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Statistical Evaluation of *Calopogonium mucunoides* Leaf Extract as Natural Inhibitor for Mild Steel in alkaline Media

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ABSTRACT: The potentiality of *Calopogonium mucunoides* leaf (CML) extract for alleviating the corrosion of mild steel samples subjected to 1M KOH was evaluated from experimental and statistical perceptions. Weight loss experiments were employed in the corrosion process and Response Surface Methodology (RSM) in optimizing the process. A box-Behnken design (BBD) of Design Expert 10.0.7, implementing RSM was used to evaluate the effects and interactions of three factors: Temperature, concentration of inhibitor and time of immersion on inhibition efficiency. The optimal conditions obtained were Temperature of 37.16°C, inhibitor concentration of 0.38g/l, immersion time of 5.11hrs and inhibition efficiency of 90.12% (desirability value of 1.0). These are in agreement with the experimental optimum value for the inhibitor. The model adequacy was elucidated using Analysis of variance (ANOVA). Similarly, the 3D graphical results unveiled that the interactions of the *variables* significantly influenced the prevention of surface damage. The resulted outcomes from the analyses further reflected RSM to be suitable method for optimization of this process.

KEY WORDS: alkaline corrosion, alkaline inhibition, *Calopogonium mucunoides,*Box-Behnken design, validation,

I.INTRODUCTION

Corrosion inhibitor is a chemical substance which, when added in small concentration to any environment, minimizes corrosion [1-3]. Corrosion inhibitors are used to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection, required, for example, to prevent corrosion that may result from accumulation of small amount of an aggressive phase.

Natural inhibitors like plant extracts exhibit moderate to high antioxidant activities. Natural antioxidants may be found in any plant part. Fruits, vegetables, spices, nuts, seeds, leaves, roots and barks are potential sources of natural antioxidants. The plant extract are environmental friendly, non-toxic, biodegradable and readily available. These plant extracts contain several organic compounds which have polar atoms such as O, N, P and S [4]. They are adsorbed into the metal surface through these polar atoms. Adsorptions of these ingredients obey various isotherms. Plant extract has been used to control the corrosion of bronze [5].

Environmentally friendly corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compounds. Some research groups have reported the successful use of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment. As reported by [6], several studies have been carried out on the corrosion inhibition of metals by plant extracts. Rosaline-Vimela, *et al*,[7] examined the corrosion inhibition of mild steel by leaves extract of *Annona muricata* leaf in 1N HCl. Plant extracts of tobacco from stems, twigs as well as leaves have been reported to show significant corrosion inhibition of aluminium and steel in both saline solutions and strong acids [8]. Extracts from leaves were investigated and found to be effective corrosion inhibitors for mild steel in 2M HCl solutions.

This work centred on using the novel *Calopogonium mucunoides* leaf extract ascorrosioninhibitor in alkaline medium. The inhibitory action of *Calopogonium mucunoides* on mild steelin KOH environments was clearly analysed with statistical tools at various temperatures and time.

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II. METHODOLOGY

The preparation of stock solution was done as previously described in [9]and the weight loss experiment performed in accordance with [9, 10].Determination and optimization of the corrosion inhibition efficiency of the plant extract on mild steel in alkaline media was done by application of Response Surface Methodology (RSM). A three-factor Box-Behnken Design (BBD) implementing RSM using Design Expert 10.0.7 was employed in designing the RSM weight loss experiment. A total of 17 runs were required for the experiment. This method was fitted into a quadratic polynomial model using equation (1).

$$Y = b_0 + \sum_{i=1}^{K} b_0 \times_i + \sum_{i=1}^{K} b_{ii} \times_i^{2} + \sum_{i}^{K}\sum_{j} b_{ij} \times_i \times_j \quad (1)$$

Where y is the response variable to be modeled; Xi, and Xj are the independent variables which influence y, bo, bi, bii and bij are the offset terms, the ith linear coefficient, the quadratic coefficient and the ijth interaction coefficient, respectively.

Table 1: Experimental range and levels of BBD

Variables			**Range and levels**		
Independent variables	**Symbols**	**Units**	**-1**	**0**	**1**
Temperature	X1	(°C)	30	50	70
Inhibitor concentration	X2	(g/l)	0.2	0.4	0.6
Time	X3	(Hrs)	1	3	6

The responses of the variables was analysed using RSM, and elucidated with ANOVA and graphical interpretations of the surface plots.

III. EXPERIMENTAL RESULTS

RSM analysis

Optimization of the process variables was done by RSM. Table 1 presents the factor levels with the corresponding values. A total of seventeen experiments was carried out as predicted by BBD and their results are shown in Tables 2.

Table 2: RSM result of corrosion inhibition of mild steel in KOH by *CML* extract

		Factor 1	**Factor 2**	**Factor 3**	**Response 1**	**Response 2**	**Response 3**
Std	**Run**	**X_1:temperature (°C)**	**X_2:Inh.conc (g/l)**	**X_3:time (hrs)**	**weight loss (g)**	**CR (g/cm²/hr)**	**Inhibition Efficiency (%)**
1	1	30	0.2	4.5	0.2	0.036	82.01
15	2	50	0.4	4.5	0.31	0.027	63.43
5	3	30	0.4	3	0.52	0.034	63.43
2	4	70	0.2	4.5	0.12	0.14	80.12
7	5	30	0.4	6	0.31	0.17	84.10
13	6	50	0.4	4.5	0.22	0.027	63.43
8	7	70	0.4	6	0.14	0.11	77.25
6	8	70	0.4	3	0.34	0.13	50.06
4	9	70	0.6	4.5	0.023	0.014	78.12
10	10	50	0.6	3	0.13	0.017	65.34
3	11	30	0.6	4.5	0.53	0.092	84.45

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17	12	50	0.4	4.5	0.23	0.027	84.46
11	13	50	0.2	6	0.24	0.079	80.31
14	14	50	0.4	4.5	0.31	0.027	90.22
16	15	50	0.4	4.5	0.42	0.027	88.04
12	16	50	0.6	6	0.21	0.039	76.50
9	17	50	0.2	3	0.21	0.017	80.21

A) Validation of the Model

The models obtained in this study were tested statistically using analysis of variance (ANOVA) as seen in Table 3. The model equations developed were tested based on p-values ($p < 0.05$). The p-values greater than 0.05 were insignificant and detached quadratic and interaction effects of temperature and time which are significant model terms.The model reduces to Eq. (2) after removing the insignificant terms.

$$Y = -0.083063 - 3.77500E - 003X_1 + 0.94500X_2 - 8.00000E - 003X_3 - 0.011375X_1 * X_2 - 1.30000E - 003X_1 * X_3 - 0.033333X_2 * X_3 + 1.45625E - 004X_1^2 - 0.36875X_2^2 + 0.011444X_3^2 \quad (2)$$

Where X_1 = Temperature, X_2= Inhibitor concentration, X_3= Immersion time respectively. The coefficient in front of Temperature, Inhibitor concentration and immersion time, represent the linear coefficient while coefficient in front of $X_1 * X_2, X_1 * X_3$ *and* $X_2 * X_3$ represent the interaction between factors and X_1^2, X_2^2 *and* ${X_3}^2$ represent the quadratic effect respectively.

The quadratic model for inhibition efficiency show that the models were significant since the F-value of 122.91 is high. Also, P-value for the quadratic model is less than 0.05, indicating that the model is statistically significant. The coefficient of determination (R^2) of the model were 0.9937 disclosed a good fit between predicted values and experimental data. High value of R^2 (near to 1) reveals good relationship between the calculated and observed results. The predicted (R^2) for CML extract reasonably agree with the adjusted R^2.

Table 3: ANOVA results for the study

(A)

ANOVA for Response Surface Quadratic model

Analysis of variance table [Partial sum of squares - Type III]

Source	**Sum of Squares**	**df**	**Mean Square**	**F Value**	**p-value Prob > F**	
Model	0.040	9	4.442E-003	122.91	< 0.0001	significant
A-temp	*4.805E-004*	*1*	*4.805E-004*	*13.29*	*0.0082*	
B-conc	*1.513E-003*	*1*	*1.513E-003*	*41.85*	*0.0003*	
C-time	*5.000E-003*	*1*	*5.000E-003*	*138.34*	*< 0.0001*	
AB	*8.281E-003*	*1*	*8.281E-003*	*229.12*	*< 0.0001*	
AC	*6.084E-003*	*1*	*6.084E-003*	*168.33*	*< 0.0001*	
BC	*4.000E-004*	*1*	*4.000E-004*	*11.07*	*0.0126*	
A^2	*0.014*	*1*	*0.014*	*395.28*	*< 0.0001*	
B^2	*9.161E-004*	*1*	*9.161E-004*	*25.35*	*0.0015*	
C^2	*2.792E-003*	*1*	*2.792E-003*	*77.24*	*< 0.0001*	
Residual	2.530E-004	7	3.614E-005			
Lack of Fit	*2.530E-004*	*3*	*8.433E-005*			
Pure Error	*0.000*	*4*	*0.000*			
Cor Total	0.040	16				

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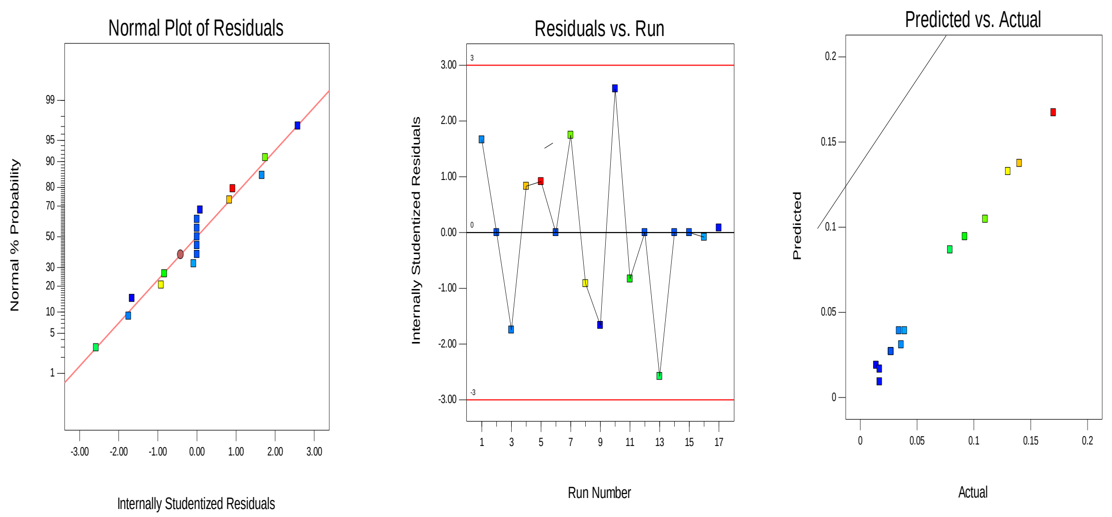
Response (B)

Std. Dev.	6.012E-003	R-Squared	0.9937
Mean	0.060	Adj R-Squared	0.9856
C.V. %	10.09	Pred R-Squared	0.8994
PRESS	4.048E-003	Adeq Precision	34.267
-2 Log Likelihood	-140.72	BIC	-112.38
		AICc	-84.05

There is correlation and high dependence between the observed and predicated values of the response [12]. "Adeq Precision" of 34.267 indicates an adequate signal for the model. The coefficient of variation (CV) and standard deviation (SD) indicates the degree of precision. Low values of CV and SD show the adequacy with which the experiment was conducted. In this current study, CV value of 10.09 and SD value of 6.012E-003 was adequate for the model.

B) Test for Significant of Regression

Normalization plots shown in Figure 1 helps to justify the satisfactory nature of the developed model. Figure 1a shows the normal probability plot. The data were plotted against a theoretical normal distribution such that the points should form a straight line and a parting from this line would indicate a departure from a normal distribution. From the result, the data points are slightly deviating from the normal distribution given, but not very acute [13]. Again, the second plot of residuals versus the fitted value (Figure1b) shows that the data points are scattered randomly and does not form a trend. However, all the data points in the plot are within the boundaries marked by the red lines. Therefore, there are no outlier data. Finally, the predicted versus the actual (Figure 1c), the data point are distributed randomly on the 45 degree line, indicating that the model provides an acceptable fit for the experimental data. The data also indicate an adequate agreement between experimental data and the output from the model [14].



(a) (b) (C)

Figure 1: Normalization plots: (a) Normal plot of residual, (b) residual vs runs and (c) predicted vs actual

Figures 2 and 3 show the 3-D surface respectively. The response surface plots are the graphical representative of the model used to visualize the relationship between the response and experimental data. The curvilinear profile of the 3D plots in Figures 2 are in accordance with the quadratic models.

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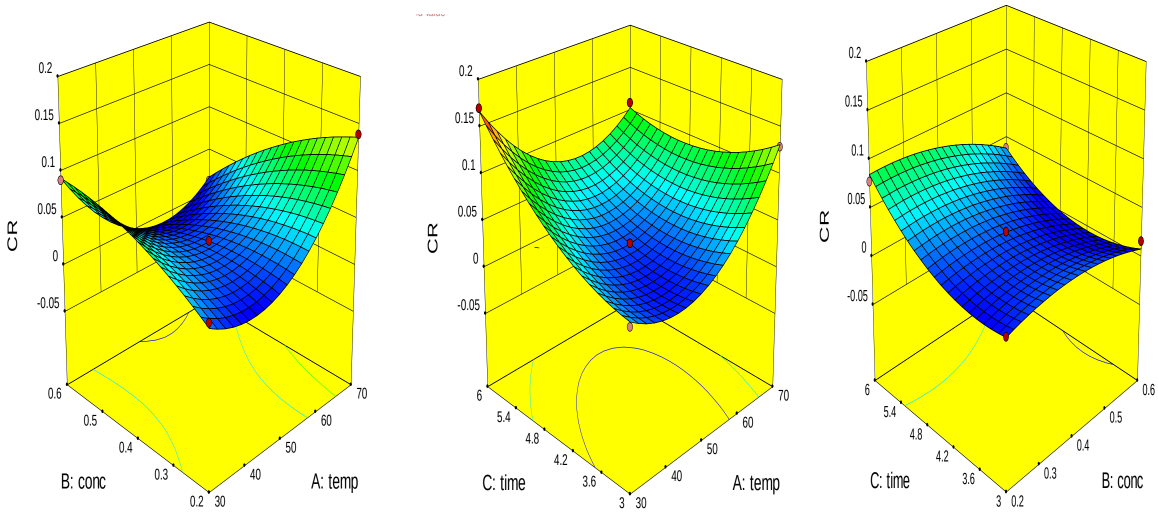
C) Optimization using the Desirability Functions

The optimization process was done to find out the values of the optimal variables that would provide high inhibition efficiency of CML extract. The result of the optimization study has been illustrated in Figures 3 and 4 showing the surface, and ramp plot for optimization of chosen factors within range and maximized response. A desirability function was used to explore the optimum conditions of three variables, which are temperature, inhibitor concentration and immersion time. The input variables were given specific values, using the desirability function in the software under BBD to be optimized in order to maximize the response inhibition efficiency (Figure 3). Using these conditions, the maximum achieved SP removal was 88.21% at temperature of 69.99°C, inhibitor concentration of 0.537g/l and immersion time of 3hrs with desirability of 1.00 for CML extract.



(a) (b) (C)

Figure 2: Surface plots of (a) inhibitor concentration versus temperature, (b) time versus temperature and (c) time versus inhibitor concentration

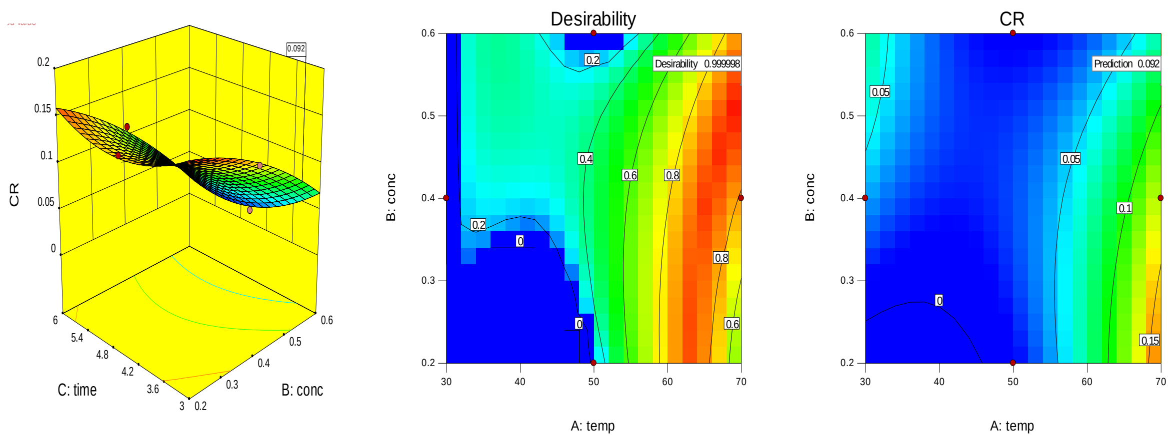


Figure 3: Desirability fitted 3D surface and contour plots for optimization of inhibitor concentration and temperature

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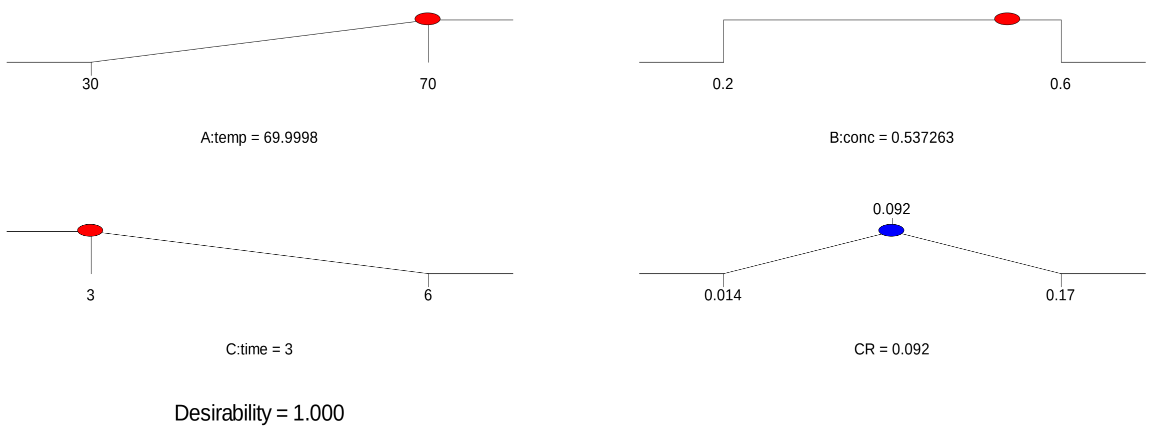

Figure 4: Desirability ramp of optimized inhibition efficiency of CML extract

IV. CONCLUSION AND FUTURE WORK

This work has demonstrated the application of RSM in obtaining optimal conditions for this process with respect to corrosion inhibition efficiency. RSM using BBD was applied to evaluate effects of temperature, inhibitor concentration and immersion time on the inhibition effective effectiveness, and then determine the optimum conditions. The results showed that the three factors considered in this study performed actively in corrosion inhibition process. The optimum conditions obtained for temperature, inhibitor concentration and immersion time were69.998°C, 0.537g/l and 3 hrs. This demonstrates that RSM can be successfully applied for modeling and optimizing the corrosion inhibition process and it is the economical way of obtaining the maximum inhibition efficiency information within a very period and with the least number of experiments. Conclusively, the *Calopogonium mucunoides* leaf extract proved to be an excellent and efficient inhibitor of mild steel in alkaline solutions.

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