, E P Oliveira, L S Villar and L A Escalera 2008 Response surface methodology (RSM) as a tool for optimization in analytical chemistry *Talanta.* **76** 965–977.

- [12] M R Hubble 2012 Engineering statistics, Uma Ética Para Quantos XXXIII 81–87.
- [13] T Lundstedt, E Seifert, L Abramo, B Thelin, Å Nyström, J Pettersen and R Bergman 1998 Experimental design and optimization *Chemom. Intell. Lab. Syst.* **42** 3–40.
- [14] M E Meibodi, M Vafaie-Sefti, A M Rashidi, A Amrollahi, M Tabasi and H S Kalal 2010 The role of different parameters on the stability and thermal conductivity of carbon nanotube/water nanofluids, *Int. Commun. Heat Mass Transf.* **37** 319–323.
- [15] J C Hsu, C J Lin, C H Liao and S T Chen 2008 Evaluation of the multiple-ion competition in adsorption of As(V) onto reclaimed iron-oxide coated sands by fractional factorial design, *Chemosphere.* **72** 1049–1055.
- [16] S H Chang, T T Teng and N Ismail 2011 Screening of factors influencing Cu(II) extraction by soybean oil-based organic solvents using fractional factorial design *J. Environ. Manage.* **92** 2580–2585.
- [17] J L Pilkington, C Preston and R L Gomes 2014 Comparison of response surface methodology (RSM) and artificial neural networks (ANN) towards efficient extraction of artemisinin from *Artemisia annua* *Ind. Crops Prod.* **58** 15–24.
- [18] R N Raja Sulaiman, N Othman and N A Saidina Amin 2016 Recovery of ionized nanosilver by emulsion liquid membrane process and parameters optimization using response surface methodology *Desalin. Water Treat.* **57** 3339–3349.
- [19] N Othman, N F M Noah, K W Poh and O Z Yi 2016 High Performance of Chromium Recovery from Aqueous Waste Solution Using Mixture of Palm-oil in Emulsion Liquid Membrane, in: *Procedia Eng.* **148** 765–773.
- [20] N Sathyamoorthy, D Magharla, P Chintamaneni and S Vankayalu 2017 Using Box Behnken design *J. Basic Appl. Sci.* **6** 362–373.
- [21] Z Y Ooi, N Othman and N F Mohamed Noah 2016 Response surface optimization of kraft lignin recovery from pulping wastewater through emulsion liquid membrane process *Desalin. Water Treat.* **57** 7823–7832.
- [22] W N N Wan Omar and N A Saidina Amin 2011 Optimization of heterogeneous biodiesel production from waste cooking palm oil via response surface methodology *Biomass Bioenergy.* **35** 1329–1338.

Acknowledgments

The authors would like to acknowledge the Ministry of Higher Education (MOHE) for the financial support under Research grant: Vote 4F949 and Universiti Teknologi Malaysia to make this research possible.