

Tetrameles Nudiflora Leaves Extract as Green Corrosion Inhibitor for Mild Steel in Hydrochloric Acid Solution

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Abstract: The efficiency of alcoholic extract of *Tetrameles Nudiflora* (TN) leaves as an environmentally friendly inhibitor for mild steel in 1N HCl solution has been investigated by weight loss method, potentiodynamic polarization measurements and electrochemical impedance spectroscopy techniques. Inhibition efficiency was found to be about 84.26 % at 15 v/v. Polarization curves revealed that TN leaves extract act as mixed type of inhibitor. Organic moieties present in the extract are found responsible for effective performance of the inhibitor which was well supported by FTIR studies. Corrosion current increases and inhibition efficiency decreases with temperature increasing in HCl solutions with and without *Tetrameles Nudiflora* leaves extract. The surface morphology analysis was confirmed by Scanning Electron Microscopy (SEM). Inhibition efficiencies obtained from electrochemical techniques and weight loss method are in good agreement.

Keywords: Corrosion inhibition, Polarization techniques, Scanning Electron Microscope, Weight loss method.

I. Introduction

The study of mild steel corrosion is theoretical and practical importance [1]. Acid solutions are widely used for the removal of rust and scale in several industrial processes such as pickling, chemical and electrochemical etching, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling, resulting in huge economic losses and many potential safety questions due to metallic corrosion [2-11]. Corrosion inhibitor of organic matter is preferred because it has relatively high affinity to the metal, its value of high efficiency, and also eco-friendly. The effectiveness of organic compounds as inhibitor has been greatly influenced by the presence of hetero atoms (O, N, P and S), polar groups, pi-bond, and the lone pair as it becomes a mean for inhibitors to do coordinated chemisorption/binding to the metal [12-17]. There has been extensive research done to develop inhibitors that are cost effective and environmentally friendly. Most of the inhibitors developed from natural sources such as plants are found to have the presence of heterocyclic compounds, nitrogen, Sulfur and oxygen atoms and these contribute greatly to inhibit ion of corrosion via various mechanisms [18-19]. Thus natural products (derived from plant materials) are being studied for their corrosion inhibition potential as they are showing good corrosion protection and are more environment friendly [20-21]. The goal of the present paper is to test the extract of *Tetrameles Nudiflora* leaves as an environmentally friendly inhibitor for the acid corrosion of mild steel, by various techniques such as weight loss method, polarization techniques and phytochemical studies.

II. Materials and Methods

2.1 Preparation of mild steel specimen

Mild steel strips were mechanically cut into strips of size 4 cm x 2 cm x 0.1cm containing the composition of (C- 0.030 %, Mn- 0.169 %, Si- 0.015 %, P- 0.031 %, S - 0.029 %, Cr- 0.029 %, Ni- 0.030 %, Mb- 0.016 %, and Cu- 0.017 %) and the remainder Fe and provided with a hole of uniform diameter to facilitate suspension of the strips in the test solution for weight loss method. For electrochemical studies, mild steel strips of the same composition but with an exposed area of 1cm² were used. Mild steel strips were polished by using emery paper of (400, 600, 800, 1000, and 1200) grade, it was then dried and stored in a desiccator to avoid moisture before using it for corrosion studies. Accurate weight of the metal was taken using four digital electronic analytical balances (Shimadzu ay 220).

2.2 Preparation of the plant extract

The *Tetrameles Nudiflora* (TN) plant leaves were taken and cut into small pieces, and dried in room temperature and ground well in to powder. 20 g of the powder was refluxed in 200 ml ethanol and it was kept overnight. The refluxed solution was filtered and the filtered liquor was evaporated to 250 ml dark green residue and extracted with separating funnel. The solution was evaporated and the dark green solid residue obtained after complete drying was preserved in a desiccator. The residue so obtained was used in preparing different concentrations of the extracts in hydrochloric acid solution. The solution was expressed in v/v.

2.3 Weight loss method

Mild steel specimens were immersed in 200 ml of 1N HCl solution of various concentration of the inhibitor in the absence and presence of mild steel for 24 hours. The weights of the specimens before and after immersion containing were determined using four digit analytical balances (Shimadzu ay 220).

From the mass loss measurements, the corrosion rate was calculated using the following relationship.

$$CR \text{ (mmpy)} = \frac{K \times \text{Weight Loss}}{D \times A \times t \text{ (in hours)}} \quad (1)$$

Where, $K = 8.76 \times 10^4$ (constant), D is density in gm/cm^3 (7.86), W is weight loss in grams and A is area in cm^2 . The inhibition efficiency (%) was calculated using equation (2) respectively,

$$IE \text{ (\%)} = \frac{W_0 - W_i}{W_0} \times 100 \quad (2)$$

Where, W_0 and W_i are the weight loss in the absence and presence of the inhibitor.

2.4. FTIR measurements

FTIR spectra were recorded in a Bruker ALPHA 8400S spectrophotometer. The film was carefully removed, mixed thoroughly with KBr made in to pellets and FTIR spectra were recorded.

2.5. Potentiodynamic polarization methods

Potentiodynamic polarization measurements were carried out using IVIUM electrochemical analyzer. The polarization measurements were made to evaluate the corrosion current, corrosion potential, and Tafel slope. Experiments were carried out in a conventional three electrode cell assembly with mild steel specimen of 1cm^2 as working electrode. Platinum electrode was used as counter electrode and calomel electrode was used as reference electrode. A time interval of 15 minutes was given for each experiment to attain the steady state open circuit potential (OCP). The polarization was carried from a cathodic potential of -800 mV (vs. SCE) to an anodic potential of -200 mV (vs. SCE) at a sweep rate of 1 mV per second. The inhibitor efficiency was calculated using the formula:

$$IE \text{ (\%)} = \frac{I_{\text{Corr}} - I_{\text{Corr}}^*}{I_{\text{Corr}}} \times 100 \quad (3)$$

Where I_{corr} and I_{corr}^* are corrosion current in the absence and presence of inhibitors.

2.6. Electrochemical impedance method

The electrochemical AC- impedance experiments were carried out in a conventional three electrode cell assembly as that used for potentiodynamic polarization studies. A sine wave with amplitude of 10 mV was superimposed on the steady state open circuit potential. The real part (Z') and the imaginary part (Z'') were measured at various frequencies in the range of 100 KHz to 10 MHz. A plot of Z' versus Z'' was made. From the plot, the charge transfer resistance (R_{ct}) was calculated, and the double layer capacitance (C_{dl}) was then calculated using formula:

$$C_{\text{dl}} = \frac{1}{2\pi} f_{\text{max}} R_{\text{ct}} \quad (4)$$

Where R_{ct} is charge transfer resistance, and C_{dl} is double layer capacitance. The experiments were carried out in the absence and presence of different concentration of inhibitor.

$$IE\% = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \times 100 \quad (5)$$

Where R_{ct} and R_{ct}^0 are the charge resistance values in the inhibited and uninhibited solution respectively.

2.7. Phytochemical analysis

Phytochemical screening were performed to assess the qualitative chemical composition of the different samples of plants extract using commonly employed precipitation and coloration reactions to identify the major secondary metabolites like alkaloids, flavonoids, glycosides, proteins, phenolic compounds, saponins, starch, steroids, tannins and terpenoids.

2.8. Scanning electron microscopy

The mild steel specimen immersed in blank and in the inhibitor solution for a period of one day was removed, rinsed with double distilled water, dried and observed in a scanning electron microscope to examine the surface morphology. The surface morphology measurements of mild steel were examined using (JEOL) computer controlled scanning electron microscope.

III. Results and Discussion

3.1 Weight loss method

Weight loss studies were carried out at four different concentrations ranging from 5-20 v/v and the inhibition efficiency (IE %) values calculated are presented in Table 1. From the table, it is noted that the IE increases with increasing concentration of the inhibitor. The extract showed the maximum inhibition efficiency of 84.26 % in hydrochloric acid at the optimum concentration of 15 v/v. This result indicated that TN Plant leaves extract could act as an excellent corrosion inhibitor.

TABLE 1. Data from Weight Loss Method for Mild steel corrosion in 1 N HCl solutions at various concentrations of TN leaves extract

Conc. of TN leaves extract (v/v)	Corrosion rate (mmpy)	Inhibition Efficiency (%)
Blank	0.0198	*
5	0.0054	72.51
10	0.0040	79.66
15	0.0031	84.26
20	0.0036	81.65

3.2 FT-IR measurement

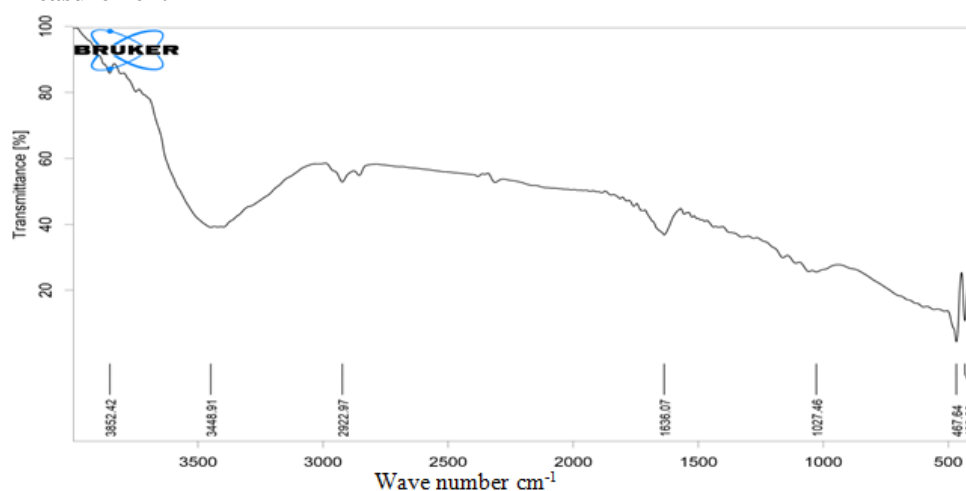


Figure 1: FTIR Spectrum of Tetrameles Nudiflora (TN) leaves extract

The chemical constituents that contribute to the corrosion inhibition have specific functional groups. The inhibitors samples were analysed with FTIR to identify the functional groups present in the extracts. TN leaves extract showed strong and sharp absorption peak at 3448 cm^{-1} , which indicates the presence of hydroxyl group. The strong stretching vibration was observed at 2922 cm^{-1} indicates the presence of CH_3 (or) N-H group. The peak occurs at the range of 1636 cm^{-1} indicated the presence of C=O group. The absorption peak at 1027 cm^{-1} indicates the presence of C-O group. From the FTIR spectrum, the TN leaves extracts may be containing the desirable chemical constituents that are common in good green inhibitors.

3.3 Potentiodynamic polarization studies

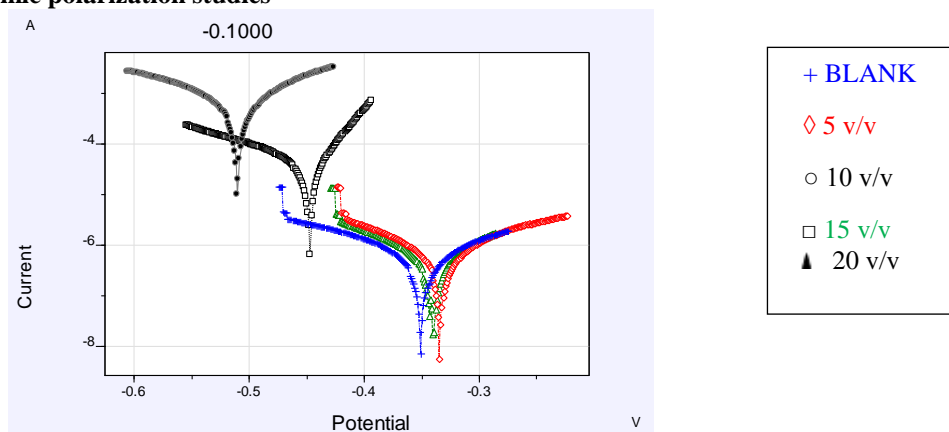


Figure. 2 Tafel plots without and with different concentrations of TN leaves extract in 1N HCl.

The potentiodynamic polarization data are plotted in Fig. 2 as the Tafel plots for mild steel in 1N HCl with the addition of different concentrations of the plant extract. The corrosion kinetic parameters, such as corrosion potential (E_{corr}), corrosion current (I_{corr}), anodic Tafel slope (b_a) and cathodic Tafel slopes (b_c), were derived from these curves are given in Table 2. It was observed from the table the I_{corr} values were progressively decreased with the steady increase in the concentration of the leaves extract. The maximum inhibition efficiency of 92.77 % was obtained at 15 v/v, was considered as the optimum concentration of the inhibitor. When compared with the blank 1N HCl, the TN leaves extract showed a mixed mode of inhibition. Moreover in the presence of inhibitor system, the corrosion current decreased from 0.695 to 0.0502 $\mu\text{A}/\text{cm}^2$. These observations confirmed the decrease in the oxidation of the metal and the formation of protective film on the metal surface [22].

Table 2. Potentiodynamic polarization parameters obtained from Tafel plots for the corrosion of mild steel in 1N HCl with various concentrations of TN leaves extract.

Conc. of TN leaves (v/v)	E_{corr} (mV) vs. SCE	I_{corr} ($\mu\text{A}/\text{cm}^2$)	CR (mmpy)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
0	-0.5046	0.695	2.273	0.128	0.087	-
5	-0.3357	0.0677	0.0022	0.154	0.091	90.25
10	-0.3378	0.0610	0.0026	0.105	0.130	91.22
15	-0.3300	0.0502	0.1641	0.148	0.036	92.77
20	-0.4391	0.0551	0.0018	0.105	0.063	92.07

3.4 Electrochemical impedance studies

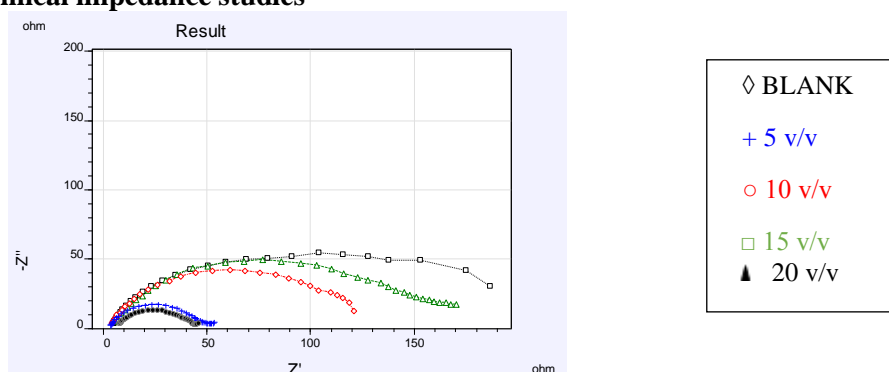


Figure 3: Nyquist plots for mild steel in 1N HCl acid solution without and with various concentration of TN leaves extract.

The corrosion behavior of mild steel in 1N HCl in absence and presence of TN leaves extract were investigated by EIS. Nyquist plots for mild steel in uninhibited and inhibited acid solutions containing different concentrations of TN leaves extract are shown in Fig 3 and data are given in Table 3. The impedance spectra showed a single semicircle and as the concentration of inhibitor increases diameter of the semicircle increases. It is evident from the results that TN leaves extracts inhibited the corrosion of mild steel in 1N hydrochloric acid at all the concentrations used, and the inhibition efficiency increased continuously with increasing concentration.

The AC impedance of the inhibited system amplified with the inhibitor the C_{dl} values decreased with inhibitor. This decrease in C_{dl} results from a decrease in local dielectric constant and / or an increase in the thickness of the double layer, suggested that inhibitor molecules inhibit the mild steel corrosion by adsorption at the metal / acid interface [23]. The depression in Nyquist semicircles is a feature for mild steel electrodes and often referred to as frequency dispersion and attributed to the roughness and other inhomogeneties of the mild steel [24]. The increase in R_{ct} values is attributed to the formation of protective film at the metal solution interface [25-26]. These observations suggest that TN leaves extracts function by adsorption at the metal surface thereby causing decrease in C_{dl} values and increase in R_{ct} values.

Table 3. Electrochemical impedance parameters for mild steel in 1 N HCl acid solution in the absence and presence of various concentration of inhibitor

Conc. of TN leaves extract (v/v)	R_{ct} (\square cm^2)	C_{dl} ($\mu\text{F cm}^{-2}$)	b_c (mV/dec)	b_a (mV/dec)	IE (%)
0	2.07	1.57×10^{-5}	0.128	0.087	*
5	2.56	1.97×10^{-5}	0.154	0.091	23.67
10	3.09	0.80×10^{-5}	0.105	0.130	33.00
15	3.38	1.06×10^{-5}	0.105	0.063	63.28
20	4.03	0.67×10^{-5}	0.148	0.036	48.63

3.5. Phytochemical screening method

Phytochemical screening of the aerial parts of plant's powder (alcoholic) extract was tested in order to find the presence of various chemical constituents included alkaloids, carbohydrates, proteins, saponins, triterpenoids and tannins, which are listed in Table 4.

Table. 4 Phytochemical screening test of TN leaves extract

S.No	Phytochemical Test	Alcoholic extract of TN leaves
1	Alkaloids	-
2	Carbohydrates	+
3	Proteins	-
4	Glycoside	+
5	Flavonoids	+
6	Tannins	-
7	Phenolic compounds	+

(+) is Present,

(-) is absent

3.6. Scanning electron microscopy (SEM)

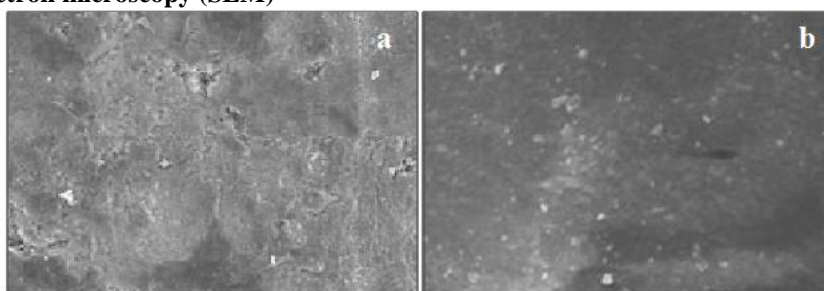


Figure. 4 SEM images of (a) Polished mild steel coupon without inhibitor and (b) mild steel coupon with inhibitor.

The surface morphology of the mild steel samples in 1N HCl in the absence and in presence of TN leaves extract are shown in Fig 4. The image (4a) shows badly damaged surface obtained when the metal was kept immersed in 1N HCl for 24 h without inhibitor indicates significant corrosion. However, in the presence of inhibitor (Fig. 4b), the surface has remarkably improved with respect to its smoothness indicating considerable reduction of corrosion rate. This improvement in surface morphology is due to the formation of a good protective film of TN leaves extract on mild steel surface which is responsible for inhibition for corrosion.

IV. Conclusion

Tetrameles Nudiflora leaves acts as efficient corrosion pickling inhibitor on mild steel in 1 N HCl acid. The use of TN plants as corrosion inhibitor is environmentally safe, nontoxic, eco-friendly, cost effective and easily available. The TN leaves extracts showed maximum inhibition efficiency of 84.26 % at the optimum concentration of 15 v/v for one day immersion time at room temperature. Results obtained in non-electrochemical methods (weight loss method) have good agreement with the electrochemical methods. The TN leaves extracts act as a mixed type inhibitor on the metal surface. SEM examination showed that there was an improvement in the surface morphology of the as corroded inhibited mild steel compared to uninhibited samples. The results of the electrochemical tests and weight loss measurements are consistent and show that this green inhibitor, which was isolated from the ethanolic extract of TN leaves, can be potentially applied as an anticorrosive agent for mild steel in hydrochloric acid environment.

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