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Use of Experimental Designs to Evaluate the Influence of Ziziphus Leaves Extracts as a Corrosion Inhibitor for Mild Steel in (3.5 M) NaCl

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Abstract

In this study, a full factorial experiment was designed to study the effect of three variables (immersion time, inhibitor concentration, and solution temperature) on the corrosion rate of mild steel by calculating the optimum inhabitation efficiency of extract of Ziziphus plant leaves in 3.5 NaCl solution at (25-35) Cº. In this experiment, one response recorded that was the determination of the inhibitor efficiency with the respect to the lose in weight recorded before and after the mild steel immersed in the inhibitor solution. The design of experiments used to investigate the best conditions required to increase the inhibitor efficiency for the mild steel existed in the corrosive media by using the tested inhibitor. Also, it introduces a new statistical approach to optimize the efficiency of new chemical inhibitors by using further analysis and tests, such as the ANOVA test.

Clearly, this paper attempted to investigate the best conditions for the use of acid extracts of leaves - Ziziphus plant as a new corrosion inhibitor for the mild steel by employing the experimental design method. The results showed that the extract solution of Ziziphus plant is an excellent corrosion inhibitor for the mild steel at specific conditions.

Keywords: experimental designs, corrosion inhibition, regression analysis, two levels factorial designs.

INTRODUCTION

In every single industry there are different plans to prevent failure, corrosion prevention plan is the most important whenever liquid – metals are existed in one system. Corrosion inhabitation requires profound study the operation conditions and material properties to set the control parameters that can help to reduce the ecological risk of corrosion (Aoki, Guedes, & Taqueda, 1998), (Naderi, Mahdavian, & Attar, 2009), (Bueno, Taqueda, de Melo, & Guedes, 2015). Corrosion inhabitation process with single or mixed inhibitors are the focus of researchers to reach better inhabitation efficiency with lower cost (Malik, Hashim, Nabi, Al-Thabaiti, & Khan, 2011), (Prathibha, Kotteeswaran, & Bheemaraju, 2013). However, a literature survey revealed that most of the conducted researches discussed the effect of using only one or two inhibitors and only a few discussed using three inhibitors.(Alexander & Moccari, 1993).

Experimental Design is a statistical tool that can be used to reduce the number of experiment with high quality conclusion. The relationships among all the experiments input and output factors can be studied with the respect of the correlation relationship between them as well as their impacts on the output responses (Silva, Camargo, & Ferreira, 2011), (Montgomery Douglas, 2001). In the most cases, the traditional method can be used to identify and determine predominant factors, but sometimes it is difficult to determine the optimum value of common working parameters without measuring the interactions between them (Nkuzinna et al., 2014). Therefore, using Design of Experiments (DOE) is a better alternative to study the effect of variables and their responses with minimum number of experiments with ability of measuring the interaction between different factors (Montgomery, 2009), (Silva et al., 2011). Two or more factors can be evaluated simultaneously by using a combination of their levels which are widely implemented in different fields but still limited in corrosion experimental studies (Mesquita, Nogueira, & Bastos, 2011).

ANOVA analysis is a useful statistical technique based on variance which can be used to determine whether or not significant differences exist among the means of several groups of observation. ANOVA has been used in order to determine the effect of inhibitor concentration, temp, and immersion time on inhibition efficiency. (Jayakumar Ramakrishnan, Kaleekal Janardhanan, Sreekumar, & Parayil Mohan, 2014) (Colas, Robledo, Martínez-Villafañe, & Almeraya-Calderón, 2012).

EXPERIMENTAL PART PRACTICAL

Specimens Preparation (Previous Work)

The analysis of mild Steel specimens of chemical composition is given in Table 1, obtained from petrochemical Industry Limited, Basrah, Iraq. The specimens were prepared into coupon size of 2 cm x 5.0 cm of thickness 1.00 mm mechanically polished with emery papers of 150, 300 and 600 grade, washed in double distilled water and finally dried. The cleaned specimens were weighed before and after immersion in 3.5 M NaCl for different durations in the absence and presence of various concentrations of the inhibitors at different temperatures in the range of 25-35 Cº.

Table 1: The Analysis of Mild Steel Specimens – Chemical Composition

Elements	% of Chemical composition
Carbon	0.14
Silicon	0.03
Manganese	0.32
Sulphur	0.05
Phosphorus	0.20
Nickel	0.01
Copper	0.01
Chromium	0.01
Iron	Balance

Preparation of plant extract:

In this work, the leaves were collected, dried and powdered in 150 g of dry Ziziphus leaves, then an appropriate solvent (deionized water) was added, and the mixture heated until boiling subsequently the mixture was cooled for 24 hours and then filtrated. The extract was placed in a standard flask (250 ml capacity) and DT water was added. From the stock solution, a series of diluted solutions in 3.5 M NaCl were prepared with concentrations ranging from 0.5 to 2 g/l.

Weight-Loss Method:

3.5 M NaCl electrolytes that used in experiments was prepared by dissolving 204.75 grams of NaCl salt in 1.0 liter distilled water. The solution was stirred until the salt particles were completely dissolved. Mild steel specimens were immersed in 100 ml of the tested solution, with and without the extracts of different concentrations. specimens weights were determined before and after immersion by using a Digital Balance (Model AUY 220 SHIMADZU). The corrosion rate (*C.R*) was evaluated using the formula proposed by Krisher (Krisher, A. S., 2006).

$C.R\ (mm/yr) = 87.6\ W / DAt$ ………………………………… (1)

$IE = 100\ [1-(C.R_2/C.R_1)]\ \%$.. ....(2)

The degree of surface coverage Θ for different concentrations of the inhibitor has been evaluated from weight loss using equation 3

$\Theta = 1-(C.R_2/C.R_1)$……………………………………… (3)

This procedure was repeated for a variety of inhibitor concentrations ranging from 0.5 to 2 g/l and at temperatures ranging from 25 - 35˚C.

Design of Experiments Strategy:

Since the implementation of experimental design in this study is important to identify the significant factors that impact the efficiency of the tested inhibitor, an experimental design matrix created with the following assumptions:

1- Full factorial design with three factors (immersion time, inhibitor concentration, and temperature of the solution).

2- Each factor has two levels (high level and low level).

The following characteristics of the practical study need designing a new matrix (mixed), which is created by using Minitab 16 Software (2^k factorial design):

1- The concentration factor has four levels (0.5, 1, 1.5, and 2) g/l.

2- Immersion time factor also has four levels (72,144,216, and 288) hrs.

3- Temperature factor has four levels (298,305, and 310) K^0.

The general polynomial model of the second degree is established to quantify the influence of the specified factors on tested inhibitor from prospective of inhibitor efficiency:

$Y = b0 + b1X1 + b2X2 + b3X3 + b12X1X2 + b13X1X3 + b23X2X3 + b11X1^2 + b22X2^2 + b33X3^2$

Where:

X_1, X_2, and X_3: independent variables representing the concentration of inhibitor, immersion time, and temperature.

b_0: constant, b_1, b_2, and b_3: coefficients reflecting the effect of factors X_1, X_2, and X_3.

b_{12}, b_{13}, and b_{23}: coefficients reflecting the interaction between two factors X_1X_2, X_1X_3, and X_2X_3.

b_{11}, b_{22}, and b_{33}: coefficients reflecting the influence quadratic X_1, X_2, and X_3.

Study Area:

The field of variation of 3 studied experimental factors was selected in order to approach the natural conditions which can be met in experimental field. Practically, the various levels were expressed in a system of coded variables which were presenting the actual efficiency values at different factor levels. The correspondence between real variables and coded ones was done starting from the following equation:

$$X_j = \frac{U_j - U_j^o}{\Delta U_j}$$

Where: X_j = value of the variable factor in J-coded; U_j= corresponding value of factor j in natural variable; and U_j^o = central value in the field of variation:

$$\Delta Uj = \text{Variance pace } \Delta Uj = \frac{U_j^{\max} - U_j^{\min}}{2}$$

All fields of variation for the 3 studied factors are warranted in the following table:

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Table 2: Factors Values at Low and High Level

Factor No.	Name	Unit	Low Level	High Level
1	Concentration of Inhibitor	g/l	0.5	2
2	Immersion Time	hr.	72	288
3	Temperature	K^O	298	310

Experimental Response:

The only experimental response followed in the current study was the inhabitation efficiency of mixtures E%; it is calculated by using the following equation:

$$E\% = (\frac{V_0 - V}{V_0}).100$$

Where: V0 and V are the weight loss of steel without and with inhibitor/ mixtures respectively.

Used matrix:

Table (3) displays the mixed matrix that was designed by using Minitab 16 software. All experiments were achieved in duplicate, with or without studied inhibitor. A point was also added to the center of the domain that was achieved in triplicate. The use of factor coding relations permitted to transform the experience matrix in design of experimentations that were expected to be fulfilled. Reponses measured for the inhibitor efficiency of different mixture were represented in Table (3).

RESULTS AND DISCUSSIONS

Statistical analysis is very important for results interpretation. This analyses including estimating, least square method, coefficients determination through regression analysis, calculating different gap between the observed values and values foreseen by the model were achieved. Tests of multiple regressions lead to development of mathematical model and permitting the inhibition reaction's efficiency simulation as a function of three studied factors in tentative domain of interest:

Regression Model:

Efficiency = 629.236 - 141.535 X_1 + 0.08125 X_2 -1.91972 X_3 - 0.017963 X_1X_2 + 0.509862 X_1X_3

Table 3: Factorial Design Matrix

X1	X2	X3	X1X2	X1X3	X2X3	Effeciency
1	1	1	2	2	2	64
2	1	1	1	1	2	57
1	2	1	1	2	1	45
2	2	1	2	1	1	73
1	1	2	2	1	1	65
2	1	2	1	2	1	53
1	2	2	1	1	2	77
2	2	2	2	2	2	70
1	1	1	2	2	2	60
2	1	1	1	1	2	80
1	2	1	1	2	1	75
2	2	1	2	1	1	66
1	1	2	2	1	1	70
2	1	2	1	2	1	66
1	2	2	1	1	2	50
2	2	2	2	2	2	78
1	1	1	2	2	2	70
2	1	1	1	1	2	62
1	2	1	1	2	1	83
2	2	1	2	1	1	74
1	1	2	2	1	1	70
2	1	2	1	2	1	84
1	2	2	1	1	2	80
2	2	2	2	2	2	74
1	1	1	2	2	2	77
2	1	1	1	1	2	70
1	2	1	1	2	1	53
2	2	1	2	1	1	81
1	1	2	2	1	1	75
2	2	2	2	2	2	64
1	1	2	2	1	1	85
2	1	2	1	2	1	77
1	2	1	1	2	1	73
2	2	1	2	1	1	87
1	1	1	2	2	2	80
2	1	1	1	1	2	76
1	2	2	1	1	2	81
2	2	2	2	2	2	74
1	1	2	2	1	1	60
2	1	2	1	2	1	84
1	2	1	1	2	1	77
2	2	1	2	1	1	69
1	1	1	2	2	2	87
2	1	1	1	1	2	82
1	2	2	1	1	2	76
2	2	2	2	2	2	89
1	1	2	2	1	1	85
2	1	2	1	2	1	78

VALIDITY OF THE MODEL AND RESULTS

The statistical analyses that led to the validity of the model are displayed as variance analyses in Table (4). This table provides the percentage of variance explained by the mathematical model in comparison to the variance contained within the experimental results. From the results obtained by the variance analysis, any probability value smaller than < 0.05 is confirmed the validity of the suggested model.

Table 4: Statistical Validation – Minitab 16 outputs

Analysis of Variance for efficiency (coded units)

Source	DF	Seq SS	Adj SS	Adj MS
Main Effects	3	4609.72	4534.54	1511.51
Concentration	1	1622.40	1562.64	1562.64
Immersion time	1	1075.27	1059.85	1059.85
Temperature	1	1912.05	1912.05	1912.05
2-Way Interactions	3	131.49	132.88	44.29
Concentration*immersion time	1	31.36	32.75	32.75
Concentration*temperature	1	94.45	94.45	94.45
Immersion time*temperature	1	5.68	5.68	5.68
3-Way Interactions	1	4.02	4.02	4.02
Concentration*immersion time*temperature	1	4.02	4.02	4.02
Residual Error	40	238.02	238.02	5.95
Total	47	4983.25		

Source	F	P
Main Effects	254.01	0.000
Concentration	262.61	0.000
Immersion time	178.11	0.000
Temperature	321.32	0.000
2-Way Interactions	7.44	0.000
Concentration*immersion time	5.50	0.024
Concentration*temperature	15.87	0.000
Immersion time*temperature	0.95	0.335
3-Way Interactions	0.67	0.416
Concentration*immersion time*temperature	0.67	0.416

Interpretation:

From Anova analysis, both three way interactions and interactions between X_1X_3 factors are not significant because the P-value is higher than (0.05); indicating there is no inter-correlation between the concentration and immersion time.

Graphic Analysis of the Model:

Now, it is important to validate the results of this study and present them graphically with respect to inhibitor efficiency and the most significant factors that were highlighted from data analysis as it can be noticed in the following figures, the main effects plot for the efficiency showed that the highest inhibitor efficiency can be obtained when the significant factors have the following values:

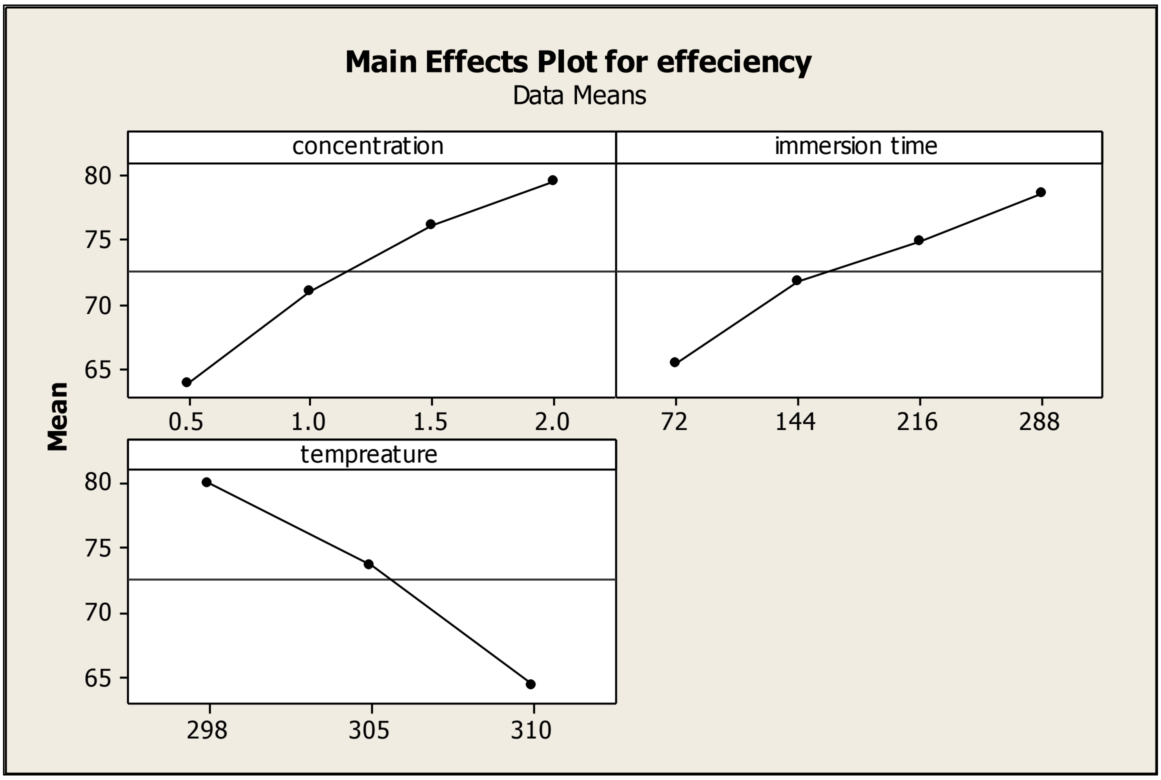

Figure 1: Main Effect Plot for Inhibitor Efficiency

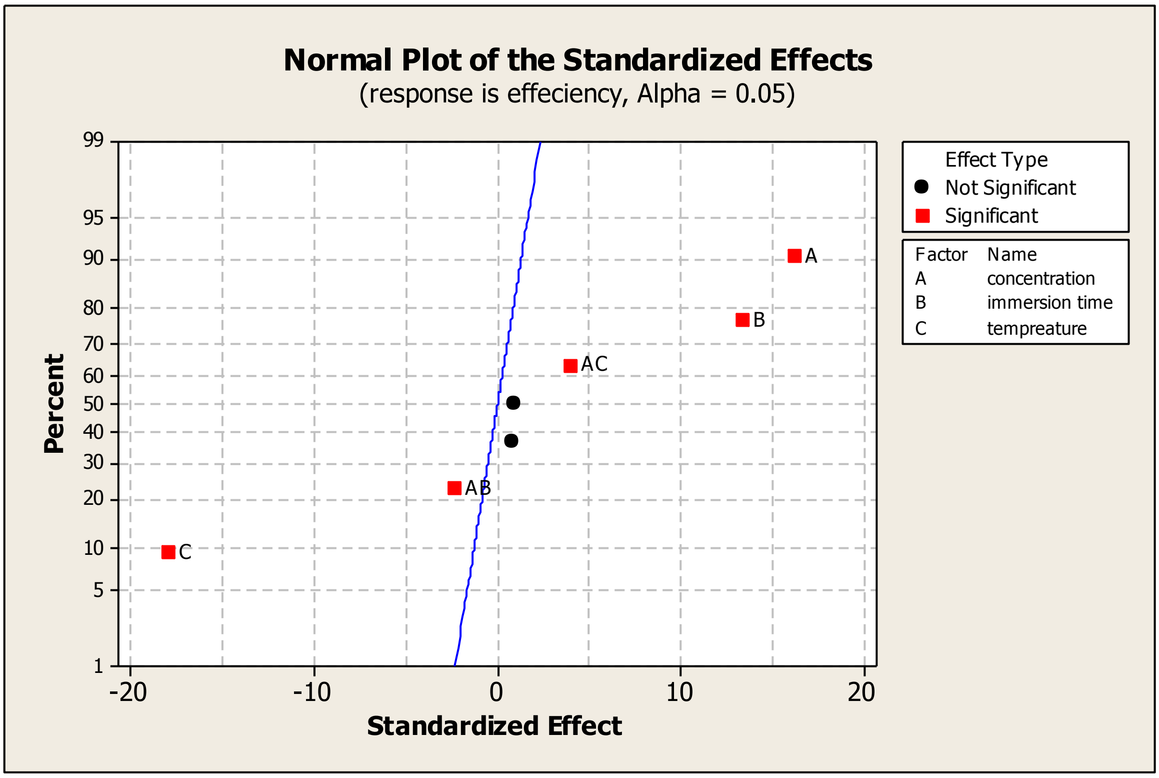

Figure 2: Normal Plot of the Standardized Effects

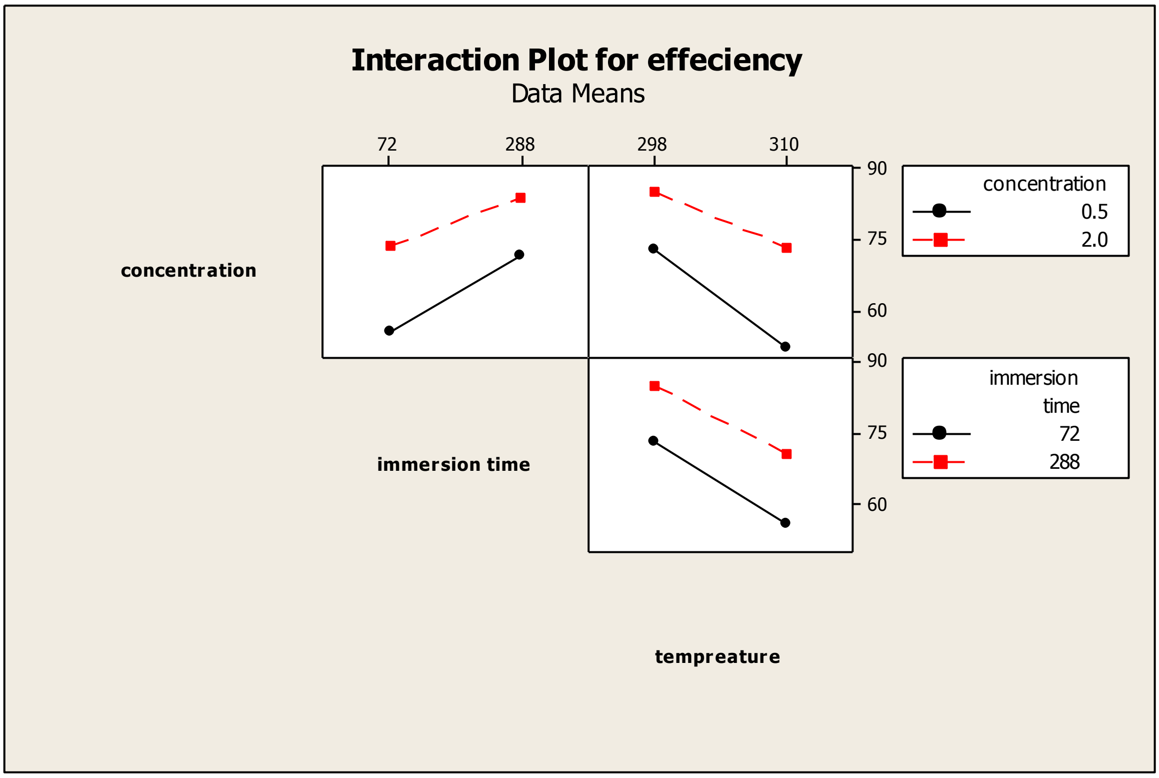

Figure 3: Interaction Plot for Efficiency

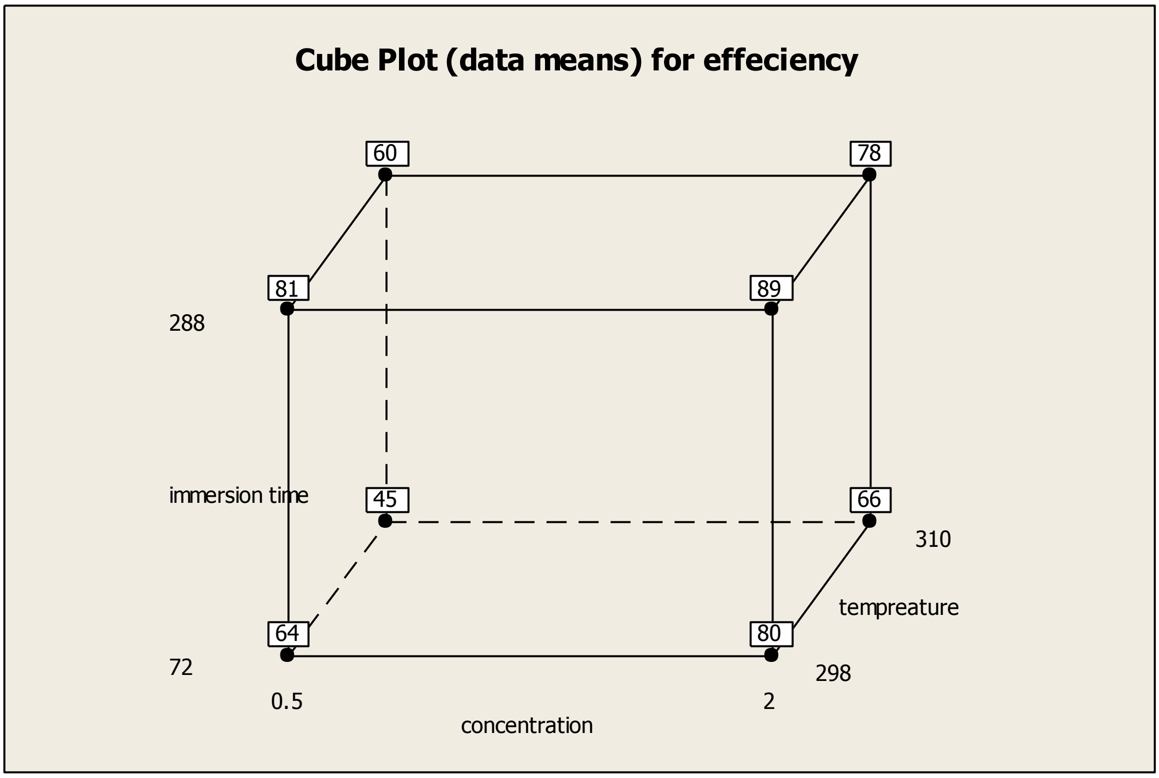

Figure 4: Cube Plot (Data Means) for Efficiency

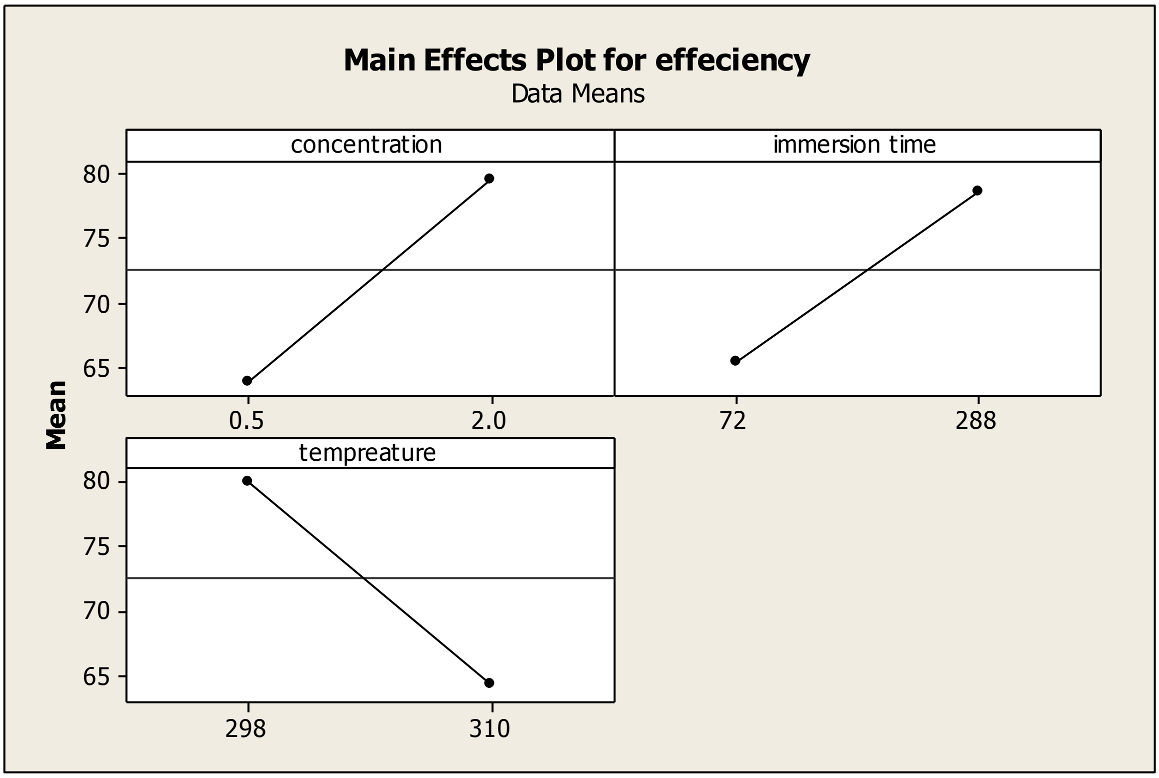

Figure 5: Main Effects Plot for Efficiency

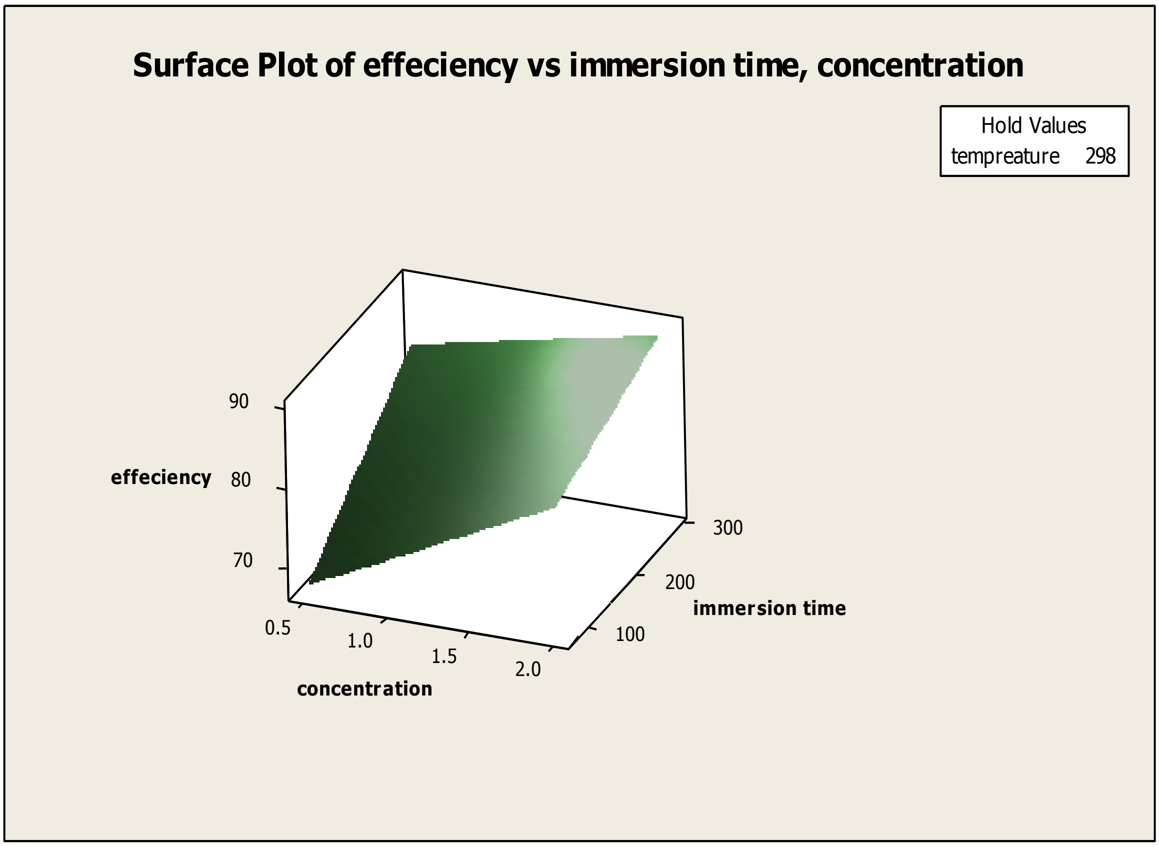

Figure 6: Surface plot of Efficiency vs. Immersion Time and Concentration

CONCLUSIONS

In this study, the experimental design was conducted to study the corrosion inhabitation efficiency of a mild steel in 3.5 M NaCl by using acid extract of leaves of Ziziphus plant under various independent variables. These variables were immersion time, inhibitor concentration and medium temperature. It showed that employing design of experiment was possible to study the effects of the variables on corrosion rate. A full factorial design was successfully used for experimental design and analysis by using Minitab 16 software. By solving the regression equation with the help of the 3-D plots, it was possible to locate the optimum variables levels. The optimum inhibition concentration, time and temperature were 2 g/L, 288 h and 298 K, respectively with inhabitation efficiency equals to 89% as an optimum response recorded at each tested level.

Indeed, the study showed that factorial design of experiment is an efficient tool for predicting the effects of independent variables on the process responses. Also, From ANOVA analysis, both the three way interactions and interactions between X_1X_3 (Inhibitor Concentration and Immersion Time) factors are not significant because the P-value more than (0.05); And that indicates there is no inter-correlation between both the concentration and the immersion time.

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