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Factorial design application for the Protection of mild steel from corrosive medium using Castor seed oil as inhibitor

Abida Begum[1]*, HariKrishna S[2]

[1]Department of Science and Humanities, PESIT-Bangalore South Campus, Bangalore-100, India.
[2]Department of Chemistry Shirdi Sai Engineering, Anekal, Bangalore-562106, India.

*Corres.author: abida.altaf@gmail.com

Abstract: A polynomial equation is developed to relate the concentration of hydrochloric acid as corrosive medium for mild steel to the variables like inhibitor concentration, temperature and time. The inhibitor used is castor seed oil. The effect of variables has been investigated and these are optimized using 3 level full factorial design method. The model allows the prediction of the extent of corrosion inhibition at different conditions. ANOVA is used to evaluate the validity of model. The correlation coefficient between the calculated and the experimental data indicates good performance of the model. From ANOVA, the variables and their interaction effect on the corrosion rate were significant. A maximum of 84.1% of Inhibition efficiency was achieved under the optimum conditions of 50 %v/v inhibitors concentration, 48 hours time and at 303K temperature.
Key words: Mathematical model; Factorial design; corrosion of mild steel; castor seed oil.

Introduction

Castor oil is a vegetable oil extracted from the castor plant its Scientific Name is *Ricinus communis* L. and familyis Euphorbiaceae (Spurge). Castor oil a colourless to pale yellow with mild or no odour or taste has a wide range of uses. It is commonly used as a laxative and for the induction of labor. In the food industry it is used as food additives. In medicine, its derivative is used for skin problem and for skin conditioning. Castor oil is an effective motor lubricant. The presence of OH groups in all the fatty acid chains makes the oil unusually polar. It is because of this hydroxyl groups only that castor oil becomes valuable as chemical feedstock. It is a monosaturated fatty acid in which about 90% of fatty acid chains are ricinoleic acid, remaining is oleic acid, linoleic acid, stearic acid and palmitic acid. Its boiling point is found to be 313 ^{0}C[1]. Since castor oil has high percentage of fatty acid and the presence of ricin & ricinoleic acid, castor oil could be used as inhibitor in 2M HCl solution. The oil formed a thin film on the surface of the metal (Fe) due to adsorption obeying Langmuir adsorption isotherm. It offers large surface coverage due to long chain hydrocarbons. In this work, castor seed oil gas been used to study the corrosion inhibition of mild steel in acid medium. A full factorial design is used for the experiments and a polynomial equation is developed to relate the inhibition efficiency to the variables such as inhibitor concentration, time and temperature. The validity of the model is evaluated by the analysis of variance (ANOVA).

Experimental:

Castor seeds were obtained from local area .The seeds were cleaned and sun dried to a moisture content of 10 %, a level considered safe for long term storage. About 1 kg seeds were dehulled and used for the experiments. 250 gram sample seed kernels were cleaned and then coarsely minced at low speed in a blender for 10 seconds[4]. The condenser with soxhlet extractor was preheated to 80 ^{0}C with round bottom flask was fixed and then heated to 70 ^{0}C (temperature slightly higher than the boiling temperature of the solvent n- hexane). The seed samples were placed with 250 ml of n-hexane in the round bottom flasks, and extracted for 8 hr. The oil was extracted and solvent was separated under vaccum. Separated oil was dried over anhydrous sodium sulphate.

Physicochemical analysis of the seed oil for iodine value, acid value, saponification value, viscosity, flashpoint, specific gravity, refractive index and free acid value has been performed according to the standard methods is shown in table -1. Removal of color and oxidizing bodies, residual gums, soap and trace metals by mixing oil with special adsorbents activated clay and heated to about 100 ^{0}C. The adsorbents containing impurities and oxidation product are removed and then filtered.

Table-1: Physicochemical analysis of Castor seed oil

Sl. No.	Parameter	Castor seed oil
1	Refractive index	0.9102
2	Viscosity (st)	5.9
3	Iodine Index	118
4	Ash content %	2.5
5	Acid Index(mg KOH/g)	2.4
6	Saponification value	179
7	Flash Point (C)	179
8	Fatty acid value (as Oleic) mg. KOH/g oil	0.99

Weight loss method

All corrosion inhibition data were obtained through weight loss experiments based on mild steel of surface area 5x1cm^2 with elemental composition of, C (0.043%), Mn (0.338%), Si (0.031%), P(0.041%) ,S (0.023%), Cr(0.047%), Mo (0.016%), Ni (0.019%) and Fe (99.437%). The blank solution was 2M Hydrochloric acid. From the stock solution of the extract, different concentrations of the inhibitor test solutions ranging from 5% to 50 % v/v were prepared. The steel specimens were cleaned with acetone, washed with water, dried and weighed to 0.0001 g precision. Two results were averaged for each inhibitor. The specimens were immersed in acid solutions containing various concentrations of the inhibitor for 24 hours and 48 hours at 303 and 313 K. The specimens were removed washed with water and dried. The mass of the specimens before and after immersion was determined using an electronic digital balance[2].

Factorial design: The experiments were conducted as per standards to investigate the given parameters affecting significantly the corrosion rate and also the independently controllable predominant process parameters. The parameters considered for the investigation are temperature, concentration and time[3]. Two levels of each of the three factors were used for the statistical analysis. The treatment combinations for the two levels and three factors are tabulated in Table-2.

Table -2: Factorial design of the corrosion process showing treatment combination

Variables	Actual value		Coded value	
	Low level	High level	Low level	High level
Inhibitor (%v/v) (A)	10	50	-1	+1
Time (Minutes) (B)	12	48	-1	+1
Temperature 0C (C)	303	311	-1	+1

The factorial design describes which factor shows more impact and influences the variation of one factor on the other factors. A full factorial design with three variables [Amount of inhibitor % v/v, Reaction time (minutes) and temperature (k)] is shown in the table-3. The optimum values of the variables were calculated with MINITAB 16.

To calculate the main effect we average the responses for the variable at high level and subtract the response at the low level .This will be equivalent to multiplying the response (% IE) by coefficients column for the variable (A,B,C) and dividing by half the number of experiments as shown in table-3. The main effect gives the relative importance of each variable. Numerically largest effect is for inhibitor concentration (variable A), followed by time (variable B) and temperature (variable C). A positive effect means the response is higher at the higher range of variable.

Table- 3: Statistical parameter design and Main effects to determine the significance of response for the given variable

A	B	C	% I.E	A	B	C
1	-1	-1	**65.00**	50	-12	-30
1	1	1	**41.76**	50	48	38
-1	1	-1	**45.67**	-5	48	-30
-1	1	1	**36.33**	-5	48	38
1	1	-1	**83**	50	48	-30
1	-1	1	**47.34**	50	-12	38
-1	-1	-1	**32.33**	-5	-12	-30
-1	-1	1	**29**	-5	-12	38
Main Effects :				45	36	8

A mathematical expression to describe the design matrix combination mentioned in Table (2) as low and high level of each factor and its corresponding corrosion rates mentioned in Table (3) in code :corrosion Rate = f (A,B,C) Where A is inhibitor concentration, B is the time and C is the temperature. The above model includes the effects of main variables first order and second order interactions of all variables. Therefore the general model equation is given as:

Corrosion Rate = $\beta 0 + \beta 1*A + \beta 2*B + \beta 3*C + \beta 4*AB + \beta 5*BC + \beta 6*CA + \beta 7 *ABC$

Where β0 is the average response of corrosion Rate and β1, β2 β3, β4, β5, β6 and β7 are coefficients associated with each variables A,B ,C and interactions. The regression coefficients and the associated affects are shown in tables-4. The significant factors are identified by analysis of variance technique[5]. Based on the experimental results, a multiple linear regression model is developed and the effect of 95 % confidence levels for the extract was presented in the table 4. A regression thus generated establishes correlation between the significant terms obtained from ANOVA, namely temp, inhibitor and time on the corrosion rate were statistically significant. Substituting the coded values of the variables for any experimental conditions in the above equation the corrosion rate vales for the corrosion control behavior of the mild steel can be calculated. The developed model equation is expressed as

Corrosion Rate = 47.54 +11.13 A +4.136B -8.946 C – 1.031AB - 5.779 BC -3.699 AC -1.196*ABC

The above equation has been used to predict the corrosion rate of the mild steel. The results of the linear regression model table -4 for castor oil showed that the inhibitor is the most important variable with the main effect of +11.13 mpy followed by temperature (C) with -8.946 mpy and time B with +4.136 mpy. The regression revealed that temperature negatively impacted the inhibition efficiency of castor seed oil on mild steel. The effect of inhibitor concentration was most pronounced as seen from the value of coefficient of that variable in comparison with the other. It can be concluded that when the effect of a factor is positive an increase in the value of the inhibition efficiency is observed when the factor changes from low to high level. In contrast, if the effect is negative, a reduction in inhibition efficiency occurs for high level of same factor.

Table-4: Statistical parameters for 2^3 design

Factor	Degree of freedom	Coefficient	Effect
Average		47.54	
Inhibitor Concentration	1	11.136	23.442
Time	1	4.136	8.273
Temperature	1	-8.946	-17.893
Inhibitor concentration *Ti	1	-1.031	-2.063
Inhibitor concentration * Temperature	1	-5.779	-11.558
Time * Temperature	1	-3.699	-7.397
Inhibitor concentration * Temperature * time	1	-1.196	-4.392

Analysis of variance

The results of ANOVA are presented in the table-5. The analysis was evaluated for a confidence level of 95 % that is for significance level of $F_{0.05,1,7}$=5.59,all effects presenting F higher than 5.59 have statistical insignificance. The F –value for all models was less than 0.05, and then the parameter or interaction can be considered as statistically significant. From the table-6 it is observed that the temperature (C),inhibitor (A) and time (B) are significant model terms influencing corrosion rate of mild steel, since they have obtained F- value less than 0.05. Although the interaction effect of temperature with inhibitor (AC) was considered statistically insignificant since their F- values are greater than 0.05, and hence it is neglected. From the P values, it appears that the main effect of each factor and the interaction effects are statistically significant when p is less than one. Therefore the two ways interaction time and temperature is statistically insignificant.

Table- 5: Analysis of variance-full fitting model for Castor seed oil

Factor	Sum of	Degree of	Mean	F value	P –value
Inhibitor concentration	1099.10	1	1099.10	3.90	0.120
Time	136.87	1	177.379	0.57	0.492
Temperature	640.28	1	728.284	2.34	0.201
Interactions					
Inhibitor concentration *Time	8.51	1	2.344	0.01	0.928
Inhibitor concentration	267.15	1	231.08	0.12	0.750
Time * temperature	38.59	1	38.59	7.23	
Residual	0.00	2	311.200		
Total	1995.95	7			

Multiple R =0.903206 , R-Sq = 0.815781, R-Sq(adj) =0.67717 and Standard Error= 10.29191

The various parameters chosen for the confirmation test are shown in the table -6. The results of the confirmation tests were obtained and comparisons were made between the actual corrosion rate values and predicted values[6-8]. The model predicts much more increase in inhibition efficiency with high and low levels of inhibitor concentration, time and temperature.

Table-6: Comparison of the Actual with the predicted result for mild steel using Castor seed oil in 2 M hydrochloric acid.

Sl. No.	Inhibitor concentration	Time (min)	Temperature (k)	Inhibition Efficiency (%)	Predicted	Residuals
1	1	-1	-1	65	64.085	0.915
2	1	1	1	41.76	54.465	-12.705
3	-1	1	-1	45.67	48.915	-3.245
4	-1	1	1	36.33	31.0225	5.3075
5	1	1	-1	83	72.3575	10.6425
6	1	-1	1	47.34	46.1925	1.1475
7	-1	-1	-1	32.33	40.6425	-8.3125
8	-1	-1	1	29	22.75	6.25

The inhibition efficiency decreases with increase in temperature shown in table-7. The maximum inhibition efficiency is lower at 311K than at 303 K. This is due to the dependence of adsorption on temperature. As the temperature rises, the quantity adsorbed decreases and as a result, the isotherm of higher temperatures is below the isotherm of lower ones. The decrease in inhibition efficiency with increasing temperature may be due to weak adsorption interaction which is physical in nature. The values of the rate constant was calculated using the first order rate law, $k = (2.303/t) \log ([A_0/A])$, where $[A_0]$ is the initial mass of the metal and [A] is the mass corresponding to time‘t’. The half-life ($t_{1/2}$) was calculated using the relationship[5], $t_{1/2} = 0.693/k$. The values of rate constant and half-life obtained from the above relations were summarized in Table-7. Half life values were found to be constant at different concentration level.

Table-7: The values of rate constant and half-life for the corrosion inhibition of mild steel in castor seed oil

Concentra Tion, (% v/v)	Corrosion Rate (mpy)	Surface coverage (θ)	Rate constant (k/s)	Half life(s)	Corrosion Rate (Mpy)	Surface coverage (θ)	Rate constant (k/s)	Half life (s)
Temperature 303 k and Time 12 hours, 2M HCl					**Temperature 303 k and Time 48 hours, 2 M HCl**			
Blank	27212.33				27212.33			
5	18368.32	0.325	0.0098	70.41	14694.66	0.46	0.0069	99.66
10	17143.77	0.37	0.0086	80.16	14150.41	0.48	0.0066	103.99
15	16599.52	0.39	0.0082	84.49	12653.73	0.535	0.0059	115.91
20	16599.52	0.423	0.0076	91.64	12653.73	0.567	0.0056	122.84
25	15701.51	0.436	0.0073	94.46	11782.94	0.589	0.0054	127.61
30	14041.56	0.484	0.0066	104.86	10912.14	0.599	0.0053	129.77
35	13225.19	0.514	0.0062	111.36	9714.801	0.643	0.0049	139.31
40	11891.79	0.563	0.0057	121.98	8245.335	0.697	0.0046	151.01
45	10694.44	0.607	0.0052	131.51	6286.048	0.769	0.0041	166.61
50	9524.315	0.65	0.0049	140.83	4353.972	0.84	0.0038	181.99

The effect of temperature was studied for the given concentration of inhibitor. ΔG^0_{ads} is a thermodynamic property, which shows a strong correlation with the energy, volume and with the inhibition polarisability. Values of the free energy of adsorption (ΔG^0_{ads}) at various temperatures were calculated using the following equation, $\Delta G^0_{ads} = -RT \ln (55.5K)$, Where K is equilibrium constant $K = \frac{\theta}{(1-\theta)C}$, θ = degree of coverage on the metal surface, T is the temperature in Kelvin, C is the concentration of the inhibitor and R is the gas constant. With the help of the temperature studies results, thermodynamic parameters such as the entropy of adsorption (ΔS^0) and enthalpy of adsorption (ΔH^0) can be calculated from the from the slope and intercept respectively. The ΔG^0_{ads} values obtained indicate that adsorption of castor seed oil is spontaneous and follows physical adsorption mechanism. Generally if ΔG^0_{ads} values are up to -20 kJ/mol there is consistence in electrostatic interaction between the charged metal and charged molecules, which signifies physical adsorption, while values more negative than -40 kJ/mol signify chemical adsorption. The values of ΔH and ΔS (table-8) infer that the adsorption of esters present in castor seed oil on mild steel is enthalpic and entropic controlled.

Table-8: Calculated values of ΔG^0_{ads} ΔH^0 and ΔG^0 for the corrosion of mild steel in 2M Hydrochloric acid in various concentration of Castor seed oil

Temp. (K)	**ΔH^0**	**ΔS^0**	**ΔG^0_{ads}**									
			Inhibitor Concentration (% v/v)									
			5	10	15	20	25	30	35	40	45	50
303 K	-0.117	-8.555	-8.08	-9.72	-10.71	-11.39	-11.95	-12.38	-12.78	-13.16	-13.55	-13.94
311K	-0.147	-7.945	-7.76	-9.54	-10.59	-11.38	-11.99	-12.48	-13.00	-13.56	-14.31	-15.30

The isotherm models such as Langmuir and Freundlich were studied and described the equilibrium characteristics of adsorption. Assumptions of Langmuir relate the concentration of the adsorbate in the bulk of the electrolyte (C) to the degree of surface coverage (θ) according to equation :$C/(\theta) = 1/Q_m b + C/Q_m$, Where Qm and b are Langmuir constants related to sorption efficiency and energy of adsorption respectively. The linear plot of C/(θ) vs C suggest applicability of Langmuir isotherm. The values of Qm and b are calculated from slope and intercept of the plot and are listed in the table-9. From the results, it is clear that the value of adsorption efficiency Qm and adsorption energy increases on increasing the temperature. Freundlich isotherm represents repulsive interaction between adsorbed solute particles is based on heterogenous surface representing the binding sites which independent[9]. The logarithmic form of Freundlich equation is represented as $\log C/(\theta) = \log K_f + 1/n \log C$,Where (θ) is surface coverage and C is the concentration of castor seed oil (% v/v) , K_f and n are constants which integrate the factors affecting the adsorption capacity and intensity of adsorption, respectively. Linear plots of log C/(θ) versus log C shows that adsorption of castor seed oil obeys the

Freundlich isotherm[9]. The K_f and n values are given in table-9 indicating the spontaneity of adsorption, hence stability of adsorbed layer is higher at 303 K.

Table- 9: Langmuir and Freundlich isotherm results

Temperture in Kelvin	Langmuir Isotherm Results			Feundlich Isotherm results		
	Statistical constants			Statistical constants		
	R^2	Q_m	b	R^2	K_f	n
303	0.939	0.7412	0.081	0.938	5.358	1.416
311	0.938	0.903	0.098	0.938	3.5399	1.326

Conclusion

ANOVA results revealed that the parameters (A, B & C) are statistically significant with F-values less than 0.05 for the inhibitor. The interactions exhibited sufficient influence except for higher temperature and were statistically significant. The results obtained by regression equations closely correlate each other which validate the regression equations developed. A good agreement between the predicted and actual corrosion rate was observed. The developed mathematical models can be used to predict the corrosion values in terms of corrosion control process parameters obtained from any combinations within the ranges studied and also employed for optimization of the process parameters of mild steel with respect to corrosion control values. Experimental data showed that in the presence of different concentration (5 – 50% v/v), castor seed oil inhibited the corrosion of mild steel in acidic medium. The inhibition efficiency increased with increase in the inhibitor concentration and with decrease in temperature leading to a physical adsorption. The highest efficiency of 84.1 % was observed at the optimum of 50 % v/v for castor seed oil in the acid solution and the effect of immersion time of the inhibitor was attained at 48 hours and at the temperature of 303 Kelvin.

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