Investigation of *Citrus aurantiifolia* Leaves Extract as Corrosion Inhibitor for Mild Steel in 1 M HCL

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Abstract: The inhibition efficiency of acid extract of leaves of *Citrus aurantiifolia* [CAL] plant on the corrosion of mild steel in 1 M HCl was investigated by weight loss measurements and electrochemical studies. The corrosion rate of mild steel and the inhibition efficiencies of the extract were calculated. The results obtained show that the extract could serve as an effective inhibitor for the corrosion of mild steel in HCl media. Inhibition was found to increase with increasing concentration of the plant extract. The inhibitive action of plant extract is discussed on the basis of adsorption of stable complex at the mild steel surface. Theoretical fitting of different isotherms, Langmuir, Temkin, Freundlich, Frumkin, Flory-Huggins and the kinetic thermodynamic model, were tested to clarify the nature of adsorption. Polarisation curves revealed that this inhibitor act as a mixed type inhibitor and the inhibition efficiency of up to 97.51% can be obtained. The surface analysis study confirms the corrosion of mild steel and its inhibition by the inhibitor CAL.

Keywords: *Citrus aurantiifolia* (CAL), Mild steel, Adsorption isotherm.

Introduction

Mild steel (MS) has been extensively used under different conditions in chemical and allied industries in handling alkaline, acid and salt solutions. Chloride, sulphate and nitrate ions in aqueous media are particularly aggressive and accelerate corrosion. One way of protecting

MS from corrosion is to use corrosion inhibitors. The known hazardous effects of most synthetic corrosion inhibitors are the motivation for the use of some natural products. The recent trend is towards environmentally friendly inhibitors. Most of the natural products are non-toxic, biodegradable and readily available in plenty. Several investigations have been reported using such naturally occurring substances as corrosion inhibitor for several metals in different media¹⁻¹⁶. The aim of the present work is to find a naturally occurring cheap and environmentally safe substance that could be used for inhibiting the corrosion of mild steel. The use of natural product will establish, simultaneously, the economic and environmental goals.

Experimental

Sample preparation

Mild steel specimens of following compositions were used for the experiment (wt %). The composition of the sample was analyzed using ARL 3460 Metal Analyzer, Optical Emission Spectrometer. The composition of the specimen was analyzed and given in Table 1.

Table 1. Elemental analysis.

Elements	% of Chemical composition	Elements	% of Chemical composition
Carbon	0.0577	Niobium	0.0007
Manganese	0.1756	Tungsten	0.0002
Silicon	0.0722	Argon	0.0015
Phosphorus	0.0168	Lead	0.0015
Sulphur	0.0165	Boron	0.0001
Chromium	0.0096	Antimony	0.0011
Molybdenum	0.0015	Bismuth	0.0014
Nickel	0.0041	Calcium	0.0004
Vanadium	0.0004	Zinc	0.0001
Aluminium	0.0392	Cerium	0.0002
Copper	0.0061	Iron	99.5904
Titanium	0.0009		

Rectangular samples of area $5 \times 1 \text{ cm}^2$ have been cut from a large sheet of mild steel. The samples were polished, drilled a hole at one end and numbered by punching. During the study the samples were polished with 400 grade emery papers, degreased in a solution of non-toxic detergent, washed with distilled water, dried, weighed and stored in desiccators for further use.

Choice of acid medium

Acids are widely used in industry, the most important areas of application being acid pickling, industrial acid cleaning, acid descaling and oil well acidizing¹⁷. HCl is widely used to pickle iron and steel because HCl quickly removes oxide scale and iron rust and filth during acid pickling. Side effects of these processes are corrosion of the substrate metal and atmospheric pollution caused by acid vapour. Inhibitors are generally used in these processes to control the metal dissolution as well as acid consumption.

Selection of the inhibitor

Use of inhibitors is an important task in the protection of metals from corrosion. Till now the majority of metal corrosion inhibitors used is toxic for human being and environment. The choice of the present inhibitors is based on the following considerations:

- Less-expensive
- Non toxic
- Possess no threat to the environment
- Easy availability

For the present study, extract of CAL is used as corrosion inhibitor for mild steel in 1 M HCl. The leaves were collected from a farm in Duraiyur, Trichy.

Extraction of plant materials

The leaves were collected, shade dried and powdered. Plant materials are dried in shade so as to enrich the active principles in them, by reducing their moisture content. The extract was prepared by refluxing 25 g of powdered dry leaves and seeds in 500 mL of 1 M HCl for 3 h and kept overnight. Then it was filtered and the volume of the filtrate was made up to 500 mL using the same acid and this was taken as stock solution.

Corrosion Studies

Weight loss measurements

Weighed samples are immersed in 100 mL of the acid (1 M HCl) without and with different concentrations of the inhibitor for various intervals of time. They are then taken out and immersed in saturated sodium bicarbonate solution to remove residual acids and then washed thoroughly with tap water, rinsed with distilled water, dried, stored in desiccators and reweighed.

The parameters used for the present study are given below

1. Time : 1/2 h, 1 h, 3 h, 7 h, 24 h, 48 h, 168 h
2. Concentration of the inhibitor : 0.005%, 0.05%, 0.15%, 0.5%, 2.5% (v/v)
3. Temperatures : (303 K, 313 K, 323 K, 333 K, 343 K) ± 2 K

Potentiodynamic polarisation measurement

Potentiodynamic polarisation studies were carried out using Solartron 1280 B. 100 mL of 1 M HCl without and with different concentrations of the inhibitor was taken in an electrochemical cell. The polished electrode was then introduced. The electrode was placed at 0.8 mV to its open circuit potential. Thus the potential was scanned at -0.2 mV/sec towards the anodic direction in Tafel extrapolation. Applied potential vs. current was plotted and on extrapolation of linear portion to the corrosion potential gives the corrosion current. In anodic and cathodic plot, the slope of the linear portion gives Tafel constants 'b_a' and 'b_c' respectively. According to the Stern-Geary equation, the steps of the linear polarization plot are substituted to get corrosion current.

$$I_{\text{corr}} = \frac{b_a \times b_c}{2.303 (b_a + b_c)} \times \frac{1}{R_p}$$

Where, R_p is polarization resistance.

Determination of inhibition efficiency

By Tafel method

$$\text{I.E. (\%)} = \frac{I_{\text{corr}} - I_{\text{corr}}(1)}{I_{\text{corr}}} \times 100$$

where, I_{corr} is corrosion current without inhibitor

$I_{\text{corr}}(1)$ is corrosion current with inhibitor.

By LPR (Linear Polarization Resistance) method

$$\text{I.E. (\%)} = \frac{\text{Rp(inh)} - \text{Rp(blank)}}{\text{Rp(inh)}} \times 100$$

Where, Rp(inh) is the polarization resistance in the presence of inhibitor.

Rp(blank) is the polarization resistance in the absence of inhibitor.

Impedance studies

Impedance measurements were carried out at various corrosion potentials. An ac sine wave of 10 mV amplitude was applied to the electrode. The frequency which is varied from 10 KHz to 100 MHz was superimposed at the open circuit potential. The results are presented in the form of Nyquist and Bode plots. All the measurements were presented in the corrosion potential. In Impedance method, the charge transfer resistance (R_{ct}) is obtained from the plots of Z' vs. Z'' (real part Vs imaginary part; Nyquist plot). The value ($R_p + R_s$) corresponds to the point where the plot cuts Z axis to the point where the semicircle cuts the Z axis at high frequency. The difference gives the R_p values, which were substituted in the Stern-Geary equation to get I_{corr} ,

$$I_{corr} = \frac{b_a \times b_c}{2.3(b_a + b_c) R_{ct}}$$

The b_a and b_c values were experimentally obtained as mentioned in the case of linear polarization for each system.

Surface examination

The mild steel specimens were immersed in various test solutions for a period of 168 h. The specimens were taken out and dried. Optical microscope (NIKON– Model EPI-PHOT) was used for this investigation.

Results and Discussion*Weight loss data*

The inhibitor was tested for six different concentrations and their corresponding weight loss data are presented in Table 2. The addition of inhibitors increases the IE, irrespective of the time of immersion. This may be due to the adsorption of phytochemical constituents of the extracts on the metal surface. The IE is 97.51 % at a concentration of 2.5% v/v. The results concerned with the effect of period of immersion at various concentrations of the inhibitors on mild steel in 1 M HCl are also shown in Table 2. The IE increases from ½ h to 24 h period of immersion and decreases in IE from 24 h to 48 h period of immersion. The decrease in IE with time may be attributed to various factors such as an increase in the ferrous ion concentration.

Table 2. Inhibition efficiency of MS in 1 M HCl in the presence of CAL at 303 K.

S. No	Conc. % v/v	½ h	1 h	3 h	7 h	24 h	48 h	168 h
1	0.005	34.96	37.17	71.77	76.60	81.89	45.47	72.47
2	0.05	55.34	58.52	80.36	82.47	93.19	80.06	90.03
3	0.15	67.19	69.23	83.49	86.78	94.75	85.43	93.60
4	0.5	69.34	72.43	87.79	88.20	96.82	88.15	95.05
5	2.5	73.65	85.51	91.71	93.53	97.51	91.42	96.74

Effect of temperature

The effect of temperature on the inhibitory action of the inhibitor was determined by weight loss method at various concentrations at different temperatures (303, 313, 323, 333 and 343)

± 2 K for a fixed immersion time of $\frac{1}{2}$ h. The tabulated data (Table 3) reveal that, as the concentration of the inhibitor increases the corrosion rate has decreased at all temperatures. Though the C.R has increased with temperature for a given concentration of the inhibitor, there is no regular trend in the change of inhibition efficiency. This may be explained on the basis of the time lag between the process of adsorption and desorption. However, the inhibitor could be effectively used at 343 K and maximum efficiency being 86.61%.

Table 3. Protection performance of CAL on MS in 1 M HCl ($\frac{1}{2}$ h) at different temperatures.

S. No	Conc. %, v/v	303 K		313 K		323 K		333 K		343 K	
		CR, mpy	I.E, %	CR, mpy	I.E %	CR, mpy	I.E, %	CR, mpy	I.E, %	CR, mpy	I.E, %
1	Blank	607.38	-	360.82	-	530.29	-	591.78	-	3375.55	-
2	0.005	395.10	34.96	3131.11	12.75	368.06	30.59	435.65	26.38	1291.71	61.75
3	0.05	271.25	55.34	230.69	35.72	262.96	50.41	359.34	39.27	1279.93	62.10
4	0.15	199.29	67.19	198.48	44.69	219.79	58.55	290.06	50.98	780.17	76.90
5	0.5	186.21	69.34	181.41	49.45	179.67	66.11	242.03	59.10	707.34	79.05
6	2.5	160.04	73.65	139.98	60.99	138.24	73.93	174.00	70.59	452.23	86.61

Interpretation of thermodynamic data

Activation energy (E_a) and thermodynamic data, such as change in free energy (ΔG_{ads}°), enthalpy (ΔH°), and entropy (ΔS°) for mild steel in 1 M HCl in the presence and in the absence of the inhibitor was calculated and listed in Table 4. The activation energy at different concentration of the inhibitor in HCl is calculated by plotting $\log C.R$ vs. $1/T$ (Figure 1). E_a values for inhibited systems are lower than those for uninhibited system indicating that all the inhibitors exhibit high I.E at elevated temperatures. The range of E_a is 32.77-20.12 kJ/mol for CAL in 1 M HCl. The negative values of ΔG_{ads}° (9.22-27.90 kJ) suggest the strong interaction of the inhibitor molecules whereas low value of ΔG_{ads}° indicated spontaneous adsorption of inhibitors on MS surface. The negative values of ΔH° (6.65-27.59 kJ/mol) indicate that the adsorption of inhibitor molecules is an exothermic reaction. The change in entropy was found to be greater than zero (0.09-0.15). This indicates that the reaction is irreversible. It is clear that, the complete desorption of the inhibitor is not possible.

Table 4. Activation parameters for the dissolution of mild steel in the presence of CAL in 1 M HCl.

S. No	Conc. %, v/v	$-E_a$ kJ / mole	$-\Delta H^\circ$ kJ / mole	ΔS° J / mole	$-\Delta G_{ads}^\circ$ kJ				
					303 K	313 K	323 K	333 K	343 K
1	Blank	32.77	-	-	-	-	-	-	-
2	0.005	22.60	27.59	0.1565	21.88	19.32	22.79	22.92	27.90
3	0.05	29.81	6.65	0.0784	18.18	16.73	18.85	18.18	21.38
4	0.15	26.27	11.49	0.0882	16.68	14.81	16.78	16.45	20.26
5	0.5	25.80	12.94	0.0844	13.89	12.17	14.41	14.03	17.19
6	2.5	20.12	18.80	0.0927	10.37	9.22	11.09	10.98	14.13

Applicability of adsorption isotherms

The surface coverage (θ) values for different concentrations of the inhibitors in both medium have been evaluated from the weight loss data. The data were tested graphically to find a suitable adsorption isotherm. A plot of $\log (\theta / (1-\theta))$ against $\log C$ (Figure 2) shows a straight line ($R > 0.9$) indicating that adsorption follows the Langmuir adsorption isotherm. It is observed that although these plots are linear, the gradients are never unity, contrary to

what is expected for ideal Langmuir adsorption isotherm equation. Organic molecules having polar atoms or groups which are adsorbed on the metal surface may interact by mutual repulsion or attraction and this may be advocated as the reason for the departure of the slope values from unity. The number of active sites of the surface occupied by one molecule of the inhibitor is given by the value of $(1/y)$. A straight line was obtained when the surface coverage was plotted against $\log C$ for the inhibitor. This shows that the adsorption obeys a Temkin adsorption isotherm, which is graphically represented in Figure 3. The plots of $\log \theta$ vs. $\log C$ are shown in Figure 4. The linearity shows that the adsorption of the inhibitor on mild steel surface follows Freundlich isotherm. The plots of IE against $\log C$ are shown in Figure 5. The sigmoidal shape shows that the adsorption of the inhibitor on mild steel surface follows Frumkin isotherm.

Figure 1. Arrhenius plots for mild steel dissolution process in 1 M HCl.

Figure 2. Langmuir adsorption isotherm.

Figure 3. Temkin adsorption isotherm.

Figure 4. Freundlich adsorption isotherm.

Figure 5. Frumkin adsorption isotherm.

The equation of Flory Huggins Isotherm,

$$\log \theta/C = \log XK + X \log (1-\theta)$$

where, θ is the degree of coverage

X is the number of active sites occupied by one inhibitor molecule or number of water molecules replaced by one molecule of the adsorbate. The value of $X > 1$, implied that one inhibitor molecule replaces more than one water molecule. The plots of $\log (\theta/C)$ against $\log (1-\theta)$ are shown in Figure 6.

Figure 6. Flory Huggins isotherm.

Potentiodynamic polarization results

The various electrochemical parameters calculated from Tafel plot (Figure 7) are given in Table 5. The lower corrosion current density (I_{corr}) values in the presence of inhibitors without causing significant changes in corrosion potential (E_{corr}) (522.29-502.15 mV) suggests that the compound is mixed type inhibitor (*i.e.*, inhibit both anodic and cathodic reactions) and are adsorbed on the surface thereby blocking the corrosion reaction. In all concentrations b_a is greater than b_c suggesting that though the inhibition is under mixed control, the effect of the inhibitor on the anodic polarization is more pronounced than on the cathodic polarization.

Figure 7. Tafel plot.

Table 5. Electrochemical parameters for mild steel in 1 M HCl containing CAL extract.

Conc. % v/v	$-E_{\text{corr}}$ mV	I_{corr} μAcm^{-2}	b_a mV/dec	b_c mV/dec	I.E., %	R_p , Ω	I.E., %
Blank	522.29	4.521	168.96	121.54	-	5.79	-
0.005	516.52	5.555	206.21	140.51	-22.87	6.76	14.34
0.05	526.49	2.877	135.71	106.03	36.36	6.18	6.31
0.15	516.85	0.859	126.31	100.47	80.99	26.31	77.99
0.5	511.78	0.311	130.07	90.71	93.10	73.90	92.16
2.5	502.15	0.094	140.31	81.79	97.91	224.11	97.41

Electrochemical impedance spectroscopy results

Impedance diagram (Nyquist plot) obtained for mild steel in 1 M HCl in the presence of various concentrations of the inhibitor is depicted in Figure 8. They are perfect semicircles and this was attributed to charge transfer reaction. Impedance parameters derived from Nyquist plots are tabulated in Table 6. It can be seen that as the concentration of inhibitor increases, C_{dl} values decrease. Decrease in C_{dl} , which can result from an increase in thickness of electrical double layer, suggests that the inhibitor molecules function by adsorption at the metal- solution interface.

Table 6. Impedance parameters for the corrosion of mild steel in 1 M HCl containing different concentrations of CAL.

S. No	Conc, % v/v	R_{ct} , $\Omega \text{ cm}^2$	C_{dl} , μFcm^{-2}	I.E., %
1	Blank	20.42	178.66	-
2	0.005	24.29	213.51	15.93
3	0.05	27.38	206.73	34.08
4	0.15	140.88	107.68	85.50
5	0.5	270.73	84.210	92.45
6	2.5	439.09	62.310	95.34

Figure 8. Nyquist plot.

Mechanism of inhibition

Constituents present in CAL

The probable mechanism can be explained on the basis of adsorption process and the structure of the constituents present in the extract. The inhibition may be due to the adsorption of phytochemical constituents present in the extract through oxygen atoms on to the surface of the metal.

Surface analysis

The polished specimen and the test specimens which are immersed in the blank (1 M HCl) and in the inhibitor CAL for 168 h, were observed under a metallurgical microscope and photomicrographs are shown in the plate 1 and 2. Photograph 1 shows the polished mild steel surface before exposure to the corrosion solution, which is associated with polishing scratches. It is clear from the photograph 2, the surface of the mild steel was heavily corroded in 1 M HCl, whereas in the presence of inhibitor in 1 M HCl, the surface condition was comparatively better (Photographs 3 and 4) depends on the concentration of the inhibitor solution suggesting that thereby the presence of a protective adsorbed layer of the inhibitor on mild steel surface which impedes corrosion rate of metal appreciably.

Plate 2. Photomicrographs of mild steel samples in the presence of CAL.

Conclusion

- The natural extract CAL was found to be effective inhibitor in the acidic medium giving up to 97.51 % efficiency. The extracts under study resist corrosion at higher temperature in 1 M HCl, the optimum temperature being 343 K.
- Adsorption models-Langmuir, Temkin, Freundlich, Frumkin and Flory-Huggins isotherm fit well as evident from the correlation coefficient values ($R \cong 1$ in all cases). This proves the applicability of all the models to the process.
- The surface analysis study confirms the corrosion of mild steel and its inhibition by the inhibitor CAL.
- The results obtained from the polarization study revealed that the extract under study behaved as a mixed type of inhibitor.
- The inhibitor CAL can be adsorbed on the metal surface through their oxygen atom of the constituents present in the extracts.

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