Optimization of Palm Oil Mill Effluent Treatment by Applying RSM and ANN

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Abstract

The optimization of the COD removal from palm oil mill effluent (POME) has done. The correlation of concentration and pH of POME, and Trans membrane pressure (TMP) of Reverse Osmosis (RO) membrane was optimized by response surface method using a second order polynomial model with Box Behken design consist of 17 runs. To determine whether the model was adequate for representing the experimental data; it was indicated by the ANNOVA table (p-value, lack of fit and R^2 values). The main factor influenced the COD removal was concentration and pH of POME. The optimum conditions were determined from 3D response surface and 2D contour graphs i.e. 28.30% of POME concentration at pH 10.75 and TMP 0.69 kPa to yield 24.1372 mg/L of COD value. The results demonstrate that the response surface method effective to minimize the number of experiment.

Keywords: POME; RO membrane; RSM; ANN; COD

Abstrak (Indonesian)

Optimisasi penghilangan COD dari palm oil mill effluent (POME) telah dilakukan. Korelasi konsentrasi dan pH POME, dan tekanan transmembran (TPM) dari membran Reverse Osmosis (RO) telah dioptimasi menggunakan metode respon permukaan dengan model polinomial orde kedua dengan desain Box Behken yang terdiri dari 17 runing. Untuk menentukan apakah model cukup cocok untuk merepresentasikan data percobaan; telah diindikasikan menggunakan tabel ANNOVA (p-value, lack of fit and R^2 values). Faktor utama yang mempengaruhi penghilangan COD merupakan konsentrasi dan Ph POME. Kondisi optimum ditentukan dari respon permukaan 3D dan grafik kontur 2D seperti konsentrasi POME 28.30% pada Ph 10,75 DAN TMP 0,69 kPa untuk menghasilkan nilai COD 24.1372 mg/L. Hasil yang diperoleh menggambarkan metode respon permukaan cukup efektif untuk meminimalisasi jumlah percobaan

Keywords: POME; RO membrane; RSM; ANN; COD

Article Info

INTRODUCTION

Palm oil mill effluent (POME) is a wastewater produced from the palm oil mill industry. The extraction of crude palm oil from the fruit requires a huge amount of water. It is estimated to produce 1 tons of crude palm oil, is required 5-7.5 tons of water. Unfortunately, 50% of the water will ends up as POME. This wastewater, if not handled properly, will contaminate the environment [1]. In Malaysia, the common methods used to handle POME are integrated anaerobic and aerobic ponds. This method requires large area and long residence times [2].

The use of RO membrane in treating POME has been a very interesting issue among researchers.

Membrane filtration has the capability to produce clear water in a relatively short amount of time, small area and energy consumption. The membrane system has been shown to be able to significantly reduce the BOD, COD, and, TSS to acceptable levels set by regulatory agency [3].

In carrying out an experiment containing many variables, it is required a tool to optimize the response of the overall variables simultaneously in one time. Response Surface Methodology (RSM) was one of famous tool used in collecting data and mathematical modeling that can be used to determine the effect of several independent variables on the response. RSM is very useful to increase the accuracy of existing design processes.

Modelling has many problems that cannot be solved with simple mathematical equations. Therefore, we need a sophisticated tools. Artificial fiber networks or artificial neural network (ANN) is a tool that is now commonly used by researchers to predict the content of the parameters.

Akratos [4] used ANN to design equations removal of BOD and COD. The results showed that the important parameters that affect the removal of BOD is pore media, waste water temperature and longtime stay. From ANN prediction, design equations hyperbole, which combines the zero-order kinetics and was first selected to predict the removal of BOD. The results of ANN and design equation models were compared with data that may be obtained from previous studies, which showed a correlation rather satisfactory. Enforced COD has been found to be strongly associated with the removal of BOD. The objectives of the present work are to test the ability of Reverse Osmosis (RO) membrane to remove the COD in POME using membrane filtration process depends on the relationship between many factors

EXPERIMENTAL SECTION

Raw POME was collected from a local palm oil mill in Selangor, Malaysia. POME was pretreated using Adsorption and Ultrafiltration membrane to reduce the suspended solids. The characterisation of the feed sample and permeate was performed and analysed using a DR/2010 portable data logging spectrophotometer (HACH, USA). The 10 L of raw POME was feed to adsorption column using dosing pump. The flow rate keep constant at 2 ml/min. POME fed at the top and flows downward along gravity, and flows into the feed samples tank of UF membrane.

Permeate from the UF membrane also simultaneously serves as feed for the RO membrane. On the RO membrane, process optimization is done

with the assistance of Response Surface Method (RSM). The permeate flux was collected and measured gravimetrically with an electronic balance. Permeate were analyzed to determine the concentration of parameters.

To get a forecast removal of COD, used Matlab 7.10.0 (R2010b The Math Works, Inc with Lavenberg-Marquardt (LM) algorithm. In the LM algorithm, there are two valid activation function is tan sigmoid function in the hidden layer and a linear function on the output layer. Data input will be divided into three parts: 70% for the training data, 15% for data validation and 15% for the test data. If the weight and bias have been determined, ANN ready for practice or training. ANN multi-layer flow can be trained to advanced mathematical functions (nonlinear regression) or determining patterns.

The circuit awoken comprised of three layers include layers of fill, one hidden layer and output layer. As we have chosen, three conditions namely POME concentration, pH, the transmembrane pressure and filtration time as independent variables in the input layer while the COD as dependent variables in the output layer to the structure of six neurons in the hidden layer.

Statistical Design of Experiments

In this study, the Box Behken was used to design the experiments (DOE) using Design Expert software version 6.0. Determination of the DOE aims to reduce the number of experiments and obtain the optimum response (Y) as the result of interaction of all the factors (X) involved. In this study, the responses were concentration of COD while the factors were concentration of POME, pH of solution and Transmembrane pressure. After conducting the experiment, the coefficients of the polynomial model were determined using the following equation:

$$Y = \beta_0 + \sum_{i=1}^{k} \beta_i X_i + \sum_{i=1}^{k} \beta_{ii} X_i^2 \sum_{i=1,i,j}^{k-1} \sum_{j=2}^{k} \beta_{ij} \qquad (1)$$

where, β_o is the constant coefficient, β_i is the linear coefficients, β_{ii} is the quadratic coefficients, and β_{ij} is the interaction coefficients. Three dimensional plots and two dimensional contour plots were obtained based on the effect of the interaction of the two factors. From these plots, the optimum region can be identified.

RESULT AND DISCUSSION
Optimization of COD removal

In this study, the concentration was varied between the ranges of 10 to 90. The pH was varied

from 3.0 to 11 using hydrochloric acid and sodium hydroxide solutions while the temperature between 0.5 to 2.5 as given in Table 1.All the experiments were based on the Box design were carried out. The total number of experimental runs was 17 as given in Table 2.The effects of the interaction between all the factors to reduce COD were evaluated through an analysis of variance (ANOVA) of the final results from the Box design. Moreover, it was important to check the adequacy of the model using diagnostic graphs and to validate the model by confirming the optimum experimental conditions as previously reported [5;6].

Model Fitting of Box Design

The effects of all the factors on the COD were investigated using the quadratic polynomial model. The final model of optimization was estimated based on the experimental results of the Box design with the respective coefficients as given below:

$COD = 78.36563 - 0.49438\,X1 - 8.46437X2 + 0.40000X3 + 0.011198X1^2 + 0.38547X2^2 + 1.25000X3^2 - 0.027594X12 + 0.10831X13 + 0.52063X23$ (2)

The predicted model that was created by the Box design involved all the coefficients which were shown as a quadratic regression. The COD using the model at each point of the experiment are listed in Table 2 as a comparison between the theoretical (predicted) and the experimental results. The analysis of variance (ANOVA) results of the Box model is given in Table 3. The degree of significance of the model and all the factors (X_1, X_2, and X_3) are presented according to the P-value, where a value that is less than 0.050 is considered to be significant, and any other value that is greater than 0.050 is not significant.

Table 1. Parameters and levels of Box design

Independent variables	X_i	Factor levels		
		-1	0	+1
Concentration	X_1	10	50	90
PH	X_2	3	7	11
TMP	X_3	0.5	1.5	2.5

The significant factors are the concentration (X_1), the pH (X_2), and the TMP (X_3) as well as the interaction between the concentration and the pH (X_{21}). Other important terms are the accuracy and variability of the model, which can be estimated according to the R-Squared (R^2) value which is between 0 to 1, with a value closer to 1 being a better prediction of the response [7]. The R^2 of the Box model showed a higher

value, which was 0.9692. On the other hand, the Adj R-Squared (R^2_{adj}) coefficient was also found to be 0.9297, which was close to the R^2 value, and this value indicated a good correlation between the factors of the process using the Box design. Adequate precision is a term that is used for evaluating the predicted range of responses relative to the associated error, where a value that is greater than 4 (18.019) is required to support the fitness of the model [8].

Adequacy Check of the Model

All the plots for investigating the optimization of COD using the Box design are given in Fig.1. The studentized residuals with normal probability show that all points were close to the line, which indicates that there were no obvious problems with the normality of the design. The general effect of the plots between the studentized residuals and the predicted COD was the random scattering of all the points rather than a funnel-shaped pattern, which confirms that the response had an original observation of variance and that there was no problem with the response variable [9].

Table 2 Experimental runs of Box design with Actual

Std	Run No.	(X_1)	(X_2)	(X_3)	COD Actual	COD Predicted
1	4	10	3	1.5	54.65	53.55
2	12	90	3	1.5	108	109.96
3	10	10	11	1,5	35	33.04
4	3	90	11	1.5	70.67	71.79
5	6	10	7	0.5	32	34.50
6	14	90	7	0.5	74	73.42
7	5	10	7	2.5	36.67	37.25
8	2	50	7	2.5	96	93.50
9	17	50	3	0.5	60.33	58.96
10	9	50	11	0.5	26	25.46
11	16	50	3	2.5	65.67	66.21
12	11	50	11	2.5	39.67	41.04
13	8	50	7	1.5	48.67	43.00
14	7	50	7	1.5	37.33	43.00
15	1	50	7	1,5	33.33	43.00
16	13	50	7	1.5	51.67	43.00
17	15	50	7	1.5	44	43.00

The values of the studentized residuals were almost at intervals of between -3.5 to +3.5, and the observed response value was not considered for any value beyond these values. This model had a studentized residual value that was lower than ± 3.5 and gives a good fitting of the model to the response surface. The outlier of the experimental runs clearly showed that all the points in the range of the outlier had a good distribution for the Box design. The actual value of the size from the experimental runs was nearly the same as

the value predicted by the model, which was evaluated by approximating the terms of R^2 and R^2_{adj}.

Response Surface Plotting and Optimization

The effects of the concentration, the pH, and the TMP on the COD were investigated by the RSM based on a Box design. 3-D response surfaces and contour graphs were used to illustrate the effects of the interaction between each of the two factors i.e. the concentration of POME, pH of solution and the TMP, on the removal COD as shown in Fig. 2.
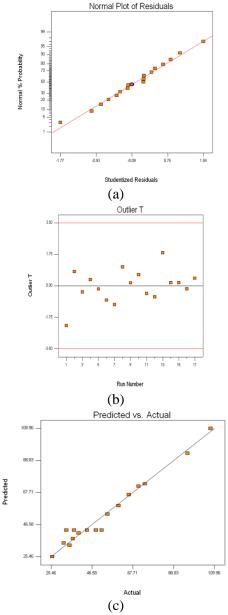
It can be observed that the COD decreased as the pH increased from 3 to 11 and that subsequently above this value the size decreased slightly shown in Fig. 2a. The main reason for this behaviour was the pH changing the character of the impurities. The higher pH means the charge of the impurities will be equal to the charge on the surface of the membrane. The similarity of these charges will be made into a more hydrophilic nature of the membrane so that the impurities do not stick to the surface and the trapped to the bulk solution. In contrast at the lower pH, the decreasing of pH increases the attraction force. The particle will easily attach to membrane surface and then pass through the pores. The particle not only contains the solid particles but also the organic molecule. The existence of organic molecule can be assumed as the COD value in solution [10].

Similarly, the effect of the concentration on the COD was observed as shown in Fig 2b. The COD was found to increase as the concentration increased. It is not surprising when the concentration increased significantly more solid particles contained in the solution. This phenomenon is probably due to the smaller concentration of POME as indicator of the presence of impurities. In addition, the increase in transmembrane pressure makes bigger chance of the small particles in the solution to pass through the membrane pores.

(a)

(b)

(c)

Figure 1 All diagnostic plots of optimization of COD using Box design, (a) Normality, (b) Outlier T, (c) Actual and predicted.

Table 3 ANOVA results for quadratic model

Source	Sum of squares	Degree of freedom	Mean square	F-value	P-value
Model	8245.45	9	916.16	24.51	0.0002
X_1	4528.19	1	4528.19	121.12	< 0.0001*
X_2	1720.79	1	1720.79	46.03	0.0003*
X_3	260.83	1	260.83	6.98	< 0.0334*
X_{21}	1351.73	1	1351.73	36.16	0.0005
X_{22}	160.16	1	160.16	4.28	0.0772
X_{23}	6.58	1	6.58	0.18	0.6874
X_{12}	77.97	1	77.97	2.09	0.1919
X_{13}	75.08	1	75.08	2.01	0.1994
X_{23}	17.35	1	17.35	0.46	0.5176
Residual	261.70	7	37.39		
Lack of fit	27.72	3	9.24	0.16	0.9193**
Pure error	233.98	4	58.49		
Total	8507.15	16			

*Significant at < 0.05% level; ** Not significant, R^2= 0.9692, R^2_{adj} =0.9297, Std. Dev. = 6.11, Mean=53.75, C.V= 11.38, Adeq Precision=18.019.

The higher value of the COD removal was obtained with a lower concentration as 10 and higher pH as 11 with lowers value of TMP. The effects of the TMP with pH and concentration with TMP are exhibited clearly by 3D graphs, which attribute greater effects of concentration, TMP and TMP, pH when these are working together as shown in Fig. 2c. These results indicated the significance of the interaction between the concentration and pH $(X_{1,2})$ from the model, which had a p-value of less than 0.05 [11].

For the optimization of all the factors to produce a lower COD, the range and the minimum options were selected for all the factors and response, respectively. The predicted conditions for all the factors for a lower COD (response) are illustrated in Fig. 3.
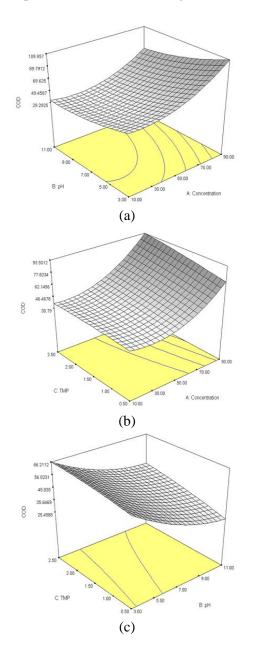
(a)

(b)

(c)

Figure 2 The effect of the factors on COD removal, (a) concentration and pH,(b) concentration and TMP, (c) TMP and pH

By applying the optimum conditions and by running the experiments, a lower COD was produced, which was close to the 24.137 predicted by the model. According to the optimization results (comparison between the predicted and experimental results), more evidence pointed to the Box Behken design for removal COD, and this was attributed to the good interaction between the selected runs of the experiment.
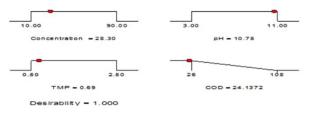
Figure 3. Predicted COD, as obtained from the RSM based on Box Behken design under optimal conditions
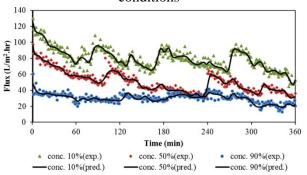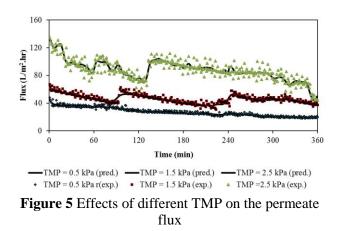
Figure 4 Effects of different POME concentration on Permeate flux

Figure 5 Effects of different TMP on the permeate flux

Neural Network for flux of membrane

The development of ANN model included two main steps i.e. training and validation. Three different

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operating conditions applied to the RO process i.e. POME concentration, pH solution and transmembrane pressure. Filtration process occurs for 360 min and the interval data was recorded for every minute. The total number of 9 experimental considers of 3 data were applied for each condition of filtration process. The relationship between the data experimental results and ANN predictions are presented in Fig. 4-6.

As shown in Fig. 4, the initial flux, J, for each pressure varies depending on the concentration of POME. At highest of POME concentration, the lowest initial flux was owned. The highest flux decline occurred when the concentration of POME was 10%. This indicates that concentration of POME was a one of significant factor effect to the flux. The increasing of POME concentration, the lower flux was found. It can be formed due to formation of a layer on the surface of membrane. However, the concentration of 10% has the highest initial flux, but it drastically declines which attributed to the lower concentration contains of particles that could be cover the membrane.
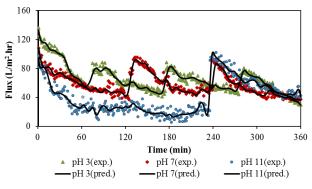

Figure 6 Effect of different pH on Permeate flux

At high TMP (2.5 kPa), initial flux reaches to 130 L/m^2 hr and declined to 80 L/m2 hr in 60 min. This situation was explained by Wu et al. [12] which that POME contains 7.05 g/L protein. The attachment of protein into the pore and retain on the surface of membrane caused the flux decline drastically. Another explanation was given by Said et al. [10]. Increasing in flux decline causes the polarization of particle deposition on the surface and blockage in the pore of the membrane. However, increasing of pressure leads to increasing the concentration polarization and thus increasing also in number of collisions between particles. Collisions between particles gives force the particles to enter the pores of the membrane. Since the size of the particles was larger than the pore size of the membrane, this causes the particles covered the pores of membrane.

In Fig. 6, it can be seen that the significant affecting of pH adjustment on stability of the flux. At low pH of 3, high flux was observed which it not continuous for long time as declined (reached to lowest) at 70 and 170 min and it is necessary cleaning the membrane. The reasonable explanation, when the pH of particle in POME lowers than the IEP of membrane, the particle carries positive charge, since the membrane has negatively charge. This results leads to interaction force between them become stronger and the particle attracted and blocked the pore membrane as shown of blocking mechanisms in Table 4. This blocking of membrane pores results the fouling which the particles were trapped inside the pore of membrane as reported earlier by Kaya et al. (13). Meanwhile at high pH of 11 shows the lowest flux which due to the high concentration of OH$^-$ ions and the solution charge almost in same of membrane charge. It increases the repulsive force between membrane and solution leads to the particle only deposited on the surface and difficult to pass through the membrane.

From the Fig. 6 seen the flux decreased rapidly and after 60 min reaches constant which attributed to particles make interaction among them to make a particle size bigger than pore membrane at starting the process. After 60 min, the particles easy to deposit on surface of membrane and other particles also deposited onto the previous particles to make a thick layer. This thick layer covered the water pass through the membrane which resulting the constant flux compared to below the initial flux. However, a flux increases to initially point on 240 min was observed due to the clean the membrane by the backwash process.

At pH of 7, the initial flux not too high with constant in longer time was found. The initial flux was lower than the pH of 3 but it could reach constant for longer time. The decreasing of flux shows totally different to both pH of 3 and 11 with constant for +120 min was obtained.

CONCLUSION

To optimize the process of reverse osmosis membrane treatment, is applied the response surface method (RSM). Factors affect parameters removal are POME concentration, solution pH and transmembrane pressure. Overall, the study showed that the optimal parameter removal. Based on the response surface and contour plots, it can be seen that the optimum of COD removal will be achieved when the concentration of POME was 28.30%, pH of POME was 10.75 and the TMP was 0:69 kPa to yield 24.1495 mg/L of COD value. Research results in line with forecast values. The prediction and validation of flux decline was

investigated using artificial neural network (ANN). All predicted results by artificial neural network (ANN) showed much closed to experimental results which confirm high accurate model produced to simulate the filtration process. However, the optimum predicted value of 90 %, 0.5 and 7 for concentration, transmembrane pressure and pH, respectively for lower flux decline. These results indicate that artificial neural network (ANN) appreciated method to develop of filtration process using the membrane for waste water treatment in future.

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