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Mild Steel Corrosion Inhibition by Various Plant Extracts in 0.5 M Sulphuric acid

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Extract of various plants *(Wrightiatinctoria, Clerodendrumphlomidis, Ipomoeatriloba)* leaves was investigated as corrosion inhibitor of mild steel in 0.5M H_2SO_4 using conventional weight loss, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopic studies. The weight loss results showed that all the plant extracts are excellent corrosion inhibitors, electrochemical polarization data revealed the mixed mode of inhibition and the results of electrochemical impedance spectroscopy have shown that the change in the impedance parameters, charge transfer resistance and double layer capacitance, with the change in concentration of the extract is due to the adsorption of active molecules leading to the formation of a protective layer on the surface of mild steel. Scanning electron microscopic studies provided the confirmatory evidence of improved surface condition, due to the adsorption, for the corrosion protection.

Keywords: Acid corrosion inhibitor; electrochemical polarization; electrochemical impedance spectroscopy; scanning electron microscopy

1. INTRODUCTION

Though many synthetic compounds have shown good anticorrosive activity, most of them are highly toxic to both human beings and environment. The safety and environmental issues of corrosion inhibitors arisen in industries has always been a global concern. Such inhibitors may cause reversible (temporary) or irreversible (permanent) damage to organ system viz., kidneys or liver, or to disturb a biochemical process or to disturb an enzyme system at some site in the body. The toxicity may manifest either during the synthesis of the compound or during its applications.

Although the most effective and efficient organic inhibitors are compounds that have π bonds, the biological toxicity of these products, especially organic phosphate, is documented specifically about their environmental harmful characteristics. From the standpoint of safety, the development of non-toxic and effective inhibitors is considered more important and desirable, nowadays, which are also called eco-friendly or green corrosion inhibitors [1-10].

These toxic effects have led to the use of natural products as anticorrosion agents which are eco-friendly and harmless. In recent days many alternative eco-friendly corrosion inhibitors have been studied and developed, they range from rare earth elements to organic compounds.

In the present work the extracts of the leaves of Wrightia tinctoria, Clerodendrum phlomidis and Ipomoea trilobaare evaluated and studied in detail.

Wrightia tinctoria, an Apocynaceae family plant is Native of central India to Burma and Timor. The leaves of Wrightia tinctoria are elliptic oblong or obovate, acute or acuminate with base acute or rounded. The leaves of this tree yield a blue dye called Pala Indigo. The leaves contain Glycosides, and certain alkaloids [11, 12].

Clerodendrum phlomidis, a Verbenaceae family plant is found on low hills, deserts of Sind, Punjab and Baluchistan.The height of the tree is 6-9m, tolerably smooth and ash coloured. The juice of Clerodendrum phlomidis leaves is used as bitter tonic [13] and also given in neglected syphilitic complaints [14].

Ipomoea triloba, a Convolvulaceae family plant is probably native to West Indies [15], but now naturalized throughout the tropical world. Leaves are heart-shaped, fine-tipped, entire or 3-lobed, mostly 2-5 cm long (but up to 12 cm), longer than wide. It has drought tolerance genes [16].

2. DETAILS OF THE EXPERIMENTAL SET UP FOR THE PRESENT STUDY

2.1. Polarization Cell

Three neck polarization cell of corning glass of half liter capacity was used in the study. The middle neck was used to accommodate working electrode (WE)of MS and the remaining two for the reference electrode (RE/SCE), and the counter electrode (CE) of platinum (99.5% pure).

2.2. Preparation of Electrodes

As described above three types of electrodes were used in the study. To prepare WE, MS rod sample **(**0.09% P, 0.37% Si, 0.01% Al, 0.05% Mn, 0.19% C, 0.06% S and the remainder Fe**)**was obtained and carefully cut into many cylindrical electrodes. After giving rough and fine finish to the edges and corners, as described earlier, one of the WE was polished through a series of emery papers starting from (rougher) 1/0 to smoother 2/0, 3/0 grades and finally through a 4/0 (finer) grade to obtain mirror finish, and was used for an electrical connection to the A C Impedance analyzer CHI 608C. Top end of WE was flattened by lathe machine so that the WE alligator key of analyzer could hold the electrode with a good grip. The upper area of the WE was then precisely covered with the Teflon and epoxy coating. The area of exposed surface of WE was measured precisely, with Vernier caliper. For the weight loss methodspecimens used (length = 2 cm, width = 2 cm, thickness = 0.1 cm) with a tiny hole on the upper part of it. For scanning electron microscopic (SEM) analysis specimens of 1×1 cm of same MS were used. This prepared WE was washed with a luke warm mild detergent (Surf) solution to remove greasy materials and then cleaned and washed repeatedly with double distilled water. It was quickly dried with a soft tissue paper and air dried then shifted into a desiccator or into the electrolyte in polarization cell. Similarly, other pieces of MS were treated to prepare WE for different sets of experiment to avoid re-use of the damaged- surfaced WE of previous set of experiment.

2.3. Weight Loss Method

The polished and pre-weighed MS specimens were tied with threads and suspended in 100 ml test solutions, with and without the inhibitor of different concentrations, for 2h of immersion at temperatures of 303K, 313K and 323K.The temperature was controlled by an aqueous thermostat. After the immersion test, the specimens were carefully washed in double-distilled water, dried and then weighed. The rinse removed loose segments of the film of the corroded samples. Duplicate experiments were performed in each set of the test and the mean value of the WL is reported. The loss in weight was determined by analytic digital micro-balance.

2.4. Electrochemical and Impedance Measurements

The AC impedance measurements are shown as Nyquist plots and polarization data as Tafel plots. The CH Electrochemical analyzer model 608 C (USA) was employed for this purpose. Polarization curves were obtained with a scan rate of 0.01 V/s in the range of ±10 mV for LPR and ± 250 mV for TI vs. the E_{corr} of the WE of the MS and measured against the SCE.Impedance measurements were carried out at the constant value of E_{corr} after the electrode had been immersed60 minutes in the test solution. The frequency range applied was 0.1Hz to 1000Hz.The A.C. signal was 5 mV peak-to-peak with 12 data points per decade.SEM analyses (images) were obtained using HITACHI model S3400 N.

2.5.Preparation of Solutions

2.5.1. Preparation of H_2SO_4 Solutions

The Analytical Reagent grade of H_2SO_4 was used for preparing the acid electrolyte in the present study. An aliquot of this acid was exactly diluted with double distilled water to prepare 0.5 M H_2SO_4 solutions. For each set of experiment freshly prepared 0.5 M H_2SO_4 solutions were used to avoid effect of any contamination.

2.5.2. Preparation of Herbal Extracts Solutions

About 25 g of dried and powdered leaves of each plant was refluxed with 0.5 M H_2SO_4 for about 5 h and was kept overnight to completely extract the basic components as these are soluble in the acid. The solution was filtered off and the filtrate was diluted to 500 ml with 0.5 M H_2SO_4 prepared as above. To know the concentration of mass of plant compounds extracted, 100 ml of the extract was taken to neutralize with 1M NaOH up to pH 8 in order to liberate the solid base from the salt formed in the extract.The neutralized solution was then extracted with chloroform. The chloroform layer consisting of basic organic compounds was evaporated and the resultant gummy material obtained was dried and powdered and weighed accurately by digital micro-balance. From the weight of extracted mass as above, the concentration in mg of the plant compounds (phyto-chemicals) in each of the diluted 100 ml extract is calculated.The concentration range studied was varied from 25 to 200ppm in 100 ml of 0.5 M H_2SO_4.Theoriginal 100 ml acid extract was containing 200 ppm of the mass and was used to study its effect on corrosion of MS in blank 0.5 M H_2SO_4.Theremaining original acid extract was then diluted by 0.5 M H_2SO_4, after calculating the volume of 0.5 M H_2SO_4 to be added to into an aliquot of the original acid extract, to obtain 25, 50, 100 and 150 ppm of concentrations in each of the separate 100 ml diluted extract solutions, as in each set of experiment 100 ml the test solutions were used, except in WL method in which similarly prepared 500 ml of the test solutions were used.

3. RESULTS AND DISCUSSION

3.1. Evaluation of Wrightia tinctoria Leaves as Corrosion Inhibitor of MS in 0.5 M H_2SO_4 Solutions

Based on the WL measurements, W_{corr} and the E_w% for various concentrations of Wrightia tinctoria leaves extract, after 2 h of immersion at the temperatures of 303K, 313K and 323K are given in Table-1. The following equation was used to determine the inhibition efficiency (E_w%):

$$E_W\,\% = 100 \times \frac{W_0 - W_{corr}}{W_0} \quad (1)$$

Where W_{corr} and W_0 are the corrosion rates of steel with and without the additive, respectively.

From the Table-1, it could be observed that the values of E_w% were gradually increased with the increase in concentration of Wrightia Tinctoria leavesextract, reaching a maximum value of 92.07 % at the highest concentration of 200 ppm at temperature of 303 K. With increase in temperature from 303 K to 313K and 323 K, there was a slight decrease in the value of E_w% which may be attributed to the negligible removal of loosely adsorbed some additive molecules by mechanical vibration of thermal energy. The results have projected that the active and adsorbed molecules present in the Wrightia Tinctoria leavesextract have effectively protected the MS even at high temperature.

The degree of surface coverage θ at different concentrations of the additive in acidic media has been evaluated from WL using the equation:

$$\theta = \frac{W_0 - W_{corr}}{W_0} \quad (2)$$

From Table-1, it could be observed that the increase in the value of $W_0$was more pronounced with the rise in temperature for the blank acid solution. In the presence of Wrightia Tinctoria leaves extract, the value of θ was decreased slightly when experimental temperature was increased, which could be caused by desorption of the extract molecules from the MS surface. The slight decrease in θ has suggested that the IE of Wrightia Tinctoria leaves extract was independent of temperature. The results have shown that Wrightia Tinctoria leaves extract could effectively protect the MS even at high temperature.

The adsorption of the inhibitor is influenced by the nature and the charge of the metal, the chemical structure of the inhibitor, distribution of the charge in the molecule, and the type of electrolyte [17-21].

Table 1. Inhibition Efficiency of different concentrations of Wrightia Tinctoria leaves extract for corrosion of MS in 0.5 M H_2SO_4 solutions at various temperatures

Temperature (K)	Concentration of additive (ppm)	W ($\mu g/cm^2$ h)	Inhibition Efficiency E_w%	θ
303	0.5 M H_2SO_4	17.25	-	-
	25	3.42	77.89	0.7789
	50	2.40	84.11	0.8411
	100	1.77	88.42	0.8842
	150	1.43	90.36	0.9036
	200	1.12	92.07	0.9207
313	0.5 M H_2SO_4	18.26	-	-
	25	4.53	75.19	0.7519
	50	3.44	81.16	0.8116
	100	2.80	84.67	0.8467
	150	2.35	87.11	0.8711
	200	1.98	89.15	0.8915
323	0.5 M H_2SO_4	19.48	-	-
	25	5.07	73.96	0.7396
	50	4.24	78.23	0.7823
	100	3.58	81.59	0.8159
	150	2.83	85.46	0.8546
	200	2.14	89.01	0.8901

Important information about the interaction between the inhibitor and steel surface can be provided by the study of adsorption isotherm. In the present work, it could be concluded that θ increased with the inhibitor concentration; this was attributed to more adsorption of inhibitor molecules onto the MS surface. If the adsorption of Wrightia Tinctoria leaves extract is assumed as belongs to the monolayer adsorption, the Langmuir adsorption isotherm could be applied to investigate the mechanism by the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (3)$$

where Cis the inhibitor concentration in the electrolyte and Kis the equilibrium constant for the adsorption/desorption process.

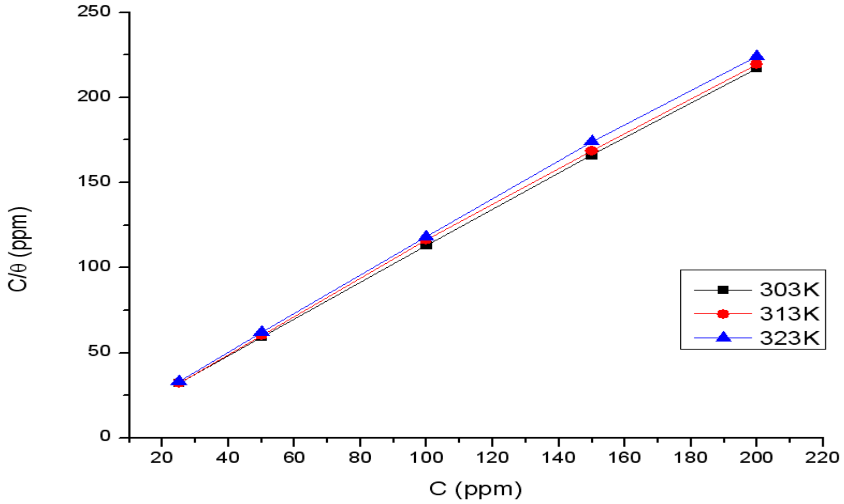

Figure 1. Langmuir adsorption plots for MS in 0.5 M H_2SO_4 at different temperatures in presence of various concentration of Wrightia Tinctoria leaves extract

Three representative Langmuir adsorption plots were obtained at different temperatures with various concentration of theWrightia Tinctoria leavesextract which are shown in Fig.1. The linear plots have the values of slopes equal to 1.06, 1.09 and 1.11for the experimental temperatures of 303, 313 and 323 K, respectively. These results could also indicate that some constituents of extract of Wrightia Tinctoria leaves units occupied more than one adsorption site on the MS surface.

A modified Langmuir adsorption isotherm [22, 23], given by the corrected equation as follows, could be applied to this phenomenon.

$$\frac{C}{\theta} = \frac{n}{K} + nC \qquad (4)$$

The potentiodynamic polarization data are shown in Fig.2 as the Tafel plots for MS in 0.5 M H_2SO_4solutions with the addition of various concentrations of the additive. The corrosion kinetic parameters such as E_{corr}, I_{corr}, anodic and cathodic Tafel slopes (b_a and b_c) were derived from these curves and are given in Table-4.2. The values of E_I% were calculated using the following equation.

$$E_I\% = 100 \times \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \qquad (5)$$

Where I_{corr} and $I_{corr(inh)}$ are the values of corrosion current densities of MS without and with the additive, respectively, which were determined by extrapolation of the cathodic and anodic Tafel lines to the value of E_{corr} by the software provided with the equipment.

The inhibiting properties of Wrightia Tinctoria leaves extract have also been evaluated by determining the values of R_p. The corresponding R_p values of MS in 0.5 M H_2SO_4solutions, in the absence and presence of different concentrations of the extract, are given in Table-2. The values of IE (E_{Rp}%) were calculated as follows:

$$E_{Rp}\% = 100 \times \frac{R_{P(inh)} - R_P}{R_{P(inh)}} \qquad (6)$$

R_p and $R_{p(inh)}$ are the polarization resistances in the absence and presence of the additive, respectively.

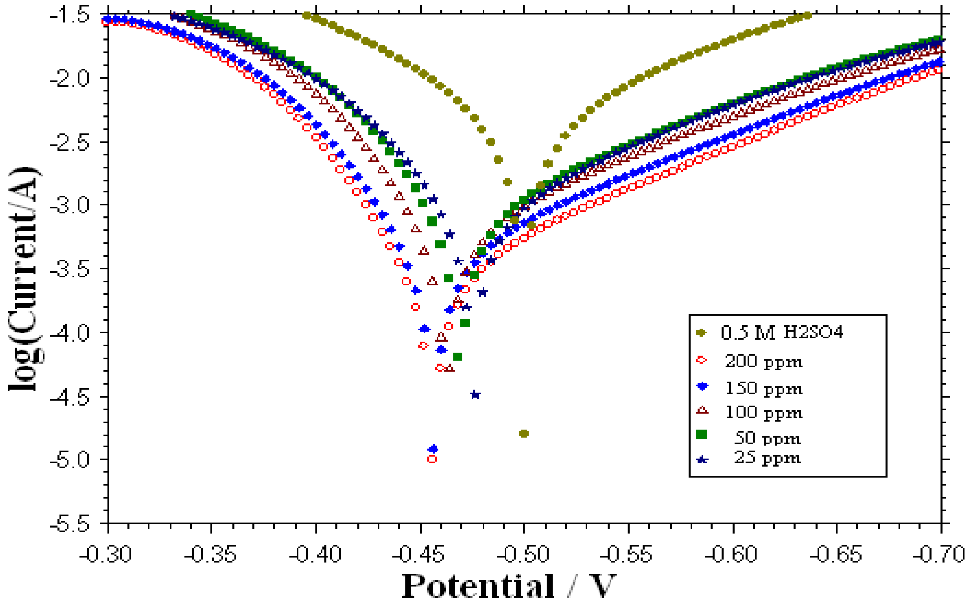

Figure 2. Tafel plots showing effect of increasing concentrations of Wrightia Tinctoria leaves extracts on corrosion of MS in H_2SO_4 solutions

From the Table-2, it could be found that the I_{corr} values were progressively decreased with steady increase in the concentration of additive up to 200 ppm from 5.91 to 0.373 mA/cm^2 leading to 94 % of IE. There was also an anodic shift of the E_{corr} value of -0.5V (blank) to -0.46 V at 200 ppm indicating that the Wrightia Tinctoria leaves extracts acted as anodic inhibitors for MS in 1 N H_2SO_4 solutions which was supported by the gradual and significant decrease of anodic Tafel slope, b_a =143 mV/decade of blank to 85 mV/ decade at 200 ppm. It could be derived from this decrease that the rate of anodic dissolution was much retarded in comparison to that of cathodic hydrogen evolution. There was decrease of only 14 mV/decade in the corresponding values of cathodic Tafel slopes to show that the extract must have acted predominantly by blocking anodic sites, and also cathodic sites to some extent, and the extract containing the active molecules were adsorbed effectively and behaved as mixed-type of the acid corrosion inhibitors.

The R_p values of MS in 0.5 M H_2SO_4solutions in the absence and presence of different concentrations of Wrightia Tinctoria leaves extract are also given in Table-2. From the results, it could be seen that the $R_p$values were gradually increased with increase in the concentration of the additive and the values of E_{Rp}% were also increased to attain 90% at 200 ppm of the concentration to confirm the effective corrosion inhibition

Table 2. Effect of Wrightia Tinctoria leaves extracts on corrosion of MS in 0.5 M H_2SO_4 solution studied by electrochemical polarizations in TI and LPR methods

Concentration of inhibitor (ppm)	E_{corr} V	Tafel Constant (mV/decade) babc		I_{corr} (mA/cm^2)	R_p (ohm cm^2)	E_I %	E_{Rp}%
0	-0.4997	143	160	5.914	06	-	-
25	-0. 4750	110	145	1.261	22	79	73
50	-0.4689	108	146	1.243	24	79	75
100	-0.4727	102	149	0.921	29	84	79
150	-0.4565	93	149	0.545	46	90	87
200	-0.4556	85	146	0.373	62	94	90

The corrosion measures of MS in 0.5 M H_2SO_4solutions, in absence and the presence of various concentrations of Wrightia Tinctoria extract were also investigated by EIS technique. The resultant Nyquist plots are shown in Fig 3. Again in this case also, there was a gradual increase in the diameter of each semicircle of the Nyquist plot due to the increase in the number of inhibitive molecules present in the extract when the concentration was raised from 25 to 200 ppm. This increase of the diameters has clearly shown that the R_t values were also increased from 7 to 269 Ohms.cm^2 at the highest concentration of 200 ppm due to the formation and gradual improvement in compactness of the barrier layer of the inhibitive molecules (IE 97 %) adsorbed, and as a result the acid corrosion rates of MS were steadily decreased.

Table-3embodies various parameters such as R_t, double layer capacitance (C_{dl}) and IE (E_R %). It was observed that there was a gradual decrease in values of C_{dl} from 155 to 60 µF/cm^2 with increase in the concentration from 25 to 200 ppm of the extract. This considerable decrease has confirmed that the inhibitive molecules of the extracts were adsorbed on the MS surface and have decreased the roughness of the MS surface created due to corrosion by 0.5 M H_2SO_4 solution. The values of E_R % were calculated by the equation as follows:

$$E_R\% = 100 \times \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \qquad (7)$$

Where R_t and $R_{t(inh)}$ are charge-transfer resistance values in the absence and presence of the inhibitor, respectively.

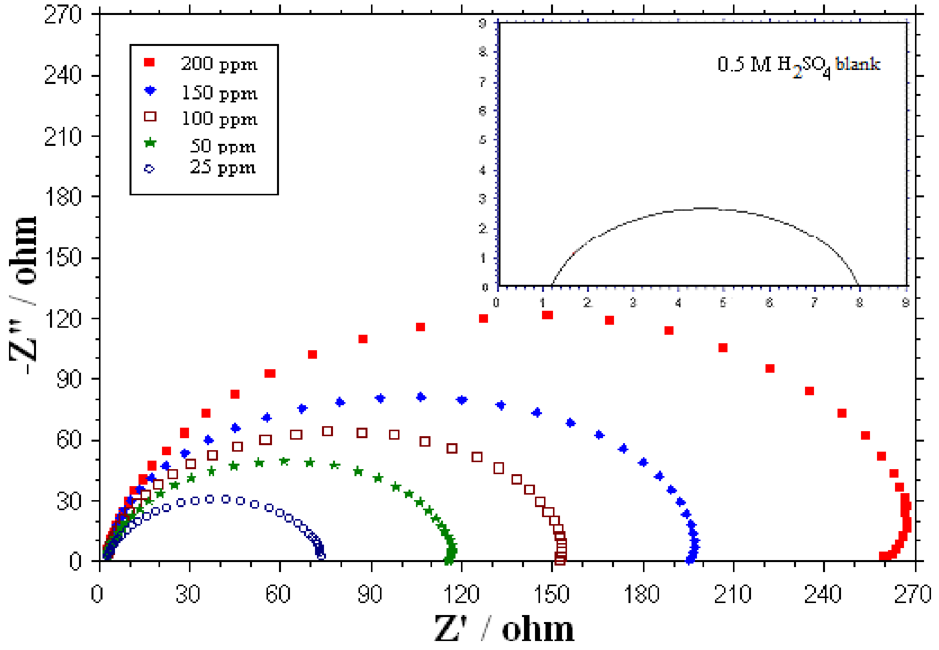

Figure 3. Nyquist plots showing effect of increasing concentration of Wrightia Tinctoria leaves extract on corrosion of MS in H_2SO_4 solutions

To calculate the values C_{dl}, the frequency (f_{max}) at which the imaginary component of the impedance is maximum $-Z_{im(max)}$was found and C_{dl} values were obtained from the following equation:

$$C_{dl} = \frac{1}{2\pi f_{max} R_t} \tag{8}$$

Table 3. Data from electrochemical impedance measurements for corrosion of MS in 0.5 M H_2SO_4 solutions at various concentrations of Wrightia Tinctoria leaves extract

Concentration of inhibitor (ppm)	R_t Ohm.cm^2	C_{dl} µF/cm^2	Inhibition Efficiency E_R %
0	07	155.27	-
25	73	84.82	90
50	118	76.39	94
100	156	69.30	96
150	198	65.15	96
200	269	59.68	97

The SEM image in Fig.4a shows that the surface of MS was awfully damaged and roughened in the absence of the extract while that in Fig.4b very clearly shows the formation of a bright grayish blue film due to adsorption of active Wrightia Tinctoria leaves constituents on the MS surface, and there was notable corrosion inhibition.

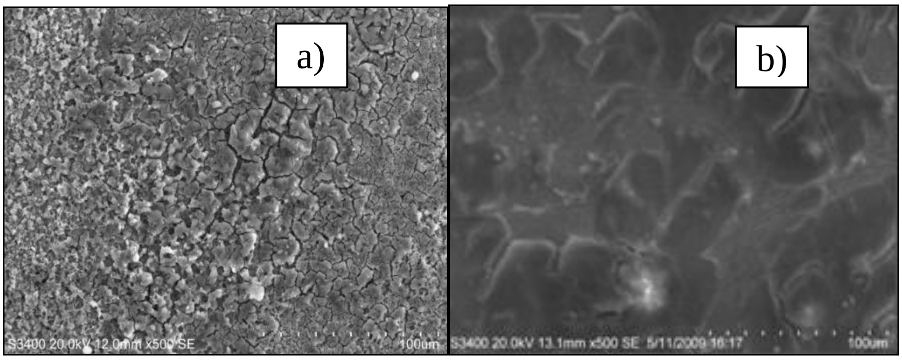

Figure 4. SEM image of MS surface, a) in 0.5 M H_2SO_4 solution, and that of b) with 200 ppm of Wrightia Tinctoria leaves extract

3.2. Evaluation of Clerodendrum phlomidis Leaves as Corrosion Inhibitor of MS in 0.5 M H_2SO_4 Solutions

From the WL measurements, W_{corr} and the E_w% at various concentrations of Clerodendrum phlomidis leaves extract, after 2 h of immersion, at the temperatures of 303K, 313K and 323K are given in Table-4.

Table 4. Inhibition Efficiency of MS in 0.5 M H_2SO_4 solutions at various concentrations of Clerodendrum phlomidis leaves extract at various temperatures

Temperature (K)	Concentration of additive (ppm)	W (µg/cm^2 h)	Inhibition Efficiency E_w%	θ
303	0.5 M H_2SO_4	18.67	-	-
	25	3.43	81.62	0.8162
	50	2.32	87.57	0.8757
	100	1.83	90.19	0.9019
	150	1.33	92.87	0.9287
	200	1.25	93.30	0.9330
313	0.5 M H_2SO_4	19.25	-	-
	25	4.06	78.90	0.7890
	50	3.02	84.31	0.8431
	100	2.50	87.01	0.8701
	150	2.06	89.29	0.8929
	200	1.68	91.27	0.9127
323	0.5 M H_2SO_4	20.21	-	-
	25	4.69	76.79	0.7679
	50	3.79	81.25	0.8125
	100	2.94	85.45	0.8545
	150	2.51	87.58	0.8758
	200	2.11	89.56	0.8956

It could be clearly observed from the table that the values of E_w% were increased with increase in the concentration of Clerodendrum phlomidis leaves extract, reaching a maximum value of 93.30 % at the highest concentration of 200 ppm at temperature of 303 K. The results have shown that Clerodendrum phlomidis leavesextract could effectively protect the steel even at high temperature. The slight decrease in E_w% at 200 ppm of the additive, due to increase in temperature, could be attributed to the removal of loosely bound inhibitive molecules of the extract on the MS surface which was due to increase in thermal vibrations.

Assuming that the adsorption of Clerodendrum phlomidis leaves extract belongs to the monolayer adsorption, the modified Langmuir adsorption isotherm could be applied to investigate the mechanism of corrosion inhibition.

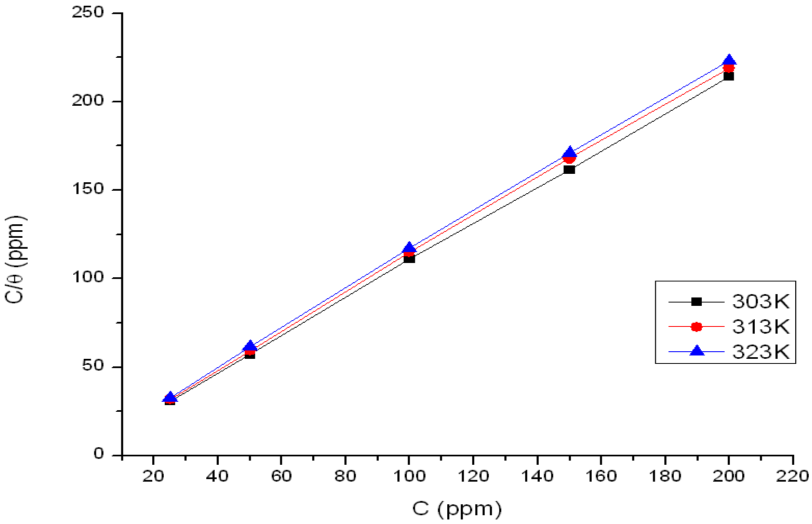

Figure 5. Langmuir adsorption plots for MS in 0.5 M H_2SO_4 at different temperatures in the presence various concentration of Clerodendrum phlomidisleaves extract

Three representative Langmuir adsorption plots at different temperatures, in absence and the presence of various concentrations of Clerodendrum phlomidis leaves extract are shown in Fig.5. These linear plots have the slopes with values equal to 1.06, 1.08 and 1.09 for the experimental temperature of 303, 313 and 323 K, respectively. These results proved that some constituents of Clerodendrum phlomidis leaves units occupied more than one adsorption site on the steel surface. A modified Langmuir adsorption isotherm could be applied in this case too.

Fig.6 shows the Tafel plots obtained by the potentiodynamic polarization for MS corroding in 0.5 M H_2SO_4solutions, without and with the addition of various concentrations of the additive-Clerodendrum phlomidis leaves extract.

From observation of the Table-5, it was found that the I_{corr} values were gradually decreased with gradual increase in the concentration of additive up to 200 ppm from 5.914to 0.412 mA/cm^2 leading to 93 % of IE. As described in earlier cases, there was an anodic shift of the E_{corr} value of -0.5V (blank) to -0.45 V at 200 ppm of the additive proving that the Clerodendrum phlomidis leaves extracts have acted as the anodic inhibitors for MS corroding in 0.5 M H_2SO_4 solutions, and it was well supported by the gradual and significant decrease of anodic Tafel slope, b_a =143 mV/decade of blank to 93 mV/decade at 200 ppm of the additive. It could confidently be derived from this decrease that the rate of anodic dissolution was much retarded in comparison to that of cathodic hydrogen evolution as there was decrease of only 19 mV/decade in the corresponding values of cathodic Tafel slopes. This means that the extract must have acted largely by blocking anodic sites, and also cathodic sites to some extent, and the extract having the active molecules behaved as mixed-type of the acid corrosion inhibitor.

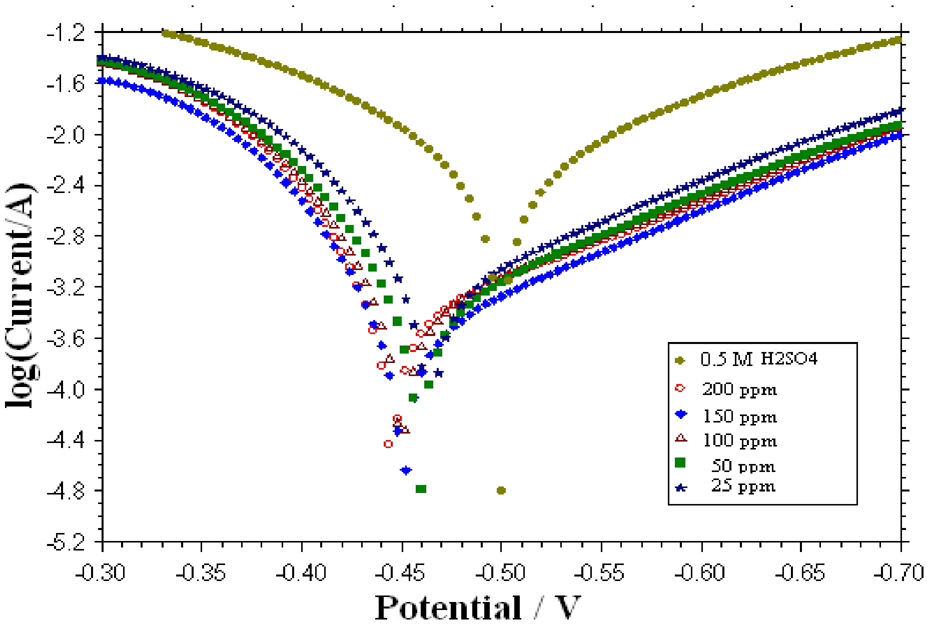

Figure 6. Tafel plots showing effect of Clerodendrum phlomidis leaves extracts on corrosion of MS in H_2SO_4 medium

The R_p values of MS corroding in 0.5 M H_2SO_4solutions in the absence and presence of different concentrations of Clerodendrum phlomidis leaves extract are also given in Table-5. From the results, it was found that the $R_p$values were gradually increased with increase in the concentration of the extract and the values of E_{Rp}% were increased to attain 90% at 200 ppm of the Clerodendrum phlomidis leaves extract.

Table 5. Effect of Clerodendrum phlomidis leaves extracts on corrosion of MS in 0.5 M H_2SO_4 solutions studied by electrochemical polarizations in TI and LPR methods

Concentration of inhibitor (ppm)	E_{corr} V	Tafel Constant (mV/decade)		I_{corr} (mA/cm^2)	R_p (ohm cm^2)	E_I %	E_{Rp}%
		ba	bc				
0	-0.4997	143	160	5.914	06	-	-
25	-0.4644	103	151	0.932	29	84	79
50	-0.4600	94	151	0.677	39	89	85
100	-0.4514	93	152	0.623	41	89	85
150	-0.4503	92	152	0.416	58	93	90
200	-0.4459	93	153	0.412	60	93	90

EIS based Nyquist plots are shown in Fig.7. As observed in previous cases, here also there was a regular increase in the diameter of each semicircle of the Nyquist plot due to increase in the number of inhibitive molecules present in the extract when the concentration was raised from 25 to 200 ppm.

This increase of the diameters has remarkably confirmed that the corresponding R_t values were also increased from 7 to 365 Ohms.cm^2 at highest concentration of 200 ppm due to the formation and gradual improvement of the barrier layer of the inhibitive molecules (IE 97 %), and as a result the acid corrosion rates of MS were gradually decreased.

Table-6 embodies various values of R_t, C_{dl} and E_R %. It was found that there was a gradual decrease in values of C_{dl} from 155 to 52 µF/cm^2 with increase in the concentration of the extract. This considerable decrease has confirmed that the inhibitive molecules of the extracts were adsorbed on the MS surface as a result there was decrease in the roughness of the MS surface.

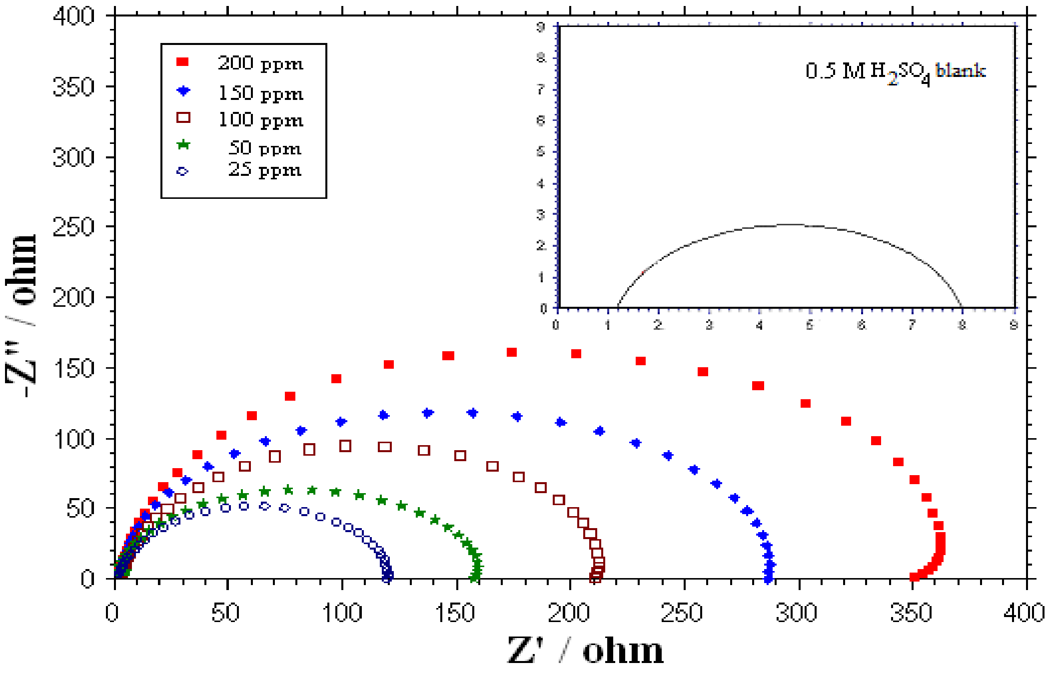

Figure 7. Nyquist plots showing effect of Clerodendrum phlomidis leaves extracts on corrosion of MS in 0.5 M H_2SO_4 solutions

Table 6. Data from electrochemical impedance measurements for MS corroding in 0.5 M H_2SO_4 solutions at various concentrations of Clerodendrum phlomidis leaves extracts

Concentration of inhibitor (ppm)	R_t Ohm.cm^2	C_{dl} µF/cm^2	Inhibition Efficiency E_R %
0	07	155.27	-
25	120	58.62	94
50	164	56.23	96
100	212	54.91	97
150	291	52.30	98
200	365	51.62	98

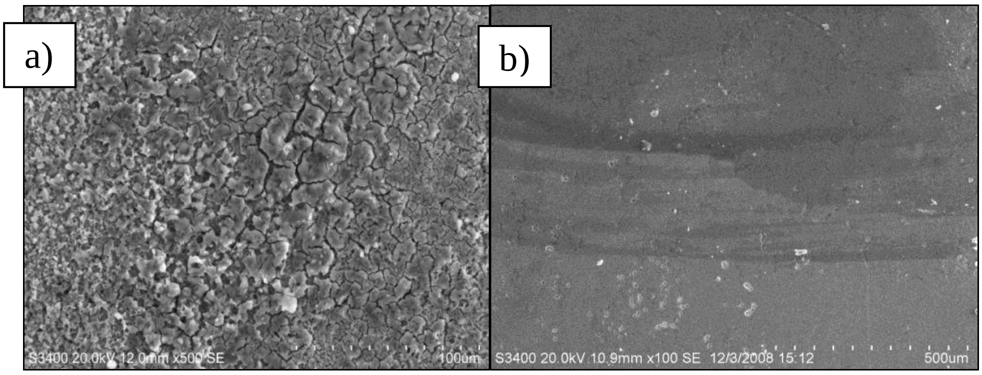

Figure 8. SEM image of MS surface, a) in 0.5 M H_2SO_4 solution, and that of b) with 200 ppm of Clerodendrum phlomidis leaves extract

The SEM photograph in Fig.8a shows that the surface of MS was tremendously damaged due to corrosion, in the absence of the extract while that in Fig.8bcould clearly confirmed the formation of a light bluish film due to adsorption of the active Clerodendrum phlomidis leaves constituents on the MS surface and that the film was responsible for the corrosion inhibition.

3.3. Evaluation of Ipomoea triloba Leaves as Corrosion Inhibitor of MS in 0.5 M H_2SO_4 Solutions

Table 7. Inhibition Efficiency of MS in 0.5 M H_2SO_4 solutions at various concentrations of Ipomoea triloba leaves extract at various temperatures

Temperature (K)	Concentration of additive (ppm)	W (μg/cm^2 h)	Inhibition Efficiency E_w%	θ
303	0.5 M H_2SO_4	15.71	-	-
	25	3.42	78.25	0.7825
	50	2.48	84.21	0.8421
	100	1.88	88.01	0.8801
	150	1.64	89.56	0.8956
	200	1.25	92.03	0.9203
313	0.5 M H_2SO_4	16.87	-	-
	25	4.04	76.03	0.7603
	50	3.02	82.11	0.8211
	100	2.47	85.36	0.8536
	150	2.00	88.13	0.8813
	200	1.66	90.14	0.9014
323	0.5 M H_2SO_4	17.63	-	-
	25	4.56	74.15	0.7415
	50	3.59	79.63	0.7963
	100	2.96	83.22	0.8322
	150	2.55	85.56	0.8556
	200	1.99	88.69	0.8869

From the WL measurements, W_{corr} and the E_w% at various concentrations of Ipomoea triloba leaves extract, after 2 h of immersion, at the temperature of 303K, 313K and 323K are given in Table-7.

From the table, it was found that the values of E_w% were increased with increase in concentration, reaching a maximum value of 92.03 % at a highest concentration of 200 ppm at the temperature of 303 K. The results have shown that Ipomoea triloba leavesextract could effectively protect the steel even at high temperature. The slight decrease in E_w% at 200 ppm of the additive, due to increase in temperature, could be attributed to the removal of loosely bound inhibitive molecules of the extract on the MS surface as a result of increase in thermal vibrations.

If it is assumed that the adsorption of Ipomoea triloba leaves extract were belonged to the monolayer adsorption, the modified Langmuir adsorption isotherm could be applied to investigate the mechanism of corrosion inhibition.

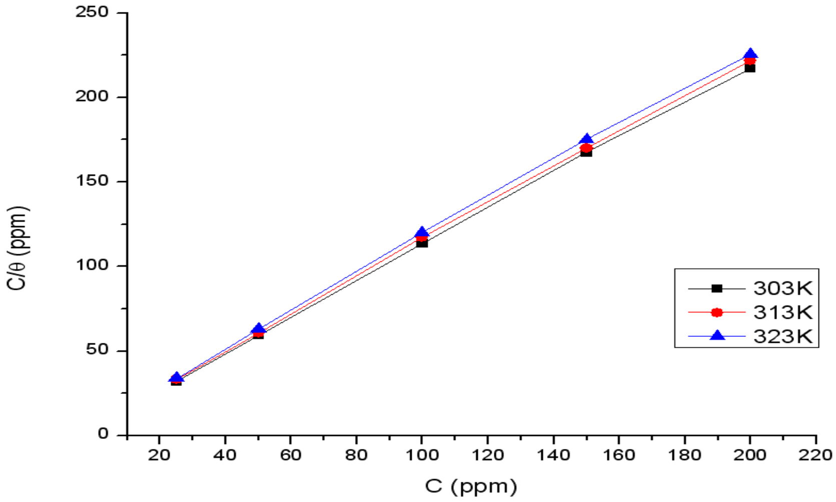

Figure 9. Langmuir adsorption plots for MS in 0.5 M H_2SO_4 at different temperatures in presence various concentration of Ipomoea triloba leaves extract

Three representative Langmuir adsorption plots at different temperatures are shown in Fig.9. These linear plots have the values of slopes equal to 1.06, 1.08 and 1.08for the experimental temperature of 303, 313 and 323 K, respectively. These results have firmly indicated that some constituents of Ipomoea triloba leaves units occupies more than one adsorption site on the steel surface. As was the case in previous section, here also a modified Langmuir adsorption isotherm could be applied.

The potentiodynamic polarization data are shown as the Tafel plots for MS in 0.5 M H_2SO_4solutions for various concentrations of the additive-Ipomoea triloba leaves extract in Fig.10.

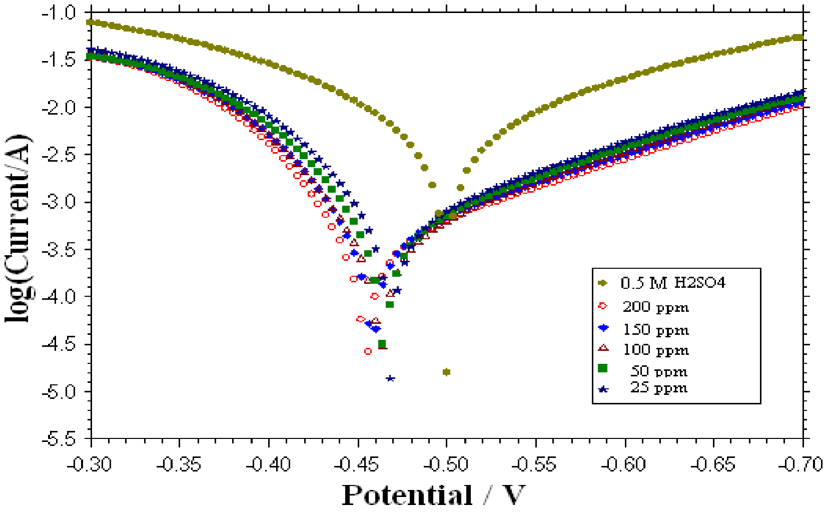

Figure 10. Tafel plots showing effect of increasing concentration of Ipomoea triloba leaves extracts on corrosion of MS in H_2SO_4 solutions

From the Table-8, it was observed that the I_{corr} values were gradually decreased with gradual increase in the concentration of the additive up to 200 ppm from 5.914to 0.432 mA/cm^2 leading to 89 % of IE. There was also an anodic shift of the E_{corr} value of -0.5V (blank) to -0.45 V at 200 ppm of the additive indicating that the Ipomoea triloba leaves extracts acted as the anodic inhibitors for MS corroding in 0.5 M H_2SO_4solutions which was supported by the gradual and significant decrease of anodic Tafel slope, b_a =143 mV/decade of blank to 92 mV/decade at 200 ppm. It could be derived from this decrease that the rate of anodic dissolution was much retarded in comparison to that of cathodic hydrogen evolution. There was decrease of only 11 mV/decade in the corresponding values of cathodic Tafel slopes to show that the extract must have acted predominantly by blocking anodic sites, and also cathodic sites to some extent, and the extract having the active molecules has behaved as mixed-type of the acid corrosion inhibitor.

The R_p values of MS corroding in 0.5 M H_2SO_4solutions in the absence and presence of various concentrations of Ipomoea triloba leaves extract are also given in Table-8. From observation of the results, it could be gathered that the $R_p$values were gradually increased with increase in the concentration of the additive, and the values of E_{Rp}% were increased to attain 89 % at 200 ppm of Ipomoea triloba leaves extract.

Table 8. Effect of Ipomoea triloba leaves extracts on corrosion of MS in 0.5 M H_2SO_4 solutions studied by electrochemical polarizations in TI and LPR methods

Concentration of inhibitor (ppm)	E_{corr} V	Tafel Constant (mV/decade) babc		I_{corr} (mA/cm^2)	R_p (ohm cm^2)	E_I %	E_{Rp}%
0	-0.4997	143	160	5.914	06	-	-
25	-0.4689	102	149	0.891	30	85	80
50	-0.4653	100	150	0.717	36	88	83
100	-0.4627	95	149	0.479	49	92	88
150	-0.4582	94	152	0.451	51	92	88
200	-0.4547	92	152	0.432	55	93	89

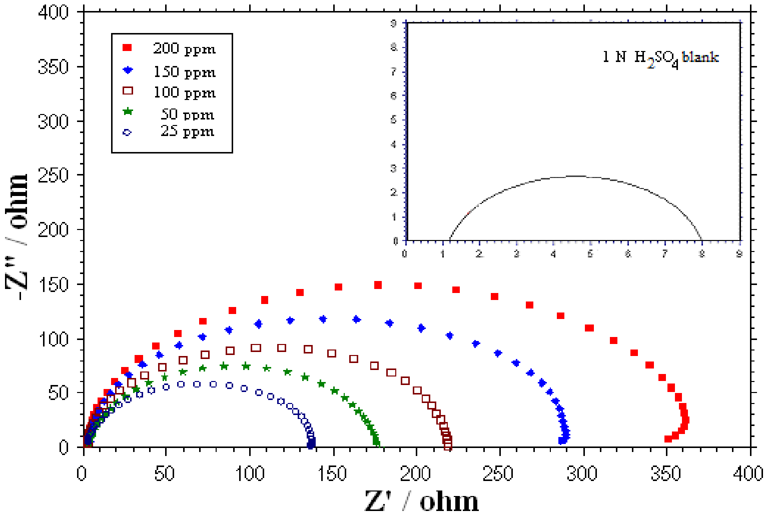

Figure 11. Nyquist plots showing effect of increase in concentration of Ipomoea triloba leaves extract on corrosion of MS in H_2SO_4 solutions

The behaviour of MS corroding in 0.5 M H_2SO_4 solutions, in absence and the presence of various concentrations of Ipomoea triloba extract were also investigated by EIS technique. The resultant Nyquist plots are shown in Fig.11. In the figure, it could be observed that there was also a gradual increase in the diameter of each semicircle of the Nyquist plot due to increase in the number of inhibitive molecules present in the extract when the concentration was raised from 25 to 200 ppm. This increase of the diameters have confirmed that the R_t values were also increased from 7 to 364 Ohms.cm^2 at the highest concentration of 200 ppm due to formation and gradual improvement of the barrier layer of the inhibitive molecules (IE 98 %), and as a result the acid corrosion rates of MS were gradually decreased.

Table-9 embodies the values of R_t, C_{dl} and E_R %. There was a gradual decrease in values of C_{dl} from 155 to 52 µF/cm^2 with an increase in the concentration of the extract. This considerable decrease also confirmed that the inhibitive molecules of the extracts were adsorbed on the MS surface, and as a result, there was remarkable decrease in the roughness of the corroded MS surface.

Table 9. Data from electrochemical impedance measurements for MS corroding in 0.5 M H_2SO_4 solutions at various concentrations of Ipomoea triloba leaves extracts

Concentration of inhibitor (ppm)	R_t Ohm.cm^2	C_{dl} µF/cm^2	Inhibition Efficiency E_R %
0	07	155.27	-
25	137	68.23	95
50	177	61.70	96
100	221	58.91	97
150	288	55.30	98
200	364	51.58	98

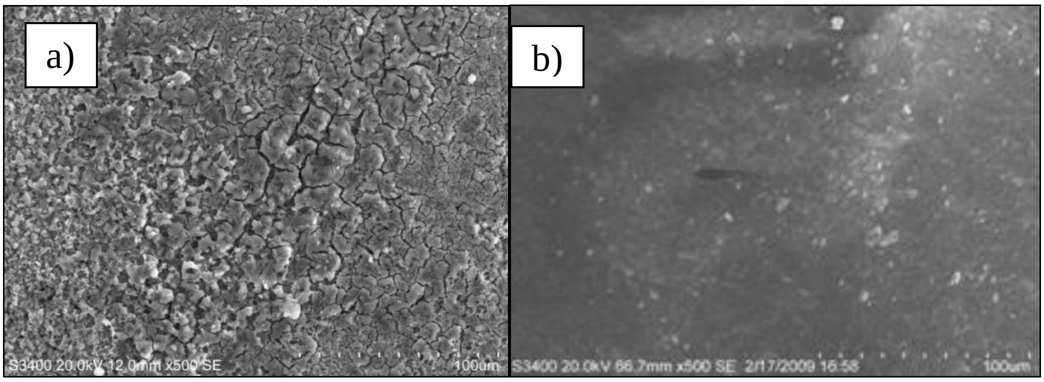

Figure 12. SEM image of MS surface, a) in 0.5 M H_2SO_4 solution, and that of b) with 200 ppm of Ipomoea triloba leaves extract

4. COMPARISON OF THE RESULTS

In order to present juicy part of the actual work carried out by the author, the results generated by three important methods are compared and summarized.

4.1. Comparisons from the Weight Loss method

A general trend of gradual increase in the weight loss with an increase in temperature is observed, and a gradual decrease in the degree of MS surface coverage and E_w% at highest concentrations of 200 ppm of each extract to establish that there was overall good stability and compactness of the barrier layers formed due adsorption of active molecules present in each extract and a gradual removal of some inhibitive molecules which were loosely adsorbed.

From these data, it could be concluded that the order of E_w% at highest concentrations of 200 ppm of each extract at the highest temperature of 323 K is as follows.

Clerodendrum phlomidis > Ipomoea triloba > Wrightia tinctoria

4.2. Comparisons from Potentiodynamic Polarization

From the comparison of the values of E_I % and E_{Rp}% obtained for various extracts, it could be concluded that the order of IE was as follows:

Wrightia tinctoria > Clerodendrum phlomidis = Ipomoea triloba

4.3. Comparisons from Electrochemical AC impedance measurements

When 200 ppm of each of the extracts were added in the blank systems, there were remarkable increases in the value of R_t to confirm that the active molecules present in each extract were efficiently and strongly adsorbed on the MS surface which was not disturbed (damaged) during AC Frequency response Analysis at OCP under no DC polarization, i.e. adverse effect of DC polarization in accessing the surface conditions of MS was nullified, and as a result, on the undisturbed surface, there was onset of strong adsorption of the molecules present in each extract. This has given much higher resistance to the phenomena of charge transfer reactions of the corrosion.

From the comparison of the values of E_R %, given in this table for various extracts, it could be concluded that the order of IE was as follows:

Clerodendrum phlomidis = Ipomoea triloba > Wrightia tinctoria

The stability of the barrier layer formed by the adsorbed molecules of Clerodendrum phlomidis extract was highest when there were no DC polarizations exerted in EIS and when the WL measurements were carried out at the highest temperature of 323 K.

The stability of the barrier layer formed by the adsorbed molecules of Ipomoea triloba extract was highest and equal to that of Clerodendrum phlomidis extract when there were no DC polarizations exerted in AC Impedance method but when the WL measurements at the highest temperature of 323 K and the DC polarizations at ambient temperature were carried out, the stability of the layers was considerably decreased due to removal of the loosely adsorbed molecules on the steel surface. The adsorbed molecules Wrightia tinctoria extracts could perform well under the adverse effect of the DC polarizations but less than those of *Clerodendrum phlomidis* extract or of Ipomoea triloba extract when EIS was employed to reveal that the stability of such layers was much less even under no influences of DC polarizations and temperature of 323 K.

Phytochemical studies of *Clerodendrum* phlomidis leaves shows presence of L-dopa, lupeol, β-sitosterol [24]; adrenaline [25]; 7-hydroxyflavone, 7-hydroxyflavone-7-Oglucoside [26]; 24β-ethylcholesta-5,22E,25-triene-3β-ol [27]; pectolinarigenin and chalcone [28]. On the basis of results, we may introduce that the inhibitory action of *Clerodendrum phlomidis* extract may be explained by the presence of infinite the presence of a large variety of compounds that act by intermolecular synergy of all constituents. [29-31].

5. CONCLUSION

From the observation of these ranges of IE, it could safely be concluded that the evaluation of the new acid corrosion inhibitors be made by the time consuming but reliable WL method for the industrial applications where thermal stability of the adsorbed layers is of much concern, and such inhibitors can be evaluated by less time consuming methods of DC polarizations under simulated conditions because above stated lower ranges of inhibition efficiencies are almost comparable and provide the opportunity to add little more amount of the inhibitors during scale-ups and applications for the safe industrial operations of the descaling, acid pickling and general cleaning of the steel surfaces.

It could also be concluded from the range of E_R % (97-98%) which was much narrow and the results quickly generated by the EIS measurements were reproducible and reliable, under no adverse influences of temperature and DC polarizations, to evaluate such eco-friendly (green) acid corrosion inhibitors, in most undisturbed and natural conditions of the systems, to save our Mother Earth and for profitable commercialization.

The results of all the experimental methods were in very good agreement to confirm the above conclusions of the corrosion of MS in stagnant 0.5 M H_2SO_4solutions and its effective inhibition by each of the herbal extracts. Each of the Photographs obtained by SEM has clearly revealed the formation of the strong protective film on the surface of MS to confirm the noticeable corrosion inhibition.

Because the leaves of various plants used here were not frequently consumed by the human beings and by the animals, the evaluation as stated above of such leaves will find a considerable eco-friendly alternative and commercial use to protect MS from the corrosion by the mineral acids like H_2SO_4.

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