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Articles

MINIMIZATION OF CORROSION RATE USING RESPONSE SURFACE METHODOLOGY

Femiana Gapsari[1*]– Rudy Soenoko[1] – Agus Suprapto[1] – Wahyono Suprapto[1]

[1] Mechanical Engineering Department, Faculty of Engineering, Brawijaya University, MT. Haryono 167 Malang, Indonesia

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Abstract:

In this paper, the corrosion rate of the austenitic stainless steel AISI 304 has been assessed via potentiodynamic polarization under the synergistic effects of environmental factors. Concentration of inhibitors, immersion time and concentration of HCL are the factors that induce the corrosion rate of the considered metal. Response Surface Methodology (RSM) is used in this research as an optimization method. The method design used is Central Compoite Design (CCD). The findings of this study reveal the combination of those three environmental factors in minimizing corrosion rate. This analysis calculates the contribution value of each parameter in changing the value of corrosion rate in both individual and synergistic cases. It has been found that minimum corrosion rate is achieved at inhibitor concentration combination of 6000ppm in 65 days and at HCl concentration of 0.5M. From the variation combination, it is seen that the concentration of inhibitor is adsorbed on the AISI 304 surface. The long period of immersion time supports the forming of thin layer which reduces the corrosion rate.

1 Introduction

The acidic media is considered as one of the environmental factors which cause corrosion. A large increase in concentration of acid solution contributes big influence to corrosion. Especially in the case when hydrochloric acid is used as acidic media. The majority of acidizing treatments carried out utilize HCl at concentrations of 5–28 % [1]. The main advantages of this acidic media are their providing other mineral acids in the acidizing operation of forming metal chlorides, which are very soluble in the aqueous phase [2]. AISI 304 is the stainless steel most widely used. Because of its formability and corrosion resistance, 304SS is one of materials which is widely applied in industries [3]. These metals are used in structural petroleum industry and petrochemical applications. In acid solutions, 304 SS is very susceptible to corrosion due to the breakage of passive film. Due to economic reason, inhibitor is widely used as an appropriate method in reducing the corrosion rate [4]. Therefore, Cera Alba (CA) used as corrosion inhibitor in this study is a novel green inhibitor for

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[*] Corresponding author. Tel.: +6281803610855; fax: +62341-554291
E-mail address: femianagapsari@gmail.com

304SS in hydrocloric acid. CA is a natural wax produced by honey bees to store honey, royal jelly, and propolis in which honey is a natural material that is good for retarding the corrosion rate of various metal [5].

Control of corrosion can be done by selecting the appropriate material which suits the condition of environment where the material is located. Minimizing corrosion is considered as optimization consisting of two forms namely minimization and maximization. Optimization is the process undertaken in order to get the right result efficiently and effectively at a low cost and restrictions [6]. By optimization and controlling the environment, the smallest effects of corrosion are known. As a result, optimization calculation is necessary to determine the effects of corrosion at the smallest rate [7].

This study analyzes the combination value of each parameter in changing the value of corrosion rate. Parameters which are often controlled at corrosion rate are concentration of inhibitor, immersion time and concentration of acid solution. *Response Surface Methodology* (RSM) is used in this research as an optimization method [8]. The method design used is *Central Composite Design* (CCD). Applying RSM analyzes shows the magnitude and quality of each parameters' effect, which is used to predict the combination of parameters to reduce the corrosion rate [9]. It determines whether one given factor, such as inhibitor concentration, has a significant effect on corrosion rate across any of the groups of considered parameters under study [10].

2 Methods

The chemical compositions of 304SS in weight % are 0.04 % C, 0.52 % Si, 0.92 % Mn, 0.030 % P, 0.002 % S, 9.58 % Ni, 18.15 % Cr, Bal.Fe. The 304 SS specimens of 1.0 mm × 4.0 cm × 1.0 cm were abraded using emery paper of grades 500 and 2000 consecutively. The density of 304SS is 7.9 g/cm^3. The electrochemical measurement used Autolab PGSTAT 128N. All measurements were done using a 200 ml corrosion cell in which 304SS was used as working electrode (WE), a reference electrode (Ag/AgCl electrode), and a counter electrode (Pt electrode). The tafel plots were obtained by polarization potentiodynamic test. The potential range from -100 mV to +100 mV at Open Circuit Potential (OCP) with scan rate 1 mV/s. CA was extracted by solid-liquid method in order to obtain the optimum conditions. The half of CA powder was extracted by maceration method using 99 % ethanol (Merck).

RSM was applied to determine the optimal combination of corrosion inhibitor, immersion time, and HCl concentration. *Central Composite Design* (CCD) is a treatment design consisting of 2^k factorial design added by some *center runs* and *axial run* (*star runs*). The function of *desirability* is as transformation from geometric response from 0 – 1. Responses in the determined limit values are between 0 – 1. The study variables were divided into three levels as follows in Table 1.

Table 1. Level of the variables

Name of Variable	Concentration of CA extract	Immersion Time	HCl Concentration
	ppm	Days	M
Low Level (-1)	2000	7	0.5
Medium Level (0)	4000	14	1
High Level (1)	6000	21	1.5

The result of RSM design with CCD was obtained using Minitab 16. Factorial 2^{k}design CCD was used in the research consisting of k factorial with each factor having low level (code -1), medium level (code 0), high level (code +1) and level at axial point (code $-\alpha$ and $+\alpha$). AS $k = 3$, $\alpha=1.682$.

3 Result and discussion

The result of RSM design of experiment is displayed in Table 2.

The corrosion rate is obtained from testing the polarization potentiodynamic. Fig. 1 shows the Tafel plots of potentiodynamic polarization testing to obtain the rate of corrosion on the draft RSM with CCD.

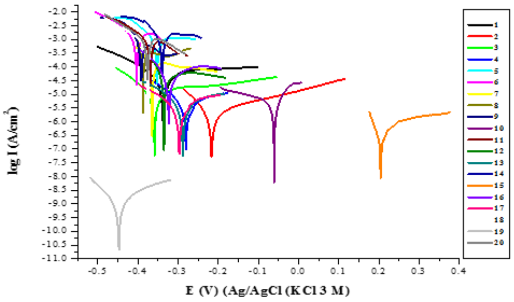

Figure 1. Tafel plots for the experimental results based on experimental design RSM with CCD.

Table 2. Research data with CCD-RSM

Exp	Cera Alba	Time	HCl	Corrosion Rate
	ppm	days	M	mmpy
1	1	-1	-1	1.48
2	-1	-1	-1	2.5
3	1	1	-1	0.41
4	-1	1	-1	0.82
5	1	-1	1	4.92
6	-1	-1	1	8.98
7	1	1	1	3.05
8	-1	1	1	6.61
9	-1.682	0	0	4.44
10	1.682	0	0	2.13
11	0	-1.682	0	4.42
12	0	1.682	0	2.14
13	0	0	-1.682	0.88
15	0	0	0	2.02
16	0	0	0	2.08
17	0	0	0	1.98
18	0	0	0	2.01
19	0	0	0	2.11
20	0	0	0	2.06

Fig. 1 shows corrosion rate. Based on Fig. 1 the largest corrosion rate is in the experiment 6, which is a combination of 2000 ppm concentration of CA extract, 7 days of immersion time and 1.5M HCl. Meanwhile, the lowest corrosion rate is obtained in the experiment extract of 6000 ppm CA, soaked within 21 days in a solution of HCl 0.5. To know the right combination for getting the lowest corrosion rate of the three variables of this research, the optimization analysis is carried out by RSM. Value corrosion rate is then analyzed by RSM using MINITAB to obtain a mathematical model of the relationship of research variables.

Linear mathematic model is the first step in the action of RSM method. Based on the testing result of the linear model, it was found that the study result did not match the first order model (linear). Thus, full quadratic model testing was conducted. Based on the CCD design, analysis of variance of (ANOVA) full quadratic response was found as shown in Table 3. ANOVA analysis has been used as a reliable method in different fields of scientific studies to evaluate the parameter effects [11]. In the field of corrosion, most of the ANOVA applications are reported in the studies that consider the interaction between inhibitors [12].

Table 3. ANOVA for full quadratic of corrosion rate

Source	Df	Seq SS	Adj SS	Adj MS	F	P
Regression	9	103.299	103.2993	11.477	109.05	0
Linear	*3*	86.383	86.383	28.7943	273.58	0.000
Square	*3*	11.695	11.6952	3.8984	37.04	0.000
Interaction	*3*	5.221	5.221	1.7403	16.54	0.000
Residual Error	*10*	1.053	1.0525	0.1053		
Lack of Fit	*5*	1.041	1.0408	0.2082	88.7	0.070
Total	*19*	104.352				

In order to obtain a good understanding of ANOVA, the average effect of factors for each level and the sum of squares and corresponding calculations need further explanation (Table 3). This study used level of significance of 5 %. Based on Table 3, p-value of regression is 0.000 times smaller than 0.05. The quadratice model is siginficant because their p-value are less than α=0.05 meaning that the right model for this case is a quadratic model. Table 3 displayed the result of lack of fit which was applied to test model adequacy. Base on Table 3, the lack of fit shows 0.00 times bigger than 0.05 which means that it rejected to resist first hypothesis. This shows that the model has been made based on the data. From the normality test of residual, tat p-value of normality is > 0.15. P-*Value* is bigger than 0.05, which is 0.15. It means that the residual has been normally distributed. Normality assumption on a regression model has been completed by the produced regression model.

Table 4. Regression of full quadratic testing

Term	Coef	SE Coef	T	P
Constant	2	0.13232	15.474	0
Inhibitor	-0.9471	0.08778	-10.789	0
Time	-0.7926	0.08778	-9.028	0
HCl	2.1908	0.08778	24.956	0
Inhibitor*inhibitor	0.4119	0.08544	4.821	0.001
Time*time	0.4102	0.08544	4.8	0.001
HCl*HCl	0.7778	0.08544	9.103	0
Inhibitor*Time	0.1387	0.1147	1.21	0.254
Inhibitor*HCl	-0.7737	0.1147	-6.746	0
Time*HCl	-0.1863	0.1147	-1.624	0.135
S= 3.244	R-sq= 99.0 %		R-sq (adj) =98.1 %	

The value of coefficient of determination from the regression of quadratic full model is displayed in Table 4. The higher the value of R^2, the greater the contribution of each variable is. The R^2 value shows correlation between X and Y suitable with the model equation being used. Model of empirical testing of full quadratic of corrosion rate based on the analysis of response surface, the empirical testing of full quadratic can be formulated as follows:

$$Y = 2.474 - 0.9471 (X_1) - 0.7926 (X_2) - 2.1908(X_3) + 0.4119 (X_1)^2 + 0.4102(X_2)^2 - 0.7778 (X_3)^2 - 0.1387 (X_1X_2) - 0.7737 (X_1X_3) - 0.1863(X_2X_3), \quad (1)$$

where, Y is corrosion rate, X_1 is concentration of CA extract (ppm). X_2 is immersion time (days). X_3 is HCl concentration (M).

Based on the analysis of response surface of full quadratic model, surface plots and contour plots of corrosion rate are seen in Fig. 2 and 3.

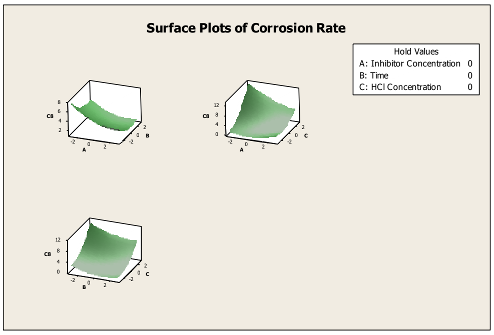

Figure 2. Surface plots of corrosion rate.

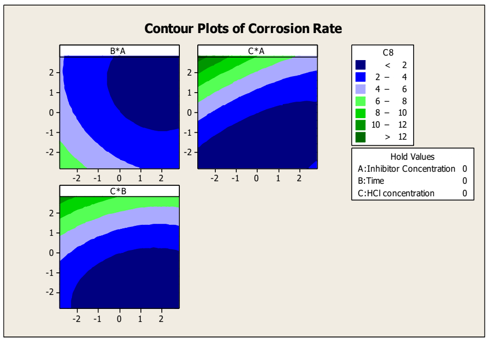

Figure 3. Contour plots of corrosion rate.

With a mathematical model of the response surface (contour plot and a surface plot) the optimum combination of corrosion environment (in this case there are study variables) has been identified to generate the minimum corrosion rate. The corrosion rate with the combination of research independent of variable inhibitor concentration, immersion time and concentration of HCl can affect the rate of corrosion which has been predicted using RSM.

From the model, the intended corrosion rate can be determined [13]. The optimization method used was *desirability function* approach. The smaller the criterion of desirability function used, the better it becomes. This criterion was conducted to determine the different rate of corrosion inhibitor concentration, immersion time, and the concentration of HCl. To perform the analysis using desirability function approach, the limit value of the response is put. Targets generated are zero corrosion rate. Based on the experimental results, the smallest corrosion rate obtained is included. The analysis desirability function as a result of a combination of process variables that produces minimal response is shown in Fig. 4.

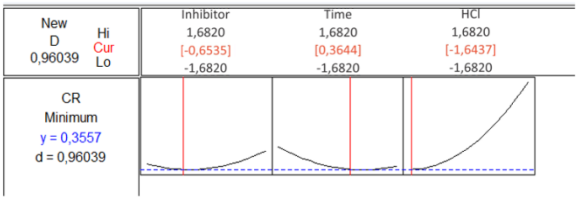

Figure 4. Response optimization.

However, corrosion rate will be minimum if the concentration of CA extract is 1307.06 ppm in 2.55 days and 0.18 M HCl. From the variation combination, it is seen that the concentration of inhibitor is adsorbed on the AISI 304 surface. The long period of immersion time supports the forming of thin layer which reduces the corrosion rate. Corrosion inhibitors are selected on the basis of solubility or dipersibility in the fluid which is to be inhibited [14]. It, therefore, shows that RSM is very effective to be applied for inhibitor concentration, immersion time and acid concentration.

4 Conclusion

Based on experiment approach using RSM, it can be concluded that:

1. Minimum corrosion rate at extract CA concentration 1307.06 ppm in 2.55 days and 0.18 M HCl has been obtained.
2. The statistical analysis shows that the model is statistically acceptable (R^2 = 99.0 % for full quadratic model).

3. Based on the result of combination of optimization variable, minimum corrosion rate has been obtained. This proves that quadratic testing model meets the requirements and has been experimentally tested. Empirical model for *full quadratic* is $Y = 2.474 - 0.9471 (X_1) - 0.7926 (X_2) - 2.1908(X_3) + 0.4119 (X_1)^2 + 0.4102(X_2)^2 - 0.7778 (X_3)^2 - 0.1387 (X_1X_2) - 0.7737 (X_1X_3) - 0.1863(X_2X_3)$.

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