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Mathematical Model of Optimum Composition on Membrane Fabrication Parameters for Treating Batik Palembang Wastewater

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Abstract: Batik Palembang wastewater is characterized by high levels Natural Organic Matter (NOM) concentration. In order to reuse the wastewater, removal of NOM and contaminants is necessary. To improve the performance of NOM removal processes we need to optimize the flux of membrane produced. Majority of the wastewater treatment processes are multi-variable and optimization through the classical method is inflexible, unreliable and time-consuming. In this study, we employ Response Surface Methodology (RSM) to optimize and analyze the effect of independent factors, namely polymer concentration (x_1), additive concentration (x_2) and dope temperature (x_3) on a treatment process to obtain the maximum removal NOM. RSM had already emerged as a tool of optimization analysis on the industry scale. Various statistical and mathematical assumptions inherent in this method and is an advantage and shortcomings in its practical application excellence. In order to fulfil the environment standardization of wastewater based on Minister Regulation No. 5/2014, the membrane was produced in optimum composition to achieve the maximum output. We use a full factorial design and Central Composite Design (CCD) of RSM to determine the significant variables and optimum condition for hybrid process of coagulation-UF membrane with respect to NOM removal and flux. Statistical analysis of full factorial design showed that the main effect of three independent factors contributed significantly. Optimum condition was achieved and showed the maximum flux of 198.82 L m^3/h and NOM removal of 90.32%.

Key words: Optimization, RSM, statistical and mathematical assumption, process parameters, design of experiment

INTRODUCTION

Response Surface Methodology (RSM) is featuring model between several explanatory variables with one or more response variables. RSM is derived from mathematical and statistical technique. It can be used for studying the effect of several factors at different level and their influence on each other. Generally, RSM has four major steps which are experimental design, model fitting, model validation and condition optimization.

Stages of a design parameter products became the starting point of the causes of defects during the manufacturing process ongoing. Experimental design to be the method that complements the off line quality control to get the optimal process settings and produce the design parameters of the product robust. Wardrop were used the method of Design of Experiment (DoE) as a tool to analyze the results of experiments in the field of agriculture (Box, 1980). Factorial design widely applied to assist researchers in investigating the effect of single and multi-factor. Until a few years later, the development of from DoE stated by Wardrop who provides an alternative design multifactorial experiment to reduce the number of experiments run (Box, 1980). Other researcher introduced modification of the DoE who not only see the influence of the experiment but also can be used to determine the optimal point of multifactor experiment (Yuliwati *et al*., 2012; Yuliwati and Ismail, 2011; Myers and Montgomery, 2002; Ghanbari *et al*., 2016). At that time, many RSM dominate the industrial engine optimization process based experiments. Viewed from the side DoE modeling in RSM that using mathematical equations basis which then developed in connection with the experiment. The level of data experimental results can only be analyzed through statistical models. Montgomery (1997) provided also the translation and analysis of DoE (Myers and Montgomery, 2002). As a tool for studying and optimizing industrial processes, RSM and its implementation was developed in

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the fields of industry from material selection, setting machines, to industrial process parameters. Batik Palembang industry is one of the industry that use RSM to optimize their produced wastewater filtration. In this study membrane technology was used to treat the produced wastewater of batik Palembang production. The membrane composition that was used in this filtration was a result of RSM. Composition of membrane could be varied in few compositions and the used parameters were total amount of polymer, additives and dope temperature. The performance of membrane was characterized by high levels Natural Organic Matter (NOM) concentration and flux. In order to reuse the wastewater as regulated by Ministry of environment of Indonesia 2014 showed in Table 1, removal of NOM is necessary. The deposition of NOM on the membrane surface leads to membrane fouling which caused the decrease of permeate flux.

Regarding the optimum composition of membrane this research was to investigate the membrane morphology and performance on batik palembang produced wastewater treatment. Hydrophilic Polysulfone (PSf) membranes were prepared via the phase inversion method by dispersing titanium dioxide (TiO_2) nanoparticles in the spinning dope in varied composition to achieve the optimum composition using RSM.

MATERIALS AND METHODS

Response surface methodology: Mathematically, RSM featuring modeling between several explanatory variable with one or more response variables. The method of RSM is based on the DoE and the main idea is to determine the optimal point on the response variable corresponds to setting the level of the explanatory variables. Experimental designs such as Central Composite Designs (CCD) are useful for RSM. It does not require an excessive number of experimental runs.

Model RSM is applied at the level of the experiment the error in the data of experiment results can not be avoided so that statistical interpretation for RSM is very attached in the implementation. RSM is developed from a linear regression model that models have relationship between the explanatory variables and the response variable. RSM has two main stages in the analysis. First, the first order regression modeling, that usual expressed as linear equations with first-order polynomial. RSM first order equations with two factors:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \varepsilon \quad (1)$$

Where:

x_i = Factors that are examined in experiments or also known as variable explanatory

y = The response variable

Table 1: Effluent standard for textile industry

Parameters	Content maximum (mg L^{-1})	Maximum pollution load (kg ton^{-1}) Source	Near by river
BOD_5	60	97	67
COD	150	105	80
TSS	50	0.900	1.000
Phenol	0.5	0.083	0.055
Total amonium Nitrogen (NH_3-N)	8.0	6.300	0.320
Turbidity (NTU)	25	32.10	29.40
Color (TCU)	50	339.0	120.0

pH = 6.0-9.0; Maximum waste = 18, 20; discharge in m^3/ton; Ministry of environment of Indonesia Number 5 (2014) and Environment Laboratory (2016)

Table 2: First order design by montgomery[3]

Natural variables N_1	N_2	Coded variables x_1	x_2	Response (Y)
30	150	-1	-1	39.300
30	160	-1	1	40.000
40	150	1	-1	40.419
40	160	1	1	5
35	155	0	0	40.3
35	155	0	0	40.5
35	155	0	0	40.7
35	155	0	0	40.2
35	155	0	0	40.6

Design of experiments appropriate with Eq. 1 is factorial as DoE and the center point are between the levels of the factor as tabulated in Table 2 that is an example of first order design. Design of experiments in Table 2 contains an optimal response points between levels factors investigated, Eq. 1 will contain the lack-of-fit (Myers and Montgomery 2002). Next, the second step can be directly applied, i.e, raises the degree of the polynomial Eq. 1 into a second order or second-degree with examples of two factors as the following Eq. 2:

$$y = \beta_0 + \beta_1 x_1 + \beta_2 x_2 + \beta_{11} x_1^2 + \beta_{22} x_2^2 + \beta_{12} x_1 x_2 + \varepsilon \quad (2)$$

The optimum response could be as differential Eq. 2 for each explanatory variable. Thus, it will obtained the setting of factors level that will optimize the response variable. This case is said be a mathematical optimization process. Superiority of RSM is not visible directly in model of first-order and second-order. When the Eq. 1 provides no lack-of-fit, then (Myers and Montgomery, 2002) states that there is no optimal point on the design first order then the factors level should be shifted in such a way towards optimizing response. This process is referred as the steepest ascent/descent which exemplified in Fig. 1 for an experiment with two factors.

Shifting factors level towards optimum response conditions is be superior in RSM. This condition is not just stop at these factors level that has been determined at experimental first order but also can track the point of

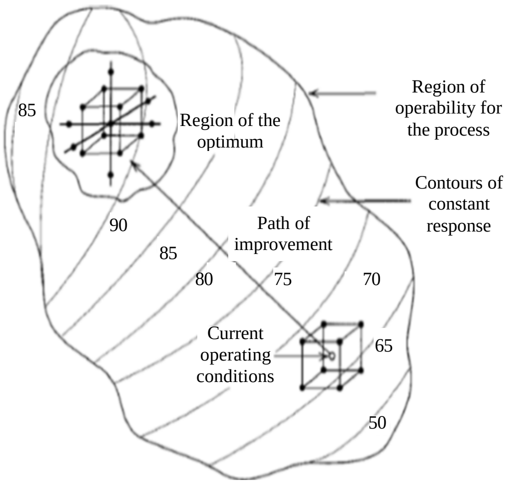

Fig. 1: Shifted factors level to optimum area

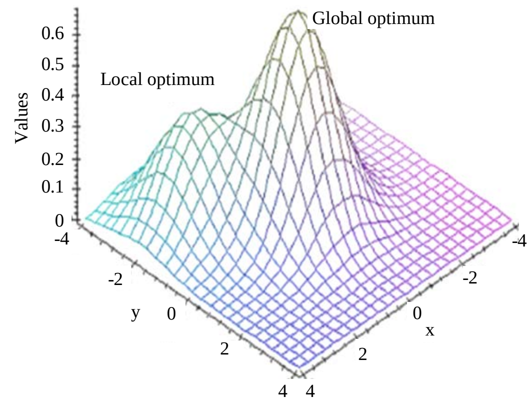

Fig. 2: Global and local optimum response surface contours

optimum response level area outside the experimental first order. Equation 2 will be applied in an area which already contains the optimal point through follow-up experiment with special designs such as central composite design.

Representation of response surface by contours: As mentioned above response surface is useful for interpreting the results of experimentations which represented the relationship between a response and the independent variables. A mesh surface generated by y is usually used in maps to show maximum and minimum values which can be achieved by the relationship among the independent variables. In certain case, in combination with another y function, the optimum conditions can be found. Thus, the finding of the optimum conditions is commonly preferred as the final compromise solution of particular boundary conditions.

As initial approach, the first order (linear) model is commonly used to find the solutions which fulfil the cutting conditions. Further approach is the second order (quadratic) model which is generated to cover more complex cutting conditions required in finding the optimum conditions. In this approach, it is possible to find the maximum or minimum values. The occurrence of hyperbolas implies that there is a saddle point (at which the response is a minimum for one direction and a maximum for other direction) somewhere on the 3D response surface contours (Fig. 2).

When an optimal point will be sought through experiments involving several factors, then the experiment should be designed in such a way that factor levels include response area containing the optimal point. The optimal point gained rather than "local optimum" but can achieve or at least closer to the position of "global optimum" variable response. Steepest Ascent or descent at RSM is a procedure that is capable of shifting levels factor experiments aiming the global optimum.

Design of experiment: The objective of the Design of Experiment (DoE) is to provide an efficient means of experimentation and analysis of experimental results.The statistical design of experiments has been used by several researchers in the analysis of machining process (Ghanbari *et al.*, 2016; Mokhtar *et al.*, 2016; Orhan *et al.*, 2011). The methodology adopted in these investigations is of recent origin and it has been demonstrated that statistical design of experiments is very economical and the analysis of the data leads to accurate and reliable conclusions.

The salient features of experimental designs for exploring response surface have been discussed by many researchers (Myers and Montgomery, 2002; Khuri and Cornell, 1996). The following properties are desirable for a sound experimental design:

- The design should allow the approximating polynomial of degree "n" to be estimated with satisfactory accuracy within the region of interest
- It should allow a check to be made on the representational accuracy of the assumed polynomial
- It should not contain an excessively large number of experimental points
- It should lend itself to blocking
- It should form a nucleus from which a satisfactory design of order "n+1" can be built in case the polynomial of degrees "n" proves inadequate

- The design should provide an economical and reliable means of experimentation
- Every design need not possess all the properties mentioned above. The relative importance of the properties depends on the particular experimental conditions

Central Composite Design (CCD): A Central Composite Design (CCD), originally proposed by (Myers and Montgomery (2002) has been used in this investigation. The factors investigated or independent variables in this study were polymer concentration, additive concentration and dope temperature. As the responses or dependent variables were NOM removal efficiency and flux. In order to investigate the effect of the type of wastewater thus the rotatable CCD design of experiments was repeated for each type of wastewater which are sources and near by river (Zularisam *et al.*, 2009).

Coding for the independent variables: There are some transformations (coding of independent variables) commonly used in machining research, the first logarithmic transformation is suggested by majority of previous researchers as follow (Ghanbari *et al.,* 2016):

$$x = \frac{\ln x_n - \ln x_{n0}}{\ln x_{n1} - \ln x_{n0}} \quad (3)$$

Where:

x = The coded value of any factor corresponding to its natural value
x_n, x_{n1} = The natural value of the factor at the level +1
x_{n0} = The natural value of the factor corresponding to the base or zero level

The second logarithmic transformation was proposed by Montgomery (1997) as follows:

$$x = \frac{\ln x_n - \ln x_{nm}}{\ln x_{nm} - \ln x_{nl}} \quad (4)$$

Where:

x = The coded value of any factor corresponding to its natural value
x_n, x_{nm} = The natural value of the factor at the medium level
x_{nl} = The natural value of the factor corresponding to the low level

The third logarithmic transformation was reported by Montgomery (1997) as follow:

$$x = \frac{2(\ln x_n - \ln x_{n1})}{(\ln x_{n1} - \ln x_{n-1})} \quad (5)$$

Where:

x = The coded value of any factor corresponding to its natural value
x_n, x_{n1} = The natural value of the factor at the level +1
x_{n-1} = The natural value of the factor corresponding to the level -1

RESULTS AND DISCUSSION

Based on the CCD of RSM with a total of 20 experiments, the three factors made up of polymer concentration, additive concentration and dope temperature were used in this study. The designs were based on two-level full factorial design which were augmented with centre and star points.

Maximum and minimum range of variables in coded form: Model fitting to equation of up to the second-order was performed to determine the goodness-of-fit. The responses were fitted to the variables by regression. The minimum and maximum range of variables were investigated and the full experimental plan with respect to their values in actual and coded form was listed in Table 3.

The experimental and predicted values of the three independent variables together with the responses are summarized in this Table 3 which took the maximum and minimum level for each variable used. The variables used are polysulfone that used in range from 15-23 wt.%, Titanium dioxide as additives was used in the wt. percentage range from 0.5-2 wt.% and dope temperature are in the range of 35 until 70° celcius. These minimum and maximum level, choised as parameters are novelty in this research that tabulated in Teble 3. In this study, for simplicity we used 3 value of level, i.e., -2, 0 and+2.

Principle of RSM was described by Mozia and Tormaszewska (2004). It is very important to choose an appropriate model for describing the shape of the surface well. To identify the right model that can fit the data, it can be started with the simplest model forms like first and second-degree Scheffe's polynomial. After testing these models for adequacy of fit they were augmented to simplex centroid and second order linear differential models by adding the appropriate terms.In this study, the second order linear differential models model used for predicting the optimal point was according to equations.

Response surface methodology approach for optimization of factors: Based on the RSM approach, the runs were conducted in CCD model-designed experiments to

Table 3: The minimum and maximum range of variables in coded form

Variables	Unit	Symbols coded	Levels -2	-1	0	+1	+2
Polimer	wt.%	x_1	15	17	19	21	23
Additive	wt.%	x_2	0.5	0.8	1.0	1.5	2
Dope temperature	°C	x_3	35	45	55	65	70

Table 4: Optimum value of factors

Factors	Optimum value
Y_1 (Flux, L m^3/h)	198.82
Y_2 (NOM removal efficiency, %)	90.32
X_1 (Polymer, wt.%)	17
X_2 (Additive, wt.%)	20 (from PSf wt.%)
X_3 (Dope temperature, °C)	50

Table 5: Predicted and experimental values of maximum responses

Variables	Maximum value of responses Flux	NOM removal
Predicted	198.92 L m^{-3}/h	90.32
Experimental	182.56 L m^{-3}/h	90.01
Residual	0.7900	0.240
Percentage error	0.4500	0.230

visualize the effects of independent factors on the response and the results along with the experimental conditions. According to the sequential model sum of squares, the model were selected based on the highest order polynomials where the additional terms were significant. An empirical relationship between the response and the variables expressed by the following fitting the equation second degree. The experimental results were evaluated and approximating function of NOM removal and flux as shown in Eq. 6 and 7 were obtained in the final equation in terms of coded and actual factors are:

$$\hat{y}_1 = +59.15+4.53\,x_1+4.03\,x_2+8.63\,x_3+1.35x_1^2+1.80\,x_2^2-7.86x_1\,x_2+5.24x_2x_3 \quad (6)$$

Where:

y_1 = The NOM removal

x_1-x_3 = Polymer, additive and dope temperature

$$\hat{y}_2 = +25.75-3.14\,x_1+1.92\,x_2+4.73\,x_3-2.95\,x_1^2-2.80\,x_3^2+3.00\,x_1x_2+2.98\,x_2x_3 \quad (7)$$

Where:

$\hat{y}_2$ = The flux of the permeate solution

x_1, x_2, x_3 = Polymer, additive and dope temperature

Those equations are mathematical correlation models that can be employed to result the optimum value of factors and predict the maximum flux and NOM removal within the range of variable factors of this experiment as shown in Table 4 and 5.

CONCLUSION

Based on the above study several conclusions can be drawn as follows; A Full factorial design and Central Composite Design (CCD) of Response Surface Methodology (RSM) can be used to determine the significant variables and optimum condition for hybrid process of coagulation-UF membrane with respect to NOM removal and flux. Statistical analysis of full factorial design showed that the main effect of polymer concentration (x_1) additive concentration (x_2) and dope temperature (x_3) were significant model terms. Whereas experimental design based on RSM revealed that the main effect of additive concentration is the most significant factor that influences the NOM removal efficiency and this is followed by the two level interactions of polimer concentration and dope temperature. In the case of membrane permeability, the second order effect of polimer and additive concentration and dope temperature are accurate for prediction the maximum fluks. This indicated that the three factors contributed significantly. Optimum condition of 17 wt.% PSf with adding 20 wt.% titanium dioxide in dope temperature of 50°C was achieved and showed the maximum flux of 198.82 L m^{-3}/h and NOM removal of 90.32%.

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