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Anticorrosive Activity of *Schreabera swietenioids* Leaves as Green Inhibitor for Mild Steel in Acidic Solution

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The corrosion inhibitive effect of *Schreabera swietenioids* plant leaves extracts on mild steel in 1 N HCl was studied by using mass loss method, polarization measurements and electrochemical impedance spectroscopy at room temperature. Polarization studies showed that the *Schreabera swietenioids* plant extracts behaved as mixed type inhibitor. Nyquist plot revealed that the addition of extracts increases the charge transfer resistance and hence increases the inhibition efficiency. Photochemical constituents and organic moieties that were adsorbed on the metal surface were also found responsible for the effective performance of the inhibitor, which was well supported by FTIR studies. Protective film formation against corrosion was confirmed by SEM analysis.

Keywords: Mild steel, Corrosion inhibitor, Mass loss method, EIS, SEM.

INTRODUCTION

Corrosion of metal cannot be completely stopped, but it can be drastically reduced using various approaches, such as upgrading the materials and blending production fluids, quite popular methods for prevention and control using chemical corrosion inhibitors. One technique of protecting mild steel from corrosion is to use green inhibitors, which help to decrease the corrosion attack on materials [1-5]. Organic compounds have widely been tried as the corrosion inhibitor for metals and alloys. The corrosion inhibition of mild steel in acidic medium in the presence of various polymers, inorganic and organic compounds has been reported [6-8]. Attention has been focussed on the corrosion inhibiting properties of plant extracts because, it is environmentally acceptable, non-toxic, inexpensive, readily available and renewable sources of materials and can be extracted by simple procedures [9-16]. In this article, the inhibitors properties of *Schreabera swietenioids* plants extract to be used as corrosion inhibitors for mild steel in HCl media are reported.

EXPERIMENTAL

Preparation of the specimen: The composition of mild steel used in this study was C: 0.030 %, Mn: 0.169 %, Si: 0.015 %, P: 0.031 %, S : 0.029 %, Cr: 0.029 %, Ni: 0.030 %, Mb: 0.016 %, Cu: 0.017 % and the remainder Fe. The mild steel specimens were mechanically cut into sizes of 4 cm × 2 cm × 0.1 cm and were used for mass loss method.

Preparation of *Schreabera swietenioids* extract: Freshly collected aerial parts of *Schreabera swietenioids* leaves were dried in room temperature and ground well into powder. The plant extracts was prepared by refluxing 10 g of *Schreabera swietenioids* powder with 150 mL of double distilled water and kept overnight. The resultant solution was then filtered and the filtrate was made to 250 mL, which was used as stock solution. The various concentrations of the extracts ranging from 5-20 ppm were then prepared from the stock solution by using double distilled water.

Mass loss method: The test specimens were immersed in 200 mL of 1 N HCl solution in the absence and presence of various concentrations of the *Schreabera swietenioids* extract using glass hooks and rods for a predetermined time period (24 h) at room temperature. Before and after the immersion, the surface of specimens was cleaned and sample was weighed. The corrosion rate was determined using equation:

$$\text{Corrosion rate (CR) (mmpy)} = \frac{K \times \text{Mass loss}}{D \times A \times t\ (h)} \quad (1)$$

where, $K = 8.76 \times 10^4$ (constant), D is density in g/cm^3 (7.86), W is mass loss (g) and A is area (cm^2).

$$\text{Inhibition efficiency (IE) (\%)} = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

W_0 and W_i are the mass loss in the absence and presence of the inhibitor.

FTIR studies: FTIR spectrum (KBr pellets) of the surface film was recorded using Bruker ALPHA 8400 S spectrophotometer in the wave number range of 4000-400 cm^{-1}.

Electrochemical studies: Electrochemical (polarization and impedance) measurements were obtained using CHI 660 E Electrochemical workstation. An electrochemical cell with a three electrode cell set up was used. Mild steel (1 cm^2) was used as a working electrode; Pt electrode was used as counter electrode and a saturated calomel electrode as reference electrode. Prior to experiment the working electrode was immersed in the test solution for 15 min to reach open circuit potential (OCP). The anodic and cathodic polarization curves were obtained from -800 to -200 mV at a scan rate of 1 mV s^{-1}. The percentage inhibition efficiency are calculated using equation:

$$\text{Inhibition efficiency (\%)} = \frac{I_{corr} - I_{*corr}}{I_{corr}} \times 100 \quad (3)$$

where, I_{corr} and I_{*corr} are corrosion current without and with inhibitors.

The impedance measurements were carried using the same cell assembly employed for the polarization measurements. AC signal with amplitude of 10 mV at open circuit potential in the frequency range from 100 KHz to 10 MHz. The impedance parameters were obtained from Nyquist plots. The double layer capacitance (C_{dl}) was determined using formula:

$$C_{dl} = \frac{1}{2\pi} f_{max} R_{ct} \quad (4)$$

where, R_{ct} is charge transfer resistance and C_{dl} is double layer capacitance.

The percentage inhibition efficiency (IE %) was calculated using the following formula:

$$\text{Inhibition efficiency (\%)} = \frac{R_{ct} - R^0_{ct}}{R_{ct}} \times 100 \quad (5)$$

where, R_{ct} and R^0_{ct} are the charge resistance values for inhibited and uninhibited solution.

Surface analysis: The mild steel specimens were immersed in 100 mL of 1 N HCl with the optimum concentration of green inhibitor solution for a period of 1 day. After termination of the experiment the specimen were removed, rinsed with double distilled water, dried and examined for their surface morphology using scanning electron microscope.

Effect of immersion time: The test specimens were immersed in 100 mL of 1 N HCl solution in the absence and presence of *Schreabera swietenioids* extract of various concentrations for 1, 3, 5, 7 and 24 h. Inhibition efficiency of mild steel was then calculated.

Influence of temperature: The mass loss measurement were carried out in the absence and presence of *Schreabera swietenioids* extract of all concentration for mild steel in 1 N HCl at temperature range of 303-323 K using water thermostats.

RESULTS AND DISCUSSION

Mass loss method: The mild steel specimens were immersed in 1 N HCl acid without and with various concentration of the extract for 24 h. The data obtained from the mass loss method are listed in Table-1. The observed values clearly indicated that with the addition of increase in concentration of the inhibitor, decreases the mass loss as well as corrosion rate distinctly. The maximum inhibition efficiency (92.73 %) was obtained at 15 ppm and this concentration was chosen to be the optimum concentration of the inhibitor.

TABLE-1
CORROSION PARAMETERS OBTAINED FROM MASS LOSS OF MILD STEEL IN 1 N HCl

Concentration of inhibitor (ppm)	Mass loss (g)	Corrosion rate (mmpy)	Inhibition efficiency (%)
Blank	0.3557	206.47	*
5	0.0545	46.41	83.79
10	0.0560	46.57	83.72
15	0.0315	20.00	92.73
20	0.0893	37.77	68.82

FTIR measurement: The FTIR spectrum (Fig. 1) of the extract of *Schreabera swietenioids* present similarity with the IR spectra which contain bands corresponding to hydroxyl group (3397.45 cm^{-1}), carbonyl group (1636.58 cm^{-1}), as well as several bands between 1383.61 and 1102.25 cm^{-1} are C-H and C-O stretching [17]. FTIR spectroscopy is not capable to determine exactly the main compound of the present extracts, but manifest what it is the more abundant chemical compound. Numerous compounds are present in the aqueous extract in lesser concentration, except for phenolic/ligands, according to previous report [18].

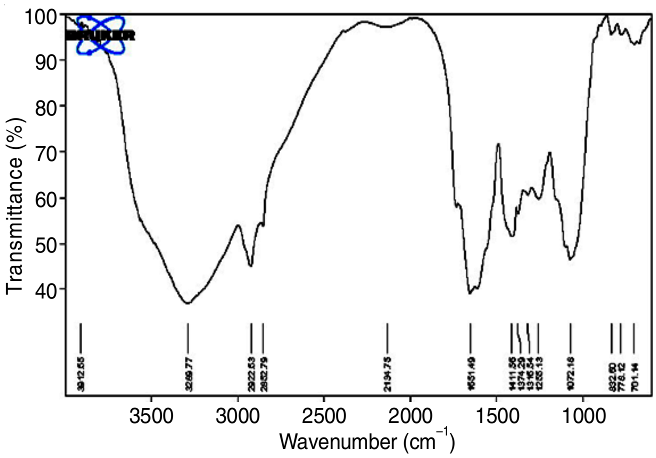

Fig. 1. FTIR spectrum of *Schreabera swietenioids* leaves extracts

Potentiodynamic polarization measurement: The effect of addition of different concentrations of the *Schreabera swietenioids* plant extracts on the Tafel plots for mild steel in 1 N HCl are shown in Fig. 2 and the corrosion data obtained from these curves are listed in Table-2. It was observed that the corrosion current density (I_{corr}) decreased considerably with increase in concentration of *Schreabera swietenioids* extract and thus increases the inhibition efficiency. At the same time, the corrosion potential (E_{corr}) value shifted towards negative potential. However, the shift in the values of corrosion potential (E_{corr}) of the extract is not significant. Irregular trends b_a and b_c value indicate the involvement of more than one type of species adsorbed on the metal surface. This observation clearly showed that the extract control both cathodic and anodic reactions and thus the inhibitor acts like mixed type inhibitors.

TABLE-2
ELECTROCHEMICAL PARAMETER FROM POLARIZATION MEASUREMENT AND CALCULATED VALUES OF INHIBITION EFFICIENCY

Concentration of inhibitor (ppm)	E_{corr} (mV/SCE)	I_{corr} (mA/cm^2)	b_c (mV/dec.)	b_a (mV/dec.)	LPR (Ohm*cm^2)	Inhibition efficiency (%)
Blank	-0.471	4.706×10^{-3}	209	153	8.2	*
5	-0.471	7.625×10^{-4}	160	102	35.2	83.79
10	-0.479	7.662×10^{-4}	147	101	34.0	83.72
15	-0.479	3.424×10^{-4}	139	085	67.0	92.73
20	-0.476	0.146×10^{-4}	167	129	21.6	83.51

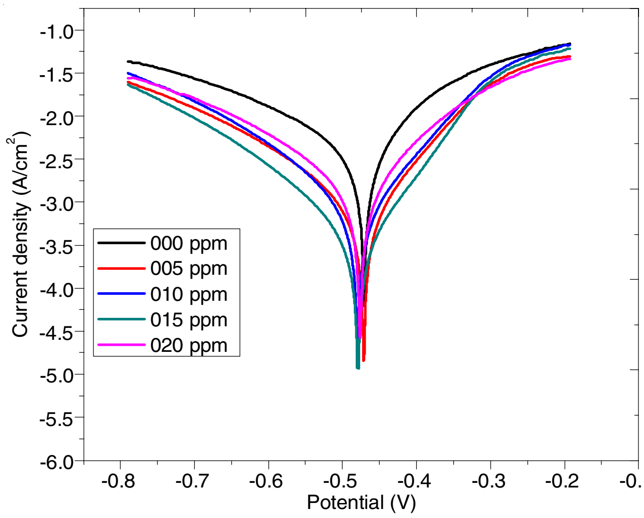

Fig. 2. Tafel plots for mild steel with different concentration of *Schreabera swietenioids* in 1 N HCl

Electrochemical impedance methods: The Nyquist plots for mild steel in 1 N HCl with different concentration of *Schreabera swietenioids* leaves extract are shown in Fig. 3 and the electrochemical parameters obtained are given in Table-3. It was noted that a single depressed semicircle was obtained for mild steel. in both blank and inhibitor solution and the diameter of the semi-circle increased with increasing concentration of the *Schreabera swietenioids* extract. These observations clearly contribute to the control of mild steel corrosion due to the charge transfer reaction occurring at the electrode/ solution interface. It was found that the increase in the concentration of the extract increases the R_{ct} and decreases the C_{dl} values respectively. The higher R_{ct} value obtained for higher concentration is attributed to the formation of protective film at the metal - solution interface [19]. Yen *et al.* [20] studied that the irregular value of C_{dl} at the inhibitor concentration of 7.266×10^{-3} μF/cm^2 was not defined. The decreased in the C_{dl} values showed that the adsorption of the inhibitor takes place on the metal surface in acidic solution.

TABLE-3
IMPEDANCE PARAMETER AND INHIBITION VALUES FOR MILD STEEL IN 1 N HCl ACID SOLUTION CONTAINING VARIED CONCENTRATION OF *Schreabera swietenioids* EXTRACT

Concentration of inhibitor (ppm)	R_{ct} (ohm cm^2)	C_{dl} (μF/cm^2)	Inhibition efficiency (%)
Blank	8.937	7.266×10^{-3}	*
5	31.894	4.271×10^{-4}	71.97
10	32.019	4.555×10^{-4}	72.08
15	62.048	1.168×10^{-4}	85.59
20	18.326	0.153×10^{-4}	51.23

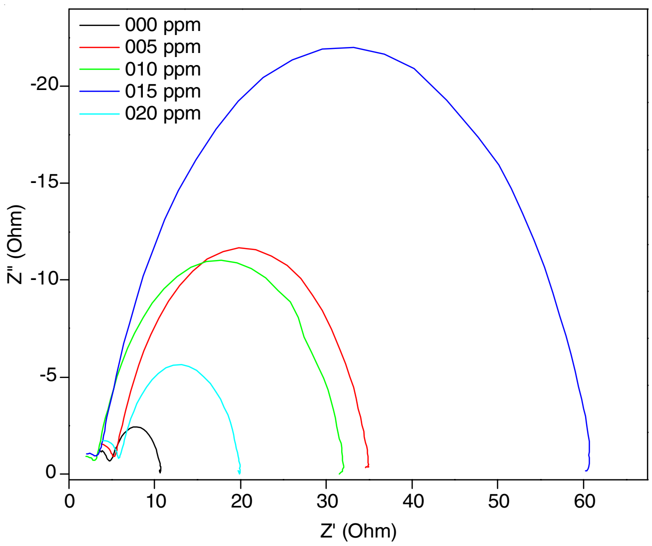

Fig. 3. Nyquist plots of mild steel in absence and presence of different concentration of extract in 1 N HCl

Phytochemical analysis: Phytochemical analysis was carried out on the aqueous *Schreabera swietenioids* leaves extracts freshly prepared according to the common phytochemical methods described by Harborne [21]. The findings of the phytochemical screening of the aerial parts aqueous extract are given Table-4.

TABLE-4
PHYTOCHEMICAL SCREENING TEST OF EXTRACT OF *Schreabera swietenioids* PLANTS LEAVES

Phytochemical test	Aqueous extract	Phytochemical test	Aqueous extract
Alkaloids	Presence	Tannins	Presence
Xanthopretins	Presence	Flavanoids	Presence
Diterpenes	Absence	Phenol	Presence
Saponins	Presence	Steroids	Presence
Phytosterols	Absence	Quinones	Absence

Surface analysis: The morphologies of the mild steel immersed in blank 1 N HCl and with optimum concentration of the inhibitor for 24 h was analyzed by scanning electron microscopy and are shown in Fig. 4(a) and 4(b). Fig. 4(a) revealed that the specimen immersed in 1 N HCl was rough and highly damaged due to the attack of aggressive acids. Fig. 4(b) revealed that the plants extract which was adsorbed on the metal surface decreased the metal surface from corrosion attack [22].

Effect of immersion time: The inhibition efficiency of *Schreabera swietenioids* extract on mild steel as a function of time was presented in Table-5. The highest inhibition efficiency

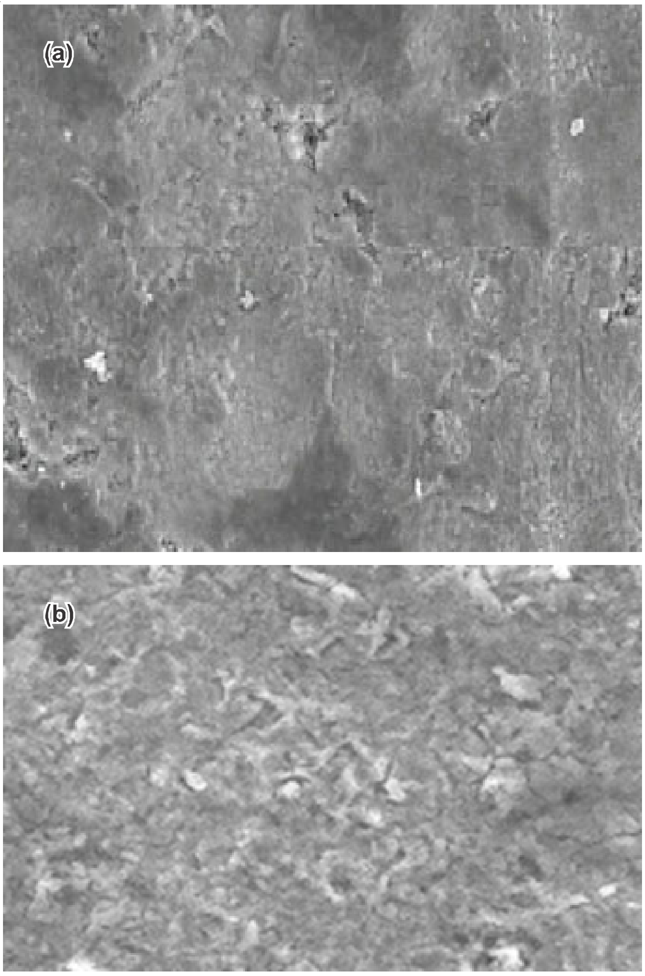

Fig. 4. SEM micrographs of mild steel surface (a) in blank 1 N HCl (b) in the presence of *Schreabera swietenioids* extract

TABLE-5
PERCENTAGE INHIBITION EFFICIENCY AT VARIOUS IMMERSIONS TIME

Concentration inhibitor (ppm)	Inhibition efficiency (%)				
	1 h	3 h	5 h	7 h	24 h
5	60.37	56.15	65.14	78.00	81.30
10	78.89	62.39	76.22	83.36	83.72
15	88.92	72.97	82.14	89.75	92.73
20	89.56	80.16	87.15	91.00	94.82

94.82 %) at 24 h was obtained for 20 ppm concentration of the inhibitor.

Influence of temperature: In order to elucidate the temperature on the inhibitive properties of leaves extract the mild steel was exposed in the blank and in the presence of different concentration of the *Schreabera swietenioids* extract at 303-323 K and corresponding data are listed in Table-6. It was observed that the *Schreabera swietenioids* leaves extract inhibit mild steel in 1 N HCl effectively up to 313 K and decreases thereafter. The inhibition showed a maximum of 77.89 % at 313 K at 20 ppm of the *Schreabera swietenioids* leaves extract.

Adsorption isotherms: The data of mass loss study (Table-6) showed that the percentage of inhibition efficiency increases with increase in the concentration of inhibitor. This suggests that the corrosion inhibitive activity is mainly because

TABLE-6
PERCENTAGE INHIBITION EFFICIENCY OF *Schreabera swietenioids* PLANTS AT VARIOUS TEMPERATURES

Concentration of inhibitor (ppm)	Inhibition efficiency (%)		
	303 K	313 K	323 K
5	49.40	44.90	42.00
10	62.50	57.57	47.09
15	72.90	70.62	69.86
20	75.88	77.89	75.16

of the different constituents of plant species on to the mild steel surface, especially alkaloids, flavonoids, polyphenols, hydrolysis products of proteins, amine compounds. In the case of *Schreabera swietenioids,* increase of temperature increases the inhibition efficiency, but in most of the cases the temperature increases, the inhibition efficiency decreases. It suggests that the inhibition occurred through chemisorption of phytoconstituents on the mild steel surface. Mass loss data (Table-6) was applied for constructing adsorption isotherms which give detailed information on adsorption mechanism. Temkin isotherm was tested for all the data. For Temkin isotherm, surface coverage (θ) was plotted against ln C (Fig. 5). A straight line was obtained for all the plants indicating that the green inhibitors follow Temkin isotherms.

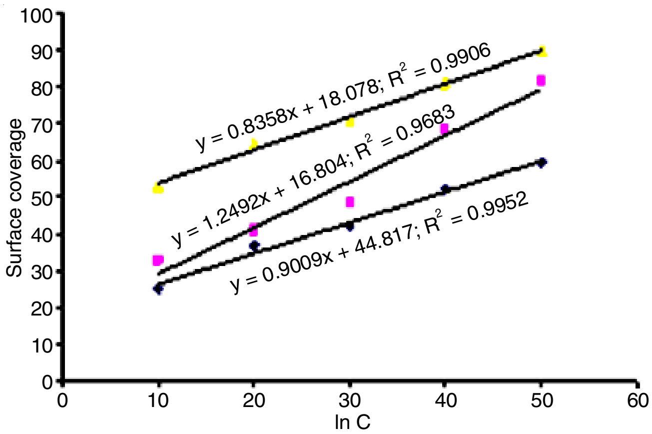

Fig. 5. Temkin isotherm for the *Schreabera swietenioids* extract on the surface of mild steel in 1 N HCl

Mechanism of inhibition: The probable mechanism of inhibition can be explained on the basis of adsorption process and the structure of the constituents present in the *Schreabera swietenioids* extracts. The main constituent of *Schreabera swietenioids* plants contains carbohydrates, alkaloids, proteins, steroids, flavanoids, tannins with the hetero atoms whose structure having multiple bonds through which they get adsorbed on the metal surface. The compounds have to block the active corrosion sites on the metal surface. This assumption could be further confirmed by the formation of the protective film on mild steel surface through adsorption and was well supported by SEM and FTIR.

Conclusion

Schreabera swietenioids plants leaves performed as efficient corrosion pickling inhibitor on mild steel in 1 N HCl. The use of *Schreabera swietenioids* plants as corrosion inhibitor is environmentally safe, nontoxic, eco-friendly, cost effective and easily available. The extracts of *Schreabera swietenioids* plants showed maximum efficiency of 92.73 % leaves at the optimum concentration of 15 ppm for one day immersion time at room temperature. The data obtained from Mass loss, Polarization and EIS methods are in good agreement to each other. Polarization studies showed that the *Schreabera swietenioids* plants extracts behave as a mixed type inhibitor on the metal surface. The adsorbed film over the mild steel surface has been confirmed by SEM analysis. The adsorption fits well to Temkin adsorption isotherm. Finally, it was concluded that *Schreabera swietenioids* leaves extract act as a corrosion inhibitor for mild steel in HCl and they can be used to replace toxic and non-biodegradable inhibitors.

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