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Der Chemica Sinica, 2012, 3(3):582-588

Pelagia Research Library
ISSN: 0976-8505
CODEN (USA) CSHIA5

A study on the phytochemical analysis and corrosion inhibition on mild steel by Annona Muricata .L leaves extract in 1 N hydrochloric acid

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ABSTRACT

Extract of Annona muricata L. leaves was investigated as a corrosion inhibitor of mild steel in 1 N HCl using conventional weight loss, electrochemical polarization, electrochemical impedance spectroscopy, and scanning electron microscopic studies. The weight loss results showed that the extract of Annona muricata L leaves is an excellent corrosion inhibitor, electrochemical polarization data revealed the mixed mode of inhibition, and the results of electrochemical impedance spectroscopy have shown 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 microscope studies provided the confirmatory evidence of an improved surface condition, due to the adsorption, for the corrosion protection.

Key words: Annona muricata L, acid corrosion inhibitor, electrochemical polarization, electrochemical impedance spectroscopy, scanning electron microscopy, mild steel.

INTRODUCTION

A huge amount of HCl is used in the chemical industry for removal of undesired scales and rust. The addition of corrosion inhibitors effectively secures the metal against an 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 hetero-atoms having higher electron density, making them the reaction centers. These compounds are adsorbed on the metallic surface and block the active corrosion sites, and most of them are highly toxic to both human beings and the environment. Hence, use of natural products as eco-friendly and harmless corrosion inhibitors has become popular [6–15]. Comparisons have been made over the years between the toxic inhibitors, like chromates and other organic inhibitors, and the natural inhibitors and it has been observed that the natural inhibitors could serve as an effective substitute for the currently preferred organic inhibitors; sometimes they show significantly better inhibitive properties than the currently employed organic corrosion inhibitors [16-19].

Annona muricata L, a anonaceae family plant, is found throughout Asia and in India. The leaves of Annona muricata L are smooth , alternate and the blades leathery and oblonglanceolate[20]. The phytochemical screening of Annona muricata L leaves demonstrated the presence of flavonoids, saponins, terpenes, and alkaloids, tannins. However, the leaves have never been exploited as a corrosion inhibitor in an acid medium. The aim of this work was to investigate

the potential of the leaves of Annona muricata L extract to act as an inhibitor of mild steel corrosion in hydrochloric acid.

MATERIALS AND METHODS

2.1. Inhibitor Preparation

About 10 grams of the dried powder of leaves of Annona muricata .L are taken in the round bottom flask and continuously flushed with an extraction agent, ethanol. After maceration, the suspension is centrifuged and the extract is collected. It is successively extracted with 6ooml of ethanol for 48hrs. The extract was filtered using whatmann No.1 filter paper. The liquid extract is concentrated by distilling off the solvent and then evaporating the solvent to dryness on a water bath to remove all the alcohol from the extract and weight of the extract is taken and kept at 4°C use. This aqueous plant extract solution is used for analyzing the phytoconstituents and also from the crude extract various inhibitor concentration ranging from 65ppm to 95ppm is prepared to evaluate the corrosion inhibition efficiency.

2.3 Phytochemical screening

Phytochemical screening were perfomed using standard procedure[21-22].

2.31 Test for reducing sugars (Fehling's test)

The aqueous ethanol extract (0.5 g in 5 ml of water) was added to boiling Fehling's solution (A and B) in a test tube. The solution was observed for a colour reaction.

2.32 Test for anthraquinones

0.5 g of the extract was boiled with 10 ml of sulphuric acid (H_2SO_4) and filtered while hot. The filtrate was shaken with 5 ml of chloroform. The chloroform layer was pipetted into another test tube and 1 ml of dilute ammonia was added. The resulting solution was observed for colour changes.

2.33 Test for terpenoids (Salkowski test)

To 0.5 g of the extract was added 2 ml of chloroform. Concentrated H_2S0_4 (3 ml) was carefully added to form a layer. A reddish brown colouration of the interface indicates the presence of terpenoids.

2.34 Test for flavonoids

Three methods were used to test for flavonoids. First, dilute ammonia (5 ml) was added to a portion of an aqueous filtrate of the extract. Concentrated sulphuric acid (1 ml) was added. A yellow colouration that disappear on standing indicates the presence of flavonoids. Second, a few drops of 1% aluminium solution were added to a portion of the filtrate. A yellow colouration indicates the presence of flavonoids. Third, a portion of the extract was heated with 10 ml of ethyl acetate over a steam bath for 3 min. The mixture was filtered and 4 ml of the filtrate was shaken with 1 ml of dilute ammonia solution. A yellow colouration indicates the presence of flavonoids.

2.35 Test for saponins

To 0.5 g of extract was added 5 ml of distilled water in a test tube. The solution was shaken vigourously.and observed for a stable persistent froth. The frothing was mixed with 3 drops of olive oil and shaken vigourously after which it was observed for the formation of an emulsion.

2.36 Test for tannins

About 0.5 g of the extract was boiled 10 ml of water in a test tube and then filtered. A few drops of 0.1% ferric chloride was added and observed for brownish green or a blue-black colouration.

2.37 Test for alkaloids

0.5 g of extract was diluted to 10 ml with acid alcohol, boiled and filtered. To 5 ml of the filtrate was added 2 ml of dilute ammonia, 5ml of chloroform was added and shaken gently to extract the alkaloidal base. The chloroform layer was extracted with 10 ml of acetic acid. This was divided into two portions. Mayer's reagent was added to one portion and Draggendorff's reagent to the other. The formation of a cream (with Mayer's reagent) or reddish brown precipitate (with Draggendorff's reagent) was regarded as positive for the presence of alkaloids.

2.38 Test for cardiac glycosides (Keller-Killiani test)
To 0.5 g of extract diluted to 5 ml in water was added 2 ml of glacial acetic acid containing one drop of ferric chloride solution. This was underlayed with 1 ml of concentrated sulphuric acid. A brown ring at the interface indicated the presence of a deoxysugar characteristic of cardenolides. A violet ring may appear below the brown ring, while in the acetic acid layer a greenish ring may form just above the brown ring and gradually spread throughout this layer.

2.4 Gas Chromatography-mass spectrometry analysis
The Gas chromatography-Mass spectrometry(GC-MS) analysis of the extract was performed using a GC-MS Model;QP 2010 series, equipped with a VF-5ms fused silica capillary column of 80m length, 0.25mm diameter and 0.25μm film thickness. For GC-MS detection , an electron ionization system, ionization energy of 70ev was used. Helium gas (99.99%) was used as a carrier gas at a constant flow rate of 1.51ml/min. injector and mass transfer line temperature were set at 200 and 240□C respectively. The oven temperature was programmed from 70 to 220□C at 10□C/min, held isothermal for 1min and finally raised to 300□c at 10□C/min. 2μl of repective dilute sample was manually injected in the split less mode, with split ratio of 1:40 and with the mass scan of 50 – 600 amu. Total running time of GC-MS is 35 min. The relative percentage of the extract constituents was expressed as percentage with peak area normalization.

2.41 Identification of the components
The identity of the components in the extract was assigned by their comparison of their retention indices and mass spectra fragmentation patterns with those store on the computer library and also with the published literature. NISTO8S. LIB(23) WILEY8 , literatures sources were used for matching the identified components from the plant material.

2.5 Preparation of Specimens
Cylindrical working electrodes of mild steel (MS) containing the weight percentage composition was found to be carbon = 0.13%, silicon=0.03% manganese=0.65%, Sulphur=0.26%, phosphorus=0.15%, copper=0.016%, nickel=0.018%, Chromium=0.029% and the remainder Fe, were used for the electrochemical polarization and impedance measurements The sheets were mechanically pressed and cut into samples of size 1x 5x 0.2cm^3 , with tiny holes on their upper parts. For 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 papers, repeatedly rinsed with warm distilled water, degreased with acetone, dried at room temperature, and then stored in a desiccator before use [10].

2.6 Weight loss method
Pre-weighed mild steel specimens (in triplicate) were suspended for 1 hour in 1N HCl with and without the inhibitor in different concentrations ranging from 65ppm to 95ppm. After the specified time the coupons were removed from test solution, thoroughly washed with $NaHCO_3$ solution and de-ionised water, dried well and then weighed. The percentage of inhibitor efficiency (IE %) for various concentrations of the inhibitor were calculated as

$$\text{I.E.\%} = \frac{W_0 - W \quad X \quad 100}{W_0}$$

2.7 Polarisation and impedance studies
Potentiodymamic anodic and cathodic polarization curves were obtained with a scan rate of 2 mv/s in the potential range from -0.2 mv to -0.8 mv relative to the corrosion potential (Ecorr). Values of the corrosion current density (Icorr) were obtained by extrapolation of the cathodic branch of the polarization curve back to Ecorr. Measurements of Rp in the vicinity of Ecorr were also carried out. Impedance spectra were recorded at Ecorr in the frequency range 0 to 10000 Hz. The values were computed using Solatron 1280B.

2.8 SEM observation:
The texture and pore structure were observed under a F E I Quanta FEG 200 – High Resolution Scanning Electron Microscope.

RESULTS AND DISCUSSION

3.1 Phytochemical screening of plant material and GC-MS study:

The phytochemical screening of the plant studied showed the presence of flavonoids, terpenoids, reducing sugar, anthraquinone ,tannins and cardiac glycosides(Table 1),and their corresponding phytocomponents list is shown in table 2 and mass spectra in fig 1.

3.2 Analysis Of The Mass Loss Data:

Table 3. Shows the percentage of inhibition efficiency obtained with different concentrations of the plant extract in HCL medium by weight loss method. The IE was found to increase with increase in the concentration of the extract with maximum IE of 80.61% at 95ppm concentration. There is a gradual increase in inhibition efficiency from 65ppm to 95ppm of the inhibitor concentration. From the values of IE % it is evident that the corrosion inhibition may be due to adsorption of the plant constituents on the metal surface. The adsorption of the phytoconstituents on the metal surface makes a barrier for mass and charge transfers thus protecting the metal surface from corrosion. The degree of protection increases with the increasing surface fraction occupied by the adsorbed molecules.

3.3 Potentiondynamic polarization and impedance spectroscopy results:

Polarisation and impedance behaviour of mild steel in 1N HCL in the presence and absence of the plant extract is shown in the Figures 2 & 3respectively. The polarization and impedance parameters are presented in the Tables 4 & 5 respectively. From the shape of the polarization curves it is seen that both the anodic as well as cathodic reactions are inhibited. The Tafel regions of the plot further indicate that the electrode reactions are kinetically controlled. The values given in the Table 4 show that corrosion current (Icorr)decreases markedly in the presence of extract and the magnitude of change increases with increasing extract concentration This confirms the inhibitive action of the extract in HCL medium. With increase in plant extract concentration, the corrosion potential (Ecorr) is not varying much. The values of both anodic and cathodic Tafel constants ba and bc respectively are markedly changed in the presence of the extract. This confirms the mixed mode of inhibition of the extract. The increasing linear polarization (Rp) values also confirm the corrosion inhibitive nature of the plant extract. The calculated values of inhibition efficiency indicate that IE % increases with increasing extract concentration.

The Nyquist plot (Figure 3) shows semicircles with single capacitive loop and increasing diameter as the concentration of the plant extract increases. The C_{dl} values shown in the Table 5 are found to decrease with increase in the inhibitor concentration. This shows that the plant constituents are adsorbed on the metal surface resulting in a decrease in double layer capacitance. The increasing charge transfer resistance Rct values imply reduced corrosion rate in the presence of the plant extract. Thus it is confirmed that the plant extract MAL shows good corrosion inhibition efficiency. The results of weight loss, polarization and impedance studies are in good agreement .

3.4 Sem Observation:

The SEM photograph in Figure 4a shows that the surface of MS was extremely damaged in the absence of the extract, while Figure 4b clearly shows the formation of a film by the active Annona muricata leaves constituents on the MS surface which was responsible for the corrosion inhibition

Table 1: Qualitative analysis of phyto chemical compounds of *Annona muricata L*

S.No.	Phytochemical components	Ethanol extract
1	Reducing sugar	+
2	Anthraquinone	+
3	Flavonoids	+
4	Terpenoids	+
5	Saponins	-
6	Tannins	+
7	alkaloids	+++
8	Cardiac glycosides	+

3.5 Mechanism of adsorption:

Phytoconstituents in the leaves of *Annona muricata L* contain an alkaloidal principle named 6-Hydroxyundulatine and other alkaloids. Due to the presence of these heterocyclic compounds ,adsorption of the plant constituents on the metal surface is facilitated. Inhibition efficiency of ***Annona muricata L*** extract may be explained as due to the

adsorption of these compounds on the metal surface thereby blocking the surface and protecting the metal from the aggressive atmosphere.

Table 2: List of phytocomponents in the leaf extract of *Annona muricata. L*

S.No.	RT	Name of the compound	Molecular formula	Molecular weight	Peak area %	Nature of the compound
1	151	13 – α Benzoyloxylupanine	$C_{22}H_{28}N_2O_3$	368.47	2.3 2	Alkaloid
2	205	Unknown	-	-	6.8	-
3	230	3-Isobutyryloxy-6-hydroxytropane	$C_{12}H_{21}NO$	227	5.7	Alkaloid
4	235	6-Hydroxyundulatine	C18H21NO6	347.362	22.8	Alkaloid
5	248	Unknown	-	-	36	-
6	361	Stylopine	$C_{19}H_{17}NO_4$	323.3	20	Alkaloid

Table 3. Effect of *Annona muricata L* on corrosion of mild steel in HCL (Weight lossmethod).

S.No.	Inhibitor Concentration(ppm)	Weight loss in (g)	Percentage Inhibition Efficiency
1	Blank	0.1186	-
2	65	0.0738	37.33
3	75	0.0509	57.08
4	80	0.0277	76.64
5	85	0.0251	78.84
6	90	0.0244	79.40
7	95	0.0230	80.61

Table 4. Potentiodynamic polarization parameters for mild steel in 1N HCL in the presence of *Annona muricata L* extract

S.No.	Environment	E_{corr} (mv)	b_c (mv/dec)	b_a (mv/dec)	I_{corr} (A/cm^2)	LPR (Ohm/ cm^2)	%IE
1	Blank	-566	0.1838	0.1344	$1.253x10^{-5}$	2694.2	
2	inhibitor	-509	0.1281	0.1352	9.860×10^{-6}	2900.7	21.31

Table 5. Impedance parameters for mild steel in 1N HCL in the presence of *Annona muricata L.*

S.No.	Environment	R_t(ohm)	$C_{dl}(F/cm^2)$
1	Blank	32.34	1.5770×10^{-7}
2	inhibitor	43.33	1.179×10^{-7}

Fig 1. GC-MS spectra of leaf extract of *Annona muricata L*

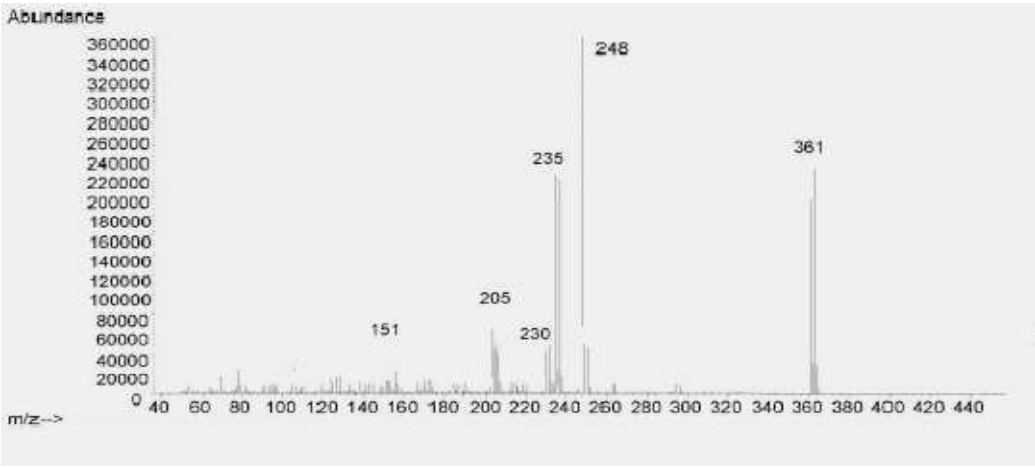
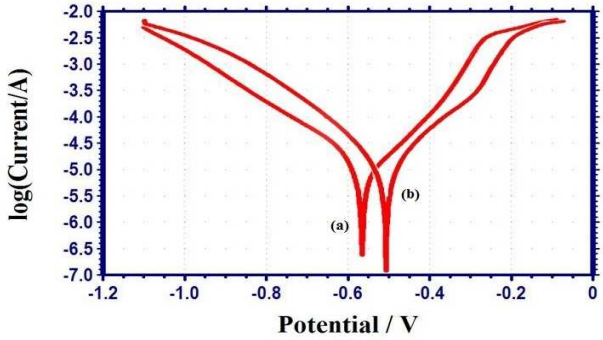
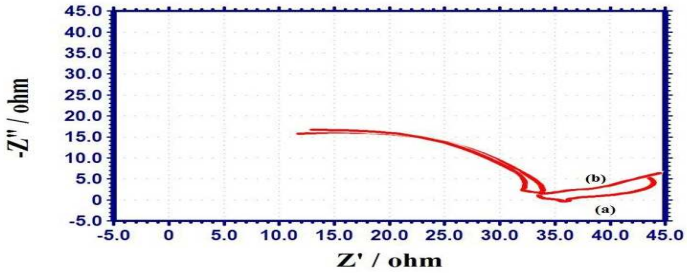


Figure 2. Potentiodynamic polarisation of mild steel in 1N HCL with and without *Annona muricata .L* extract



(a) Potentiodynamic polarisation of corrosion of Mild Steel in1M HCl
(b) Potentiodynamic polarisation of corrosion of Mild Steel in the presence of Annona muricata L

Figure 3. Nyquist plot of mild steel immersed in 1N HCL with and without plant extract



a. Niquist plot for 1MHCL
b. Niquist plot for Annona muricata L extract.

Fig 4a **Fig 4b**

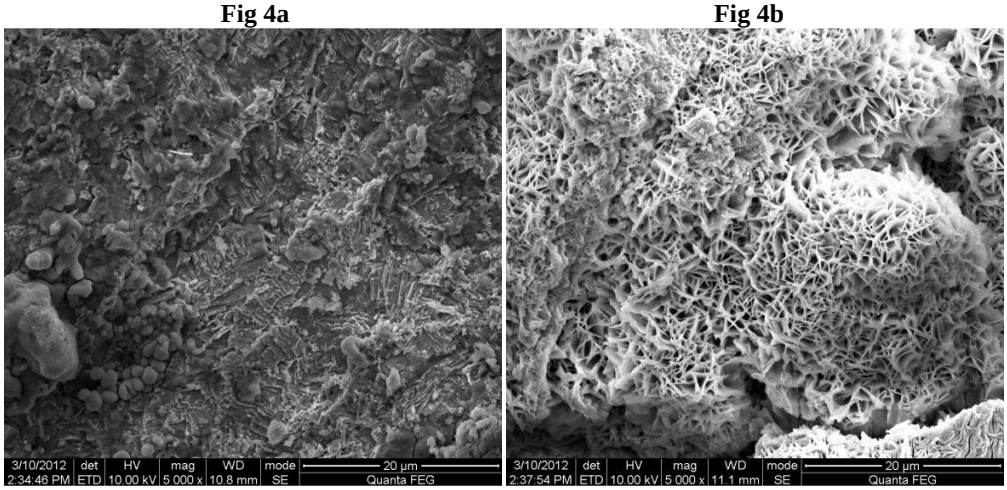


Figure 4. SEM images of MS a) in 1 N HClmedia and b) with Annona muricata leaves extract (95 ppm)

CONCLUSION

Acid extract of *Annona muricata L* leaves acts as good corrosion inhibitor for mild steel in 1N HCL medium. Inhibition efficiency increases with inhibitor concentration and maximum inhibition efficiency was 80.61% at the inhibitor concentration 95ppm. Corrosion inhibition may be due to the adsorption of the plant constituents on the mild steel surface. Polarisation studies indicate the inhibitor to be of a mixed type inhibiting both cathodic as well as anodic reactions.

Acknowledgement
We express our sincere thanks to the Head, Department of Chemistry,the Principal and the management (teaching and non-teaching) staff for successful completion of this research work.

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