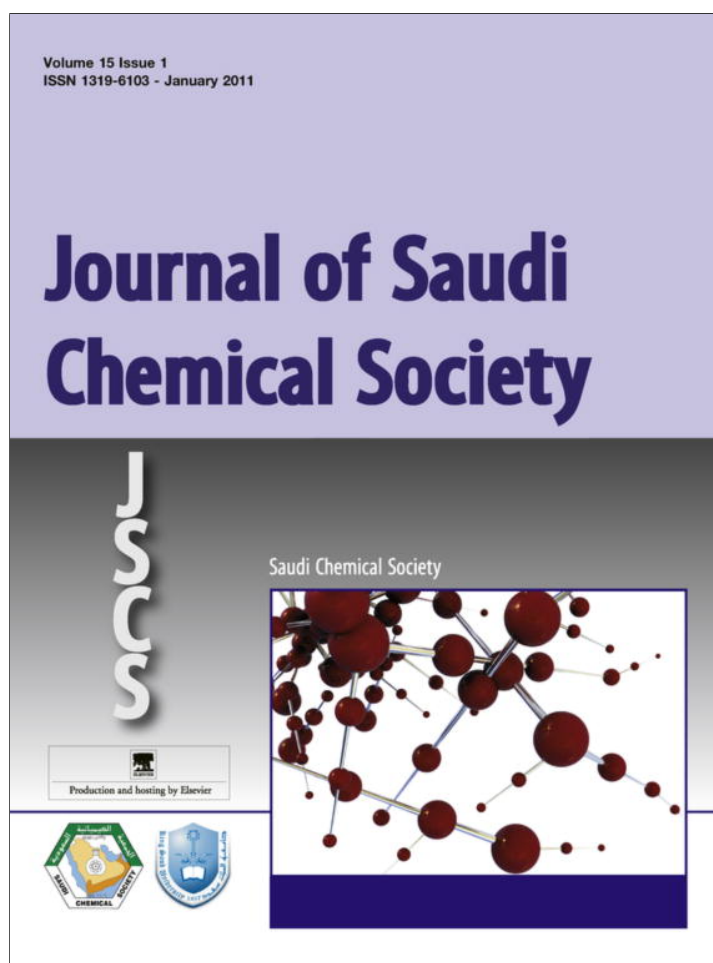


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ORIGINAL ARTICLE

Medicago Sativa plant as safe inhibitor on the corrosion of steel in 2.0M H₂SO₄ solution

A.M. Al-Turkustani ^{a,*}, S.T. Arab ^a, L.S.S. Al-Qarni ^b

^a King Abdulaziz University, Girls College of Education, Chemistry Department, Jeddah, Saudi Arabia

^b Al-Baha University, Girls College of Education, Chemistry Department, Baha, Saudi Arabia

Received 4 January 2010; accepted 28 March 2010

Available online 16 October 2010

KEYWORDS

Steel;
Medicago Sativa;
Corrosion;
Corrosion inhibitors;
Acidic solutions

Abstract The inhibitive effect of water and alcoholic extracts of *Medicago Sativa* (*MS*) on the corrosion of steel in 2.0 M H₂SO₄ containing 10% EtOH has been studied using chemical (weight-loss(ML), hydrogen evolution(HE)), electrochemical (potentiodynamic polarization (PDP) and impedance spectroscopy (EIS)) techniques. Also, scanning electron microscopy (SEM) is used to support the obtained results. The results showed that the inhibition efficiency increases with the increase of *M. Sativa* (*MS*) concentration. The water and alcoholic extracts of *MS* plant act as mixed type inhibitors with nearly the same efficiency. The inhibition action of *M. Sativa* (*MS*) extracts was discussed in terms of their horizontal adsorption on the metal surface. The adsorption follows Langmuir adsorption isotherm.

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1. Introduction

Corrosion is the atmospheric oxidation/degradation of metals. It is an electrochemical process by which metallic surfaces react with their environment causing the metal to lose its mate-

rial properties due to surface deterioration (Chaieb et al., 2005; Abd El-Rehim et al., 2001).

Inhibitors are required to protect metals against acid attack. The need is growing in corrosion inhibitors more and more necessity to stop or delay the process of corrosion (Abdallah, 1994).

Iron is a metal which is silvery and shiny in nature; row iron is not as strong and hard as needed for construction, building and other purposes (Abd-El Nabey et al., 1986; Abdel-Gaber et al., 2006). So, about 98% of the row iron is alloyed with a variety of elements such as, tungsten (W), manganese (Mn), nickel (Ni), vanadium (V), and chromium (Cr) to strengthen and harden it, making useful steel – one of the greatest invention and most useful materials ever created – for construction, automobiles and other forms of transportation such as tracks, train and train tracks (Arab and Abd-El Nabey, 1991). Many studies have been made on the corrosion inhibition of steel in

* Corresponding author.

E-mail addresses: A.M.Turkustani@hotmail.com (A.M. Al-Turkustani), S.T.arab@hotmail.com (S.T. Arab), L.S.S.Al-Qarni@hotmail.com (L.S.S. Al-Qarni).



acid media (Arab and Al-Mhyawi, 2008; Arab and Emran, 2008; Arab et al., 2005, 2008; Azim et al., 1995).

The known hazard effects of most synthetic corrosion inhibitors are the motivation for the use of some nature products as safe (green) inhibitors.

Recently, plant extracts have again become important as an environmentally acceptable, readily available and renewable source for a wide range of needed inhibitors. Plant extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost (Barakat et al., 1998).

Medicago Sativa is the first plant used as fodder; the green parts of the plant contain about 9.1% carbohydrates, 5.0% protein, 0.9% oils and 2.4% minerals such as phosphorus and calcium, while the dry green parts of the plant contain 30.0% carbohydrates, 14.7% protein, 2.2% oils, 7.9% minerals and vitamins A, E, B12 and K.

This plant is relish by the presence many of chemical compounds such as: biotin, cytidine, inosine, guanine, guanosine and riboflavin (Bastidas et al., 1997; Bentiss et al., 1999a) (Table 1).

The aim of this study is to investigate the ability of *M. Sativa* (MS) as friendly and environmentally safe inhibitors to protect the steel against corrosion in 2.0 M H₂SO₄.

2. Experimental

2.1. Specimen

The experiments were performed with steel sample from Shaban steel company of weight percentage composition as follows: Table 2

Table 2 Chemical composition of steel.

Element	C	Cr	Mo	S	P	Si	Mn	Fe
Amount%	0.38	0.9	0.15	0.03	0.035	0.40	0.50	97.61

2.2. Solutions

All chemicals used were of analytic grade. The blank corroding solution was 2.0 M H₂SO₄ (PAI-Panreac) containing 10% EtOH ethyle alcohol (PAI-Panreac).

2.3. Preparation of extracts (inhibitor)

The preparation of *M. Sativa* plant extracts was carried as follows:

2.3.1. Water extract

Weighed 200 g of dry and milled *M. Sativa* plant is boiled with water several times, then filtered and the filtrate product is placed in a standard flask and completed to 250 ml by distilled water.

2.3.2. Alcoholic extract

The dry and milled *M. Sativa* plant 250 g can be extracted by ethyl alcohol several times until the obtained color become light green. The collected extract was dissolved in ethyl alcohol and placed in a standard flask 250 ml.

2.4. Measurement methods

2.4.1. The chemical techniques

These measurements were carried out by two methods; hydrogen evolution method (HEM) and mass-loss method (MLM).

2.4.1.1. Hydrogen evolution measurements (HEM). A clean weighed rod of 5.0 cm in length and 1.0 cm in diameter was polished by emery paper starting with 100–1200 then it was immersed in the test solution and immediately the volume of the evolved hydrogen gas was measured as a function of time as described elsewhere (Bentiss et al., 1999b). In each new study the measurements of the sample area were checked and the change in volume of hydrogen gas was recorded every 5 min for 60 min.

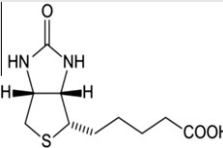
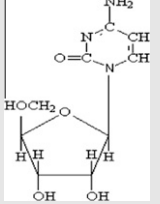
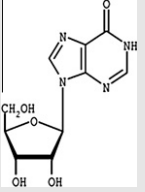
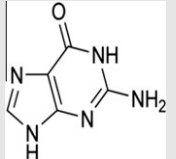
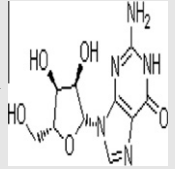
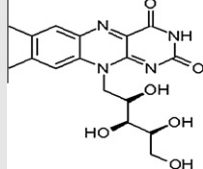
2.4.1.2. Mass loss measurements (MLM). The clean weighed rod of mild steel was suspended in the test solution and at the end of each experiment of (HEM), the sample was withdrawn from the test solution, washed thoroughly with deionized water followed by ethanol and dried with a stream of air, and reweighed.

2.4.2. The Electrochemical techniques

2.4.2.1. Potentiodynamic polarization measurements (PDP).

The polarization curves were determined over a wide range of electrode potentials using AMEL-potentiostat Mod.533 Italy, with 1 ranges from 1.0 μA to 1.0 A and positive feedback for IR drop compensation, using the usual electrolytic cell as described elsewhere (Dehri and Ozcan, 2006).

Table 1 Main constituents of *Medicago Sativa* (MS) plant.

Biotine		Cytidine	
Inosine		Guanine	
Guanosin		Riboflavin	

2.4.2.2. *Electrochemical impedance spectroscopy measurements (EIS)*. EIS measurements were carried out using an impedance spectrum analyzer (ACM Gill AC) connected to a Samsung computer (Bridge DVD ASUS 8X max). All experiments were in the frequency range between 30 kHz and 0.5 Hz. The input signal amplitude was 10 mV peak to peak in both high and low frequency ranges. The data emulation program of the type Setup_ZSimDemo_320 was used to treat the impedance data and know the equivalent circuit which describes the reaction between solution and sample surface.

2.4.3. *Scanning electron microscopy (SEM) analysis*

SEM analysis of the electrode surface was carried out using Scanning Electro Microscope XL 20 PHILIPS.

3. Results and discussion

3.1. Chemical study

The chemical measurements were carried out by hydrogen evolution (HE) and mass loss (ML) methods. Fig. 1a and b show the plots of hydrogen volume with time curves for steel in 2.0 M H₂SO₄ containing 10% EtOH solutions in absence and presence of different concentrations of MS water extract and alcoholic extract at 30 °C, respectively.

Inspection of the plots reveals that hydrogen gas evolution commences only after an induction period, which corresponds to the time interval needed by the corrodent to break down the pre-immersion oxide film on the steel surface (Ebenso et al., 2009). After the induction period, the volume of evolved H₂ gas varies linearly with reaction time.

It is clear that as the concentration of MS water extract and alcoholic extract increases, the rate of hydrogen evolution is decreased, i.e., the rate of steel corrosion decreases, which indicates inhibition of the corrosion process. This implies that MS extracts retard steel corrosion in the studied solutions.

The corrosion rates (*R* and \dot{R}) for steel sample in absence and presence of different concentrations of MS water and alcoholic extracts at 30 °C are given in Tables 3 and 4.

The inhibition percentages were calculated from hydrogen evolution (Inh._{HEM}%) and mass-loss (Inh._{MLM}%) measurements using the following two Eqs. (1) and (2) (El-Etre, 2006; Elkadi et al., 2000; El-Mahdy and Mahmoud, 1995):

$$\text{Inh.}_H\% = 100(1 - R/R_0) \tag{1}$$

$$\text{Inh.}_M\% = 100(1 - R'/R'_0) \tag{2}$$

Where *R*₀, *R*, *R*'₀ and \dot{R} represent the corrosion rates from hydrogen evolution and mass-loss in absence and presence of studied extracts, respectively.

3.2. 2. Electrochemical study

3.2.1. Potentiodynamic polarization measurements (PDP)

The potentiodynamic polarization curves for steel corrosion in 2.0 M H₂SO₄ containing 10% EtOH in absence and presence of different concentrations of MS water extract and alcoholic extract at 30 °C are shown in Fig. 2. The electrochemical parameters (corrosion potential (*E*_{corr.}), corrosion current (*I*_{corr.}), anodic and cathodic Tafel slopes (*b*_a and *b*_c) and the

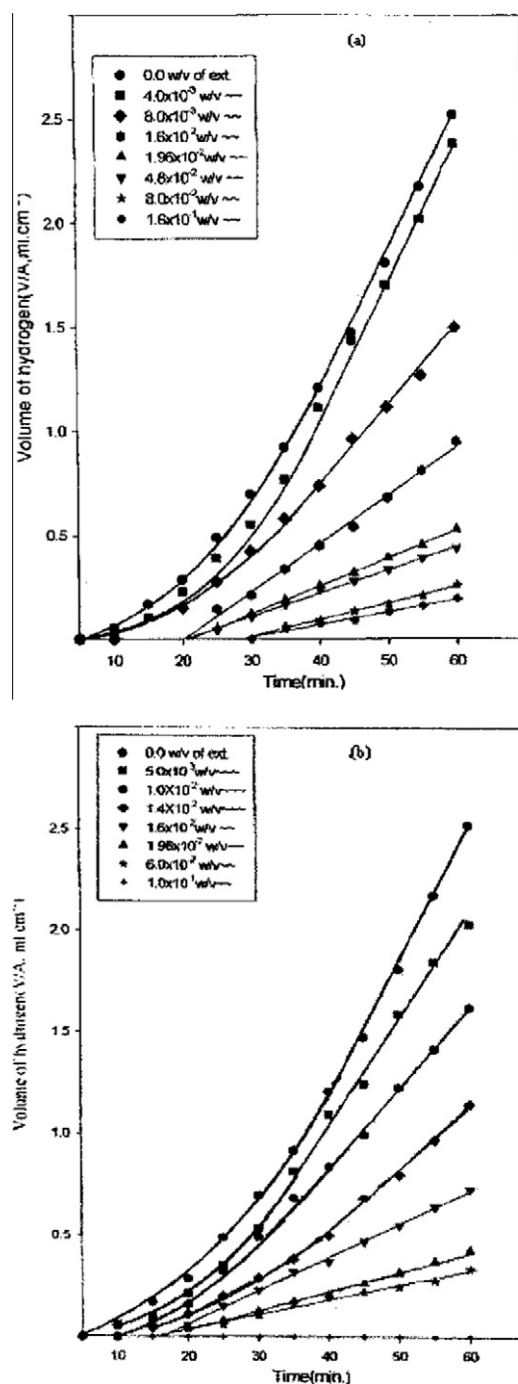


Figure 1 Volume of hydrogen/time curves of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in absence and presence of different concentrations of MS; (a) water and (b) alcoholic extracts at 30 °C.

inhibition percentages (Inh._p%) for water extract and alcoholic extract of MS plant are recorded in Tables 5 and 6.

Fig. 2 shows that water extract and alcoholic extract of MS plant retard both cathodic and anodic processes (metal dissolving and hydrogen evolution); this appears in the displacement of Tafel lines (cathodic and anodic), i.e., these extracts of MS plant act as mixed type inhibitors.

As can be seen from Tables 5 and 6 that there is irregular displacement in the corrosion potential (*E*_{corr.}) values for steel

Table 3 The corrosion rates of steel sample in 2.0 M H₂SO₄ + 10%EtOH in absence and presence of different concentrations of *MS* water extract at 30 °C.

C (w/v)	0.0	5 × 10 ⁻³	1 × 10 ⁻²	1.4 × 10 ⁻²	1.6 × 10 ⁻²	1.96 × 10 ⁻²	6 × 10 ⁻²	1 × 10 ⁻¹
<i>R</i>	9.709 × 10 ⁻⁵	7.519 × 10 ⁻⁵	5.364 × 10 ⁻⁵	4.46 × 10 ⁻⁵	2.163 × 10 ⁻⁵	2.093 × 10 ⁻⁵	1.397 × 10 ⁻⁵	4.337 × 10 ⁻⁶
<i>Ṙ</i>	6.660 × 10 ⁻²	5.040 × 10 ⁻²	3.740 × 10 ⁻²	2.910 × 10 ⁻²	1.640 × 10 ⁻²	1.026 × 10 ⁻²	7.257 × 10 ⁻³	0.0

Table 4 The corrosion rates of steel sample in 2.0 M H₂SO₄ + 10%EtOH in absence and presence of different concentrations of *MS* alcoholic extract at 30 °C.

C (w/v)	0.0	4.0 × 10 ⁻³	8.0 × 10 ⁻³	1.6 × 10 ⁻²	1.96 × 10 ⁻²	4.8 × 10 ⁻²	8.0 × 10 ⁻²	1.6 × 10 ⁻¹
<i>R</i>	9.709 × 10 ⁻⁵	9.330 × 10 ⁻⁵	6.104 × 10 ⁻⁵	4.456 × 10 ⁻⁵	2.492 × 10 ⁻⁵	1.865 × 10 ⁻⁵	1.123 × 10 ⁻⁵	7.753 × 10 ⁻⁶
<i>Ṙ</i>	6.66 × 10 ⁻²	6.100 × 10 ⁻²	3.690 × 10 ⁻²	2.330 × 10 ⁻²	1.350 × 10 ⁻²	1.130 × 10 ⁻²	8.120 × 10 ⁻³	6.189 × 10 ⁻³

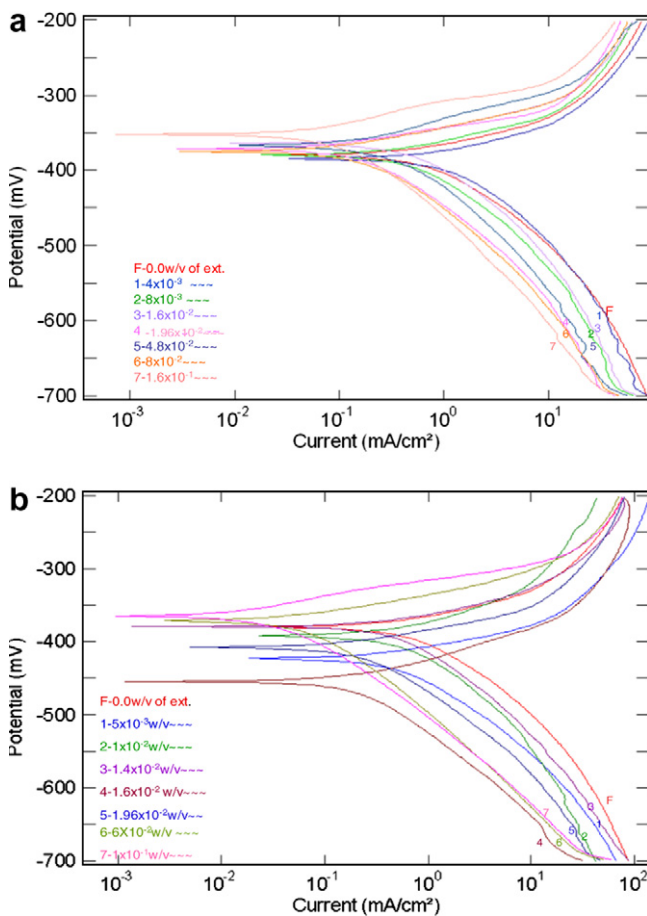


Figure 2 Polarization curves of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in absence and presence of different concentrations of *MS* (a) water and (b) alcoholic extracts at 30 °C.

sample in *MS* water extract and alcoholic extract under study to less negative (more positive) values with regard to the free acid solution and decrease of *I*_{corr} values was associated with a shift in the corrosion potential *E*_{corr}. to less negative values especially at high concentrations.

Both anodic and cathodic Tafel slopes (*b*_a and *b*_c) values for the corrosion of steel sample in 2.0 M H₂SO₄ containing 10%EtOH in presence of *MS* water and alcoholic extracts

are varied in irregular shape; this behavior was previously observed in many others studies (Farooqi et al., 1997; Fouda and El-Semongym, 1982; Hopson and Tales, 1990; Kertit et al., 1994a,b). Also, it is clear that the values of *b*_a and *b*_c are decreased with increase in the concentration of *MS* plant water and alcoholic extracts; this means that the extracts of *MS* plant are acting as mixed type inhibitors.

The values of Inh.% were determined from polarization measurements according to the following equation:

$$\text{Inh.p}\% = (1 - I_{\text{corr}}/I_{\text{corr}}^0) \times 100 \quad (3)$$

Where *I*⁰_{Corr.} and *I*_{corr.} are the corrosion current densities in the absence and presence of inhibitor, respectively.

3.2.2. Electrochemical Impedance Spectroscopy Measurements (EIS)

The corrosion behavior of steel sample in 2.0 M H₂SO₄ solution containing 10% EtOH in absence and presence of water extract and alcoholic extract of *MS* plant was investigated by the EIS method at 30 °C. The obtained Nyquist plots of studied *MS* water and alcoholic extracts are shown in Figs. 3a and 3b). It can be seen that the obtained impedance diagrams show almost a semicircle for the free acid and in the presence of *MS* extracts (water and alcoholic). The differences have been attributed to frequency dispersion. The semicircle appearance indicates that the corrosion of steel is mainly controlled by the charge transfer process and the presence of water extract and alcoholic extract of *MS* plant in acidic solution do not alter the mechanism of dissolution of steel surface (Kertit et al., 1994b; Khamis and Al-Andis, 2002).

Inhibition percentage efficiencies obtained from EIS measurements are calculated from the following equation (Kiby, 1990; Mansfeld et al., 1980, 1982; Muralidharan et al., 1995, 1996):

$$\text{Inh.R}_{\text{ct}}\% = (R_{\text{cto}}^{-1} - R_{\text{ct}}^{-1}/R_{\text{cto}}^{-1}) \times 100 \quad (4)$$

Where *R*_{cto}⁻¹ and *R*_{ct}⁻¹ are the values of charge transfer resistance for steel in 2.0 M H₂SO₄ solution containing 10% EtOH without and with the extract, respectively. The values of inhibition efficiency calculated from Eq. (4) are listed in Tables 7 and 8.

Fig. 4a shows Nyquist curves for steel in 2.0 M H₂SO₄ containing 10% EtOH in presence low concentration (4.0 × 10⁻³ w/v) of *MS* water extract at 30 °C as a model for example

Table 5 Electrochemical parameters of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in absence and presence of different concentrations of *MS* water extract at 30 °C.

Conc. (w/v)	Polarization (PDP)				Impedance (EIS)		
	$-E_{\text{corr.}}$ (mv)	b_a (Vdec ⁻¹)	b_c (Vdec ⁻¹)	$I_{\text{corr.}}$ (mA cm ⁻²)	$R_{\text{corr.}}$ (mmday ⁻¹)	$R_{\text{sol.}}$ (Ωcm ²)	$R_{\text{ct.}}$ (Ωcm ²)
0.0	380.46	103.96	95.68	6.586	76.331	2.253	14.15
4.0×10^{-3}	395.48	79.27	151.99	7.389	57.60	1.074	11.52
8.0×10^{-3}	385.65	58.85	142.47	3.776	31.47	1.852	23.96
1.6×10^{-2}	364.14	46.06	130.77	2.161	25.05	4.019	41.41
1.96×10^{-2}	378.18	39.29	113.40	1.388	16.09	5.816	69.27
4.8×10^{-2}	376.05	41.89	75.890	1.299	15.05	5.648	88.60
8.0×10^{-2}	374.66	31.82	67.090	1.069	13.95	2.560	110.10
1.6×10^{-1}	352.55	30.60	61.830	0.619	7.177	17.97	230.90

Table 6 Electrochemical parameters of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in absence and presence of different concentrations of *MS* alcoholic extract at 30 °C.

Conc. (w/v)	Polarization (PDP)				Impedance (EIS)		
	$-E_{\text{corr.}}$ (mv)	b_a (Vdec ⁻¹)	b_c (Vdec ⁻¹)	$I_{\text{corr.}}$ (mA.cm ⁻²)	$R_{\text{corr.}}$ (mmday ⁻¹)	$R_{\text{sol.}}$ (Ωcm ²)	$R_{\text{ct.}}$ (Ωcm ²)
0.0	380.46	103.96	95.68	6.586	76.331	2.253	14.15
5.0×10^{-3}	437.20	47.85	76.53	4.383	50.80	1.124	19.85
1.0×10^{-2}	396.06	72.17	139.11	3.276	37.96	5.040	23.58
1.4×10^{-2}	379.88	35.56	83.86	2.147	24.89	1.344	33.24
1.6×10^{-2}	453.38	25.45	44.60	1.834	21.26	1.592	58.56
1.96×10^{-2}	407.22	20.69	36.85	0.980	11.36	2.402	79.14
6.0×10^{-2}	371.65	26.05	66.32	0.953	11.04	9.092	467.7
1.0×10^{-1}	363.32	23.44	37.47	0.782	9.06	1.923	551.7

which it contains from half incomplete circle with inductive loop at low frequencies, and by using Setup_ZSimDemo_320 program an equivalent circle as $[R_s(Q(R_{ct}(CR)))]$ (Musa et al., 2009; Mylius and Niethen, 1957; Payer et al., 1980) is obtained, where R_s represents the solution resistance, R_{ct} is charge transfer resistance and Q is constant phase element (CPE) which is used as a condenser. Analysis of the impedance spectra was done by fitting the experimental data using the nonlinear least square fitting procedure. The quality of fitting to the equivalent circuit (EC) was judged firstly by the chi-square (χ^2) values and secondly by the error distribution versus frequency, comparing experimental with simulated data. Excellent agreement between the fitted and experimental data was obtained ($\chi^2 = 10^{-2} - 10^{-3}$). It is clear that the presence of fitting corrosion and corrosion cell is as shown in Fig. 4b.

Also Fig. 5a shows Nyquist plot for the corrosion of steel in 2.0 M H₂SO₄ containing 10%EtOH in presence of high concentrations (6.0×10^{-1} w/v) of *MS* water extract at 30 °C, which it emulates by the equivalent Randal-circle $[R_s(C_d(R_{ct}))]$ (Fig. 5b) where Q is used as ideal condenser.

Tables 5 and 6 show that R_{ct} values increased by increasing the concentration of the *MS* water extract and alcoholic extract, respectively, and decreasing the corrosion rate of steel sample is obtained.

The increase of charge transfer resistance in the presence of the studied extracts may be due to the gradual replacements of water molecules by the adsorption of the molecule of water extract and alcoholic extract of *MS* plant on the metal surface.

Tables 7 and 8 show the inhibition percentages which obtained from chemical (HE and ML) and electrochemical

(PDP and EIS) measurements for the corrosion of steel sample in H₂SO₄ containing 10% EtOH in absence and presence of water and alcoholic extract of *MS* plant at 30 °C.

Inspection of these Tables reveals that the inhibition percentages are increased as the concentration of *MS* water and alcoholic extracts is increased for all used methods but the chemical methods and polarization method for all concentrations show a considerable differences at the low concentrations of water and/or alcoholic extract and good agreement is observed at high concentrations (Rengamani et al., 1993, 1994; Sakthivel et al., 1999). The extracts give nearly equal values of inhibition, which indicate to the effectiveness of the *MS* extracts on the inhibition of steel in H₂SO₄ solution.

Also, the inhibition percentages calculated from polarization measurements for all concentrations of the extracts are always higher than those obtained from chemical measurements. A similar observation on the difference between chemical and electrochemical measurements has been reported before Rengamani et al., 1994. The differences observed can be attributed to the fact that the chemical methods give average corrosion rates, whereas electrochemical methods give instantaneous corrosion rates (Sakthivel et al., 1999).

Good consistency is observed only at high concentrations of *MS* plant extracts for results obtained from chemical and electrochemical methods, probably because the higher bulk concentration of *MS* plant extracts leads to an increase in adsorption and blocking the metal surface (Stupnisek-Lisac et al., 1988; Trabaneli and Corassiti, 1991).

The results also show that the alcoholic extract gives more inhibition efficiency than the water extract. The inhibition effi-

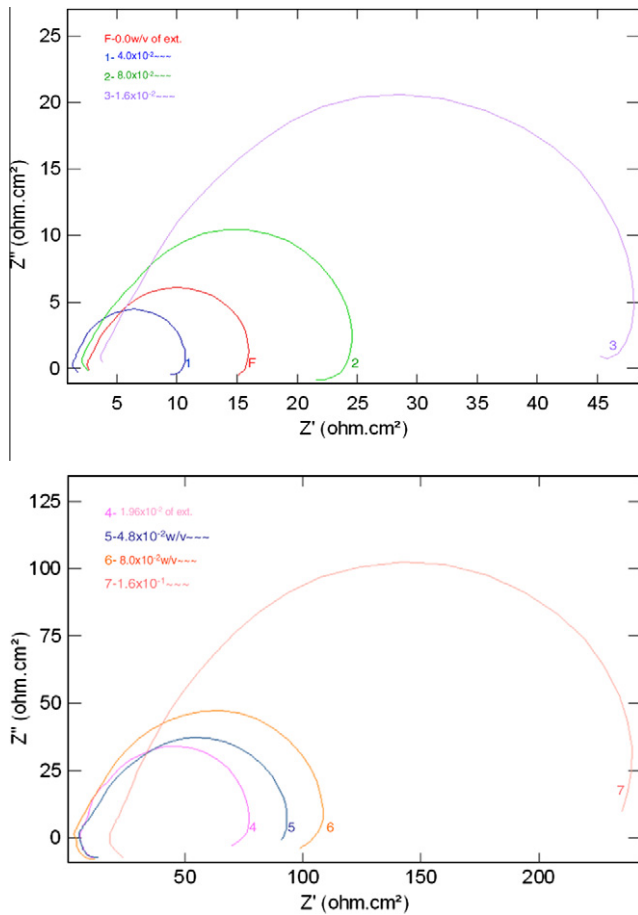


Figure 3a Nyquist curves of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in absence and presence of different concentrations of *MS* water extract at 30 °C.

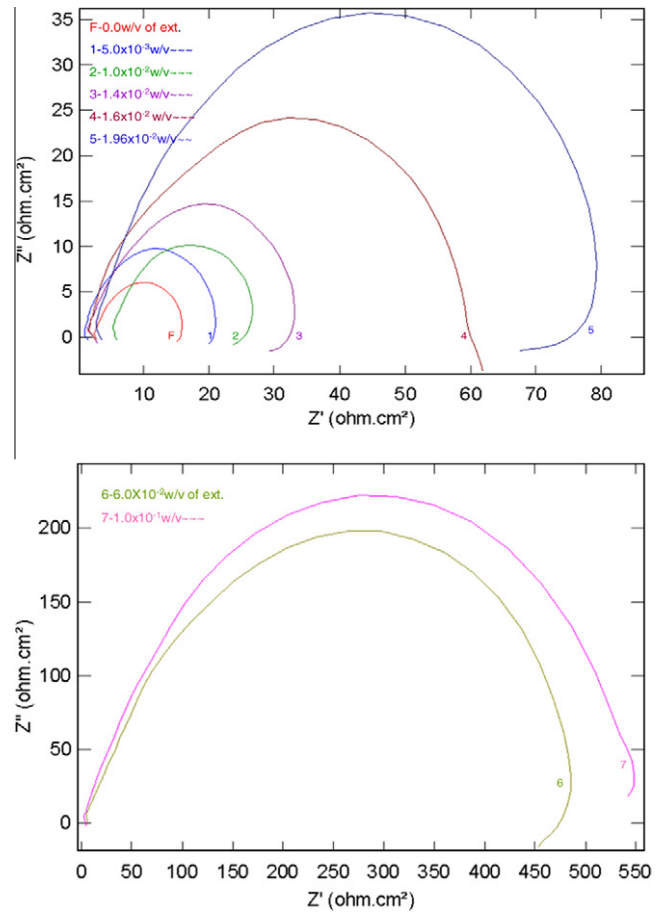


Figure 3b Nyquist curves of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in absence and presence of different concentrations of *MS* alcoholic extract at 30 °C.

ciency was close to 100% at the concentration 1×10^{-1} w/v of alcoholic extract; this is attributed to the nature of the substances extracted from the solvents.

3.3. Adsorption isotherm

The decrease in the corrosion rate by the addition of water extract and alcoholic extract of *MS* plant is attributed to either adsorption of the plant components on the metal surface or

the formation of a barrier film separating the metal surface from the corrosive medium (Vincent and Okhio, 2005; West, 1970; Zhao and Liang, 2005;X, 1984).

Fig. 6 shows the relation between Inh.% and $\log C_{inh}$. of the investigated extracts from all methods used. As can be readily seen, almost the plots have the form of S-shaped adsorption. This indicates that these extracts (water and alcohol) of *MS* plant inhibit the acid dissolution of steel by adsorption the

Table 7 Inhibition percentages of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in presence of different concentrations of *MS* water extract at 30 °C.

Conc. (w/v)	Inhibition%			
	Inh.p %	Inh.R _{ct} %	Inh.M %	Inh.H%
0.0	—	—	—	—
4.0×10^{-3}	-12.20	-22.83	3.900	8.350
8.0×10^{-3}	42.67	40.94	37.13	44.50
1.6×10^{-2}	67.19	65.83	54.10	64.99
1.96×10^{-2}	78.92	79.57	74.33	79.97
4.8×10^{-2}	80.28	84.03	80.79	83.03
8.0×10^{-2}	83.77	87.15	88.43	87.81
1.6×10^{-1}	90.60	93.87	92.01	90.70

Table 8 Inhibition percentages of steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in presence of different concentrations of *MS* alcoholic extract at 30 °C.

Conc. (w/v)	Inhibition%			
	Inh.p %	Inh.R _{ct} %	Inh.M %	Inh.H%
0.0	—	—	—	—
5.0×10^{-3}	33.44	28.71	22.56	24.31
1.0×10^{-2}	50.26	39.99	44.95	43.78
1.4×10^{-2}	67.40	57.43	54.06	56.30
1.6×10^{-2}	72.15	75.03	77.72	75.38
1.96×10^{-2}	85.11	82.12	78.45	84.59
6.0×10^{-2}	85.53	96.97	85.61	89.10
1.0×10^{-1}	88.13	97.44	95.53	100

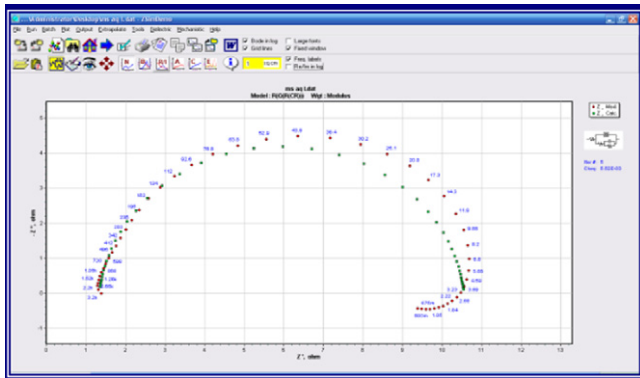


Figure 4a Circuit simulation proposed electrochemical impedance spectrum for steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in presence of 4.0×10^{-3} w/v of *MS* water extract at 30 °C.

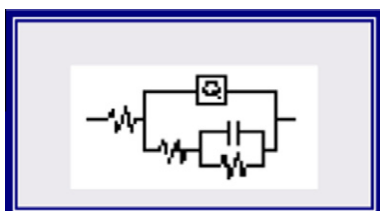


Figure 4b Equivalent circuit model for steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in presence of 4.0×10^{-3} w/v of *MS* water extract at 30 °C.

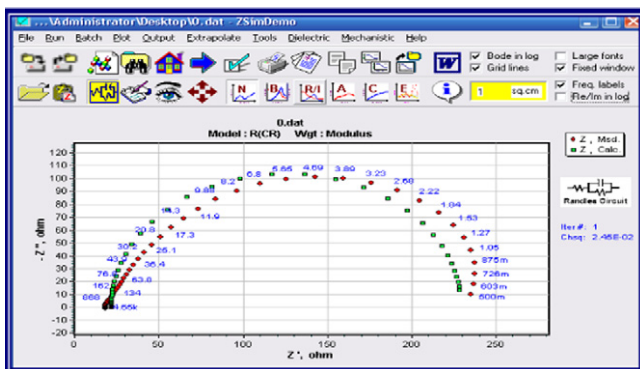


Figure 5a Circuit simulation proposed electrochemical impedance spectrum for steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in presence of 1.6×10^{-1} w/v concentration of *MS* water extract at 30 °C.

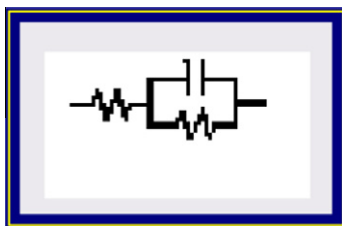


Figure 5b Equivalent circuit model for steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH in presence of 1.6×10^{-1} w/v of *MS* water extract at 30 °C.

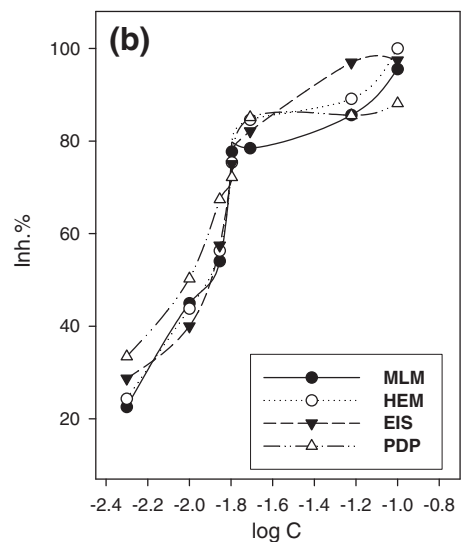
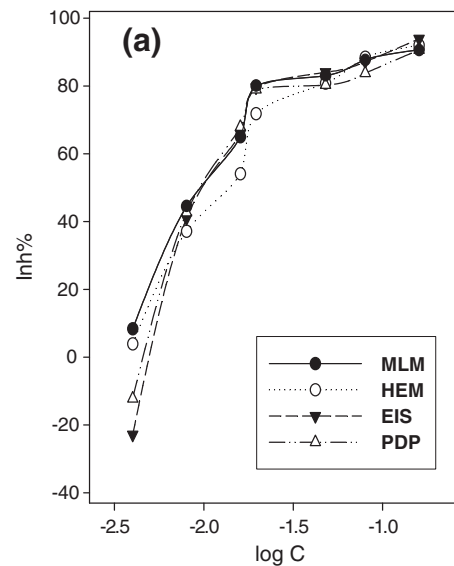


Figure 6 The variation of inhibition efficiency (Inh.%) against log C of (a) water extract and (b) alcoholic extract of *MS* for steel sample corrosion in 2.0MH₂SO₄ + 10%EtOH at 30 °C.

molecules of the *MS* plant at steel acid solution interface; also the obtained figure indicated one step of adsorption.

An excellent fit was obtained for water extract and alcoholic extract of *MS* plant, using the following Langmuir adsorption isotherm equation:

$$\Theta = KC_{Ex}/1 + KC_{Ex} \quad (5)$$

$$C/\Theta = 1/K + C \quad (6)$$

Where C_{Ex} is the concentration of *MS* water and/or alcoholic extract, K constant of adsorption and H is degree of coverage.

It can be seen from Fig. 7 using Eq. (6) that the straight lines of a slope less than unit are found.

Tables 9 and 10 give the average of adsorption constant (K_{ads}) and the standard free energy of adsorption ($-\Delta G_{ads}^o$), the value of constant K which is related to the standard free energy of adsorption, $-\Delta G_{ads}^o$, by the following Eq. (7):

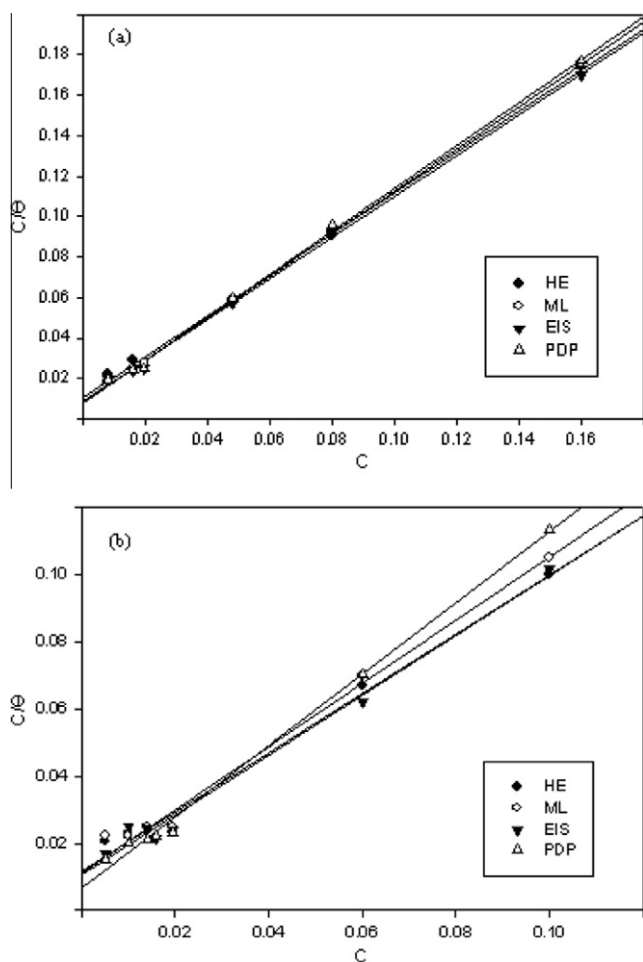


Figure 7 The relation between C/H against C of (a) water extract and (b) alcoholic extract of *MS* for steel sample corrosion in 2.0 M H₂SO₄ + 10% EtOH at 30 °C (Langmuir isotherm).

Table 9 The adsorption constants (K_{ads} , and $-\Delta G_{ads}^{\circ}$) obtained from Langmuir isotherm for *MS* water extract in 2.0 M H₂SO₄ + 10% EtOH.

Method	K_{ads} , (ml/gm)	Slope	$-\Delta G_{ads}^{\circ}$, (kJ ml gm ⁻¹)	C.C.%
HE	94.34	1.01	21.57	99
MS	125	1.05	22.28	99
EIS	116.28	1.01	22.10	99
PDP	126.58	1.06	22.31	99

Table 10 The adsorption constants (K_{ads} , and $-\Delta G_{ads}^{\circ}$) obtained from Langmuir isotherm for *MS* alcoholic extract in 2.0 M H₂SO₄ + 10% EtOH.

Method	K_{ads} , (ml/gm)	Slope	$-\Delta G_{ads}^{\circ}$, (kJ ml gm ⁻¹)	C.C.%
HE	86.96	0.89	21.37	98
MS	87.72	0.94	21.39	98
EIS	93.46	0.89	21.55	98
PDP	149.25	1.06	22.73	99

$$K = 1/55.5 \exp(-\Delta G_{ads}^{\circ}/RT) \quad (7)$$

The value of 55.5 mol L⁻¹ is the concentration of water at electrode/electrolyte interface in solution.

As can be seen from Tables 9 and 10, negative values of $-\Delta G_{ads}^{\circ}$ are characteristic features of spontaneously and strong, also, adsorption for *MS* plant molecules which also reflect the high values of inhibition. The tables show that the value of the binding constant K almost the same. As it is clear from the tables resemble the values of K_{ads} . The adsorption is happening are physical adsorption.

From the inspection of chemical composition of *M. Sativa* plant, it appears that this plant is available source of many natural organic components such as in Table 1. These components are chemical organic compounds that contain nitrogen atom with free electron pair. This compound can adsorb on steel sample through the electron pair on nitrogen atom. The adsorption of these components led to decrease the reaction between steel metal and acid media (H₂SO₄) and then decrease corrosion rate (X, 1996).

3.3.1. Microstructure study of steel surface by SEM at 30 °C

Fig. 8 shows the SEM micrographs of the steel sample exposed in 2.0 M H₂SO₄ containing 10% EtOH in absence and presence *MS* water and alcoholic extracts at 30 °C after 60 min immersion. The clean surface of studied sample before immersion in test solution is shown in Fig. 8a; it appears that a solid and homogenous surface Fig. 8b exhibits the effect of 2.0 M H₂SO₄ solution on the corrosion of steel sample at 30 °C.

Uniform corrosion along with pits is observed in this micrograph in absence of *MS*, general and pitting corrosion (deep and irregular pits) were detected on the metal surface.

SEM examination of steel surface in 2.0 M H₂SO₄ containing 10% EtOH in presence of low and high concentrations of *MS* (water and alcoholic) extracts was carried out at 30 °C. Fig. 8c and d appear that in the presence of low concentration of *MS* extracts (water and alcoholic); the pits turn to distinct and spherical ones which are less than that in presence of acid without inhibitor. This indicates to the formation of porous film on steel surface. As the concentration of the *MS* extract increases, the micrograph shows the formation of a nonporous film on the metal surface with no evidence of pits on the surface (Fig. 8e and f). This layer is due to the adsorption of the inhibitor molecules around the pits in the first stage of formation (initiation and propagation). These observations were in good agreement with those obtained from chemical and electrochemical measurements.

4. Conclusion

It can be concluded that:

- (1) When the concentration of *MS* water and alcoholic extracts increased the rate of steel corrosion is decreased, which indicates that the inhibition of the corrosion process is produced.
- (2) The electrochemical results of polarization showed that the extract of *MS* plant acts as mixed type inhibitor, they retarded both anodic and cathodic corrosion reactions.

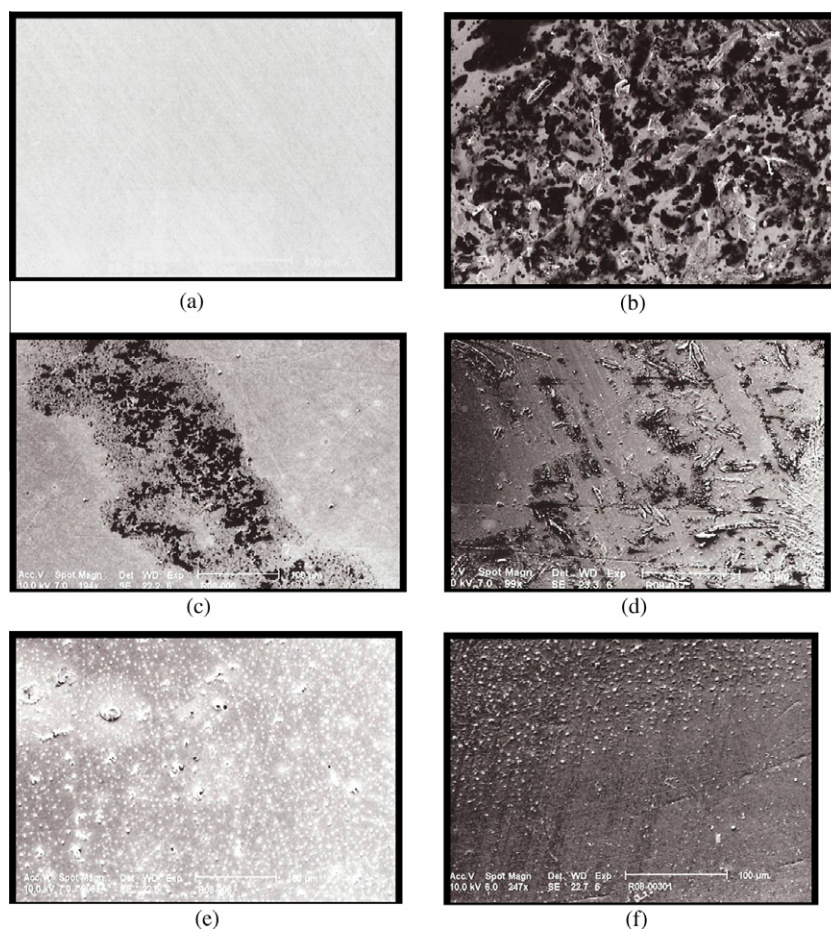


Figure 8 SEM of steel surface after 60 min. of immersion in 2.0 M H₂SO₄ containing 10% EtOH in absence and presence of ((c) 4×10^{-3} , (e) 1.6×10^{-1}) *MS* aqueous and (d) 5.0×10^{-3} , (f) 1.0×10^{-1} *MS* alcoholic extracts at 30 °C.

- (3) Electrochemical impedance spectroscopy results showed that the corrosion and corrosion inhibition of steel occurred mainly by charge transfer.
- (4) Also, the experimental results from chemical and electrochemical studies were fit Langmuir adsorption isotherm.
- (5) The scanning electron microscopy for steel in 2.0 M H₂SO₄ containing 10% EtOH in absence and presence of low and high concentrations of water and alcoholic extracts of *MS* plant showed that the changes (pits) on the steel surface are due to the effect of acid corrosion of *MS* plant as inhibitor; the steel surface appears unchanged especially at high concentrations of the extract.

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