Anal. Bioanal. Electrochem., Vol. 7, No. 6, 2015, 701-718

Analytical & Bioanalytical Electrochemistry

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Full Paper

Optimization of Corrosion Inhibition of Mild Steel by Ethanol Extract of Prosopis Juliflora in HCl Medium using Factorial Analysis

Thiruvengadam Venugopal,* Kolanthi Kannan and Nasarullnah Zulfareen

Department of Chemistry, Government College of Engineering, Salem-636011, India

* Corresponding Author, Tel.: +919381325813

E-Mail: t.venu1973@gmailcom

Received: 11 August 2015 / Received in revised form: 27 November 2015 / Accepted: 3 December 2015 / Published online: 31 December 2015

Abstract- Inhibition of corrosion of mild steel by ethanol extract of Prosopis Juliflora was studied by both potentiodynamic method and weight loss method. A 2^4 full factorial design was performed to determine the optimal condition of corrosion inhibition and to determine the variable which affects the inhibition of corrosion of mild steel by the ethanol extract of Prosopis Juliflora. The variable that was studied were concentration of the medium (HCl, 0.1 M and 1 M), concentration of the inhibitor (100 ppm and 700 ppm), temperature (303 K and 333 K) and time (1h and 5 h). A linear mathematical model was applied to the experimental results, to determine the effect of each variables and their relationship were determined. Statistical analysis such as ANNOVA (Analysis of Variance), F-test and student t-test, surface analysis were carried out in experimental data and the results indicated that the effect of the temperature is greatest followed by the concentration of the inhibitor and least effect was shown by the concentration of the time. Concentration of medium on the corrosion inhibition of mild steel by ethanol extract of Prosopis Juliflora was found to show a negative effect. The statistical model was found to have most excellent fit with high coefficient of determination (R^2=0.997) for the inhibition of corrosion. The effect of the factor on the Corrosion inhibition was also investigated by the response surface methodology (RSM) based on Box-Behnken design (BBD).

Keywords- Factor analysis, Prosopis juliflora, t-test, ANNOVA

1. INTRODUCTION

Inhibition of corrosion is considered as one of the vital importance for the industries as yearly millions of dollars was lost due to the corrosion and its related activities. So inhibition of corrosion becomes vital and absolute necessary as almost all the industries use metal and/or alloys. Various synthetic inhibitors were used to prevent corrosion, the main functional group that should be present in such inhibitors are Nitrogen, oxygen or sulfur. These synthetic inhibitors are hazardous to the human which may cause health hazard and are also costly and difficult to synthesis in large scale [1-3]. So search for ecofriendly and cheap inhibitor has led to use of different plant extract. The plant extract may contain various functional groups which can inhibit the corrosion. Various authors have used different plant extracts for the inhibition of corrosion [4-7].

Plants contain many bioactive constituents like terpenes, alkaloids, flavonoids and phenolic compounds [8-10] these compound can be extracted by various solvent and these compounds are soluble in acid and invariably contains hetero atom like nitrogen or sulfur which can act as corrosion inhibitor. Prosopis Juliflora is a member of Leguminosae family, which was found in arid and semi-arid regions of India. The plant is not of much commercial use and is found in the barren land all over India. In the present study corrosion protection is carried out using the ethanol extract of seeds of Prosopis Juliflora as corrosion inhibitor on mild steel. Statistical technique is used for the first time to analysis the optimum condition using four variables. Extensive survey of literature has indicated that there is no work report on optimization of corrosion parameter using ANNOVA and t-test. So in this study four parameters namely temperature, concentration of inhibitor, time and concentration of the acid medium were analyzed using ANNOVA, t-test, F-test and surface response plot and optimization of the experimental data was carried out.

2. MATERIALS AND METHODS

2.1. Plant Material

Plant material (seed and skin) of Prosopis Juliflora was collected from the arid areas of India. The plant material was washed thoroughly in tap water and dried in an oven for 48 h at 50 ˚C. The dried material was beached to form fine powder and filtered through the sieve and it is stored in refrigerator at 5 ˚C.

2.2. Preparation of Extract

400 grams of the dried seeds of powdered Prosopis Juliflora was taken in a round bottomed flask and ethanol is added until the plant material was fully immersed in the solvent. The whole setup was kept for 8 hours with constant shaking. The entire process was

repeated for two to three times until the supernatant i.e., the extract was collected and pooled together. Finally the extract was concentrated in a rotary evaporator at 54 °C and it is kept in air tight bottle at 5 °C. (Shachi singh, 2012). 1 g of the extract is weight accurately in 1 L flask and dissolved in required concentration of HCl (1 M or 0.1 M) and made up to the mark with the same solution. From this stock solution required amount of concentration was diluted and used for the analysis.

2.3. Specimen preparation

Mild steel having a composition of Fe: 99.75%, Mn: 0.01%, Cu: 0.01%, Si: 0.02%, P: 0.02% and C: 0.18% is used in this work. The specimens of dimension 5 cm 1.5 cm width are used. The specimens were polished using 1/0, 2/0, 3/0 and 4/0 grade emery papers and pickling solution was used to wash the mild steel till the metal is clear and washed with distilled water, acetone and kept in oven for immediate usage.

2.4. Weight loss method

Mild steel is used here because the percentage of iron is more in mild steel, which enhances the corrosion rate in industries. Here by adding the methanol extract the Prosopis Juliflora the inhibition efficiency of mild steel increases with increase in concentration, temperature by minimizing the rate of corrosion. Weight loss methods were carried out by weighing the specimens before and after immersion in 1 M HCl in the absence and presence of inhibitor. From the initial and final mass of the specimen, the weight loss was calculated. From this weight loss value, inhibition efficiency (IE) and corrosion rate were determined.

$$\mathrm{I.E\ (or)}\eta\ \% = \frac{\Delta \mathrm{Wu} - \Delta \mathrm{W\,i}}{\Delta \mathrm{Wu}} \times 100 \quad (1)$$

$$\mathrm{CR(mmpy)} = \frac{87.65 \times \Delta \mathrm{W}}{\mathrm{A} \times \mathrm{T} \times \mathrm{D}} \quad (2)$$

$$\theta = \frac{\Delta \mathrm{Wu} - \Delta \mathrm{W\,i}}{\Delta \mathrm{Wu}} \quad (3)$$

Where, ΔW_u, ΔW_i Weight loss of the metal in the absence and presence of inhibitor.

2.5. Electrochemical studies

The surface of electrode is prepared by taking mild steel specimen of an area of 1 cm and embedded with Teflon coating. The coated mild steel was polished with1/0, 2/0, 3/0 and 4/0 grade emery papers and degreased with acetone before usage.

2.6. Electrode cell assembly

Electrochemical workstation (CH instruments) Model 608 D/E Series was used for polarization and AC Impedance studies. Three electrode systems was used for this purpose, Platinum electrode acts as an auxiliary electrode ,saturated calomel electrode (SCE) act as a reference electrode and mild steel of an area of 1 cm was used as working electrode.

2.7. Procedure and calculation

In Electrochemical workstation, polarization and AC Impedance was carried out in the presence and absence of inhibitor and the readings were recorded from these values the percentage of inhibition efficiency and the degree of surface coverage θ was calculated [3]:

$$\text{I.E (or) } \eta\,\% = [1 - (i'\,\text{corr} / i\,\text{corr})] \times 100 \qquad (4)$$

Where, i'_{corr} and i_{corr} are the corrosion current density of mil steel in the absence and presence of inhibitor.

After polarization measurements electrochemical impedance was carried out by varying the frequency from 100 MHz to 100 KHz (Musa et al., 2009). The following equation is used to calculate inhibition efficiency (η%) and double layer capacitance (Cdl) of BFC was calculated by

$$(\eta\,\%) = \frac{R^{i}_{ct\,1} - R^{0}_{ct\,1}}{R^{i}_{ct\,1}} \qquad (5)$$

$$Cdl = \frac{1}{2 \times 3.14 \times f_{max} \times R_{ct}} \qquad (6)$$

Where $R^{0}_{ct\,1}$ and $R^{i}_{ct\,1}$ is charge transfer resistance in the absence and presence of BFC, f_{max} is the frequency and Rct are the charge transfer resistance.

2.8. Screening Method

Prosopis Juliflora extract was subjected to phytochemical screening and the following test for alkaloids, flavonids, terpenes, tannin, saponin, phenolic compounds was carried out and the results were shown in Table 1.

2.9. Statistical Technique

Inhibition of corrosion depends upon many criteria such as the concentration of the acid, concentration of the inhibitor, temperature and time. Normally experiments were carried out in which only one factor like concentration of the inhibitor, is varied at a time while the other factors remains constant. The optimum amount of that factor (like concentration of the inhibitor) is fixed and the other factors are varied one by one and the optimum level of the inhibitions is then found out. This method of finding the optimum condition is time consuming and sometime leads to results which are not correct, since some factor may be optimized incorrectly [12, 13].

Table 1. Phytochemicals present in the extract, obtained from the seed and skin of Prosopis Juliflora

Phytochemicals	Result
Alkaloid	+
Flavonids	+
Tannin	+
Phenol	+
Saponin	-
Amino acid	-
Terpenoid	+
Steroids	+
Carbohydrate	-

Mathematical model of analysis of the data were widely used in almost all field of science, to interpret the results got from the experiment and also to model the experiments and to find the optimum values. Many mathematical models are available for the interpretation and evaluating the results, Factorial analysis is one of the important method used by Chemist, Physicist and Biologist. Factorial analysis is used to interpret and evaluate results where there is no continuous link between the factors and the responses. Factorial analysis gives relation between the different factors which are not related to each other, thereby the dependency of the one factor over the other can be studied. Another important advantage of the factorial analysis is that not only individual parameter effects are studied but their relative importance in the given experiment can also be studied and the relation between other factors can be derived from the mathematical analysis. This is not possible by the classical corrosion inhibition analysis by varying one factor only. Factorial approach has an important advantage of minimizing the time, effort and cost of doing a lot of experiment (Although in this work lot of experiments were done for other reporting purposes). Here the main effect of the interaction of all the factor is important, and arrived equation will give the effect of the variation of the factor on the results of the analysis. Variance analysis and factorial design of the experiment are used to express the percentage of inhibition of the corrosion by the given inhibitor by a polynomial model.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic Polarization Studies

As the concentration of ethanol extract of Prosopis Juliflora increases the inhibition efficiency also increases with decrease in corrosion rate (Table 2 and Fig. 1). Corrosion parameters such as corrosion potential , anodic slope and cathodic Tafel slope, corrosion current, and inhibition efficiency were calculated (Table 2). It implies that, the addition of the inhibitor shifts the anodic polarization to more positive side and cathodic to more negative values. This implies that the addition of ethanol extract of Prosopis Juliflora reduces the anodic dissolution and the added ethanol extract of Prosopis Juliflora act as a mixed type inhibitor.

The i_{corr} values of inhibitor decrease with increase in inhibitor with a shift of E_{corr} to more negative potential. This indicates that, the ethanol extract of Prosopis Juliflora suppresses cathodic reaction predominantly than anodic process. The maximum inhibition efficiency of ethanol extract of Prosopis Juliflora was found to be 80.21% in 700 ppm at 60 °C. The inhibition efficiency of ethanol extract of Prosopis Juliflora obtained from the Tafel plot was good compared with the inhibition efficiency obtained from the weight loss method. Polarization curves of ethanol extract of Prosopis Juliflora in 1 M HCl at 60 °C was shown in Fig. 1.

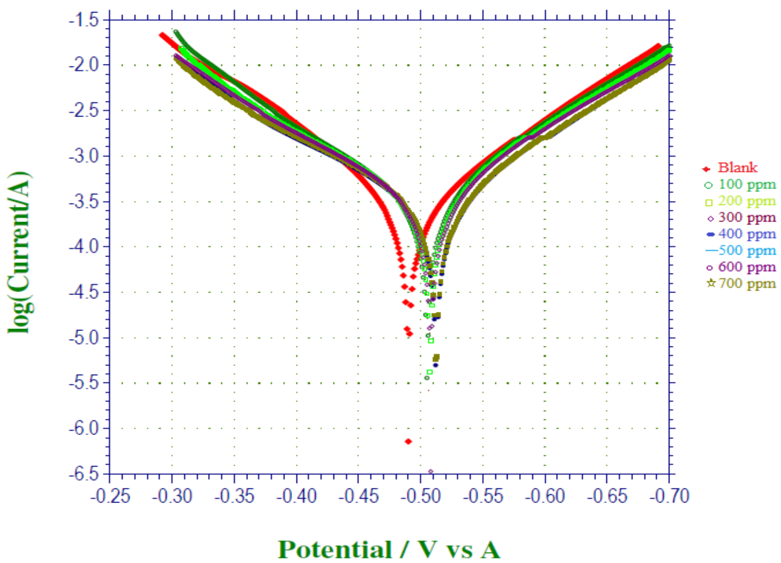


Fig. 1. Polarization curves of mild steel in 1 M HCl in the absence and presence of inhibitor at 60 °C

3.2. AC Impedance Study

The Nyquist plot for mild steel in 1 M HCl in the presence and absence of inhibitor was shown in Fig. 2. Impedance parameters derived from Nyquist plots were given in Table 3. From the table, it is observed that the value of charge transfer resistance (R_{ct}) increases with an increase in concentration of ethanol extract of Prosopis Juliflora. But the value of double layer capacitance (C_{dl}) decreased with increase in the concentration of inhibitor. The inhibition efficiency increases with increase in concentration of inhibitor. The maximum inhibition efficiency of ethanol extract of Prosopis Juliflora was found to be 83.33% in 700 ppm at 60 $^{\circ}$C. The impedance diagram has almost semicircular appearance due to the electrical double layer and charge transfer resistance, which indicates that the corrosion of mild steel is mainly controlled by the addition of the inhibitor (Figs. 2 & 3). The inhibition efficiency obtained from AC impedance method is in good agreement with the inhibition efficiency obtained from conventional weight loss and polarization method.

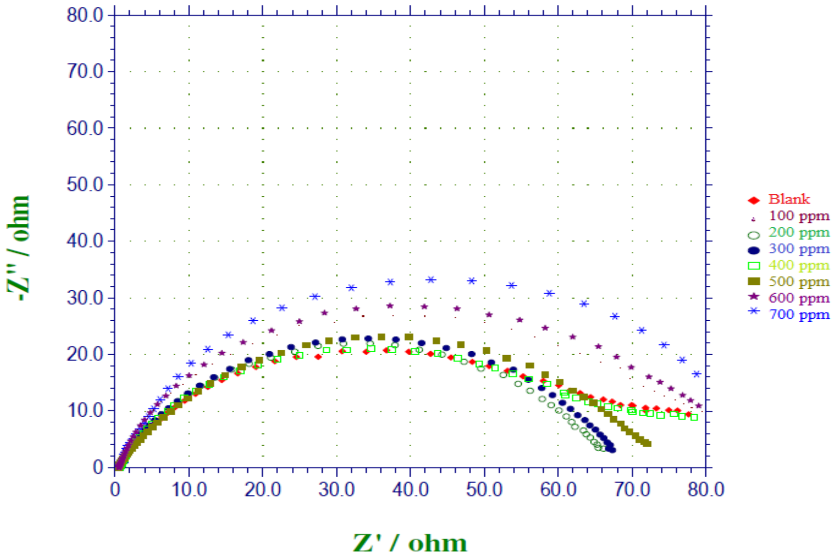
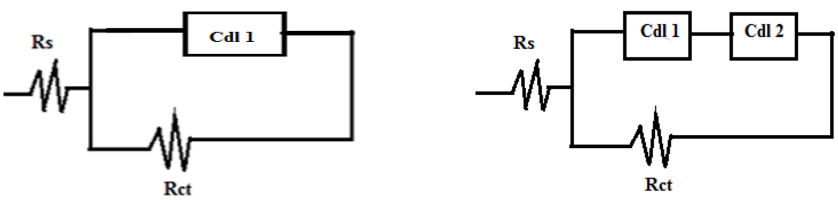


Fig. 2. AC impedance curves of mild steel in 1 M HCl in the absence and presence of inhibitor at 60 $^{\circ}$C



(a) **(b)**

Fig. 3. Equivalent circuit for mild steel in 1 M HCl in the (a) absence and (b) presence of inhibitor at 60 $^{\circ}$C

Table 2. Tafel polarization parameters for Mild Steel in 1 M HCl in the ethanol extract of Prosopis Juliflora from 30 ˚C to 60 ˚C

S.No.	Temp. (^{0}C)	Conc. of inhibitor (mM)	E_{corr} (V/SCE)	$-b_a$ (mV dec^{-1})	$-b_c$ (mV dec^{-1})	i_{corr} (mA cm^{-2})	IE%
1	30^{0}C	Blank	-0.471	6.85	7.02	3.458	-
		100	-0.502	11.63	11.8	1.651	52.27
		200	-0.525	10.54	10.71	1.649	52.32
		300	-0.547	11.77	11.94	1.552	55.12
		400	-0.551	11.10	11.27	1.375	60.23
		500	-0.567	11.62	11.79	1.341	61.23
		600	-0.578	11.82	11.99	1.310	62.12
		700	-0.589	12.04	12.21	1.651	64.32
2	40^{0}C	Blank	-0.454	5.663	5.833	5.821	-
		100	-0.456	6.631	6.801	2.614	55.10
		200	-0.458	6.178	6.348	2.438	58.12
		300	-0.454	8.817	8.987	2.314	60.24
		400	-0.462	8.875	9.045	2.200	62.21
		500	-0.466	9.957	10.127	2.005	65.55
		600	-0.47	13.25	13.42	1.739	70.12
		700	-0.476	12.66	12.83	1.529	73.74
3	50^{0}C	Blank	-0.421	6.307	6.477	8.785	-
		100	-0.434	6.128	6.298	3.677	58.14
		200	-0.439	8.695	8.865	3.502	60.14
		300	-0.447	13.30	13.47	3.236	63.17
		400	-0.454	13.81	13.98	2.976	66.12
		500	-0.46	11..68	11.85	2.625	70.12
		600	-0.461	8.105	8.275	2.264	74.23
		700	-0.464	8.113	8.283	1.893	78.45
4	60^{0}C	Blank	-0.411	5.681	5.851	9.546	-
		100	-0.424	7.897	8.067	3.321	65.21
		200	-0.425	11.32	11.49	3.128	67.23
		300	-0.43	12.92	13.09	2.874	69.89
		400	-0.436	10.91	11.08	2.566	73.12
		500	-0.439	10.17	10.34	2.061	78.41
		600	-0.445	10.33	10.5	1.889	80.21
		700	-0.456	13.15	13.32	1.602	83.22

A simple Randle’s equivalent circuit was fixed to fit the mechanism of inhibitor with charge transfer resistance (Rct), double layer capacitance (Cdl 1) (Cdl 2), and solution resistance (Rs).

Table 3. AC impedance parameters for Mild Steel in 1 M HCl in the ethanol extract of Prosopis Juliflora from 30 ˚C to 60 ˚C

S.No.	Temp. (˚C)	Conc.of inhibitor (mM)	Rct (ohm cm^2)	Cdl (ohm $\mu F/cm^2$)	I.E %
1.	30 ˚C	Blank	5.2	157.67	-
		100	10.95	88.62	52.52
		200	10.98	82.01	52.63
		300	11.56	78.99	55.01
		400	13.24	74.97	60.73
		500	13.67	72.06	61.96
		600	13.96	71.64	62.74
		700	14.85	68.57	64.98
2.	40 ˚C	Blank	7.5	202.12	-
		100	16.67	142.17	55.00
		200	18.23	121.16	58.85
		300	18.96	113.76	60.45
		400	20.08	110.58	62.65
		500	21.96	103.54	65.85
		600	25.73	101.38	70.85
		700	28.82	99.74	73.98
3.	50 ˚C	Blank	8.9	515.87	-
		100	21.32	308.15	58.25
		200	22.73	301.59	60.85
		300	24.64	296.19	63.88
		400	26.26	282.01	66.11
		500	30.20	274.02	70.53
		600	34.24	268.52	74.01
		700	40.92	257.51	78.25
4.	60 ˚C	Blank	10	595.77	-
		100	28.58	504.76	65.01
		200	30.49	488.25	67.20
		300	33.05	465.08	69.74
		400	37.30	435.45	73.19
		500	47.57	402.38	78.98
		600	51.33	386.77	80.52
		700	59.99	370.21	83.33

3.3. Statistical design and analysis

Statistical design with four independent variables which affect the corrosion are taken and coded as A, B, C and D at two levels of interval and 2^4 model is used to obtain the results in MINITAB 17 software. The high level was designated as +1 and the low level was designed as -1. (Table 4). Table 5 represents the factorial design of the analysis. % inhibition efficiency for both experiment and the predicted model are presented in the same table and it was found that experimental and predicted values are close to each other. So the model fits well for the inhibition of corrosion on mild steel by ethanol extract of Prosopis Juliflora extract.

Table 4. High and Low level of the experimental condition (Factors)

Experimental Condition (Factor)	Low Level (-1)	High Level (+1)	Code of the Factor
Temperature	303 K	333 K	A
Concentration of the Inhibitor	100 ppm	700 ppm	B
Time	1 h	5 h	C
Concentration of Acid	0.1 M	1 M	D

Table 5. Factorial design of the data and the predicted value of the data

Run No.	Coded values of independent variables				Inhibition efficiency (%)			
	A	B	C	D	Trail 1	Trail 2	Average	Predicted
1	-1	-1	-1	1	51.16	52.27	51.71	51.07
2	-1	1	-1	1	64.52	64.12	64.32	63.68
3	1	-1	-1	1	69.31	69.21	69.26	68.62
4	1	1	-1	1	83.72	84.01	83.86	83.22
5	-1	-1	1	1	54.17	53.19	53.68	53.04
6	-1	1	1	1	66.21	66.11	66.16	65.52
7	1	-1	1	1	69.82	69.81	69.81	69.17
8	1	1	1	1	84.01	84.25	84.13	83.49
9	-1	-1	-1	-1	59.86	59.44	59.65	59.01
10	-1	1	-1	-1	69.19	70.12	69.65	69.01
11	1	-1	-1	-1	75.12	76.12	75.62	74.98
12	1	1	-1	-1	89.11	88.75	88.93	88.29
13	-1	-1	1	-1	60.71	60.82	60.76	60.12
14	-1	1	1	-1	70.12	70.91	70.51	69.87
15	1	-1	1	-1	76.71	76.11	76.41	75.77
16	1	1	1	-1	90.12	90.53	90.32	89.68

Sixteen experiments were taken for the Factorial analysis from the wide data collected from the average value EIS (Electrochemical impedance spectroscopy), Polarization studies and weight loss method. The results of the all the methods were close enough hence average of the all the three has been taken for the statistical analysis. The sixteen experiments were duplicated for consistent results, other data of the experiments were used elsewhere.

The polynomial regression model used for the analysis of the results are given as

$$Yi=\lambda_o+\lambda_1X_{1i}+\lambda_2X_{2i}+\lambda_3X_{3i}+\lambda_4X_{4i}+\lambda_{12}X_{1i}X_{2i}+\lambda_{13}X_{1i}X_{3i}+\lambda_{14}X_{1i}X_{4i}+\lambda_{23}X_{2i}X_{3i}+\lambda_{24}X_{2i}X_{4i}+ \lambda_{34}X_{3i}X_{4i}+ \lambda_{123}X_{1i}X_{2i}X_{3i}+ +\lambda_{234}X_{2i}X_{3i}X_{4i} ++ \lambda_{124}X_{1i}X_{2i}X_{4i} + + \lambda_{134}X_{1i}X_{3i}X_{4i} + + \lambda_{1234}X_{1i}X_{2i}X_{3i}X_{4i} \quad (7)$$

Where Y_i is the predicted response from the model, X_{ji} (where j=1,2,3,4 and i=1,2 ……15,16) indicate the experimental variable in the coded form, λ_o is the constant which gives the average value of the results and λ_1, λ_2, λ_3 and λ_4 are the coefficient of the response and higher coefficient is the interaction between various factor, for example λ_{13} show the interaction between the concentration of the acid and temperature, λ_{123} show the interaction of the concentration of the acid, concentration of the inhibitor and the temperature.

In this study only two factors for each variable were considered and the percentage inhibition efficiency of the inhibitor was studied as a result of the change of factor from lower level to higher level. Since it refers to the major experimental factor of interest in this experiment it is commonly called as main effect.

The inhibition efficiency of the ethanol extract of Prosopis Juliflora can be expressed in the equation as

$$R=70.9259+8.8684\,A+6.3116\,B+0.5491\,C-3.0578\,D+0.7066\,A*B-0.1734\,A*C+0.0309\,A*D-0.0041\,B*C+0.4391\,B*D+0.0291\,C*D+0.0434\,A*B*C-0.2272\,A*B*D-0.1997\,A*C*D-0.0478\,B*C*D-0.0641\,A*B*C*D \quad (8)$$

Where R is the percentage efficiency of the inhibition of corrosion on mild steel by the ethanol extract of seeds of Prosopis Juliflora.

The positive value of the coefficient means that the increase in the factor (like concentration of acid, inhibitor etc.) leads to increase in the inhibition capacity of the ethanol extract whereas a negative indicates that the increase in the factor of the variable would decrease the inhibition capacity of the ethanol extract.

Table 6 gives the effects, regression coefficient, standard errors and t value of the experimental data. It can be inferred from the table that the coefficient were found by dividing the net effect by two. When regression coefficient is divided by standard error, standardized effect is obtained.

3.4. Student t-test

Student t-test can be considered as statistically important method to determine whether the calculated main and interaction effects varies significantly from zero. The data of the result of the t-test was shown in Table 3 and Pareto chart (Fig. 4) can provide valuable information of the main effects and interaction of various variables. At 95% confidence level and sixteen degree of freedom, it was found that value variable or the interaction between the variables should be more than 2.1 (i.e. t>2.1) to make a significant contribution to inhibition of corrosion.

Table 6. Statistical parameter of 2^4 factorial design

Term	Effect	Coefficient	Standard error	t-value
Constant		70.9259	0.0756	938.42
A	17.7369	8.8684	0.0756	117.34
B	12.6231	6.3116	0.0756	83.51
C	1.0981	0.5491	0.0756	7.26
D	-6.1156	-3.0578	0.0756	-40.46
A*B	1.4131	0.7066	0.0756	9.35
A*C	-0.3469	-0.1734	0.0756	-2.29
A*D	0.0619	0.0309	0.0756	0.41
B*C	-0.0081	-0.0041	0.0756	-0.05
B*D	0.8781	0.4391	0.0756	5.81
C*D	0.0581	0.0291	0.0756	0.38
A*B*C	0.0869	0.0434	0.0756	0.57
A*B*D	-0.4544	-0.2272	0.0756	-3.01
A*C*D	-0.3994	-0.1997	0.0756	-2.64
B*C*D	-0.0956	-0.0478	0.0756	-0.63
A*B*C*D	-0.1281	-0.0641	0.0756	-0.85

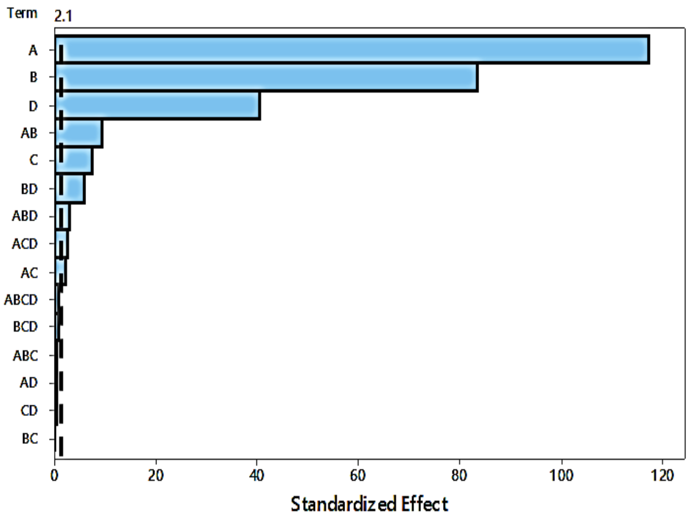


Fig. 4. Pareto Chart of the standardized effects (Response is R, α=0.05) for the inhibition of corrosion on mild steel by the ethanol extract of Prosopis Juliflora seeds

A reference line was drawn on the Pareto chart at 95% significant level and effects which were inside the line are considered as insignificant on the experiment. It has been found that all the main effect are statistically important in the study as all of them lies outside the reference line in Pareto chart, but few interaction like AD, BC, CD, ABC, BCD and ABCD remains well inside the reference line in the Pareto Chart, which indicates that these interaction is least significant in the inhibition of corrosion on mild steel by the ethanol extract of Prosopis Juliflora seed.

3.5. Analysis of Variance (ANNOVA)

Analysis of variance can also be used to find the significant main and interaction effects of the various variables which may influence the inhibition of corrosion on mild steel. Table 7 represent the sum of squares (SS) and mean square (MS) of each factor. The Ratio of the means square effect and the mean square error of each factor gives the F-ratio and P-value for each factor are also represented in Table 4. At 95% confidence level, with degree of freedom 1 and 16 factorial tests $F_{0.05,\,1,16}$ [13] the value of significant contribution by the factor should be above 4.49 and the values of the factor variable with lower value of 4.49 was considered as insignificant in the inhibition of corrosion. Statistical significance of the factor can be determined using Probability value or P-value. For 95% confidence level for a factor to be significant the P-value should be less than or equal to 0.05 and when P-value is zero or near zero then that factor contributes more towards the inhibition of corrosion on mild steel [11].

From the Table 7 it can be seen that according to the F value, P value and also from t-test the most significant factor that affects the inhibition of the corrosion was temperature (factor A)which was followed by concentration of the inhibitor (factor B) and concentration of medium (factor D), with time (factor C) contributing the least to the inhibition of corrosion, but the effect of time cannot be considered as insignificant as it has F-value greater than 4.49 and P value of zero. In the interaction effect the most important was found to between temperature and concentration of inhibitor (A X B), followed by concentration of inhibitor and concentration of the medium (BXD) and then the significantly least interaction between temperature and time (A X C) showing value of F more than 4.49. In three way interactions, two group of factors was found to be significant, interaction of temperature, concentration of inhibitor and concentration of the medium and next was temperature, time and concentration of the medium.

The difference between the t-test and the ANNOVA (f-value and P-value) is that the latter does not give any idea of whether a factor is significant in the positively or negatively. A negatively significant factor affects the corrosion inhibition by decreasing the inhibition when the factor is increased.

Table 7. Analysis of variance on data for the inhibition of Corrosion on Mild steel by the ethanol extract of Prosopis Juliflora

Factor	Degree of Freedom	Sum of Squares (SS)	Mean Square (MS)	F-Value	P-Value
A	1	2516.77	2516.77	13768.14	0.000
B	1	1274.75	1274.75	6973.57	0.000
C	1	9.65	9.65	52.77	0.000
D	1	299.21	299.21	1636.83	0.000
A*B	1	15.98	15.98	87.39	0.000
A*C	1	0.96	0.96	5.27	0.036
A*D	1	0.03	0.03	0.17	0.688
B*C	1	0.00	0.00	0.00	0.958
B*D	1	6.17	6.17	33.75	0.000
C*D	1	0.03	0.03	0.15	0.706
A*B*C	1	0.06	0.06	0.33	0.573
A*B*D	1	1.65	1.65	9.04	0.008
A*C*D	1	1.28	1.28	6.98	0.018
B*C*D	1	0.07	0.07	0.40	0.536
A*B*C*D	1	0.13	0.13	0.72	0.409
Error	16	2.92	0.18		

T-test gives the positive or negative interaction more precisely. With F-value and P-value it can be inferred whether a factor is significant or not and T-test gives the negative or positive significance so ANNOVA and T-test are both complimentary to each other. Fig. 5 represent the normal probability plot of standardized effect. The significant factor are represented as square and placed away from the center line while factors which were insignificant were represented as circles and occur along the axis. The plot is consistent with the analysis of significant results.

The factors which are not considered to be significant from the t-test and F-test were discarded and new equation for the inhibition of corrosion found was

$$R=70.9259+8.8684\ A+6.3116\ B+0.5491\ C-3.0578\ D+0.7066\ A*B-0.1734\ A*C+0.4391\ B*D-0.2272\ A*B*D-0.1997\ A*C*D \quad (9)$$

Based on the equation 9 the parameters of ANNOVA were recalculated eliminating the insignificant factors and the values of the SS, MS, F-value and P-value are given in the Table 8. The F-value for the lack of fit associated with elimination of some of the interacting factors was found to be 0.29 which was well below 4.49 for $F_{0.05,\ 1,16}$. Hence elimination of the interacting factor does not affect statistically the model.

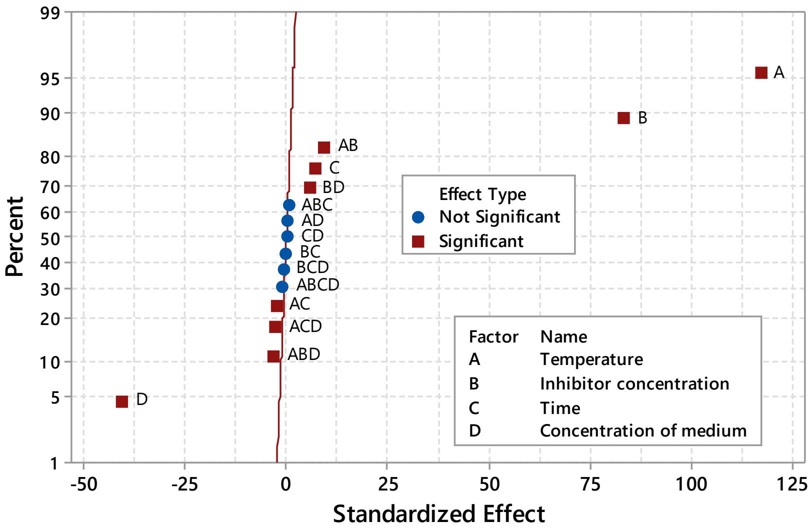


Fig. 5. Normal plot of Standardized Effects (response is R, α=0.05) for the inhibition of corrosion on mild steel by the ethanol extract of Prosopis Juliflora

Table 8. Analysis of variance on data reduced model for the inhibition of Corrosion on Mild steel by the ethanol extract of Prosopis Juliflora

Factor	Degree of Freedom	Sum of Squares (SS)	Mean Square (MS)	F-Value	P-Value
A	1	2516.77	2516.77	17048.20	0.000
B	1	1274.75	1274.75	8634.91	0.000
C	1	9.65	9.65	65.35	0.000
D	1	299.21	299.21	2026.78	0.000
A*B	1	15.98	15.98	108.21	0.000
A*C	1	0.96	0.96	6.52	0.018
B*D	1	6.17	6.17	41.79	0.000
A*B*D	1	1.65	1.65	11.19	0.003
A*C*D	1	1.28	1.28	8.64	0.008
Error	22	3.25	0.15		
Lack-of-Fit	6	0.32	0.05	0.29	0.931
Pure Error	16	2.92	0.18		
Total	31	4129.66			

3.6. Main and interaction effects

Individual effect of the factor on the corrosion inhibition was shown in Fig. 6. The response line for each factor would give the contribution of the factor towards the inhibition of the corrosion. Vertical line in the main effect would imply that the contribution of the factor towards the corrosion inhibition would be greatest whereas horizontal line indicates that the contribution of the factor towards the inhibition of corrosion would be least significant. A positive slope response line indicates that the effect has positive response when the factor is increased, whereas the negative slope indicates that the effect has negative response when the factor is increased. Analysis of the equation 8 and Fig. 3 shows that the temperature was the most important factor which affects the corrosion inhibition since the coefficient of the factor was the largest (8.8684) and around 17.7368% increase when the factor is increased from 303 K to 333 K. This effect can be explained by the fact that numerous functional group present in the inhibitor would be chemically adsorbed on the mild steel at high temperature contributing to the higher inhibition of corrosion.

Next important factor which affects the inhibition of corrosion was found to be inhibitor concentration with a change of 12.6232% when the concentration of the inhibitor is changed from 100 ppm to 700 ppm. The increase in the inhibitor can increase the rate of adsorption on the mild steel and less number of active sites would be available for the corrosion to take place. With increase in the inhibitor concentration decreases the surface available on the mild steel for the corrosion to take place. Interesting fact in this study is that it would normally expected that concentration of the inhibitor would have the highest significance, but rather it was the temperature which has higher significance.

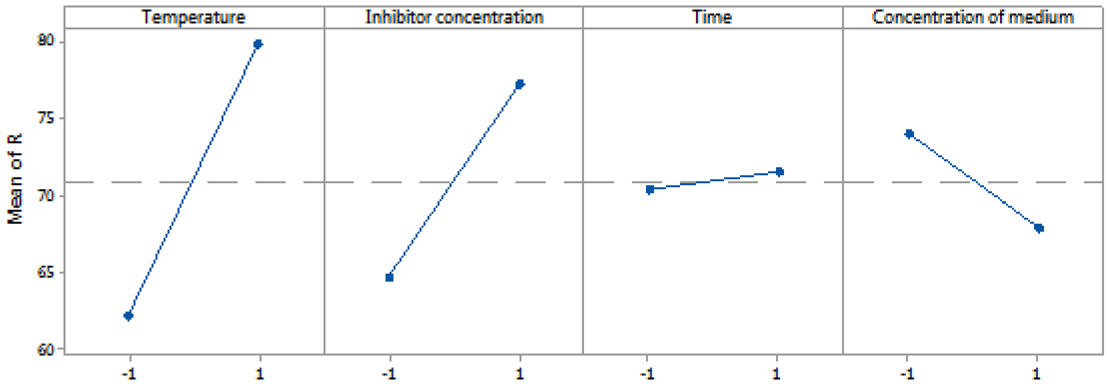


Fig. 6. Main effect plot of inhibition of corrosion on mild steel by ethanol extract of seeds of Prosopis Juliflora

The negative slope of the response line showed that concentration of the medium affects the inhibition of corrosion in the negative way with a decrease of 6.1156% when the medium concentration was changed from 0.1 M to 1 M. This trend was highly expected as increase in the HCl medium would increase the attack on the metal by the acid. At low concentration of the acid the attack by the medium would be lower since the active molecules for the attack would be lower, when the concentration of the acid increases the active molecules increases and hence the attack by the medium increases. Although the presence of inhibitor may slow down the corrosion, increased active molecules of HCl increases the corrosion.

The least significant factor which was found in the experiment was time with change of only 1.0982% when the exposure time of the steel to the inhibitor was increased from 1 h to 5 h. Although the change is very small the statistical design does not reject the data as both the t-test and F-test gave significant value to that factor. The low value may be attributed to the fact that the equilibrium of adsorption between the mild steel and inhibitor would have been attained in a short period of time. With increase in time after the equilibrium has been reached there would be only mild change in the adsorption. This fact would be useful for determining the efficiency of the inhibitor, a good inhibitor would reach equilibrium adsorption at a shorter time interval and hence the control of corrosion would be high. In this regard the ethanol extract of seeds of Prosopis Juliflora can be considered as efficient inhibitor.

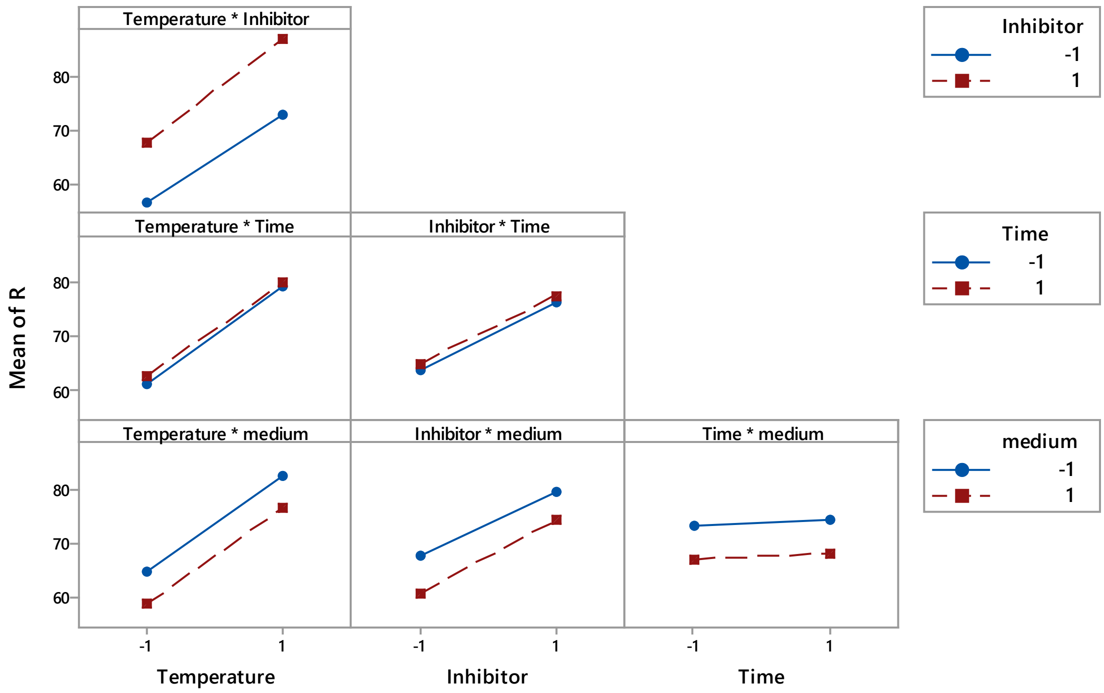


Fig. 7. Plot of interaction effect of various parameter for the inhibition of corrosion on mild steel by ethanol extract of seeds of Prosopis Juliflora

Fig. 7 shows the interaction plot of various variables. The non-parallel line would indicate that the interactions between the variables are significant. Fig. 4 and equation 8 shows that there would be a negative interaction between temperature and time (A X C) and a positive interaction between temperature and concentration of the inhibitor (A X B) and between concentration of inhibitor and the medium (B X D). The positive interaction between the variable is more than factor C (time).

4. CONCLUSION

Electrochemical polarization and impedeance studies showed that the ethanol extract of the seed of Prosopis Juliflora can be used as green inhibitor. Optimum condition of various parameters which affects the inhibtion of corrosion was determined using ANNOVA, t-test and Surface response diagram. An equation has been arrived for the inibition efficiency and the equation was found to fit well with the experimental data of the various parameters analyzed the order of significance of importance was found to be: tem perature> concentration of inhibitor>time>concentration of the medium. Time factor showed a negative significance where as all other factors showed positive significance level.Two way and three way interaction was also found be out using the model. And these interaction was found to have a lesser significance except for few on the experimental condition.

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