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Inhibitor for the Corrosion of Mild Steel in H_2SO_4

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ABSTRACT

An extract of *Terminalia chebula* fruits was investigated as a corrosion inhibitor of mild steel in 0.5 M H_2SO_4 by means of conventional mass loss, electrochemical polarization, electrochemical impedance spectroscopy and scanning electron microscopy. The mass loss results showed that the extract of *Terminalia chebula* is an excellent corrosion inhibitor, electrochemical polarization data revealed the mixed mode of inhibition and the results of electrochemical impedance spectroscopy showed 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 confirmatory evidence of an improved surface condition, due to adsorption, for corrosion protection.

KEYWORDS

***Terminalia chebula,* acid corrosion inhibitor, electrochemical polarization, electrochemical impedance spectroscopy, mild steel.**

1. Introduction

Large amounts of sulphuric acid are used in the chemical industry for the removal of undesired scale and rust. The addition of corrosion inhibitors effectively protects the metal against acid attack. Many studies in this regard using organic inhibitors have been reported.[1–5] Most of the inhibitors are organic compounds with N, S and O heteroatoms that have high electron densities, making them the reaction centres. These compounds are adsorbed on the metallic surface and block the active corrosion sites and most of them are highly toxic to both humans and the environment. Hence, the use of natural products as eco-friendly and harmless corrosion inhibitors has become popular.[6–14]

Terminalia chebula, a plant from the Combretaceae family, is abundant in North India and southwards to the Deccan tablelands.[15] *Terminalia chebula* is a tree with a rounded crown and spreading branches. The fruit contains a constituent which has a wide antibacterial and antifungal spectrum. It is rich in tannin. The chief constituents of tannin are chebulic acid, chebulagic acid, corilagin and gallic acid.[16] So, *Terminalia chebula* is a good potential inhibitor but little has been reported about its inhibition behaviour.

2. Experimental

2.1. Inhibitor Preparation

About 5 g of dried and powdered fruits of *Terminalia chebula* was refluxed with 0.5 M H_2SO_4 for about 5 h and was kept overnight to extract the basic components. The solution was filtered and the filtrate was diluted to 500 mL with 0.5 M H_2SO_4. This extract was used to study the corrosion inhibition properties. To know the mass of plant extract, 100 mL of the extract was taken and neutralized with 1 M NaOH up to pH 8 in order to liberate the base from the salt. The neutralized solution was then extracted with chloroform. The organic (chloroform) layer consisting of basic organic compounds was evaporated and the resultant gummy material obtained was dried and powdered. From the mass of the obtained powdered material per mL, the mass of plant compounds in the extract was calculated. The aggressive acid solutions used were made of AR grade H_2SO_4 and diluted with doubly distilled water. The concentration range taken was varied from 25 to 200 ppm in 0.5 M H_2SO_4.

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2.2. Preparation of Specimens

Cylindrical working electrodes of mild steel (MS) containing 0.09 % P, 0.37 % Si, 0.01 % Al, 0.05 % Mn, 0.19 % C, 0.06 % S and the remainder Fe, were used for the electrochemical polarization and impedance measurements. For the mass loss method and scanning electron microscopic (SEM) analysis specimens of 1 ×1 cm of the same MS were used. The surface preparation of the mechanically polished specimens was carried out using different grades of emery paper, degreased with acetone, dried at room temperature and then stored in a desiccator before use.

2.3. Mass Loss Method

The polished and pre-weighed MS specimens were suspended in 100 mL of the test solutions, with and without the extracts of different concentrations, for a fixed period and were washed, dried and weighed. From the mass loss data, the percentage inhibition efficiency, E_w, was calculated.

2.4. Electrochemical and Impedance Measurements

A three-electrode cell of Borosil glass, consisting of a working electrode (WE) of MS, a pure platinum counter electrode (CE), and a saturated calomel electrode (SCE) as a reference electrode, was used for the measurements. The electrolytes used were acidic solutions maintained at 30 °C. The AC impedance measurements are shown as Nyquist plots and the polarization data as Tafel plots. A CH Electrochemical analyzer model 608 C (Austin, TX, USA) was used for this purpose. Polarization curves were obtained with a scan rate of 0.01 V s^{-1} in the range of –250 mV to +250 mV *vs.* the corrosion potential (E_{corr}) of the working electrode measured against SCE. Impedance measurements were carried out at the E_{corr} 60 min after the electrode had

Table 1 Inhibition efficiency of MS in 0.5 M H_2SO_4 at various temperatures in the presence and absence of different concentrations of *Terminalia chebula* fruit extract.

Temperature/K	Concentration/ppm	W/μg cm^{-2} h^{-1}	Inhibition efficiency, E_w/%	θ
303	0.5 M H_2SO_4	17.32	–	–
	25	4.23	76	0.76
	50	3.25	81	0.81
	100	2.51	86	0.86
	150	2.23	87	0.87
	200	1.98	89	0.89
313	0.5 M H_2SO_4	19.82	–	–
	25	5.34	73	0.73
	50	4.02	80	0.80
	100	3.23	84	0.84
	150	2.96	85	0.85
	200	2.67	87	0.87
323	0.5 M H_2SO_4	20.56	–	–
	25	5.94	71	0.71
	50	4.92	76	0.76
	100	4.03	80	0.80
	150	3.21	84	0.84
	200	2.91	86	0.86

been immersed in the test solution. The frequency range studied was 0.1 Hz to 1000 Hz. The AC signal was 5 mV peak-to-peak with 12 data points per decade. SEM analysis was carried out with a HITACHI model S3400 N (Tokyo, Japan) scanning electron microscope.

3. Results and Discussion

Based on the mass loss measurements, the corrosion rate, W_{corr}, and the values of inhibition efficiency, E_w, for various concentrations of *Terminalia chebula* fruit extract after 2 h of immersion at 303 K, 313 K and 323 K are given in Table 1. The inhibition efficiency, E_w, was determined from equation (1):

$$E_w = 100 \times \frac{W_0 - W_{corr}}{W_0} \% \tag{1}$$

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

From Table 1 it is clear that E_w increases with an increase in concentration reaching a maximum value of 89 % at a concentration of 200 ppm at 303 K. This suggests that an increase in the inhibitor concentration increases the number of molecules adsorbed over the mild steel surface, blocking the active sites of acid attack and thereby protecting the metal from corrosion. Generally, the corrosion increases with a rise in temperature, as can be seen from Table 1.

The degree of surface coverage θ for different concentrations of the inhibitor in acidic media has been evaluated from the mass loss by making use of equation 2:

$$\theta = \frac{W_0 - W'}{W_0 - W_m} \tag{2}$$

where W_m is the smallest corrosion rate. From Table 1, the increase of W_0 is more pronounced with the rise in temperature for the blank solution. In the presence of the *Terminalia chebula* fruit extract θ decreases slightly with increasing experimental temperature, which could be caused by desorption of the inhibitor from the steel surface. The slight decrease of θ suggests that the efficiency of the *Terminalia chebula* fruit extract is independent of temperature. The result shows that the *Terminalia chebula* fruit extract effectively protects the steel 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 charge in the molecule, and the type of electrolyte.[17–21] Important information about the interaction between the inhibitor and the steel surface can be provided by the adsorption isotherm. In the work cited above, it may be concluded that θ increases with the inhibitor concentration; this is attributed to greater adsorption of inhibitor molecules onto the steel surface. Assuming that the adsorption of *Terminalia chebula* fruit extract belonged to the monolayer adsorption, then the Langmuir adsorption isotherm can be applied to investigate the mechanism by the following equation:

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{3}$$

where C is the inhibitor concentration in the electrolyte and K is the equilibrium constant for the adsorption/desorption process.

Three representative Langmuir adsorption plots at different temperatures are shown in Fig. 1. Linear plots are obtained with slopes equal to 1.09, 1.11 and 1.12 for the experimental temperatures of 303, 313 and 323 K, respectively. These results indicate that some constituent of the *Terminalia chebula* fruits occupies more than one adsorption site on the steel surface. A modified Langmuir adsorption isotherm[22,23] could be applied to this phenomenon, which is given by the corrected equation:

$$\frac{C}{\theta} = \frac{n}{K} + nC \tag{4}$$

The potentiodynamic polarization data are shown as Tafel plots for MS in 0.5 M H_2SO_4 with the addition of various concentrations of the additive in Fig. 2. The corrosion kinetic parameters such as corrosion potential, E_{corr}, corrosion current density, I_{corr}, anodic and cathodic Tafel slopes, b_a and b_c, were derived from these curves and are given in Table 2. The values of E_I were calculated using the following equation:

$$E_1 = 100 \times \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \% \tag{5}$$

where I_{corr} and $I_{corr(inh)}$ are the values of the 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 corrosion potential, E_{corr}.

From Table 2, it is observed that the I_{corr} values gradually

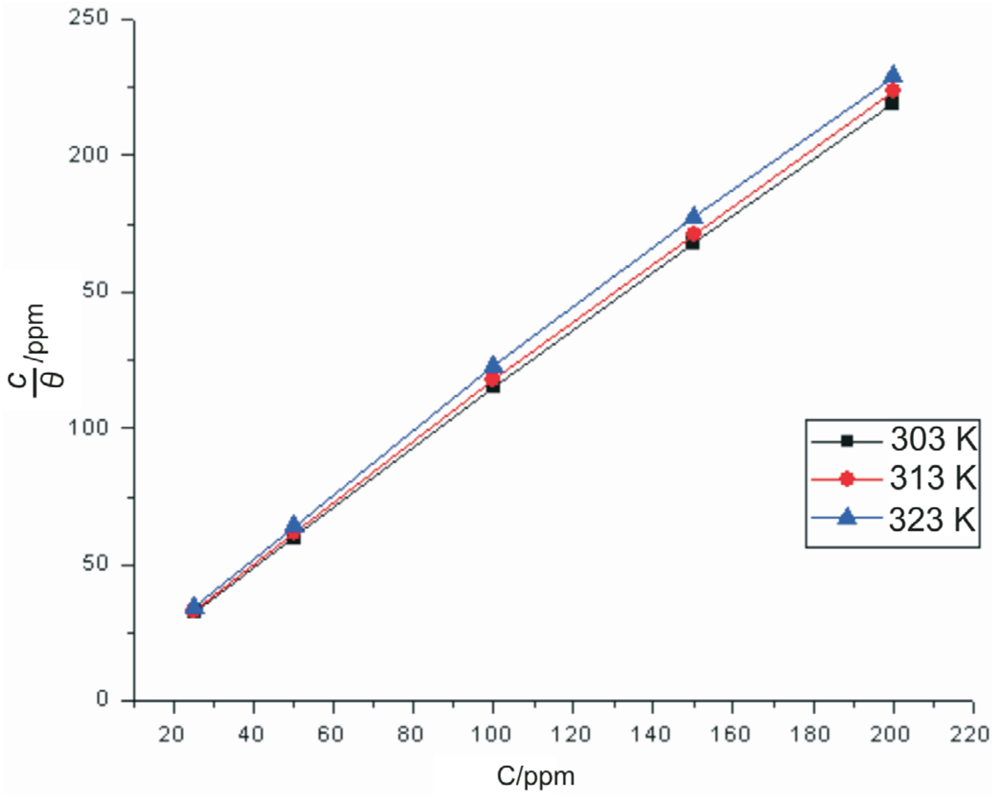


Figure 1 Langmuir adsorption plots for mild steel in 0.5 M H_2SO_4 at different temperatures.

decrease with increase in the concentration of inhibitor, with respect to the blank. Further, there was an anodic shift of the E_{corr} value with an increase in the concentration of the inhibitor indicating that the *Terminalia chebula* extract acted as an anodic inhibitor[24] for MS in 0.5 M H_2SO_4, which was supported by the gradual and significant decrease of the anodic Tafel slope. It could be derived from this decrease that the rate of anodic dissolution was much retarded in comparison with that of cathodic hydrogen evolution and there was also some decrease in the corresponding values of the cathodic Tafel slopes. This means that the extract must have acted predominantly by blocking anodic sites, and also cathodic sites to some extent, and the extract contained the active molecules which behaved as mixed-type acid corrosion inhibitors.

The corrosion behavior of MS in 0.5 M H_2SO_4, in the absence and presence of various concentrations of *Terminalia chebula* extract were also investigated by the EIS technique. The resultant Nyquist plots are shown in Fig. 3. The existence of a single semicircle in each plot shows that there was only a single charge transfer process during the anodic dissolution of MS and

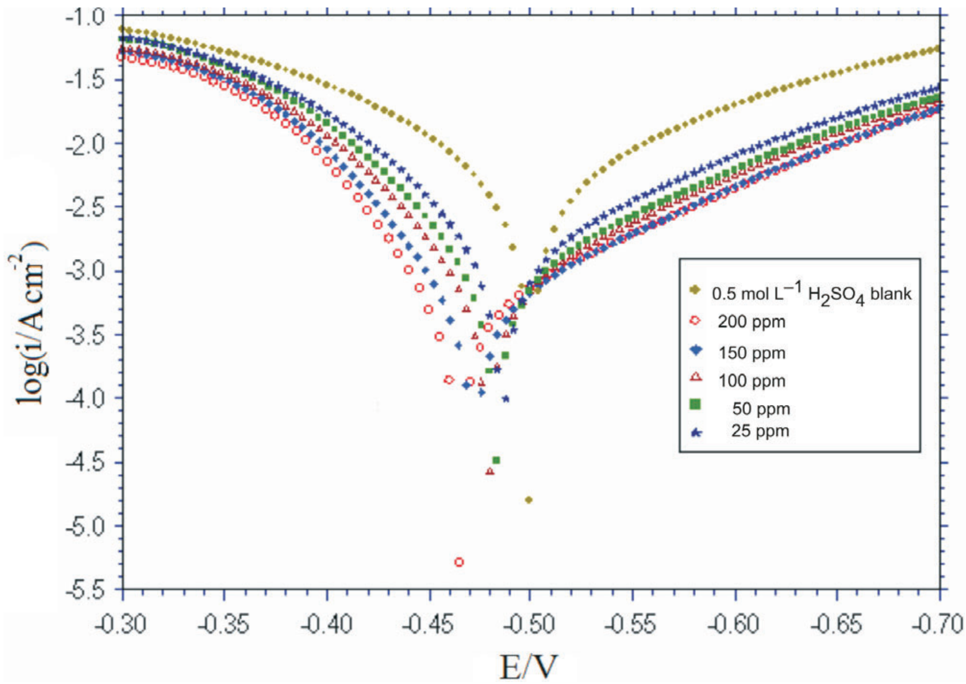


Figure 2 Tafel plots showing the effect of *Terminalia chebula* fruit extract on corrosion of MS in H_2SO_4 medium.

Table 2 Effect of *Terminalia chebula* fruit extracts on MS in 0.5 M H_2SO_4 media (Tafel polarization studies).

Concentration of inhibitor/ppm	Corrosion potential/V	Tafel constant/mV decade^{-1}		Corrosion current density /mA cm^{-2}	Inhibition efficiency, E_I/%
		b_a	b_c		
0	–0.4997	143	160	5.914	–
25	–0.4865	101	141	1.679	72
50	–0.4829	90	138	1.115	81
100	–0.4794	88	137	0.888	85
150	–0.4724	81	134	0.649	89
200	–0.4653	84	132	0.610	90

remained unaffected in the presence of inhibitive molecules of the extract added in the acid. An isolated Nyquist plot for the blank system is shown in the inset in Fig. 3, which indicated that there was least charge transfer resistance, R_t, of the corrosion reactions. There was a gradual increase in the diameter of each semicircle of the Nyquist plot due to an increase in the number of inhibitive molecules in the extract when the concentration was raised from 25 to 200 ppm. It clearly reflected that at the highest concentration of 200 ppm, formation and gradual improvement of the barrier layer of the inhibitive molecules took place, and as a result the acid corrosion rate of MS gradually decreased.

Table 3 embodies various parameters such as R_t and the double layer capacitance, C_{dl}. There was a gradual decrease in the values of C_{dl} with increase in the concentration of the extract. This considerable change indicated that the inhibitive molecules of the extracts had been adsorbed on the MS surface and decreased the roughness of the MS surface. The values of E_R were calculated from equation (6):

$$E_R = 100 \times \frac{R_{t(inh)} - R_t}{R_{t(inh)}} \% \qquad (6)$$

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

To obtain the values of C_{dl}, the values of the frequency at which the imaginary component of the impedance is maximum, $-Z_{im(max)}$, were found and used in the following equation with the corresponding R_t values:

$$C_{dl} = \frac{1}{2\pi f_{max} R_t} \qquad (7)$$

Table 3 Data from electrochemical impedance measurements of mild steel in 0.5 M H_2SO_4 for various concentrations of *Terminalia chebula* fruit extract.

Concentration of inhibitor/ppm	R_t /ohm cm^{-2}	C_{dl} /μF cm^{-2}	Inhibition efficiency, E_R/%
0	07	155.27	–
25	43	126.29	83
50	69	99.52	90
100	89	89.31	92
150	136	78.46	95
200	166	74.13	96

The SEM photograph in Fig. 4a shows that the surface of the MS was extremely damaged in the absence of the extract while Fig. 4b clearly shows the formation of a film by the active *Terminalia chebula* constituents on the MS surface which was responsible for the corrosion inhibition.

The inhibition properties of *Terminalia chebula* may be due to the presence of nitrogenous compounds in the extract[25] or tannins.[26] Tannins are complex astringent aromatic acidic glycosides found in various plants. They are made up of polyphenols and their acidic and heterocyclic derivatives. Polar organic compounds containing N, S and O are good corrosion inhibitors.[27] These may have been responsible for the formation of an oriented film layer, which essentially blocks discharge of H^+ and dissolution of metal ions. Acid pickling inhibitors containing

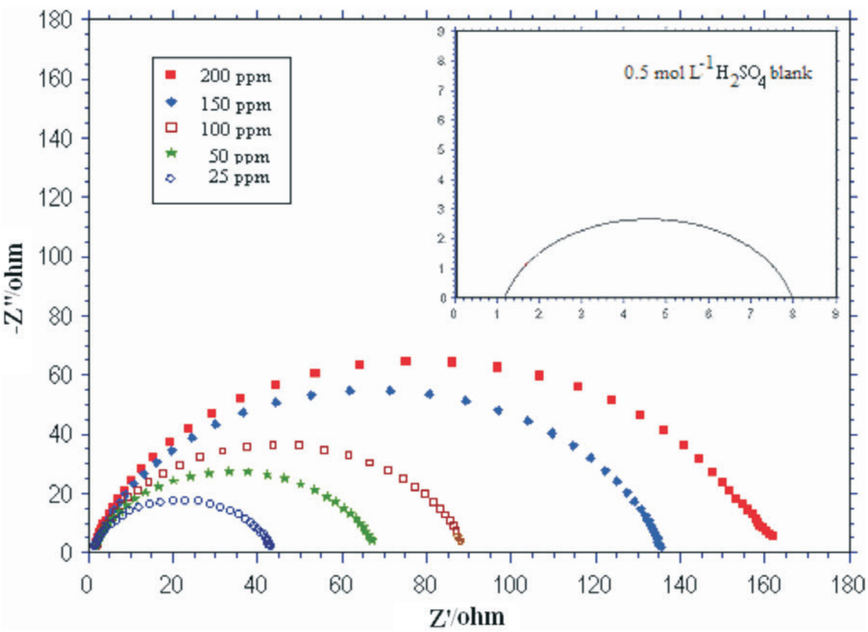
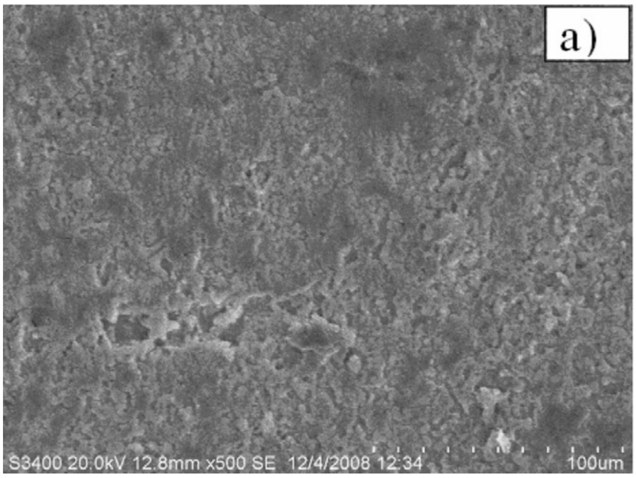


Figure 3 Nyquist plots showing the effect of the *Terminalia chebula* fruit extract on the corrosion of MS in H_2SO_4 medium.



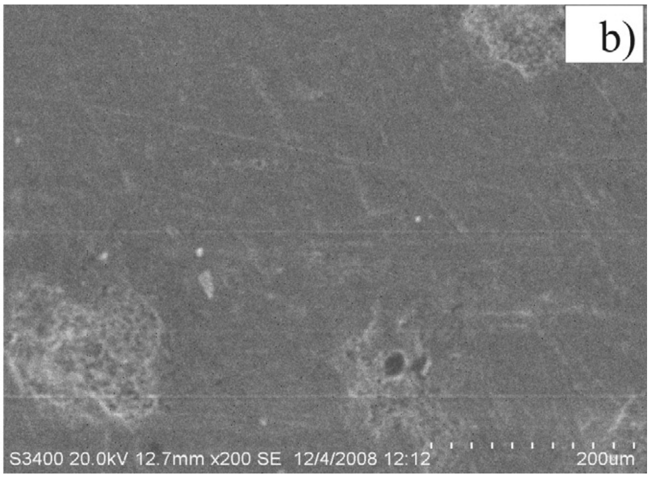


Figure 4 SEM images of MS (**a**) in 0.5 M H_2SO_4 medium and (**b**) with *Terminalia chebula* extract (200 ppm).

organic N, amine, S and OH groups behave similarly to inhibit corrosion.

4. Conclusions

The active molecules present in the extract of *Terminalia chebula* have effectively inhibited corrosion of mild steel in 0.5 M H_2SO_4 at various temperatures by forming a protective barrier layer. It adsorbs on the steel surface according to the modified Langmuir adsorption isotherm. The inhibition efficiency of the extract increased gradually with increase in concentration. Polarization measurements have shown that the extract of *Terminalia chebula* has acted as a mixed inhibitor, retarding predominantly anodic dissolution of steel in 0.5 M H_2SO_4. The results of the mass loss, electrochemical polarization and AC impedance spectroscopy were all in very good agreement to support the above conclusions. Photographs by SEM clearly showed the formation of the protective film on the surface of the mild steel. The acid extract of *Terminalia chebula* can be considered as a source of relatively cheap, eco-friendly and effective acid corrosion inhibitors.

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