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OPTIMIZATION OF THE INHIBITION EFFICIENCY OF MANGO EXTRACT AS CORROSION INHIBITOR OF MILD STEEL IN 1.0M H_2SO_4 USING RESPONSE SURFACE METHODOLOGY

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ABSTRACT

The optimization of inhibition efficiency of mango (mangnifera indica) extract as inhibitor of mild steel in 1.0M H_2SO_4 using response surface methodology is presented. The corrosion inhibition study was carried out using thermometric, gravimetric (one factor at a time and response surface methodology) and potentiodynamic polarization methods. Fourier transform infrared spectroscopy was used to analyze the mango extract and corrosion product. Analyses of the results revealed that adsorption of the mango extract on the surface of the mild steel was spontaneous and occurred according to the mechanism of physical adsorption. The inhibition efficiency was concentration, temperature and time dependent. Mango extract exhibited the optimum inhibition efficiency of 74.09 % (at optima inhibitor concentration of 0.97g l^{-1}, temperature of 305.33 K and time of 22.76 h). It inhibited both cathodic and anodic reactions and acted as mixed-type inhibitor. The analysis of mango extract and corrosion product of mild steel in H_2SO_4 (with the mango extract) showed that the stretched C=C at 1570.02 cm^{-1} peak shifted to 1415.72 cm^{-1}. Also, the stretched O-H at 3761.08 cm^{-1} peak shifted to 3668.5 cm^{-1}. The nature of the shifts indicate that there was synergy among the functional groups of C=C and O-H in the corrosion inhibition process.

Keywords: corrosion inhibitor, H_2SO_4, mango extract, mild steel, optimization.

INTRODUCTION

Mild steel is widely used in the manufacturing of installations for petroleum, fertilizers, and other industries. It is used for the production of lightly stressed machine fittings, armature shafts, turbine motors, railways axels, pipes and drums. It can be hardened by heat treatment, and it has good machining properties [1, 2]. In view of viability of mild steel and its high cost of production and installation, several steps are taken to prolong the life span of the metal in most industries. Acid solution such as H_2SO_4 is used for removal of undesirable scale and rust in several industrial processes. Acid solutions are often used in industry for cleaning, descaling and pickling of steel structure, processes which are normally accompanied by considerable dissolution (corrosion) of the metal [3]. Corrosion control by the application of inhibitor is an acceptable means of maintaining the stability of metallic structures. Furthermore, naturally occurring compounds are of interest, because they are cost effective, readily available and eco-friendly. Due to these advantages, extracts of some common plants and plant products have been tried as corrosion inhibitors for metals and alloys under different environment [4 - 7]. This work is aimed at optimizing the inhibition efficiency of leaves extract of mango (mangnifera indica) as inhibitor of mild steel in H_2SO_4. Mango belongs to the flowering plant family, Anacardiaceae. Some natural products from mangnifera indica leaves are potential therapeutics for disease [8, 9]. It is important to examine the optimal inhibitive property of the mango extract.

EXPERIMENTAL

Extraction of the Plant Extract

Leaves of mango were collected from Akpugo, Enugu state, Nigeria. There were sun-dried for three days. The dried leaves were ground to increase the surface area and stored in a closed container. For every of the extraction process, 30 grams of each of the ground mango leaves were measured and soaked in 1000ml of ethanol for 48 hours. At the end of the 48 hours, each plant mixture was filtered. The filtrate obtained is a mixture of the plant extract and the ethanol. The extract obtained in ethanol solvent was concentrated, distilling off the solvent and evaporate to dryness. The plant extract was weighed and stored for the corrosion inhibition study.

Metals Preparation

Sheet of mild steel with composition of P (0.02 %), Mn (0.11 %), Si (0.02 %), S (0.02 %), Cu (0.01 %), C (0.23 %), Ni (0.02 %), Cr (0.01 %) and Fe (99.56 %) was cut into coupons (5 cm x 4cm x 0.1cm). The coupons were cleaned followed by polishing with emery paper to expose shining polished surface. To remove any oil and organic impurities, the coupons were degreased with acetone and finally washed with distilled water, dried in air and then stored in desiccators.

Accurate weight of each coupon was taken using electronic weighing balance and the initial weight was recorded.

FT IR Analysis of the Mango Extract and Corrosion Product

The mild steel was immersed in the H_2SO_4 medium in the presence of the mango extract. At the end of the corrosion study, the corrosion products in the beakers were collected with the aid of sample bottles. Fourier transform infrared spectrophotometer (SHIMADZU, Model: IR affinity – 1; S/N A 2137470136 SI) was used for the determination of the functional groups of the leaves extract of mango and corrosion products in the presence of the leaves extract of mango.

Comparative analysis of various FT IR produced peaks were carried out so as to determine the appropriate functional groups for the corrosion inhibition process.

Thermometric method of the Corrosion Inhibition Study

The measurements were carried using a thermostat set at 30^0C for the mild steel in free and inhibited H_2SO_4. The temperatures of the system containing the mild steel and the test solution were recorded regularly until a steady temperature value was obtained. The reaction number (RN) was evaluated using eq. (1) [10, 11].

$$RN = \frac{T_m - T_i}{t} \quad (1)$$

where T_m and T_i are the maximum and initial temperatures (in ^0C) respectively, and t is the time in minutes elapsed to reach T_m.

The inhibitor efficiency was determined using Equation (2) [10].

$$IE\% = 1 - \frac{RN_{add}}{RN_{free}} * 100 \quad (2)$$

where RN_{free} and RN_{add} are the reaction numbers for the mild steel dissolution in free and inhibited corrosive medium respectively.

Weight loss (gravimetric) method

Weight loss method using one factor at a time

Considering one factor at a time, the weight loss method was carried out at different temperatures and with various concentrations of the mango extract. According to this method, weighed mild steel coupons were separately immersed in 250 ml open beakers containing 200 ml of 1.0M H_2SO_4. Also, mild steel coupons were separately immersed in 250 ml open beakers containing 200 ml of 1.0M H_2SO_4 with various concentrations of the mango extract.

The variation of weight loss was monitored periodically at various temperatures in the absence and presence of various concentrations of the extract. At the appropriate time, the coupons were taken out, immersed in acetone, scrubbed with a bristle brush under running water, dried and reweighed. The weight loss was calculated as the difference between the initial weight and the weight after the removal of the corrosion product. The experimental readings were recorded. The weight loss (Δw), corrosion rate (CR) and inhibition efficiency (IE) were determined using the eqs. (3), (4) and (5), respectively. The surface coverage was obtained using the following eq. (6) [12].

$$\Delta w = w_i - w_f \tag{3}$$

$$IE\% = \frac{\omega_0 - \omega_1}{\omega_0} * 100$$

$$E\ \% = \frac{\omega_0 - \omega_1}{\omega_0} * 100 \tag{5}$$

$$\theta = \frac{\omega_0 - \omega_1}{\omega_0} \tag{6}$$

where w_i and w_f are the initial and final weight of mild steel samples respectively; w_1 and w_0 are the weight loss values in presence and absence of inhibitor, respectively. A is the total area of the mild steel sample and t is the immersion time.

Effect of temperature on the corrosion rate

Effect of temperature on the corrosion rate was described using Arrhenius equation;

$$CR = Ae^{-E_a/RT} \tag{7}$$

where CR is the corrosion rate of the mild steel, A is the pre-exponential factor, E_a is the activation energy, R is the gas constant.

Eq. (10) can be linearized to form eq. (8).

$$\ln(CR) = lnA - (E_a/R)(\tfrac{1}{T}) \tag{8}$$

Considering the corrosion rates of the metal at T_1 and T_2 as CR_1 and CR_2, then eq. (8) can be expressed by eq. (9) [13 - 15].

$$\ln\left(CR_2/CR_1\right) = (E_a/2.303R)(\tfrac{1}{T_1} - \tfrac{1}{T_2}) \tag{9}$$

Thermodynamic parameter for the adsorption process

The heat of adsorption Q_{ads} (kJ mol^{-1}) was calculated using eq. (10) [14, 16].

$$Q_{ads} = 2.303R\left[\log\left(\frac{\theta_2}{1-\theta_2}\right) - \log\left(\frac{\theta_1}{1-\theta_1}\right)\right] * \frac{T_2.T_1}{T_2 - T_1} \tag{10}$$

where R is the gas constant, θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively.

Consideration of the adsorption isotherms

The data obtained for the degree of surface coverage were used to test for the applicability of different adsorption isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherms).

1. Langmuir isotherm

Langmuir isotherm can be expressed by eq. (11) [14, 17, 18].

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{11}$$

where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is the degree of surface coverage. In logarithmic form, eq. (11) can be expressed in eq. (12).

$$log\frac{C}{\theta} = \log C - logK \tag{12}$$

2. Frumkin isotherm

Frumkin adsorption isotherm can be expressed according to eq. (13).

$$\log\left((C) * \left(\frac{\theta}{1-\theta}\right)\right) = 2.303logK + 2\alpha\theta \tag{13}$$

where K is the adsorption-desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer.

3. Temkin isotherm

Temkin isotherm can be expressed by eq. (14) [14].

$$\theta = -\frac{2.303logK}{2a} - \frac{2.303logC}{2a} \tag{14}$$

where K is the adsorption equilibrium constant, a is the attractive parameter, θ is the degree of surface coverage, C is the concentration of the inhibitor.

4. Flory-Huggins isotherm

The Flory-Huggins isotherm can be expressed by eq. (15) [14, 19].

$$\log\left(\frac{\theta}{C}\right) = \log K + x\log(1-\theta) \qquad (15)$$

where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

The free energy of adsorption (ΔG_{ads}) was calculated according to eq. (16) [14, 19].

$$\Delta G_{ads} = -2.303RT\log(55.5K) \qquad (16)$$

where R is the gas constant, T is temperature, K values obtain from the isotherms (Langmuir, Frumkin, Temkin and Flory-Huggins isotherms) were used to obtain the values of ΔG_{ads} according to eq. (16).

Weight loss method using response surface method

Response surface method in design expert software was used to design the experiment for the weight loss method. Inhibitor concentration, temperature and time were the considered factors while weight loss, corrosion rate and inhibition efficiency were the expected responses of the study. The RSM was used to analyze the responses. The ANOVA and graphical analyses of the inhibition efficiencies were carried out. The mathematical models in terms of coded and actual factors were obtained. The model in terms of coded factors was used to make predictions about the response for given levels of each factor. The high levels of the factors were coded as +1 and the low levels of the factors were coded as -1. The optimum inhibition parameters were obtained.

Potentiodynamic Polarization Study

Electrochemical test were conducted using a potentiostat/galvanostat 263 electrochemical system workstation, with a conventional three-electrode corrosion cell. A graphite rod and a saturated calomel electrode (SCE) were used as a counter and reference electrodes, respectively. A metal specimen fixed in epoxy resin with a surface area of 1 cm^2 exposed to the test solution, served as the working electrode. Electrochemical measurements were carried out in aerated and unstirred solution at the end of 1800 s of immersion, which allowed the open circuit potential (OCP) to attain steady state. Temperature was fixed at 30 ± 1^0C. Potentiodynamic polarization studies were conducted in the potential range ±250 mV versus corrosion potential at a scan rate of 0.333mV s^{-1}. The inhibition efficiency was determined using eq. (17).

$$\text{IE}\,\% = \frac{i_{corr(uninh)} - i_{corr(inh)}}{i_{corr(unmh)}} \times 100 \qquad (17)$$

where $i_{corr(uninh)}$ and $i_{corr(inh)}$ are the corrosion current density values without and with inhibitor respectively.

RESULTS AND DISCUSSION

The FT IR Spectra of the Mango Leaves Extract and Corrosion Product.

The peaks of spectrum of the mango leaves extract are shown in Fig. 1. The functional groups of C=C-H, Ar-H bend out of plane, C-H bend in plane, C=C stretch, C=N stretch, C-H stretch and O-H stretch are present in the mango leaves extract. The peaks of spectrum of the corrosion product are shown in Fig. 2. The spectrum of each of the graph shows various peaks in the absorbance versus wave length relationship. The peaks and their

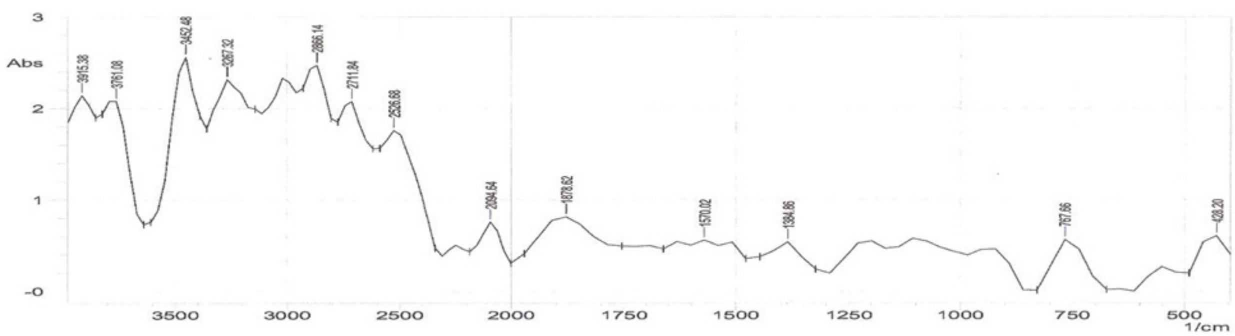

Fig. 1. The FT IR spectrum of the mango leaves extract.

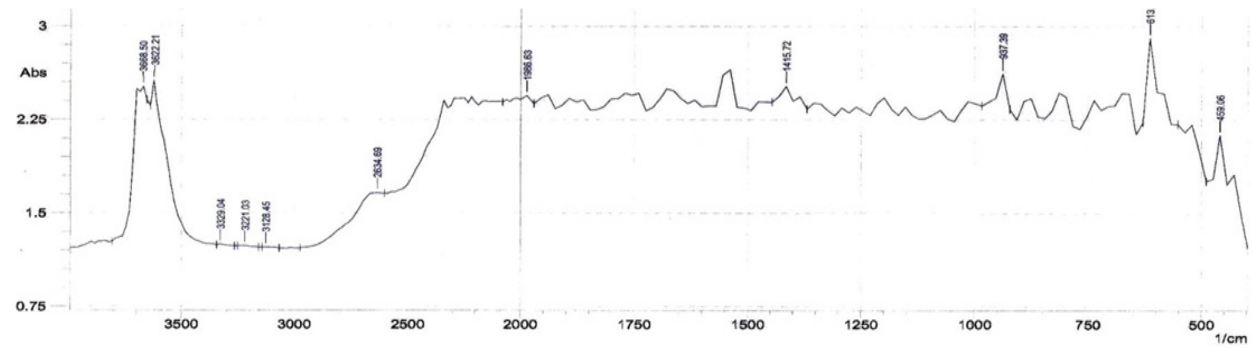

Fig. 2. FTIR spectrum of the corrosion product of mild steel in H_2SO_4 with mango leaves extract.

Table 1. Effects of concentration of the extract on the IE (%) of mild steal in the medium.

Inhibitor conc., g/l	RN	IE (%)
0.0	0.0348	
0.2	0.0181	47.92
0.4	0.0121	65.13
0.6	0.0079	77.17
0.8	0.0072	79.19
1.0	0.0069	80.29

corresponding intensities represent the functional group of the plant extract [11, 20, 21].

Results of the Corrosion Inhibition as Determined by Thermometric Results

The effect of concentration of the mango extract (inhibitor) on the reaction number (RN) and the inhibition efficiency (I.E) of the mild steal in the H_2S0_4 medium is presented in Table 1. Increase in concentration of the inhibitor lowers the reaction number. This is in agreement with previous observation [10]. Also, the inhibition efficiency increases with increasing concentration of the inhibitor.

Results of Weight Loss Method

Results of weight loss method using one factor at a time

The experimental results of weight loss and corrosion rate using one factor at a time are presented Table 2.

In graphical form, Fig. 3 presents the plot of inhibition efficiency versus inhibitor concentration and temperature at various times (in series 1, 2, 3). The inhibition efficiency increases with increase in concentration of the inhibitor (plant extract) but decreases with increase in temperature (Fig. 3 and Table 3). This observation is in agreement with previous studies [22 - 24].

The inhibition efficiency (IE) and degree of surface coverage (θ)

The inhibition efficiency and degree of surface coverage of the mild steel in the H_2SO_4 medium with mango extract are presented in Tables 3.

The inhibition efficiency increases with increase in concentration of the plant extract. But the inhibition efficiency decreases with increase in temperature.

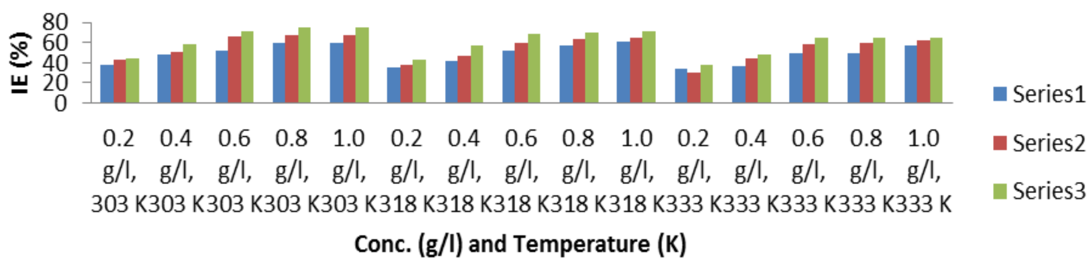

Fig. 3. IE versus concentration and temperature at various times.

Table 2. Data of corrosion inhibition of mild steel in H_2SO_4 with mango leaves extract.

Time (hr)	Parameter	0.0 g/l, 303 K	0.2 g/l, 303 K	0.4 g/l, 303 K	0.6 g/l, 303 K	0.8 g/l, 303 K	1.0 g/l, 303 K	0.0 g/l, 318 K	0.2 g/l, 318 K	0.4 g/l, 318 K	0.6 g/l, 318 K	0.8 g/l, 318 K	1.0 g/l, 318 K	0.0 g/l, 333 K	0.2 g/l, 333 K	0.4 g/l, 333 K	0.6 g/l, 333 K	0.8 g/l, 333 K	1.0 g/l, 333 K
8	Weight loss (g)	0.52	0.32	0.27	0.25	0.213	0.21	0.56	0.36	0.327	0.27	0.24	0.22	0.58	0.38	0.37	0.29	0.29	0.25
16		0.93	0.527	0.453	0.31	0.303	0.3	0.99	0.62	0.53	0.4	0.36	0.35	1.02	0.713	0.57	0.42	0.413	0.39
24		1.3	0.72	0.54	0.37	0.33	0.32	1.38	0.79	0.6	0.43	0.41	0.4	1.43	0.89	0.75	0.51	0.507	0.503
8	CR (mg/cm^2hr)	3.25	2.00	1.688	1.563	1.331	1.313	3.5	2.25	2.044	1.688	1.5	1.375	3.625	2.375	2.313	1.812	1.812	1.563
16		2.906	1.647	1.416	0.969	0.947	0.938	3.094	1.938	1.656	1.25	1.125	1.094	3.188	2.228	1.781	1.312	1.291	1.219
24		2.708	1.5	1.125	0.771	0.688	0.667	2.875	1.646	1.25	0.896	0.854	0.833	2.979	1.854	1.563	1.063	1.056	1.048

Similar trend was noticed in the relationship between the degree of surface coverage and the concentration of the plant extract.

The activation energy and heat of adsorption

The results of the activation energy and heat of adsorption for the corrosion inhibition of the mild steel in the H_2SO_4 with mango extract are presented in Table 4. The values of the activation energy indicate that the adsorption of the extract of the mango leave on the metal surface conforms to the mechanism of physical adsorption. In all the cases, the heat of adsorption is negative indicating that the adsorption of the extract on the mild steel surface is exothermic.

a) Fitting of data into the Langmuir isotherm

The experimental data were fitted into Langmuir isotherm. As presented in Figure 4, plot of log(C/ θ) versus log(C) shows linear graph.

b) Fitting data into Frumkin isotherm

The experimental data were fitted into Frumkin adsorption isotherm. As presented in Fig. 5, Plot of log((C)*(θ/(1-θ))) versus θ shows linear graph. The linear relationship indicates that Frumkim isotherm was obeyed.

c) Fitting data into Temkin isotherm

The experimental data were fitted into Temkin isotherm as presented in Fig. 6. The graph of θ versus logC shows linear relationship indicating that Temkin adsorption isotherm was obeyed.

d) Fitting data into Flory-Huggins isotherm

The experimental data were fitted into the Flory-Huggins isotherm as presented in Figure 7. Plot of log(θ/C) versus ln(1 - θ) gave linear relationship. The graph showed that Flory-Huggins isotherm was obeyed.

The adsorption parameters for the corrosion inhibition

The parameters of the Langmuir, Frumkin, Temkin and Flory-Huggins isotherms are presented in Table 5. Considering the fitted data to the Langmuir isotherm, the R^2 value is very close to unity, indicating strong adherence to Langmuir adsorption isotherm [15, 25]. From the Frumkin adsorption parameter, the lateral interaction term (α) gave positive values suggesting

Table 3. The inhibition efficiency (IE) and degree of surface coverage (θ) of mild steel in H_2S0_4 with mango leaves extract.

Mild steel area of 5cm*4cm; immersion time of 24 h						
Inhibitor conc. (g l^{-1})	Temperature at 303 K		Temperature at 318 K		Temperature at 333 K	
	IE (%)	Θ	IE (%)	Θ	IE (%)	Θ
0.2	44.62	0.4462	42.75	0.4275	37.76	0.3776
0.4	58.46	0.5846	56.52	0.5652	47.55	0.4755
0.6	71.54	0.7154	68.84	0.6884	64.34	0.6434
0.8	74.62	0.7462	70.29	0.7029	64.55	0.6455
1.0	75.38	0.7538	71.01	0.7101	64.83	0.6483

Table 4. The activation energy and heat of adsorption for the corrosion inhibition

Conc. of the plant extract (g/l)	Activation energy, E_a (kJ/mol)	Heat of adsorption, Q_{ads} (kJ/mol)
0.2	13.645	-7.935
0.4	21.175	-12.299
0.6	20.682	-9.274
0.8	27.591	-13.400
1.0	29.098	-14.191

Table 5. Adsorption parameters for the corrosion inhibition of mild steel in H_2SO_4 by mango leaves extract.

Adsorption Isotherm	Temperature (K)	R^2	Log K	ΔG_{ads} (kJ mol^{-1})	Isotherm property	
Langmuir Isotherm	303	0.9878	-0.081	-9.6		
	333	0.9709	-0.1586	-10.1		
Frumkin Isotherm	303	0.9887	-1.1092	-3.7	α	1.9663
	333	0.9716	-1.0199	-4.6		
Temkim Isotherm	303	0.964	1.660	-19.8	a	-2.444
	333	0.909	1.577	-21.2		-2.672
Flory-Huggins Isotherm	303	0.928	0.633	-13.8	x	1.144
	333	0.776	0.510	-14.4		1.334

attractive behaviour of the inhibitor on the mild steel surface. From the Temkin adsorption parameter, the attractive parameter value (a) is negative, indicating that repulsion exists in the adsorption layer [15]. The value of the size parameter (x) is positive. This shows that the adsorbed species of the plant extract is bulky [14]. The value of free energy of adsorption (ΔG_{ads}) is presented in Table 6. The value of ΔG_{ads} is negative and less than the threshold value of -40 kJ/mol required for chemical adsorption. This is in agreement with previous

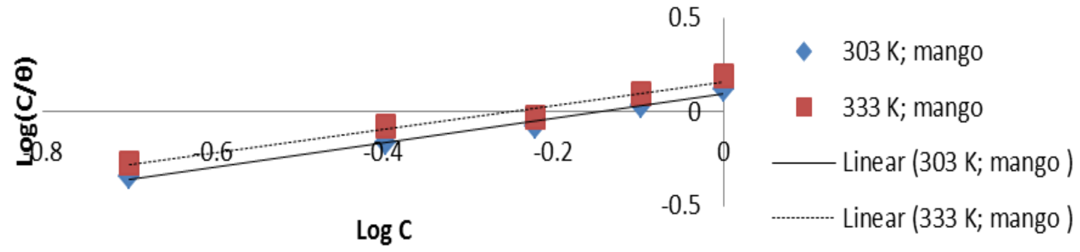

Fig. 4. The ln(C/ θ) versus lnC for the corrosion inhibition of mild steel in H_2SO_4 with mango extract.

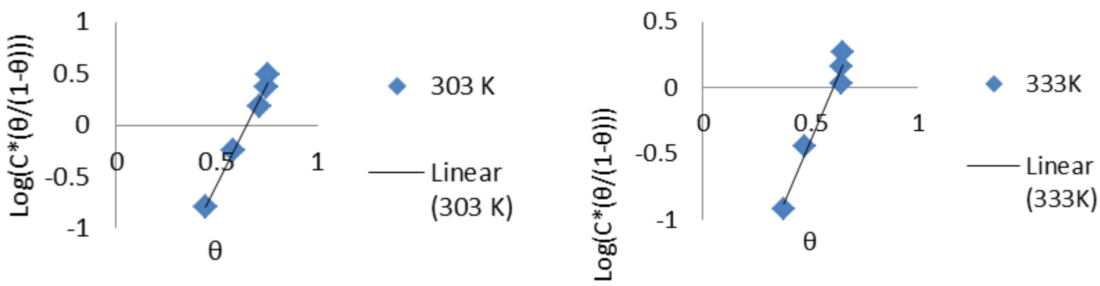

Fig. 5. The log(C*(θ/(1-θ))) versus θ for the corrosion inhibition of mild steel in H_2SO_4 by mango leaves. extract.

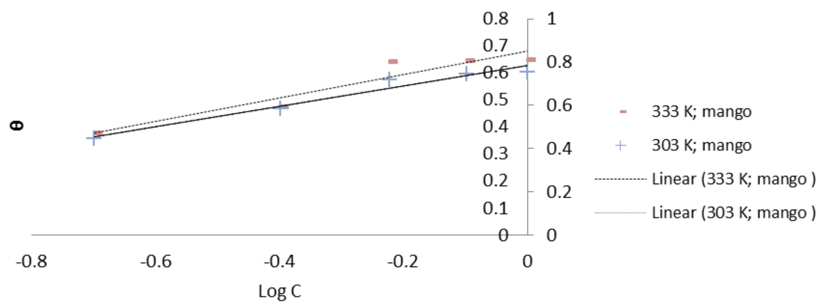

Fig. 6. Plot θ versus lnC for the corrosion inhibition of mild steel in H_2SO_4 with mango extract.

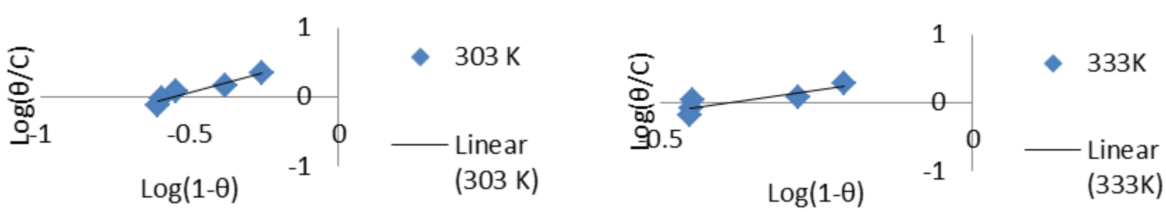

Fig. 7. Log(θ/C) versus log(1-θ) for the corrosion inhibition of mild steel in H_2SO_4 with mango leaves extract.

works [14, 23]. It is clear that adsorption of the mango extract was spontaneous and occurred according to the mechanism of physical adsorption.

The results of the weight loss method using RSM

The responses of weight loss, corrosion rate and inhibition efficiency to the factors of inhibitor's concentration, temperature and time for the corrosion inhibition of the mild steel in H_2SO_4 with the mango extract are presented in Table 6.

Graphical analysis of the inhibition efficiency, IE (%), as determined using RSM

The analysis of inhibition efficiency of the mango

Table 6. The RSM result of the corrosion inhibition of mild steel in H_2SO_4 by mango extract.

Std	Run	Factor 1; A: Inhibitor conc.(g/l)	Factor 2; B: Temperature (K)	Factor 3; C: Time (h)	Response 1; Weight loss (g)	Response 2; Corrosion rate (mg $cm^{-2}h^{-1}$)	Response 3; Inhibition efficiency (%)
1	1	0.2	303	8	0.32	2	38.46
15	2	0.6	318	16	0.4	1.25	59.6
10	3	1	318	16	0.35	1.09	64.65
9	4	0.2	318	16	0.62	1.938	37.37
19	5	0.6	318	16	0.4	1.25	59.6
18	6	0.6	318	16	0.4	1.25	59.6
3	7	0.2	333	8	0.38	2.375	34.48
4	8	1	333	8	0.25	1.563	56.9
6	9	1	303	24	0.32	0.667	75.38
7	10	0.2	333	24	0.89	1.854	37.76
13	11	0.6	318	8	0.27	1.688	51.79
8	12	1	333	24	0.503	1.048	64.83
5	13	0.2	303	24	0.72	1.5	44.62
20	14	0.6	318	16	0.4	1.25	59.6
17	15	0.6	318	16	0.4	1.25	59.6
16	16	0.6	318	16	0.4	1.25	59.6
12	17	0.6	333	16	0.42	1.313	58.82
14	18	0.6	318	24	0.43	0.896	68.84
2	19	1	303	8	0.21	1.313	59.62
11	20	0.6	303	16	0.31	0.969	66.67

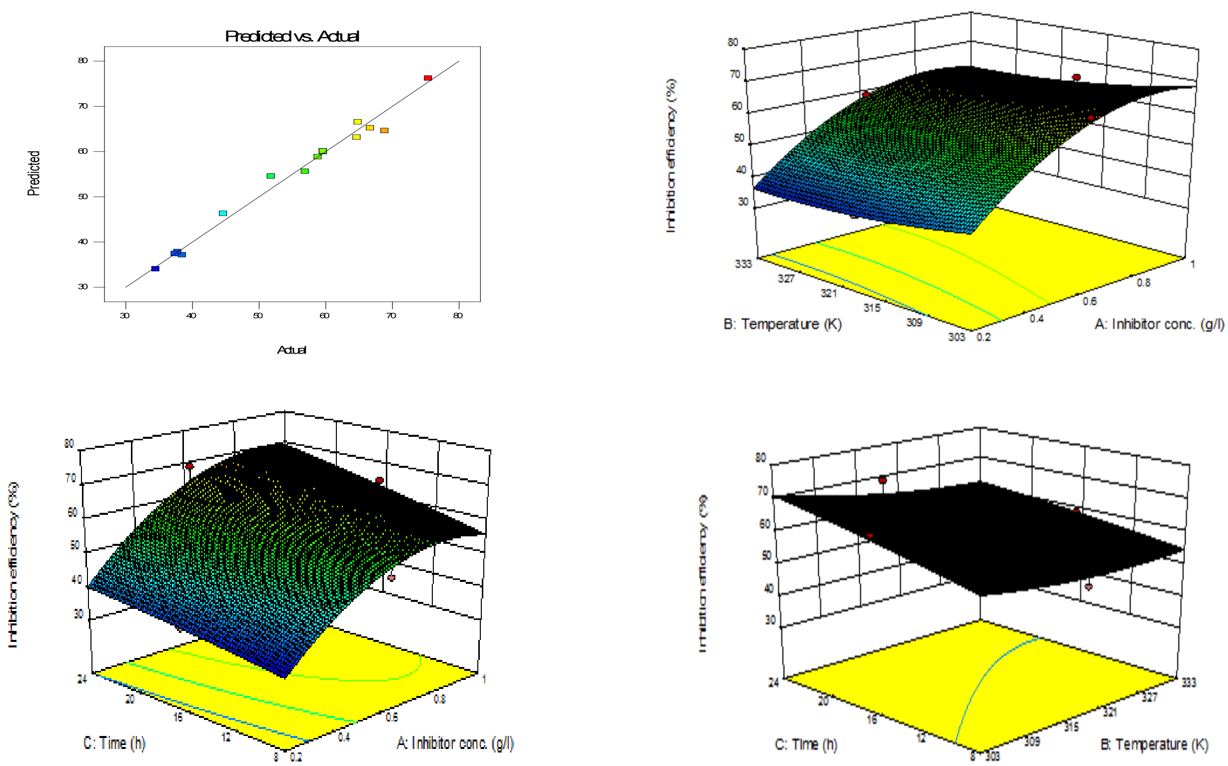

Fig. 8. IE (%) of mango leaves extract as corrosion inhibitor of mild steel in H_2SO_4.

Table 7. Optimal parameters for the corrosion inhibition process.

Optimum inhibitor conc. (g l^{-1})	Optimum temperature (K)	Optimum time (hr)	Optimum inhibition efficiency (%)
0.97	305.33	22.76	74.09

extract (inhibitor) of the mild steel in the H_2SO_4 medium is presented in Figures 8 below. Predicted versus actual plot is used to test the significance of the model's order. The predicted versus actual plot shows linear graph. The graphs (3-D surface plots) show the relationship between the factors and response (inhibition efficiency) of the designed experiment. Increase in concentration increases the inhibition efficiency. Also, inhibition efficiency reduces as temperature rises.

a) Predicted versus Actual IE (%); b) IE (%) versus inhibitor concentration and temperature; c) IE (%) versus inhibitor concentration and time; d) IE (%) versus temperature and time.

Mathematical models of the inhibition efficiency

The mathematical models for inhibition efficiency of the mango extract as corrosion inhibitor of the mild steel in the H_2SO_4 medium are shown in Equation (18a) for the coded factors and Equation (18b) for the actual factors. The model shows the relationship among the inhibition efficiency (IE), inhibitor concentration (A), temperature (T) and time (C). The model in terms of coded factors predicts the response for given levels of each factor. The coded model shows the relative impact of the factors.

IE = +60.09 +12.87*A -3.20* B +5.02*C -0.30*A*B +1.78*A*C -1.34*B*C -9.81*A^2 +1.92*B^2 -0.51*C^2 (18a)

IE = +877.05605 +112.96386 * Inhibitor conc. -5.43653 * Temperature +4.09504 * Time -0.050625 * Inhibitor conc. * Temperature +0.55664 * Inhibitor conc. * Time -0.011156 * Temperature * Time -61.33239 * Inhibitor conc.^2 +8.54141E-003 * Temperature^2 -7.94034E-003 * Time^2 (18b)

Considering the significant terms, the models of eqs. (21a) ad (21b) reduce to eqs. (19a) and (19b).

IE = + 60.09 + 12.87*A - 3.20* B +5.02*C + 1.78*A*C - 9.81*A^2 (19a)

IE = + 877.05605 + 112.96386 * Inhibitor conc. - 5.43653 * Temperature + 4.09504 * Time + 0.55664 * Inhibitor conc. * Time - 61.33239 * Inhibitor conc.^2 (19b)

From the ANOVA for the corrosion inhibition of mild steel in H_2SO_4 by mango leaves extract, the model F-value is 65.84. It shows that the model is significant. There is only a 0.01 % chance that an F-value this large could occur due to noise. Values of "Prob> F" less than 0.0500 indicate model terms are significant. In this case A, B, C, AC, A^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. The "Pred R-Squared" of 0.8591 is in reasonable agreement with the "Adj R-Squared" of 0.9685; the difference is less than 0.2. "Adeq Precision" measures

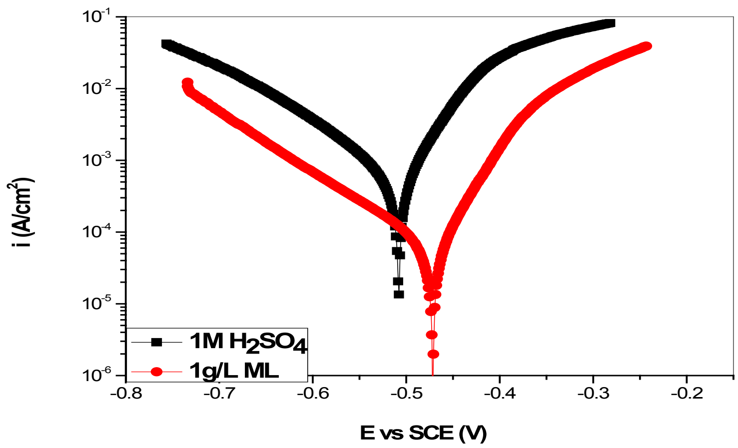

Fig. 9. The potentiodynamic polarization curves.

Table 8. The parameters from Tafel polarization of mild steel immersed in H_2SO_4 medium in the absence and presence of mango extract.

System	E_{corr}	i_{corr}	IE (%)
Mild steel [1 M H_2SO_4]	-485.3	591.3	
+ 1 g/l mango leaves extract	-480	122.1	79

Table 9. Peak, intensity and assignment of FTIR of analysis of the mango leaves and corrosion product of mild steel in H_2SO_4 (with the mango leaves extract).

Mango extract			Corrosion product of mild steel in H_2SO_4 (containing mango leaves extract as inhibitor)		
Peak (cm^{-1})	Intensity	Assignment	Peak (cm^{-1})	Intensity	Assignment
767.66	0.5606	C=C-H, Ar-H bend out of plane	613.36	2.908	C≡C-H, C-H bend
1384.86	0.5355	C-H bend in plane	937.39	2.6214	C=C-H, Ar-H bend out of plane
1570.02	0.5564	C=C stretch, C=N stretch	1415.72	2.5189	C=C
2711.84 2866.14	2.0725 2.4678	C-H stretch			
3267.32	2.3135	O-H stretch, C-H stretch	3128.45 3221.03	1.2264 1.2378	O-H stretch, C-H stretch
3452.48 3761.08	2.5574 2.0784	O-H stretch	3329.04 3622.21 3668.5	1.2491 2.5632 2.5125	O-H stretch

the signal to noise ratio. A ratio greater than 4 is desirable. The ratio of 29.250 indicates an adequate signal.

From the RSM analysis, optimal parameters of the inhibition process are presented in Table 7. The optimum inhibition efficiency of the mango extract is 74.09 %.

The Potentiodynamic Polarization Results

The potentiodynamic polarization curve is presented in Fig. 9. The mango extract inhibits both cathodic and anodic reactions and act as mixed-type inhibitors.

Pentiodynamic polarization result provided the insight into the specific effect of the inhibitor on the anodic and cathodic corrosion reactions [26, 27]. The mango extract was found to inhibit the corrosion of the mild steel in the H_2SO_4 medium, affecting both the cathodic and anodic reactions. The polarization measurements suggest a mixed-inhibition mechanism (Fig. 9). This finding is in agreement with a report [28]. The corrosion process was inhibited by adsorption of the extracted organic matter onto the metal surface. The mechanism of action of the inhibitor depended on the electron density and polarizability of the functional groups present in the molecule. The parameters from Tafel polarization of the mild steel immersed in the H_2SO_4 in the absence and presence of the inhibitor (mango leaves extract) are shown in Table 8.

The Analysis of Mango Extract and Corrosion Product

Table 9 presents the analysis of pure mango leaves extract and corrosion product of mild steel in H_2SO_4 (with the mango leaves extract). The stretched C=C at 1570.02 cm^{-1} peak shifted to 1415.72 cm^{-1}. Also, the stretched O-H at 3761.08 cm^{-1} peak shifted to 3668.5 cm^{-1}.

The shifts in peaks in the FT IR result of the corrosion product, suggest that there was interaction between the mild steel and some molecules of the mango extract. The variation of the number and the nature of the shifts indicate that there was synergy among the functional groups in the corrosion inhibition process.

CONCLUSIONS

From the analyses of the experimental results, the following conclusions can be drawn:

● The inhibition efficiency of the extract was concentration, temperature and time dependent.

● Adsorption of the mango extract on the surface of the mild steel was spontaneous and occurred according to the mechanism of physical adsorption.

● The mango extract exhibited the optimum inhibition efficiency of 74.09 % (at optima inhibitor concentration of 0.97 g l^{-1}, temperature of 305.33 K and time of 22.76 h).

● The mango extract inhibited both cathodic and anodic reactions and acted as mixed-type inhibitor.

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