Effect of Morinda Tinctoria Leaves Extract on the Corrosion Inhibition of Mild Steel in Acid Medium

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The Morinda tinctoria (MT) plant leaves extract was prepared in aqueous and hydrochloric acid media and was used as corrosion inhibitor for mild steel in hydrochloric acid medium. MT is found to be an efficient inhibitor at room temperature and the efficiency decreases with increase in temperature. Results from colorimetric studies predict the amount of iron present in the test solution and the percentage inhibition efficiency values calculated from this data fit well with the weight loss experiments. The AC impedance studies reveal that the mild steel surface is positively charged and the process of inhibition is through charge transfer. Polarisation studies indicate the mixed nature of the inhibitor. Thermodynamic parameters obtained predict that the process of inhibition is a spontaneous one.

KEY WORDS: Acid solution; Mild steel; Colorimetry; Electrochemical technique; Corrosion

1. Introduction

Synthetic and naturally occurring plant products are used as corrosion inhibitors. The mechanism of corrosion inhibition process involves formation of a protective layer which prevents the corrosive substance to the metal surface. The selection of the inhibitor is based on the availability, low cost, non-toxic, biodegradable, renewable material and the presence of groups or atoms which aid the adsorption of inhibitor to the metal surface. Plant products satisfy majority of the above criteria and hence a lot of work is being carried out using plant extracts as corrosion inhibitors in different media, on various metals^[1–11]. Naturally occurring inhibitors from plant products contain a variety of organic substances that may adsorb on the metal surface through hetero atoms, aromatic rings and multiple bonds and thereby prevent the metal surface from further corrosion^[12–14]. The plant Morinda tinctoria (MT) which belongs to the family of Rubiaceae is a weed which grows on its own in our area and is often discarded as waste. But the leaves of this plant are found to contain many active

constituents^[15]. Available literature suggests that the extract of the plant in any form has not been used for corrosion inhibition studies. Hence, in the present work an attempt has been made to study the corrosion inhibition properties of the aqueous and acid extracts of the leaves of MT on mild steel.

2. Materials and Methods

2.1 Specimen preparation

The mild steel (MS) specimen of dimension 1 cm × 5 cm × 0.2 cm with an area of 12.3 cm² was used for the weight loss study and the specimen with an exposed area of 0.95 cm² was used for electrochemical study. The surface of the specimens was mechanically polished with different grades (600, 800 and 1000) of emery papers and then degreased with acetone. The composition (wt.%) of MS is: C 0.14, Mn 0.57, Al 0.05, Cr 0.03, Si 0.02, Cu 0.01 and balance is Fe.

2.2 Extract preparation

The aqueous and acid extracts were prepared by refluxing 5 and 0.25 g of dried and powered leaves of MT for 3 h at 60 °C in 100 mL of distilled water and 1 mol/L HCl respectively. The solutions were allowed to cool to room temperature, filtered and stored. The

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aqueous and hydrochloric acid extracts are abbreviated as AE and HE respectively. Distilled water and analar grade HCl were used for preparing the extracts.

2.3 Weight loss studies

The pre-cleaned and pre-weighed MS specimens in triplicate were suspended in 100 mL test solution with and without inhibitor at different concentrations of AE and HE in 1 mol/L HCl for a period of 1 h. After that, the specimens were taken out, washed with distilled water, dried and weighed. From the weight loss data, inhibition efficiency (%IE) was calculated and the critical concentration of the inhibitor was found out for both AE and HE. The effect of halide additives was studied by adding the halide additives (KCl, KBr and KI). The influence of the temperature on corrosion behaviour of MS in the presence of MT extract was studied in the range of (30–60 °C). In addition to this the influence of the immersion time on inhibition efficiency was studied by varying the immersion time from 1 to 48 h. All these studies were carried out at (30 ± 1) °C. The inhibiting power and corrosion rate were calculated from the following equation.

$$\%IE = (W_B - W_I/W_B) \times 100\% \quad (1)$$

where W_B and W_I are the weight loss of the MS specimens in absence and in presence of the inhibitor respectively.

$$v = 87.6W/\rho At \quad (2)$$

where v is corrosion rate (mm/y), W is the weight loss (mg), ρ is the density of the specimen (g/cm³), A is the area of specimen (cm²) and t is the exposure time (h).

2.4 Colorimetric estimation

In the present study, the amount of Fe²⁺ present in the test solution before and after MS immersion was determined by colorimetric experiment. Ammonium thiocyanate is the colouring agent; the %T (percentage transmittance) of this solution was recorded and used as blank. This was mixed with standard ferric ammonium sulphate solutions of different concentrations and the %T was recorded. A standard graph was plotted between %T and the concentration of Fe²⁺. MS specimens after weight loss experiments were taken away from the inhibited and uninhibited solutions and were tested for dissolved iron by noting the transmittance after mixing with ammonium thiocyanate. From the standard graph the amount of iron was calculated. The %IE was calculated from the following equation

$$\%IE = (C - C')/C \times 100\% \quad (3)$$

where C is concentration of Fe²⁺ in blank solution, C' is concentration of Fe²⁺ in inhibited solution.

2.5 Electrochemical studies

Electrochemical studies were carried out using electrochemical analyzer of CH Instrument (Model 608D). The experiments were carried out in a three electrode cell assembly using platinum as auxiliary electrode and calomel as reference electrode. MS specimen was used as a working electrode. AC impedance studies were conducted in the frequency range of 10,000–1 Hz at the rest potential using 0.02 V sine wave as the excitation signal. R_{ct} and C_{dl} values were obtained from the Nyquist plots and the %IE was calculated from

$$\%IE = (R_{ct}^i - R_{ct}^o)/R_{ct}^i \times 100\% \quad (4)$$

where R_{ct}^o and R_{ct}^i are the charge transfer resistance in absence and in presence of inhibitor respectively. Potentiodynamic polarization studies were carried out in the potential range of –0.750 to –0.250 V at a scan rate of 0.01 V/s. The electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic slopes (b_a and b_c) were obtained from Tafel plots and the %IE was determined using the formula,

$$\%IE = (I_{corr}^o - I_{corr}^i)/I_{corr}^o \times 100\% \quad (5)$$

where I_{corr}^o and I_{corr}^i are the corrosion current densities in absence and in presence of inhibitor respectively.

2.6 Surface analysis

FT-IR was recorded using Perkin Elmer spectrophotometer for the dried HE extract and the material obtained by scrapping the specimens after the immersion experiment. Surface morphology of the mild steel in inhibited and uninhibited systems was also examined using scanning electron microscope (SEM) (JSM 6390).

3. Results and Discussion

3.1 Weight loss studies

The results obtained for the corrosion inhibition of MS in 1 mol/L HCl medium with AE and HE by weight loss studies are given in Table 1, and it is clear from the table that the %IE increases with increasing the concentrations of both AE and HE. The maximum %IE for AE and HE were noticed at the inhibitor concentrations of 12 vol.% and 15 vol.%, respectively. The increase in %IE or decrease in corrosion rate reveals the adsorption of various natural products present in the extract on MS. Table 1 indicates that the %IE increases with increase in immersion time from 1 to 6 h and decreases from 24 to 48 h for AE. In the case of HE the %IE gradually decreases from 1 to 48 h. The decrease in %IE after certain period of time might be due to the desorption of inhibitor molecules from the metal surface^[16,17].

Table 1 Effect of the concentration of the inhibitor and immersion period on the corrosion of MS in HCl medium

Inhibitor	Concentration (vol.%)	Immersion period									
		1 h		3 h		6 h		24 h		48 h	
		CR (mm/y)	%IE (%)	CR (mm/y)	%IE (%)	CR (mm/y)	%IE (%)	CR (mm/y)	%IE (%)	CR (mm/y)	%IE (%)
HE	Blank HCl	35.29		25.61		25.90		22.76		15.60	
	3	20.23	42.67	13.73	46.40	11.52	55.52	11.16	50.99	10.37	33.55
	5	10.43	70.44	8.26	67.77	8.33	67.83	6.87	69.82	7.76	50.22
	10	5.90	83.29	5.50	78.51	5.62	78.28	5.75	74.72	5.66	63.73
	15	5.17	85.35	4.48	82.53	4.82	81.38	4.25	81.35	4.00	74.35
AE	4	9.98	71.72	3.02	88.19	2.89	88.85	3.25	85.73	5.66	63.73
	6	7.53	78.66	1.94	92.44	1.66	93.58	2.80	87.71	5.00	67.95
	8	6.26	82.26	1.84	92.80	1.63	93.70	2.92	87.16	5.11	67.24
	12	4.90	86.12	1.75	93.15	1.03	96.03	2.64	88.41	4.75	69.57

Table 2 Effect of addition of halide additives (1 vol.%) on the corrosion inhibition of MS in HCl medium

System	15 vol.% HE		12 vol.% AE	
	CR (mm/y)	%IE (%)	CR (mm/y)	%IE (%)
Blank HCl	35.29		35.29	
With inhibitor	5.17	85.35	4.90	86.12
Inhibitor + KCl	4.26	87.92	4.08	88.43
Inhibitor + KBr	3.63	89.72	3.08	91.26
Inhibitor + KI	2.72	92.29	2.18	93.83

The effect of halide ions on the inhibition efficiency of various organic compounds and natural products were studied by so many authors^[18–20] and they observed that the synergistic effect increased in the order $\text{Cl}^- < \text{Br}^- < \text{I}^-$. According to the literature, the halide ions facilitate adsorption of the organic compounds in plant species during MS corrosion in acidic medium. The increase in the %IE was observed for MS corrosion in acidic medium with both AE and HE in the presence of halide additives and the results are listed in Table 2.

3.1.1 Effect of temperature

The effect of the temperature (303–333 K) on corrosion of MS was studied in the presence and in the absence of AE and HE to find the nature of interaction between the inhibitor and MS surface. The activation energy (E_a) for MS corrosion reaction was found out from the slope of the Arrhenius plot ($\lg \text{CR}$ vs. $1/T$) where slope is $-E_a/2.303R$, CR is the corrosion rate, E_a is the activation energy, R is gas constant, T is temperature in absolute scale. Analysis of Table 3 reveals that in the case of HE the %IE decreases considerably when the temperature is increased from 303 to 313 K. This might be due to the desorption of adsorbed inhibitor molecules from the metal surface. However, when the temperature is increased beyond 313 K, the %IE only slightly decreases. Table 3 also shows that with AE, the %IE is almost constant with increase in the temperature indicating that the equilibrium between adsorption and desorption is not altered considerably with increase in the temperature. The difference in the %IE between AE and HE at dif-

ferent temperatures mainly depend on the type and nature of the substituent present in the extract. Since, the %IE values are altered only to a small extent at higher temperatures; above 313 K it is obvious that the inhibitor is efficient over a wide range of the temperatures. The calculated values of E_a for both the inhibited systems are found (Table 3) to be higher than the uninhibited system. This is an indication of spontaneous adsorption of the inhibitor molecules on MS surface and is attributed to physisorption^[21].

3.1.2 Adsorption isotherm

Adsorption process is determined by using the surface coverage data and it plays an important role in the prediction of the adsorption isotherm. It also provides information about the nature of interaction between the metal surface and inhibitor. The free energy of adsorption (ΔG_{ads}) at different temperatures was calculated using the following equation.

$$\Delta G_{\text{ads}} = -RT \ln(55.5 K) \quad (6)$$

where $K = \theta/C_{\text{inh}}(1-\theta)$, θ is surface coverage, C_{inh} is the concentration of inhibitor. The constant value of 55.5 represents the molar concentration of the water in solution. The values of ΔG_{ads} less negative than -20 kJ/mol assumed for physisorption and that more negative than about -40 kJ/mol indicate chemisorption^[22]. Table 3 shows negative values of ΔG_{ads} for both AE and HE indicating the stability of the adsorbed layer and spontaneity of adsorption. Observation of the Table 3 shows that in the case of AE, ΔH_{ads} is negative and ΔS_{ads} is positive. The positive value of ΔS_{ads} and negative value of ΔH_{ads} indicate the spontaneity of the reaction at all temper-

Table 3 Effect of the temperature on the corrosion inhibition of MS in HCl medium with AE and HE

System	Temperature (K)								E_a (kJ/mol)	$-\Delta G_{\text{ads}}$ (kJ/mol)				$-\Delta H_{\text{ads}}$ (kJ/mol)
	303		313		323		333			Temperature (K)				
	CR	%IE	CR	%IE	CR	%IE	CR	%IE		303	313	323	333	
	(mm/y)	(%)	(mm/y)	(%)	(mm/y)	(%)	(mm/y)	(%)						
Blank HCl	35.29		48.54		87.01		193.06		47.25					
HE (15 vol.%)	5.17	85.35	11.98	75.33	21.50	75.29	50.90	73.64	61.91	7.71	6.29	6.48	6.44	18.24
AE (12 vol.%)	4.90	86.12	7.80	83.93	14.24	83.63	32.57	83.13	52.26	8.43	8.26	8.47	8.63	5.87

Note: $\Delta S_{ads} = -0.0362$ for HE (15 vol.%), $\Delta S_{ads} = 0.0081$ for AE (12 vol.%)

atures. This is further supported by the fact that with AE, the %IE values remain constant in the temperature range of 303–333 K. However, in the case of HE both ΔH_{ads} and ΔS_{ads} are negative suggesting the spontaneity of the reaction at lower temperature^[23,24]. The decrease in the %IE values at higher temperatures with HE further supports the above argument. Also, the values of ΔH_{ads} less negative than 25 kJ/mol relate the fact that the process of adsorption is through physisorption^[25]. The ΔG_{ads} , ΔH_{ads} , ΔS_{ads} values indicate that the process of adsorption of both AE and HE are spontaneous and exothermic in nature. Among all the adsorption isotherms tested, Langmuir adsorption isotherm was found to fit well with the experimental data and the isotherm was obtained by plotting, $\lg(\theta/1-\theta)$ vs. $\lg C$, as shown in Fig. 1.

3.2 Colorimetric estimation

The results obtained from weight loss method give the corrosion rate, %IE of the inhibitor for MS corrosion and the results obtained from colorimetric estimation give the amount of Fe^{2+} in the inhibited and uninhibited solutions which can be used to calculate %IE. The %T values were found out for inhibited and uninhibited solutions after one hour of immersion of the sample in the test solution. The %T values were then used to find out the concentration of Fe^{2+} in the above solutions using the standard graph. From the Fe^{2+} concentration, the %IE

was calculated by applying the relation described in section 2.4 and the results are given in Tables 4 and 5. Table 4 reveals that with the increase in the concentration of inhibitor, the iron content of the solution after experiment decreases suggesting the lower corrosion rate. Also, the addition of halide salts increases the %IE (Table 5). The above results predict the adsorption of the inhibitor molecules on the metal surface in the acidic medium thereby prevent the MS from further corrosion. The %IE value calculated from the colorimetric data is in accordance with the data obtained from weight loss studies.

3.3 Electrochemical studies

3.3.1 AC impedance method

Impedance studies were carried out by varying the concentration of inhibitors (HE and AE) and the added halide ions. The Randles equivalent circuit used for impedance studies is given in Fig. 2, where R_s is solution resistance, C_{dl} is the double layer capacitance and R_{ct} is the charge transfer resistance. The impedance data obtained from Nyquist plots are given in Tables 6 and 7. The representative Nyquist plots for varying the concentration of inhibitor (HE) is given in Fig. 2. The values of R_{ct} increased with increase in the concentration of inhibitors (HE and AE) as well as halide additives and corresponding C_{dl} values decreased. The increasing R_{ct} values imply reduced corrosion rate in the presence of the inhibitor and this is because of increasing surface coverage of the inhibitor molecule on the addition. A decrease in C_{dl} value increases the thickness of the electrical double layer, indicating that the inhibitor is adsorbed on the surface. The impedance diagrams have an approximately semicircular appearance and the diameter of the semicircles were varied upon increasing the concentration of inhibitor suggesting the corrosion of MS is controlled by a charge transfer process^[12,14]. Also the impedance data were used to find out the potential of zero charge and the results show the positive nature of the specimen.

3.3.2 Potentiodynamic polarization method

Fig. 3 depicts the representative Tafel plots of the corrosion inhibition studies on mild steel with different concentrations of HE. The polarisation data obtained are given in Tables 6 and 7. Results show that the addition of inhibitor alters both b_a and b_c values

Fig. 1 Langmuir adsorption isotherm for mild steel corrosion in 1 mol/L HCl in the presence of AE and HE

Table 4 Effect of the concentration of inhibitor on the corrosion of MS in HCl medium from colorimetric studies

Inhibitor	Concentration (vol.%)	$C_{\text{Fe}^{2+}}$ (10^{-5} mol/mL)	%IE (%)
	Blank HCl	7.7630	
HE	3	4.3199	44.35
	5	2.2186	71.42
	10	1.4074	81.87
	15	1.1875	84.70
AE	4	2.2186	71.42
	6	1.6908	78.22
	8	1.4074	81.87
	12	1.0018	87.10

Note: $C_{\text{Fe}^{2+}}$ is the concentration of Fe^{2+} in the test solution

Table 5 Colorimetric data on the effect of addition of halide additives (1 vol.%)

System	$C_{\text{Fe}^{2+}}$ (10^{-5} mol /mL)	%IE (%)
Blank HCl	7.7630	
HE (15 vol.%)	1.1875	84.70
HE + KCl	1.0018	87.10
HE + KBr	0.8454	89.11
HE + KI	0.6255	91.94
AE (12 vol.%)	1.0018	87.10
AE + KCl	0.8454	89.11
AE + KBr	0.6255	91.94
AE + KI	0.5620	92.76

Fig. 2 Nyquist plots for corrosion of MS in 1 mol/L HCl with different concentrations of HE

suggesting that the inhibitor reduces anodic dissolution and retard hydrogen evolution as well indicating the mixed nature of the inhibitor. On increasing the concentration of inhibitors, the I_{corr} values decrease which are due to the higher surface coverage of the inhibitor^[12,14]. The results obtained for the synergistic studies are in accordance with the gravimetric data.

3.4 Surface analysis

SEM images of uninhibited and inhibited surfaces in Fig. 4 clearly reveal that the surface of the mild steel is covered with inhibitor molecules of AE and HE. This is further confirmed by FT-IR spectroscopy. MT belongs to the same family (Rubiaceae) as that of *Morinda citrifolia* (MC). The leaves of MC are found to contain many amino acids and

Fig. 3 Tafel plots for MS corrosion in 1 mol/L HCl with different concentrations of HE

flavonoids^[26]. Hence, the extract of MT is presumed to have many functional groups like NH_2 , COOH , OH , NH *etc.* In order to study the nature of adsorption, the IR spectrum (Fig. 5(b)) of scrapped material from the MS specimen coated with HE of MT was compared with that of the crude plant extract (Fig. 5(a)). Two broad peaks at 3368 and 1639 cm^{-1} in the spectrum of the acid extract can be assigned for O-H and/or NH_3^+ symmetric stretching and $\text{C}=\text{O}$ stretching and/or NH_3^+ symmetric bending respectively^[27]. These peaks have been shifted to 3321 and 1622 cm^{-1} in the adsorbed material scrapped from the MS, indicating that the inhibitor is adsorbed on the metal surface. The peak at 1261 cm^{-1} corresponds to NH_3^+

Table 6 Electrochemical parameters for MS corrosion in 1 mol/L HCl at different concentrations of the inhibitor

Conc. of inhibitor	R_{ct} ($\Omega \cdot \text{cm}^2$)	%IE (%)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	$-E_{corr}$ vs. SCE (V)	b_a ($1/\text{V} \cdot \text{dec}^{-1}$)	b_c ($1/\text{V} \cdot \text{dec}^{-1}$)	$I_{corr} \times 10^{-4}$ (A/cm^2)	%IE (%)
Blank HCl	14.8		540.1	0.4769	6.768	5.787	14.470	
HE 3	26.63	44.42	301.6	0.4783	7.617	6.470	9.160	36.70
5	50.83	70.88	150.9	0.4740	8.862	7.367	4.682	67.64
10	92.16	83.94	78.33	0.4683	10.172	8.562	2.261	84.37
15	136.9	89.19	74.68	0.4641	10.979	9.290	1.436	90.08
AE 4	99.65	85.15	65.33	0.4783	10.192	8.932	2.427	83.23
6	153.1	90.33	55.41	0.4783	10.156	9.378	1.642	88.65
8	179.5	91.75	51.83	0.4801	9.854	9.509	1.404	90.30
12	189.3	92.18	49.51	0.4795	9.649	9.568	1.235	91.47

Table 7 Electrochemical parameters for MS corrosion in 1 mol/L HCl with halide additives (1 vol.%)

System	R_{ct} ($\Omega \cdot \text{cm}^2$)	%IE (%)	C_{dl} ($\mu\text{F}/\text{cm}^2$)	$-E_{corr}$ vs. SCE (V)	b_a ($1/\text{V} \cdot \text{dec}^{-1}$)	b_c ($1/\text{V} \cdot \text{dec}^{-1}$)	$I_{corr} \times 10^{-4}$ (A/cm^2)	%IE (%)
Blank HCl	14.8		540.1	0.4769	6.768	5.787	14.470	
HE (15 vol.%)	136.9	89.19	74.68	0.4641	10.979	9.29	1.436	90.08
HE + KCl	237.9	93.78	52.86	0.4530	10.621	9.81	1.071	92.6
HE + KBr	262.6	94.36	51.59	0.4685	9.915	9.823	0.800	94.47
HE + KI	277.8	94.67	50.61	0.4782	9.797	9.943	0.905	93.75
AE (12 vol.%)	189.3	92.18	49.51	0.4795	9.649	9.568	1.235	91.47
AE + KCl	267.4	94.47	48.61	0.4769	11.147	9.592	0.994	93.13
AE + KBr	284.8	94.8	47.83	0.4783	10.822	9.839	0.875	93.95
AE + KI	313.1	95.27	44.25	0.4832	10.296	9.908	0.785	94.57

Fig. 4 SEM images of fresh MS sample, MS dipped in 1 mol/L HCl, MS dipped in HE and MS dipped in AE

Fig. 5 FT-IR spectrum of the HE (a) and the material scrapped from MS surface (b) after immersion in inhibited system (HE)

in plane bending and/or coupled C-O stretching and O-H in plane bending vibrations^[14,27]. The shift of this peak to 1216 cm^{-1} is again a clear indication of interaction of these groups with the metal surface. The peak at 668 cm^{-1} in the IR spectrum of the scrapped material is due to $\gamma\text{-Fe}_2\text{O}_3$ ^[13,28]. The above observations clearly indicate the adsorption of the inhibitor molecule on the mild steel surface at active site.

4. Mechanism

The impedance data predicts the positive nature of the specimen in HCl medium. Also, the thermodynamic data advocate the physisorption mechanism. Further, the adsorption process is found to obey Langmuir adsorption isotherm, suggesting the possibility of multilayer adsorption. Hence, it is reasonable to conclude that while adding the inhibitor to HCl solution the anions like COO^- , OH^- present in the inhibitor solution, and the unshared pair of electrons present on the various hetero atoms present in the functional groups like C=O, O-H, N-H, NH_2 gets adsorbed on the MS. It is also possible that the Cl^- ions are adsorbed on the positively charged metal surface followed by the adsorption of positively charged species like NH_3^+ present in the crude extract and thereby preventing the metal surface from further corrosion.

5. Conclusions

Morinda tinctoria leaves extract act as effective corrosion inhibitor for mild steel in HCl medium. The thermodynamic data suggest that the process of adsorption is spontaneous, exothermic in nature and occurs *via* physisorption. The adsorption of HE and AE on MS follow Langmuir isotherm. AC impedance studies favour charge transfer mechanism. Potentiodynamic polarisation studies indicate the mixed

nature of the inhibitor. Surface analysis techniques (SEM and FT-IR) also confirm the adsorption of inhibitor molecule on the metal surface. The results from weight loss method are in good agreement with the colorimetric and electrochemical methods.

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