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Studies on the Inhibition of Mild Steel Corrosion by *Rauvolfia serpentina* in Acid Media

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Alkaloid extract of *Rauvolfia serpentina* was tested as corrosion inhibitor for mild steel in 1 M HCl and H_2SO_4 using weight loss method at three different temperatures, viz., 303, 313, and 323 K, potentiodynamic polarization, electrochemical impedance spectroscopy and scanning electron microscope (SEM) studies. It is evident from the results of this study that *R. serpentina* effectively inhibits the corrosion in both the acids through adsorption process following Tempkin adsorption isotherm. The protection efficiency increased with increase in inhibitor concentration and temperature. Free energy of adsorption calculated from the temperature studies also revealed the chemisorption. The mixed mode of action exhibited by the inhibitor was confirmed by the polarization studies while SEM analysis substantiated the formation of protective layer over the mild steel surface.

Keywords chemisorption, corrosion inhibitor, mild steel, *Rauvolfia serpentina*, SEM

1. Introduction

Mineral acids such as HCl and H_2SO_4 find use in pickling baths and descaling operations. When mild steel is used in these processes, it suffers severe corrosion. For the prevention of acid corrosion of mild steel, use of inhibitors is a common strategy. Organic compounds containing such heteroatoms like N, S and O have been used (Ref 1, 2) as corrosion inhibitors. Though these organic inhibitors reduce the corrosion rate effectively, they are toxic and cause severe environmental hazards.

The aim of the present work is to develop a naturally occurring, cheap and environmentally safe inhibitor for the corrosion of mild steel. Several authors investigated and reported natural corrosion inhibitors like henna (Ref 3), *Nypa fructicans* (Ref 4) and Opuntia extract (Ref 5). We have reported the successful use of *Andrographis paniculata* (Ref 6), *Datura metel* (Ref 7), *Datura stramonium* (Ref 8), atropine sulphate (Ref 9), black pepper extract (Ref 10) and *Strychnos nux-vomica* (Ref 11) as corrosion inhibitors for mild steel in acid medium. The use of natural products as corrosion inhibitors is well documented (Ref 12).

Rauvolfia serpentina, belonging to the family of Apocyanaceae, is a medicinally important plant found in tropical regions of India. Reserpine, the major alkaloid present in this plant, has been proved to be a very effective antihypertensive drug (Ref 13). This paper describes the study of the protection efficiency of roots of *R. serpentina* against mild steel corrosion in acid medium.

2. Experimental

2.1 Inhibitor Preparation

The plant inhibitor was prepared by refluxing 500 g of dried roots of *R. serpentina* with 10% HCl for 6 h. Then, the acid extracts were filtered off and neutralized with 10% NaOH up to pH 8 in order to liberate the basic ingredients from the salt. The neutralized solutions were then extracted with chloroform. The organic (chloroform) layers consisting of basic compounds were evaporated and the resultant gummy material obtained was dried, powdered and tested for corrosion inhibitive effect. This inhibitor showed positive test for alkaloid content. Various concentrations of the plant extracts (inhibitor) were prepared by dissolving the known quantity of the resultant powder in the acid medium.

2.2 Specimen Preparation

Mild steel (MS) specimens containing C = 0.10%, Mn = 0.34%, P = 0.08% and Fe = 99.51% were used for the study. MS specimens of size 3 × 1 × 0.21 cm were used for weight loss study, specimens with an exposed area of 1 cm^2 were used for electrochemical study and 1 × 1 cm was used for scanning electron microscope (SEM) analysis. The surface preparation of mechanically polished specimens was carried out using different grades of emery paper and then degreased with acetone.

2.3 Weight Loss Method

The polished and preweighed MS specimens of uniform size were suspended in 100 mL test solutions with and without the inhibitor at different concentrations for a period of 2 h. Then, the specimens were washed, dried and weighed. The weight loss was calculated. From these data, inhibition efficiency (IE) was calculated using the following Eq 1:

$$\mathrm{IE} = \left(1 - \frac{W_{\mathrm{i}}}{W_{\mathrm{o}}}\right) \times 100 \qquad \text{(Eq 1)}$$

where, W_o is the weight loss of MS without inhibitor and W_i is the weight loss of MS with inhibitor.

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2.4 Electrochemical Studies

CH electrochemical analyzer model 650 B was used to record Tafel polarization curve and Nyquist impedance curve. A conventional three electrode system was used for this purpose. MS specimen was used as a working electrode. Pt electrode and calomel electrode served as auxillary and reference electrodes respectively. The working electrode was polished with 1/0, 2/0, 3/0 and 4/0 grade emery papers and washed with distilled water before use. The polarization measurements were recorded at the end of 30 min of immersion of working electrode into the electrolyte. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}) using which IE was calculated as given under (Eq 2).

$$\text{IE} = \left(1 - \frac{I_{\text{corr(i)}}}{I_{\text{corr(o)}}}\right) \times 100 \qquad \text{(Eq 2)}$$

where $I_{\text{corr(o)}}$ is the corrosion current density of MS without inhibitor and $I_{\text{corr(i)}}$ is the corrosion current density of MS with inhibitor.

AC impedance measurements were carried out at E_{corr} immersion on standing in the atmosphere of air at the range from 0.1 to 1000 Hz at an amplitude of 10 mV. The impedance diagrams are given in Nyquist representation. The electrical equivalent circuit for the system is shown in Fig. 1. In the given electrical equivalent circuit, R_s is the solution resistance, R_{ct} the charge transfer resistance and C_{dl} is the double layer capacitance. The IE values were computed using Eq 3

$$\text{IE} = \left(1 - \frac{R_{\text{ct(o)}}}{R_{\text{ct(i)}}}\right) \times 100 \qquad \text{(Eq 3)}$$

where $R_{\text{ct(o)}}$ is the charge transfer resistance of MS without inhibitor and $R_{\text{ct(i)}}$ is the charge transfer resistance of MS with inhibitor.

2.5 SEM Analysis

The specimens used for surface morphological examination were immersed in acid containing various concentrations of inhibitor and in blank separately for 2 h. Then, they were removed, rinsed quickly with rectified spirit and dried. The analysis was performed on HITACHI-model S-3000 H Scanning Electron Microscope.

3. Results

3.1 Weight Loss Method

The change of corrosion inhibition efficiency in 1 M HCl and H_2SO_4 with respect to the inhibitor concentrations and the temperatures have been displayed in Fig. 2 and 3 respectively. From these figures, it is clear that the addition of inhibitor increased the inhibition efficiency in both the acid media through the adsorption of the basic constituents of *R. serpentina* on the MS surface and provide protection against corrosion.

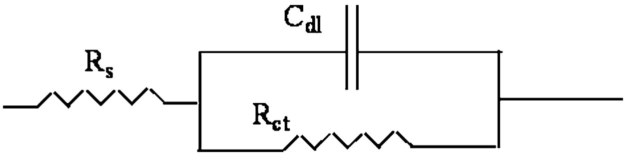

Fig. 1 The electrical equivalent circuit for a.c. impedance measurement

Further, it is observed that raise of temperature also increased the corrosion inhibition efficiency of the inhibitor. Generally, the protective action of plant extracts could be attributed to the adsorption of the phytoconstituents over the surface of the metal. The increase of temperature decreases the hydrogen evolution overvoltage that leads to the spurt in the cathodic reaction. On the other hand, increase of temperature accelerates the chemisorption of the inhibitor on the metal surface (Ref 14). When the latter effect is predominant, the final result is an increase of inhibiting effect, which was observed in our studies.

The adsorption isotherms are very important to understand the mechanism of organo-electrochemical reactions. The adsorbed layer combats the action of corrosive media (HCl and H_2SO_4) and enhances the protection of metal surface. Weight loss data are quite useful in determining the adsorption characteristics of the inhibitor and are useful in the construction of adsorption isotherms. The surface coverage (θ) values were calculated using weight loss values (Eq 4).

$$\text{Surface coverage } (\theta) = \frac{\text{Weight loss without inhibitor} - \text{Weight loss with inhibitor}}{\text{Weight loss without inhibitor}} \qquad \text{(Eq 4)}$$

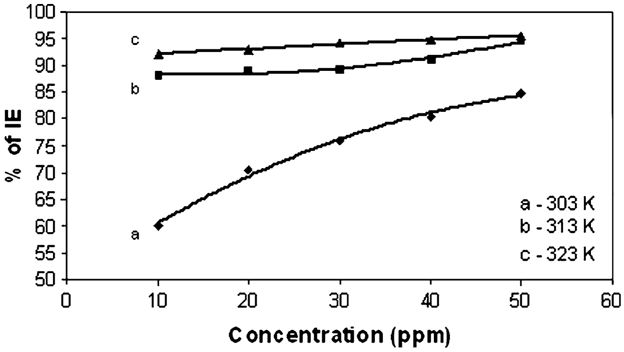

Fig. 2 Inhibition efficiency of MS in 1 M HCl in the presence of different concentrations of *R. serpentina* extract

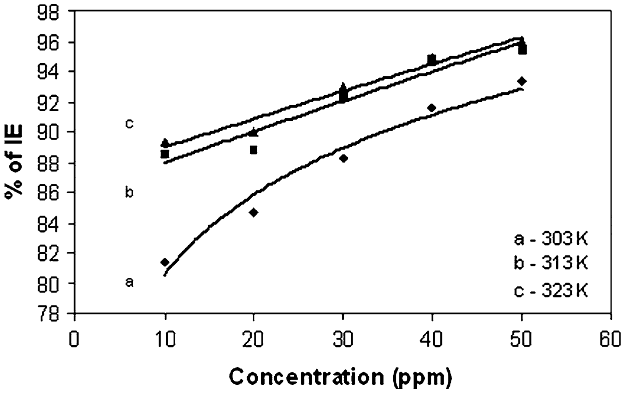

Fig. 3 Inhibition efficiency of MS in 1 M H_2SO_4 in the presence of different concentrations of *R. serpentina* extract

The θ values for different concentrations of inhibitors were tested graphically by fitting into Temkin adsorption isotherm (surface coverage versus ln C). Equation 5 represents the mathematical form of Temkin adsorption isotherm.

$$K_{\mathrm{ads}}C = \mathrm{e}^{f\theta} \qquad \text{(Eq 5)}$$

where K_{ads} is the equilibrium constant of the adsorption process.

From Fig. 4 and 5, it can be observed that the inhibitor follows Temkin adsorption isotherm. The regression coefficient (closer to unity) supports the linearity in the plot. Thus, it is evident that adsorption plays a vital role in the control of corrosion by this plant extract.

From the slope values of Temkin adsorption isotherm, free energy of adsorption ($\Delta G^{\circ}_{\mathrm{ads}}$) was calculated which was found to be −47.42 and −68.07 kJ mol^{-1} for 1 M HCl and 1 M H_2SO_4 medium respectively. The negative values of $\Delta G^{\circ}_{\mathrm{ads}}$ ensure the spontaneity of the adsorption process, stability of the adsorbed layer on metal surface and strong interaction of the inhibitor molecules on the mild steel surface (Ref 15). ΔG values confirmed the predominant chemisorption than the physisorption mode (Ref 16).

Plant extracts inhibit the dissolution reaction by adsorption at the metal surface in two different ways (Ref 17). First, the inhibitor may compete with Cl^- or SO_4^{2-} ions for sites at the water covered anodic surface. In doing so, the protonated inhibitor loses its associated protons in entering the double layer and chemisorbs by donating electrons to the metal. In addition, the protonated inhibitor electrostatically adsorbs onto the anion covered surface through its cationic form. Both the modes are depicted in Fig. 6. But, since chemisorption plays a main role, competitive adsorption of the green inhibitor which involves the donation of electron pair to the metal surface appears predominant.

3.2 Electrochemical Studies

The impedance results for the corrosion inhibition of plant extract for mild steel in 1 M HCl and H_2SO_4 at different concentrations at room temperature are presented in Fig. 7 and 8. The various impedance parameters viz., the double layer capacitance (C_{dl}), charge transfer resistance (R_{ct}) and the inhibition efficiencies computed from these graphs, are given in Table 1.

From Fig. 7 and 8, it is evident that the impedance response of mild steel in both 1 M H_2SO_4 and 1 M HCl changes significantly on the addition of green inhibitor. In the presence of the inhibitor, the diameter of the capacitive loop increases as compared to the acid, which is an indication of corrosion inhibition taking place through charge transfer process. Further, the large capacitive loop arises like semi-circle for mild steel in

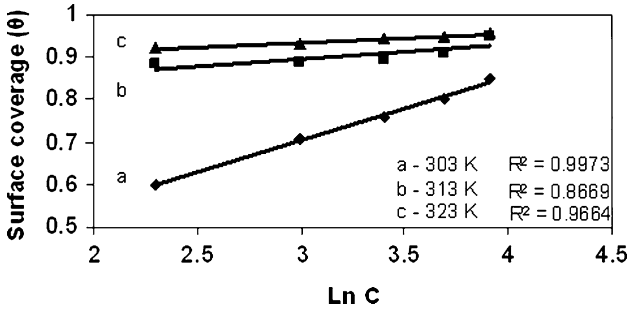

Fig. 4 Temkin plot of *R. serpentina* extract on MS corrosion in 1 M HCl medium

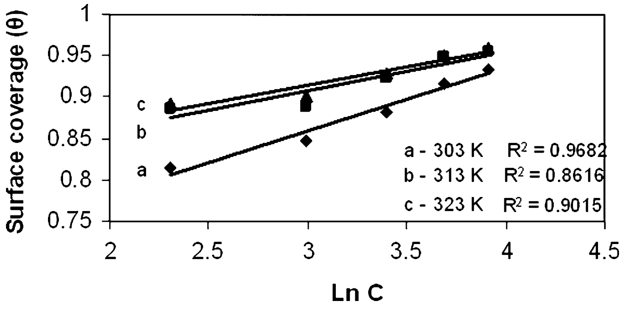

Fig. 5 Temkin plot of *R. serpentina* extract on MS corrosion in 1 M H_2SO_4 medium

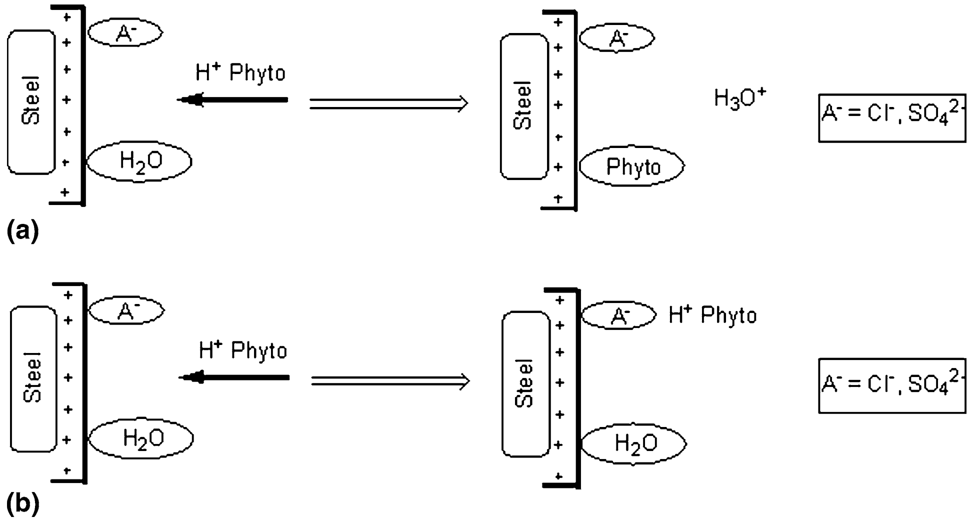

Fig. 6 (a) Competitive and (b) cooperative adsorption of green inhibitor in acid solutions

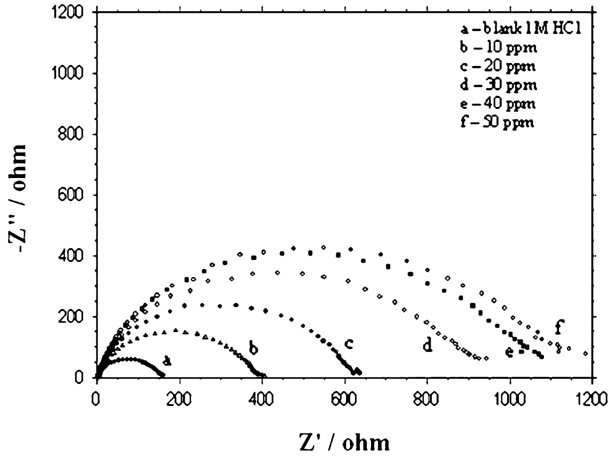

Fig. 7 Nyquist plot of *R. serpentina* extract on MS in 1 M HCl medium

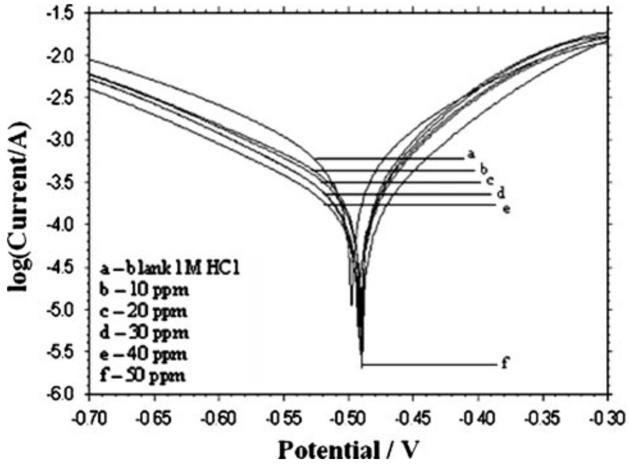

Fig. 9 Tafel plot of *R. serpentina* extract on MS in 1 M HCl medium

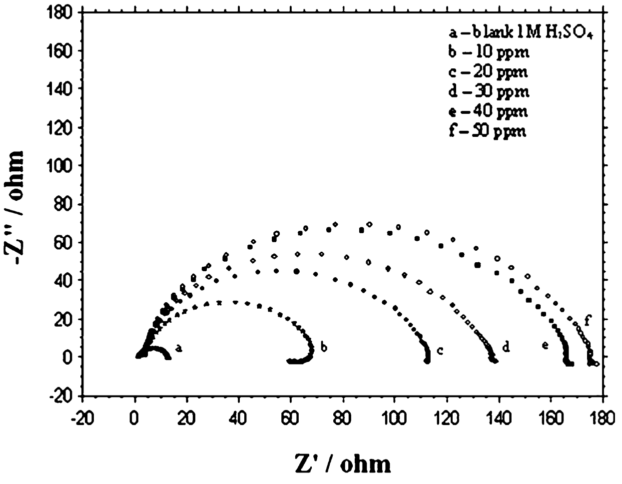

Fig. 8 Nyquist plot of *R. serpentina* extract on MS in 1 M H_2SO_4 medium

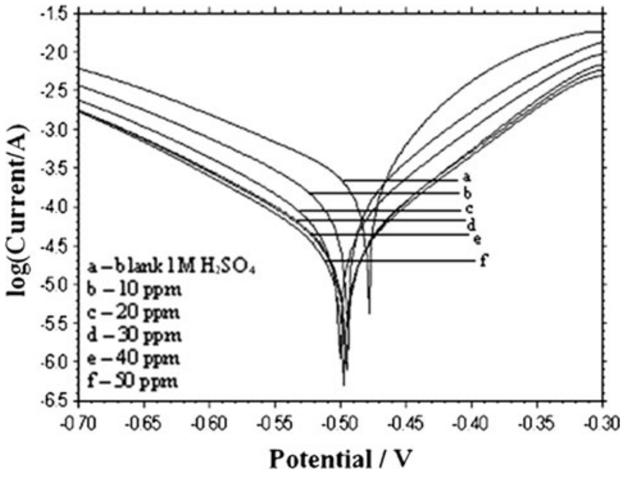

Fig. 10 Tafel plot of *R. serpentina* extract on MS in 1 M H_2SO_4 medium

Table 1 Effect of *R. serpentina* on MS in 1 M HCl and 1 M H_2SO_4 media (impedance studies)

S. no.	Acid medium	Concentration of inhibitor, ppm	R_{ct}, Ω cm^2	C_{dl}, µF cm^{-2}	% of IE
1.	HCl	0	161.61	101.17	…
		10	402.86	22.66	59.88
		20	633.98	22.41	74.50
		30	930.76	20.49	82.63
		40	1069.52	17.51	84.88
		50	1169.52	14.40	86.18
2.	H_2SO_4	0	11.77	1385.10	…
		10	64.23	25.38	81.67
		20	109.47	17.87	89.24
		30	134.18	17.01	91.22
		40	161.8	21.15	92.72
		50	172.50	16.07	93.17

1 M H_2SO_4 and 1 M HCl media in both presence and absence of green inhibitor, which indicated the reaction of electrical double layer at the acid-electrolyte interface (Ref 18). The inhibitor shows a maximum IE of 86% at 50 ppm concentration in HCl medium while in H_2SO_4 medium it is 93%.

The results of potentiodynamic polarization study are given in Fig. 9 and 10 and the parameters calculated from these figures are given in Table 2. From the table, it is evident that the I_{corr} values decreased during the addition of the plant extract, which confirms the corrosion protection. Further, the E_{corr} values are not shifted much in HCl medium while shifted up to 20 mV cathodically in H_2SO_4 medium. But the Tafel slopes values (b_a and b_c) are altered in both the acid media. Zhao et al. (Ref 18) reported that the change of E_{corr} values within ±30 mV during the addition of inhibitor indicates the mixed mode of action. These observations clearly evidenced the fact that *R. serpentina* inhibits the corrosion through mixed mode of inhibition.

3.3 SEM Analysis

The SEM micrographs obtained (with appropriate magnification) are depicted in Fig. 11 and 12. Figure 11(a) indicates the finely polished characteristic surface of mild steel and

Table 2 Effect of *R. serpentina* on MS in 1 M HCl and 1 M H_2SO_4 media (polarization studies)

S. no.	Acid medium	Concentration of inhibitor, ppm	$-b_a$, mV dec^{-1}	$-b_c$, mV dec^{-1}	$-E_{corr}$, mV (vs. SCE)	I_{corr}, μA cm^{-2}	% of IE
1.	HCl	0	95	110	495	158.48	…
		10	75	120	495	100.00	36.90
		20	85	115	500	63.09	60.50
		30	85	115	495	39.81	75.19
		40	83	97	498	31.62	80.04
		50	70	95	495	25.11	84.15
2.	H_2SO_4	0	95	110	475	1000.00	…
		10	80	160	490	316.22	68.37
		20	70	130	490	251.18	74.88
		30	79	139	491	199.52	80.04
		40	62	118	492	158.48	84.15
		50	75	120	495	100.00	90.00

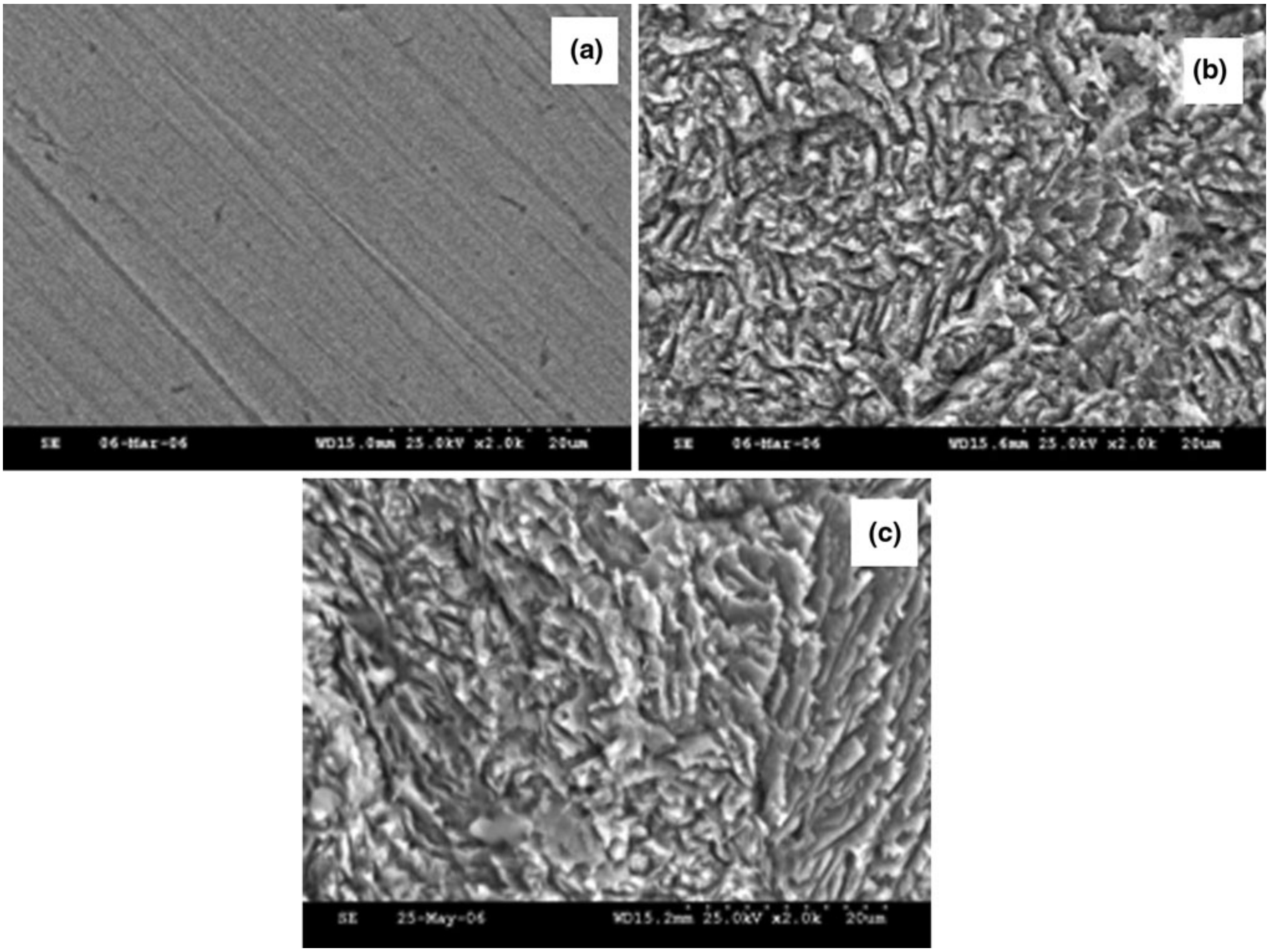

Fig. 11 SEM images of (a) polished MS plate, (b) MS in 1 M HCl, and (c) MS in 1 M H_2SO_4

shows some scratches which had arisen during polishing. Perusal of images as depicted in Fig. 11(b) and (c) revealed that the immersed specimens were highly damaged in the presence of 1 M HCl and H_2SO_4 respectively due to the direct attack of aggressive acids.

Figure 12(a) and (b) shows the formation of a protective film by *R. serpentina* extract on the metal surface which inhibits the corrosion significantly in both the acid media. The micrographs (Fig. 12a) also showed the scratches formed during metal polishing also covered well by the inhibitor.

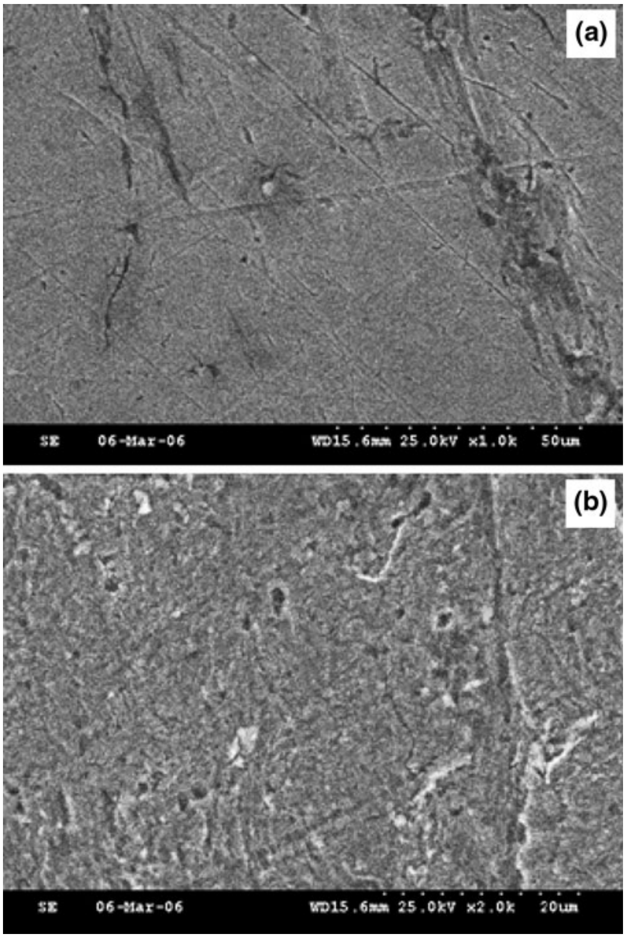

Fig. 12 SEM images of (a) MS in 1 M HCl (with inhibitor) and (b) MS in 1 M H_2SO_4 (with inhibitor)

4. Conclusion

The following are the conclusions drawn from the present study:

1. *R. serpentina* acts as a good inhibitor for corrosion of MS in both the HCl and H_2SO_4 media. The inhibition efficiency increases along with concentration of the inhibitor and temperature of the system.
2. This green inhibitor inhibits corrosion up to 95% in HCl medium and 96% in H_2SO_4 medium at a concentration of 50 ppm and at a temperature of 323 K.
3. IE of the green inhibitor increases with increase of temperature, which is due to chemisorption following Tempkin adsorption isotherm. The free energy of adsorption ($\Delta G^{\circ}_{\text{ads}}$) values obtained were more than -40 kJ mol^{-1} which also supports the chemisorption mode of adsorption.
4. Impedance measurements revealed the increase of charge transfer resistance and decrease of double layer capacitance with increase in the concentration of inhibitor.
5. From the polarization studies, it is evident that *R. serpentina* acts as a mixed type inhibitor.
6. SEM study supports the formation of protective layer over the MS surface by the green inhibitor.
7. The alkaloidal heterocyclic constituent, viz., reserpine present in the plant root, may be responsible for the anticorrosive property of *R. serpentina*.

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