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Activities of Couroupita Guianensis Flower Extract on Carbon Steel in Acid by Electrochemical Studies

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ABSTRACT

Activities of alcoholic extract of *Couroupita Guianensis* flower extract on the corrosion of carbon steel in 1.0N HCl was studied by both potentiodynamic polarisation and electrochemical Impedance spectroscopy (EIS). The observed result shows that the dissolution rate of carbon steel decreased with increase of inhibitor concentration. As we expect to decrease the corrosion current (I_{corr}) from 62.14 to 12.53 $\mu\text{A}/\text{cm}^2$ with the increase of inhibitor concentration and attained the maximum of 79.83% IE by potentiodynamic polarization. Charge Transfer Resistance (R_{ct}) value increased from 11.65 to 70.73 Ωcm^2 and also decrease of Double Layer Capacitance (C_{dl}) value from 0.01772 to 0.005684553 $\mu\text{F}/\text{cm}^2$ by EIS studies. The maximum percentage of IE observed value 83.7% at 1000ppm inhibitor concentration. The inhibitor behaved as mixed-type. Surface Analysis (SEM/EDX) were also carried out to establish the corrosion-inhibitive properties of the samples.

KEYWORDS : 1N HCl, Couroupita Guianensis Flower, Carbon steel, Electrochemical studies, SEM/EDX.

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INRODUCTION

Corrosion leads to spontaneous failure in metals and its alloys. Aside specific corrosion, even general corrosion leads to the reduction in the cross section of metal structure to the point where it can no longer support applied even minimum load. Corrosion control of metal is most economical, technical and aesthetical importance. Even though, various methods available to inhibit the corrosion, the use of inhibitors is one of the most practical methods for protection against corrosion. Corrosion inhibitors retard corrosion by adsorbing onto the metal surface and blocking the Electrochemical reaction occurring at solution /metal interface due to the presence of hetero atoms in inhibitors.¹⁻⁷.

Although many synthetic compounds show good anticorrosive action, most of them are highly toxic to living things and environment. These inhibitors may cause temporary or permanent damage to organs such as kidneys or liver, or to disturb a biochemical process or enzyme system at some sites in the body⁸. The toxicity may encounter either during the synthesis of the compound or during its applications. So in recent years, the prime investigations on anticorrosion inhibitors are to focus on the use of naturally occurring substances as a non-hazardous replacement for synthetic counterpart. Thus plant extracts have become an environmentally acceptable, readily available and easily extractable materials for wide range of corrosion prevention^{9,10,11,12,13,14}. Although lot of research progressing in plant inhibitors, there are N number of plant species still available in the nature earth for inhibition analysis. The research dimension may be in search of new plants for its photochemical compounds, efficiency, availability, adsorption quality etc.

In the present work, inhibitive action of CG flower extract as a cheap, eco-friendly, naturally occurring substance on corrosion behaviour of Carbon steel in 1.0N HCl has been investigated. through weight loss, potentiodynamic polarization and Impedance measurements. Inhibited metallic surfaces are examined by Scanning Electron Microscope (SEM) and corrosion product analysed by EDX.

MATERIALS AND METHODS

Electrochemical measurements

Electrochemical measurements were conducted by conventional three –electrode system including of carbon steel as working electrode with an exposed area 1cm^2 , a platinum electrode as counter electrode and saturated calomel electrode (SCE) as reference electrode. Before testing, the working electrode was immersed in test solution at Open Circuit Potential for 30 min to attain a steady state potential and the potential sweep rate for potentiodynamic polarisation (Tafel) curves was 10mVs^{-1} . Corrosion current density (I_{corr}) was determined from the intercept of extrapolation of

anodic and cathodic Tafel slopes at the corrosion potential (E_{Corr}). The inhibition efficiency (%) was calculated using I_{corr} values both in the presence and absence of inhibitor.

$$IE(\%) = \frac{I_{\text{corr}}(\text{blank}) - I_{\text{corr}}(\text{inh})}{I_{\text{corr}}(\text{blank})} \quad (1)$$

Where $I_{\text{corr}}(\text{blank})$ and $I_{\text{corr}}(\text{inh})$ are the corrosion current density values of carbon steel in the absence and presence of inhibitors.

Electrochemical impedance spectroscopy was performed in range of frequency 1Hz to 100KHz with the AC signal of amplitude 5 mV using CH 660E electrochemical analyser. The charge transfer resistance obtained from the diameter of the semicircle of the Nyquist plot. The inhibition efficiency (IE%) derived from EIS as calculated using the following equation

$$IE(\%) = \frac{R_{\text{ct}}(\text{inh}) - R_{\text{ct}}(\text{blank})}{R_{\text{ct}}(\text{inh})} \quad (2)$$

where, $R_{\text{ct}}(\text{Inh})$ = charge transfer resistance with inhibitor

$R_{\text{ct}}(\text{blank})$ = charge transfer resistance without inhibitor

EDX Analysis

By compositions of all elements present on the surface of the specimen, before and after immersion were identified by Energy Dispersive X-ray spectroscopy (EDX) using the Oxford Instrument Model - Jasco V670. The energy of an acceleration beam employed was 20 kV.

Scanning Electron Microscope (SEM)

Model: Jasco/Japan, Scanning Electron Microscope was used to study the nature of the corroded surface. The dissolution of metal and the protective film formed by the inhibitor on the metal surface was also studied.

RESULT AND DISCUSSION:

Electrochemical Studies

Polarisation Studies

Tafel slope of Potentiodynamic polarisation curve of carbon steel in 1.0N HCl in the presence and absence of various concentrations are shown in Fig (1). And the observed electrochemical corrosion parameters viz; corrosion potential (E_{corr} mV), anodic and cathodic Tafel slopes (b_a and b_c mVdec⁻¹), the corrosion current density (I_{corr} μAcm^{-2}) and the percentage of inhibition efficiency are given in Table-1.

Both anodic dissolution of iron and cathodic evolution hydrogen reaction were inhibited after the addition of CG extract to 1.0N HCl solution. The inhibition of these reactions was more

pronounced on increasing CG concentration, resulting that the adsorption of inhibitor on the carbon steel surface.

Table No.1: “ Electrochemical parameters of carbon steel in 1.0N HCl solution of various concentration of Couroupita Guianensis”.

Concentration (ppm)	-E _{corr} (mV)	b _a (mV dec-1)	b _c (mV dec-1)	I _{corr} (μA cm ⁻²)	IE (%)
0	484.7	96.11	104.74	62.14	-
10	489.6	86.40	95.05	29.50	52
50	488.6	96.52	110.41	20.94	66.30
100	482.7	98.02	118.48	16.01	74.23
500	492.5	84.44	92.50	14.63	76.45
1000	497.1	88.28	96.76	12.53	80

A possible of mechanism may be the adsorption of inhibitor on the specimen surface through the electron pair of heteroatom's, and the π electron in the molecular structure of inhibitor, which may blocks the carbon steel surface and reduce the corrosive attraction of carbon steel in HCl media.

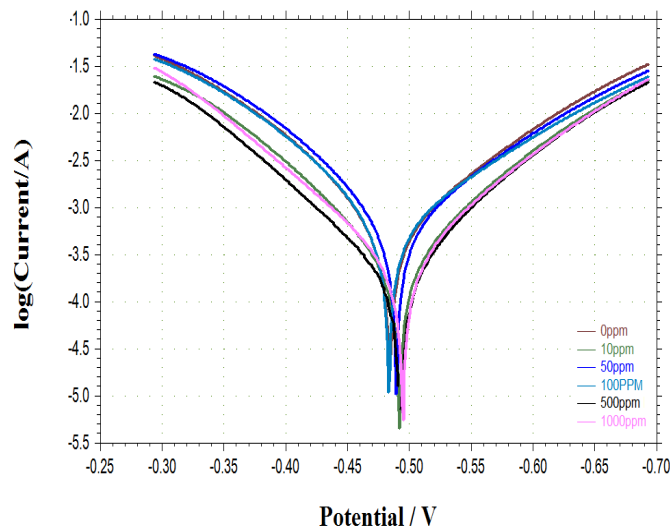


Fig.1: Polarization curves for carbon steel in 1.0N HCl in the presence and absence of different concentration of CG.

Values of corrosion current density (I_{corr}) decreased from 62.14 μA to 12.53 μA cm⁻² and the corrosion potential (E_{corr}) shifted to negative direction (-484.7 to -497.1 mV/SCE), when compared to the blank. Generally, utilizing the inhibitor can be relegated as cathodic or anodic type if the displacement in corrosion potential is more than 85mV/SCE, with respect to corrosion potential of the blank. This may confirms that the CG extract acts as mixed-type inhibitor. The decrementation of the current densities (I_{corr}) with the incrementation of CG extracts concentration, denotes that the incremented of inhibition efficiency to 79.83%

Electrochemical Impedance studies(EIS):

Figure:2,3a,3b represent the Nyquist, Bode plots and phase angle with different concentration CG extract on carbon steel specimens in 1.0N HCl. The, Charge Transfer Resistance (R_{ct}), Double Layer Capacitance (C_{dl}) and corresponding inhibition efficiency obtained from electrochemical impedance spectroscopy is represented in Table -2. It is evident from the Nyquist plots response of metal specimens showed a marked difference in the presence and absence of the inhibitor CG extract. It can found out that all the Nyquist plot shows a single capacitive loop. The capacitance loop intersects the real axis at higher and lower frequencies. A perfect semi-circle clearly indicates that the charge transfer process may control the dissolution of the specimen. The value of R_{ct} is a measure of electron transfer across the exposed area of the metal surface and it is inversely proportional to rate of corrosion.

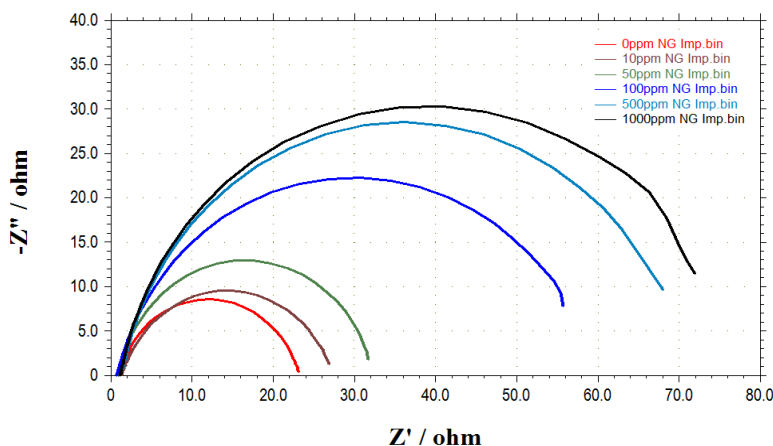


Fig.2 : Electrochemical impedance Nyquist plots for carbon steel in 1N HCl containing concentration of CG inhibitor.

Various parameters derived from these investigations are mentioned in Table- 2. It is evident from the data shown that the values of Charge Transfer Resistance (R_{ct}) were increased from 11.65 to 55.02 $\Omega \text{ cm}^2$ in the presence of alcoholic extracts of all plants when compared with those in acid solution. The double layer capacitance (C_{dl}) was computed using the Eq. (3):

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (3)$$

Where f_{max} is the frequency at which the imaginary component of the impedance is maximal. The decrease in the C_{dl} values in the presence of plant extracts could be attributed to the adsorption of the phytochemicals present in plant extracts over the carbon steel surface as organic compounds adsorption process on the metal surface is characterized by a decrease in C_{dl} value. The values of inhibition efficiency (IE %) were calculated by using the Eq. (2):

Table:2 EIS Parameters for the corrosion of carbon steel in 1.0N HCl containing CG

Concentration (ppm)	R _{ct} (Ω cm ⁻²)	f _{max} × 10 ⁻¹ (Hz)	C _{dl} (μF cm ⁻²)	IE (%)
0	11.65	1.161	0.011772	—
10	25.69	1.398	0.0024344	54.64
50	30.88	1.602	0.0032188	62.27
100	54.90	2.904	0.059865	78.78
500	55.02	1.201	0.0074098	78.82
1000	70.73	3.960	0.0096845	83.53

This data was also fitted with the values obtained from the potentiodynamic polarisation data as described earlier. Maximum inhibition efficiency was observed for alcoholic extract of CG is 83.5%.

Bode plot showed that the pitting resistance of the Carbon steel was generally increased by increasing the CG concentration which was confirmed by the relaxation of the impedance spectra (Fig.3.a).

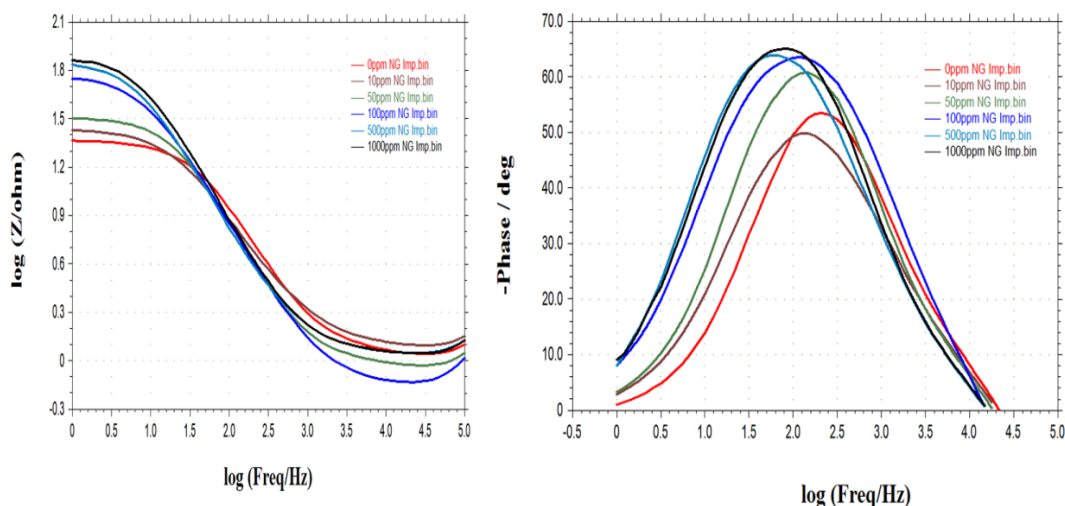


Fig:3(a-b). Electrochemical impedance plots (a) Bode plot, (b) phase angle plot for carbon steel in 1N HCl containing concentration of CG inhibitor.

In phase plots (Fig.3.b) the phase angle at higher frequencies attributed to anticorrosion performance. The depression of phase angle at relaxation frequency with the decrease in the inhibitor concentration indicates that the decrease of capacitive response with the decrease of inhibitor concentration. Such phenomenon reflected that the higher corrosion activity at low concentration of the inhibitor

Spectral Studies -EDX spectrum:

EDX spectroscopy was used to determine the elements present on the Carbon Steel surface in the presence and absence of inhibitor. Figs: 4 and 5 represents that the EDX spectra of the corrosion products on metal surface in the presence and absence of optimum concentrations of CG extract in

1.0N Hydrochloric acid. In the absence of inhibitor molecules, the spectrum may concluded that the existence of elements present in the metal and environments. However, in the presence of the concentrations of the inhibitor, the presence of hetero atoms like Oxygen and micro alloying elements is found to be present in the corrosion product on the metal surface. It clearly indicates that this micro alloying elements and oxygen present in the inhibitor molecules may involve the film formation with the metal ion during the adsorption process and prevent the further dissolution of metal against corrosion.

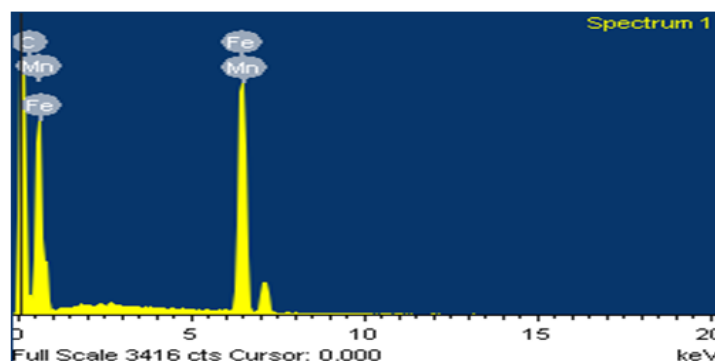


Fig: 4. EDX spectrum of the corrosion product on carbon steel surface in 1.0N HCl

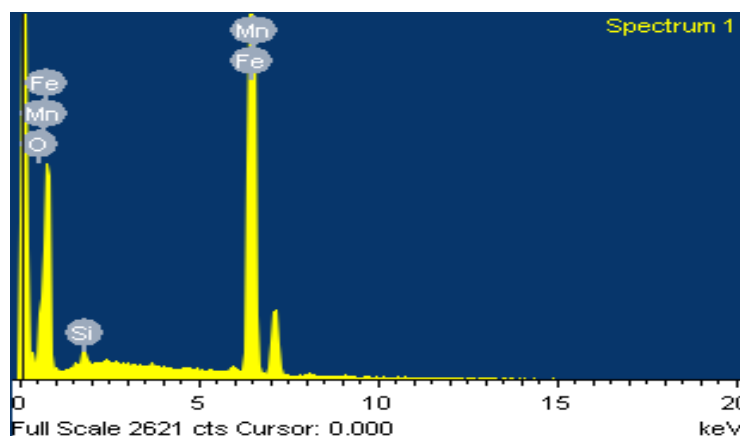


Fig :5 . EDX spectrum of the corrosion product on Carbon steel in the presence of CG extract in 1.0N HCl

SEM Analysis

Image of Surface morphology of the carbon steel was recorded by Scanning Electron Microscopy (SEM). Fig 6 (a-c) shows that the SEM micrographs of carbon steel surface before and after immersion in 1.0N Hydrochloric acid respectively. SEM photographs (fig-6b) showed that the surface of metal has number of clear pits and cracks with severe damage visible in the surface may be belong to the plug type of corrosion. But in presence of inhibitor (Fig 6-c) the dissolution process significantly reduced (i.e pits and cracks were not seen on the surface) by the formation of thin film like spongy mass covered on the entire surface of the metal completely.

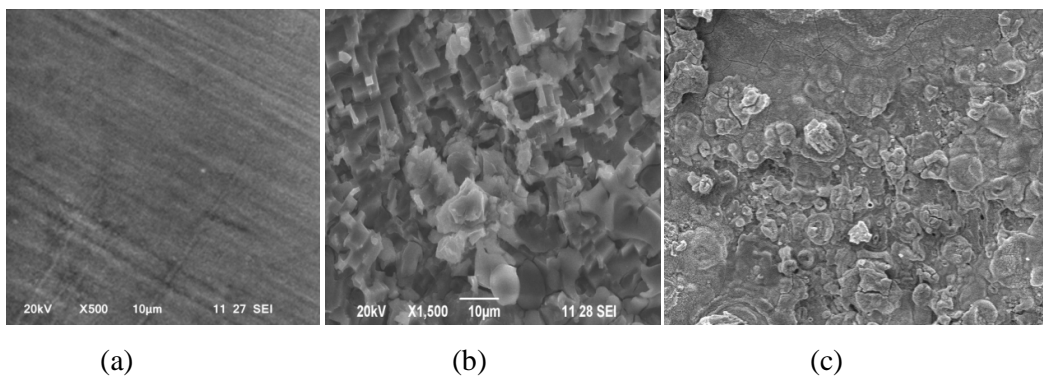


Fig: 6 (a -c) SEM image of the Polished Carbon Steel surface, Before and After immersed in 1.0N Hydrochloric acid with CG extract respectively.

CONCLUSION

Alcoholic extract of *Courouptia Guianensis* (CG) flowers may act as a good Anti- corrosion material for the Carbon steel in 1.0N HCl acid environment. The obtained results from the polarization measurements revealed that the CG extract behaves as a mixed type of inhibitor and attained maximum of 79.83% IE. In Impedance studies, the Charge Transfer Resistance (R_{ct}) increased with increases of inhibitor concentration and achieved maximum of 83.5% IE. Double Layer Capacitance (C_{dl}) also decreased with increase of extract concentration, since current resistance decreases.

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