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Corrosion inhibition of *Citrus aurantium* L. leaf extract in aqueous medium

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Abstract : The effect of *Citrus aurantium* leaf on the corrosion of carbon steel in neutral medium has been studied by mass loss measurements at different time. The present investigation revealed that the percentage of inhibition efficiency is increased with increase of inhibitor concentration and decreased with rise in period of contact. The corrosion products on the metal surface in the presence and absence of inhibitor is analysed by FTIR and UV studies. The observed results concluded that the CM leaf could serve as an effective inhibitor on carbon steel in neutral medium environment.

Keywords : *Citrus aurantium*, Mass loss, Carbon steel, FTIR

1. Introduction

Many pharmaceutical innovations are developed from a starting point of knowledge derived from the biological activities of natural organisms. In the case of the random screening of natural product, Aylward et al. [1] argued that the sheer scale of the resource, in the order of 10 to 100 million species, and the continuing evolution of new screens and new disease targets imply that biodiversity will never be fully explored for its pharmaceutical potential. The protection of metal against corrosion is a major industrial problem. The use of inhibitor is one of the best options of protecting metals against corrosion. Several inhibitors in use is either synthesized from cheap raw materials or chosen from compounds having hetero atoms in their aromatic or long chain carbon system. These organic compounds can adsorb on the metal surface, block the active sites and thereby reduce the corrosion rate considerably [2]. Most of the synthetic organic compound shows good anti-corrosive activity, which are highly toxic to cause severe hazards to both human beings and the environment during its applications [3]. The safety and environmental issues of corrosion inhibitors arisen in industries have always been a global concern. The recent trend is to save human being and environment by using eco-friendly inhibitors. Some investigator [4,5] studied the plant extracts and the derived organic species become more important as an environmentally benign, readily available, renewable and acceptable source for a wide range of inhibitors. Several efforts have been made using corrosion preventive practices and the use of green corrosion inhibitors [6]. The plant extract are rich sources of molecules which have appreciably high inhibition efficiency and hence termed as "Green Inhibitors" [7]. These inhibitors are biodegradable and do not contain heavy metals or other toxic compounds [8]. The successful use of naturally occurring substances to inhibit the corrosion of metals in acid and alkaline environment have been presented by some research groups running through references [9-14]. In our present study, we have chosen eco-friendly bio-inhibitor, a green approach to prevent environmental pollution by harmful organic chemicals. The influence of CA extract in aqueous medium on carbon using mass loss measurements have been studied. The characterization of alcoholic crystals of inhibitor and the corrosion product on carbon steel in the presence of inhibitor is also reported by UV and IR studies.

2. Experimental

2.1. Preparation of extract

The flowers 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 50 g of powdered dry leaves in 500 mL of ethanol for 12 h. The extract and solvent was separated using distillation process. The pure extract was made up to 100 mL and this was taken as stock solution.

2.2. Preparation of specimens

Rectangular samples of area 4x1 cm² 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.

2.3. Weight loss method

Carbon steel specimens in triplicate were immersed in 100 ml of the solutions containing various concentrations of the inhibitor for one day. The weight of the specimens before and after immersion were determined using Shimadzu balance, model AY 62. The corrosion products were cleansed with Clarke's solution [15]. The inhibition efficiency (IE) was then calculated using the equation;

$$IE = 100 [1 - (W_2/W_1)] \% \quad (1)$$

where W_1 is the corrosion rate in the absence of the inhibitor, W_2 is the corrosion rate in the presence of the inhibitor.

2.4. Potentiodynamic polarization measurement

Potentiodynamic polarisation studies were carried out using VSP primeton. 100 ml of DD water without and with 200 ppm 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 10 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.

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

Where, R_p is polarization resistance.

2.5. AC 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 plot. 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

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

The b_a and b_c values were experimentally obtained.

2.6. FTIR Spectroscopy

The FTIR spectra of pure *Citrus aurantium* and (b) thin film formed on the surface of the carbon steel immersed in DD water containing *Citrus aurantium* was recorded using FTIR.

2.7. UV-Vis spectroscopy

The UV-vis spectroscopy of Mn^{2+} , Fe^{2+} ion, Pure extract, Extract + Mn^{2+} , Extract + Fe^{2+} ion is measured.

3. Results and Discussion

3.1. Mass loss studies

The inhibitor was tested for six different concentrations and their corresponding weight loss data are presented in Table 1 (Figs. 1 and 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 79.2% at a concentration of 200 ppm. The results concerned with the effect of period of immersion at various concentrations of the inhibitors on mild steel in DD water are also shown in Table 2. The IE of the inhibitor system increases from 79.2% to 84.8% from first day to the third day and a slight decrease in IE is noticed on the fifth day. However, it does not decrease much after 5 days. This is attributed to the formation of a very strong and stable film on the surface of the metal that prevents the attack of oxygen, hydroxides, chlorides and other anions present in the solution.

Table 1. Corrosion rates of carbon steel in DD water in the presence and absence of the inhibitor system and the inhibition efficiencies obtained by the mass-loss method.

Inhibitor system: CA + Mn^{2+}

S.No	<i>Citrus aurantium</i> (ppm)	Mn^{2+} (ppm)	Corrosion Rate (mdd)	Inhibition Efficiency (%)
1	0	0	38	-
2	100	20	15.2	60
3	200	20	7.9	79.2
4	300	20	9.6	74.7
5	400	20	10.9	71.3
6	500	20	11.2	70.5
7	600	20	11.9	68.6

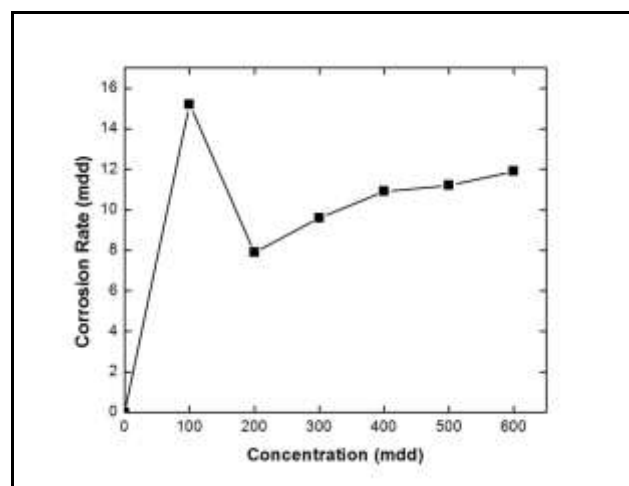


Fig. 1. Corrosion rate of carbon steel in DD water by CA + Mn^{2+} system

Table 2. Effect of duration of immersion on the IE of CA + Mn²⁺ system Corrosion rates of carbon steel in DD water in the presence and absence of the inhibitor system and the inhibition efficiencies obtained by the mass-loss method

Inhibitor System: CA + Mn²⁺

S.No	CA (ppm)	Mn ²⁺ (ppm)	Immersion period (days)	Corrosion Rate (mdd)	Inhibition Efficiency (%)
1	200	20	1	7.9	79.2
2	200	20	3	6.8	84.8
3	200	20	5	8.9	81.4
4	200	20	7	9.6	80.8
5	200	20	15	10.1	80.5
6	200	20	30	11.1	80.8

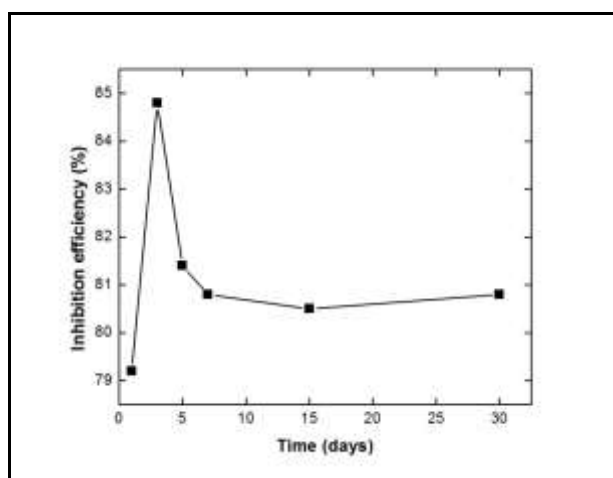


Fig. 2. Effect of duration of immersion on the CR of carbon steel CA +Mn²⁺ system

3.2. Potentiodynamic polarization results

The various electrochemical parameters calculated from Tafel plot (Fig. 3) are given in Table 3. The lower corrosion current density (I_{corr}) values in the presence of inhibitor without causing significant changes in corrosion potential (E_{corr}) (-519 to -517 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. Since 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.

1. Tafel plot for mild steel in DD water.
2. Tafel plot for mild steel in DD water with CM.

Table 3. Results of potentiodynamic polarization studies

Medium: DD water

Inhibitor system: CA (200 ppm) + Mn²⁺ (20 ppm)

S. No	Environment	E_{corr} (mV vs SCE)	b_a (mV)	b_c (mV)	R_p (Ω cm ²)	I_{corr} (A/cm ²)
1	DD water	-519	101.2	273.24	3.14×10^5	1.0218×10^{-4}
2	Inhibitor system in DD water	-517	272	124	3.68×10^4	1.1795×10^{-5}

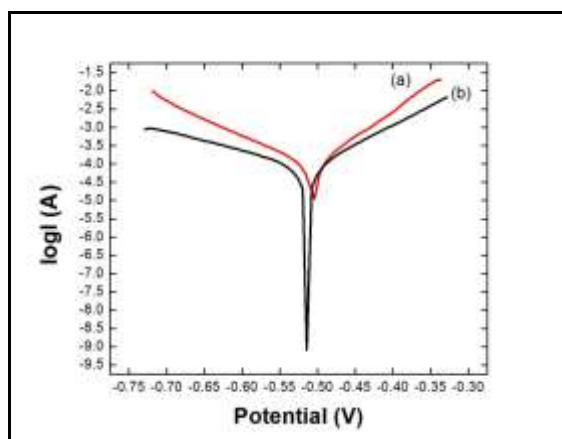


Fig. 3. Results of Potentiodynamic polarisation curves of carbon steel

Medium: DD water

Inhibitor: CA (200 ppm)

1. DD water
2. CA (200 ppm) + Mn^{2+} (20 ppm) in DD water

3.3. Electrochemical impedance spectroscopy results

Impedance diagram (Nyquist plot) obtained for mild steel DD water in the presence of various concentrations of the inhibitor is depicted in Fig. 4. They are perfect semicircles and this was attributed to charge transfer reaction. Impedance parameters derived from Nyquist plots are tabulated in Table 4. It can be seen that the resistance has increased and C_{dl} values has decreased. 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 4. Results of AC impedance studies

Medium: DD water

Inhibitor System: CA + Mn^{2+}

S.No	Environment	CA (ppm)	Mn^{2+} (ppm)	R_{ct} , ($\Omega \text{ cm}^2$)	C_{dl} (F/cm^2)
1	DD water	0	0	7.624×10^6	3.317×10^{-10}
2	Inhibitor system in DD water	200	20	1.017×10^7	1.436×10^{-10}

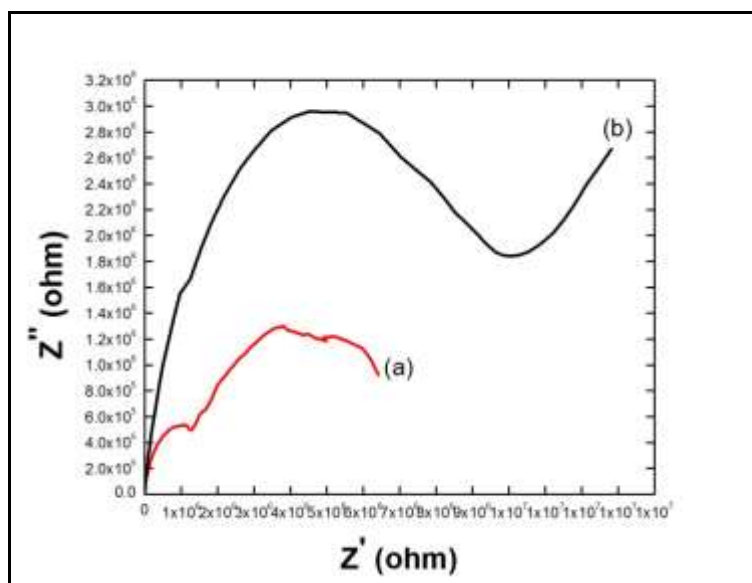


Fig. 4. AC impedance of carbon steel immersed in various environments

Medium: DD water

Inhibitor: CA (200 ppm)

1. DD water
2. CA (200 ppm) + Mn^{2+} (20 ppm) in DD water

3.4. Analysis of FTIR spectra

The FTIR spectrum of the pure extract is shown in Fig. 5a. The band at 3450 cm^{-1} is due to the presence of $-OH$. The lowering of the $-OH$ stretching frequency. The bands at 1658 cm^{-1} and 1385 cm^{-1} are due to the coupling of $-C-O$ stretching and $-C-O-H$ in-plane bending vibration. The bands at 1046 cm^{-1} and 756 cm^{-1} are due to $-C-O$ ring vibration.

Figure 5b shows the FTIR spectrum of carbon steel immersed in the presence of the extract. The $-OH$ frequency of the extract at 3450 cm^{-1} is shifted to 3459 cm^{-1} . The bands at 1658 cm^{-1} and 1385 cm^{-1} which are due to the coupling of $-C-O$ stretching and $-C-O-H$ in-plane bending of the carboxylate anion are shifted to 1660 cm^{-1} and 1392 cm^{-1} . The band at 1046 cm^{-1} (due to the ring oxygen) is shifted to 1066 cm^{-1} . The band at 756 cm^{-1} is shifted to 625 cm^{-1} . The results indicate that the carboxylate anion and the ring oxygen are responsible for the interaction between the extract and the metal surface.

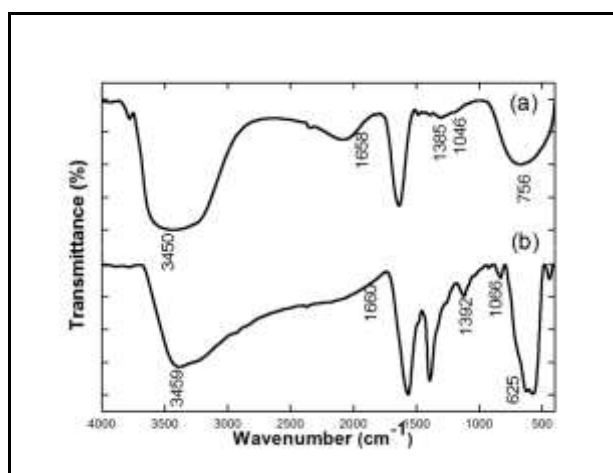


Fig. 5. FTIR Spectrum (KBr) (a) pure CA and (b) thin film formed on the surface of the carbon steel immersed in DD water containing CA

3.5. UV-visible spectral study

UV-Visible spectrum of Mn^{2+} , Fe^{2+} ion, CA, CA + Mn^{2+} , and CA + Fe^{2+} ion in DD water are given in Fig. 6a-e. The absorbance of CA at 198.88 nm is found to be 2.6027 (Fig. 6c). On increasing the λ , initially the absorbance decreases sharply, reaches a value of 0.69111 at 269.91 nm. The absorbance of Mn^{2+} ion is found to be 0.00260 at 338.11 nm and it decreases with increase in λ (Fig. 6a).

The addition of 20 ppm of Mn^{2+} to a solution containing 200 ppm of CA increases the absorbance value. The absorbance is found to be 3.3082 at 200 nm. The absorbance decreases sharply with increase in λ value and reaches 1.2554 at 271.02 nm (Fig. 6d). The value of absorbance in Mn^{2+} + CA constituent indicates the existence of strong interaction between Mn^{2+} and CA.

UV-visible spectrum of Fe^{2+} (Fig. 6b) shows that at 224 nm the solution has an absorbance of 0.12054. The absorbance decreases with increase in λ . A small peak is observed at 580 nm. When Fe^{2+} added to CA the absorbance increases tremendously to 3.5097 at 211 nm (Fig. 6e) then decreases gradually then remains constant. This implies the existence of a strong interaction between Fe^{2+} and CA.

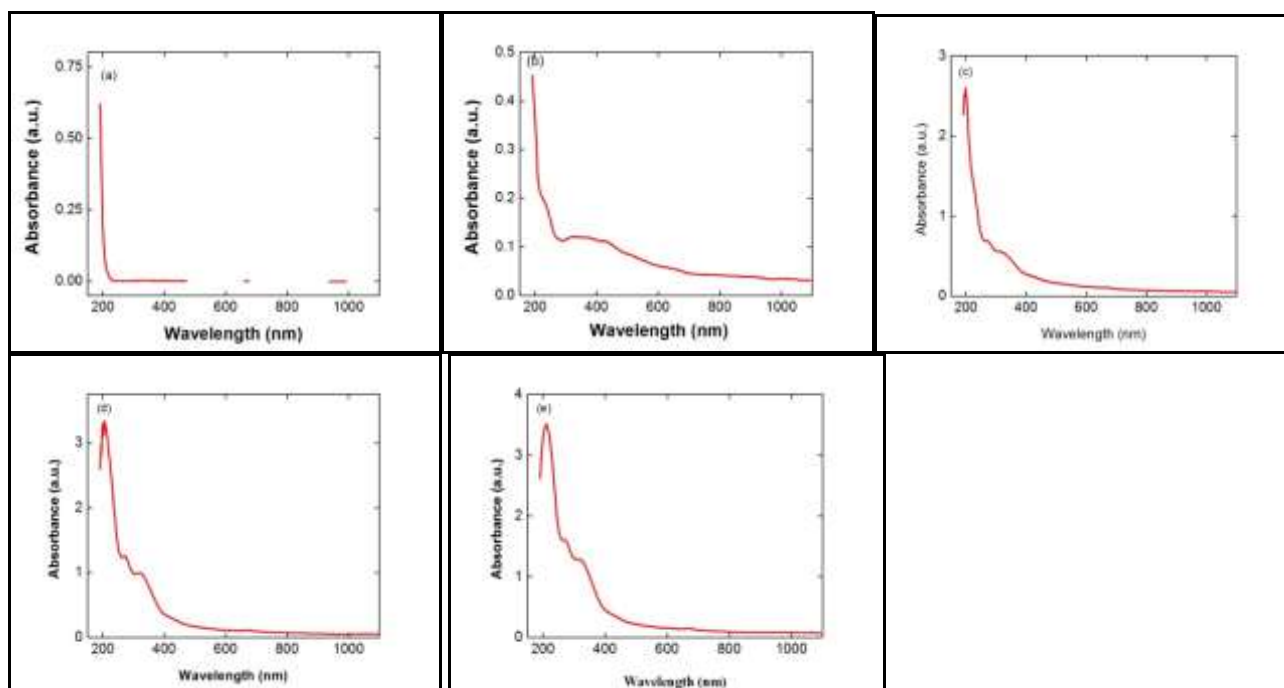


Fig. 6. UV-Visible absorption spectra of the test solutions in DD water (a) Mn^{2+} , (b) Fe^{2+} ion, (c) CA, (d) CA + Mn^{2+} , and (e) CA + Fe^{2+}

4. Conclusion

The following conclusions were made from the following studies,

1. The corrosion rate of mild steel in DD water decreases with increase in concentration of CA.
2. The maximum inhibition efficiency of CA is found to be 79.2% at 200 ppm of inhibitor from mass loss studies.
3. Electrochemical measurements revealed that incorporation of CA significantly improved the inhibition performance, and produced strong synergistic inhibition effect.
4. All EIS spectra exhibit one capacitive loop which indicates that the electrochemical reaction is controlled by charge transfer process.
5. The FTIR spectrum confirms the formation of iron-CA complex.
6. The UV-visible absorption spectra, indicates the possibility of formation of iron-CM complex and Mn^{2+} -CA complex in the presence of inhibitor formulation.

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