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A Green pickling solution for mild steel- An alternative to ASTM Std. pickling solution (Clarke solution)

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Abstract

The *Avicennia marina* extract (AME) in Conc.HCl exhibited 98% corrosion-inhibition of mild steel for 20 min. by weight-loss method at 25℃. The results obtained by the weight-loss method are in accordance with the electrochemical measurements. The pickling effect of AME in Conc.HCl was compared with the Clarke solution. A negligible base metal loss was observed in the AME-treated system when compared with Clarke solution. The 3D topography of theAME-treated system is outstanding, owing to the smoother surface than that of the polishedmetal. The adsorption process is physisorption, and it obeys the Langmuir adsorption isotherm.

Key words: Mild steel, Corrosion test, Clarke solution, Conc.HCl, Electron microscopy, Electrochemical studies

1. Introduction

Acid pickling and acidization are the most commonly used methods, which employ the acids for the cleaning and descaling of steels. In order to protect the integrity of the fabricated metal surface, corrosion inhibitors are used. Generally, 5% and 18% HCl with inhibitor are used to clean industrial equipment before and after operation [1,2].The ASTM G 1-03 recommends Clarke solution for the cleaning of iron and steel; the exposure time varies from 1-25 min. depending on the deposition of corrosion products [3]. It contains stannous chloride (5%) and antimonytri-oxide(2%) in Conc.HCl. It is believed that Clarke solution removes only the corrosion products without affecting the surfaces of the base metal. Singh et al [4] have reported that the performance of Clarke solution varies with the elemental composition of virgin carbon steel. Also, there is no synergistic or additive effect of stannous chloride with antimony tri-oxide on the dissolution of steel in Conc.HCl medium [4].

Furthermore, Clarke solution contains 7% of toxic inorganic compounds. Owing to the severe criticism on the toxicity of corrosioninhibitors,there is an emerging need for the development of easily degradable and less toxic inhibitors. Rare-earth elements [5], organics [6], and plant extracts [7]have been reported to have corrosion-inhibition on metals and alloys in various acidic media. Nevertheless, they are harmless and easily degradable.

The mangrove plant, *A.marina* is the fastest growing, cosmopolitan species distributed along the tropical and subtropical coastlines.*A.marina*has been reported for its bio-potentials andunique chemical compositions that owe to its medicinal applications [8-12]. Despite the number of studies reported the use of plant extracts as corrosion inhibitors, they concentrated mostly on the inhibition of mild steel in dilute acid medium.The plant extracts of*Ecliptaalba*[13],*Ocimum sanctum*[14],and*Adathodavasica*[15], are reported to have more than 98% corrosion-inhibition efficiency in 1 N HCl for mild steel. The work on corrosion-inhibition of mild steel in Conc.HCl is rare [16]. Therefore, in the present study, an attempt has been made to study the corrosion-inhibition efficiencyof *A.marina*leafextract (AME) in Conc.HCl medium for mild steel.To the best of our knowledge, this report is the first of its kind that explores the corrosion-inhibition efficiency of mangrove plant,*A.marina*in Conc.HClmedium for mild steel.

2. Materials and methods

2.1 Materials

Commercial grade mild steel sheets of composition C - 0.1%, Si - 0.07%, Mn - 0.5%, S - 0.05% & balance Fe, was used in this study. Mild steel coupons of size 10mm×50mm×2mm were used for weight-loss measurements and surface analysis. The mild steel coupons were de-scaled by grinding on an abrasive belt and were fine polished using the emery paper grade-1200.The coupons were degreased with acetone and washed thoroughly with double distilled water before experiment. Analytical grade HCl-37% (Merck) was used as test medium and the 4 N test solution was prepared by diluting the same with double distilled water. The Clarke solution was prepared according to ASTM-G 1-03 guidelines [3].

Freshly collected leaves of *A.marina*were washed thrice with double distilled water to remove the debris, and shadedriedfor a week. AME was prepared by extracting 100 g of dried, coarsely ground leaves using methanol (w/v) at 50^0C for 24 h. The methanol extract was filtered using Whattman filter paper No.1, and the filtrate was concentrated under reduced pressure. The AME concentrate was then freeze dried to complete dryness, weighed, and used throughout the experiment.

2.2 Characterization of AME

The presence of phytochemicals;tannins,terpenoids,phenols,flavonoids,saponins,steroids, and glycosides were analyzed following the standard protocol[17]. TheFTIR spectrum was recorded in Bruker Tensor 27 FTIR spectrophotometer, between the IR region 4000 and 500 cm^{-1}, using the KBr pellet technique. To check the stability of AME in Conc.HCl the UV-Vis spectral measurements were obtained using Shimadzu UV 1800. CHNS analysis of AME was done using the CHNS-elemental analyzer(Vario EL III).

2.3 Weight-loss measurements

The mild steel coupons were immersed in 100 ml of Conc. HCl in the absence and presence ofAME (9 g/L, 18 g/L, and 36 g/L). After the 5, 10, 15, and 20 min. exposure at 25℃, the coupons were washed using double distilled water and their weight-losses were determined using the Shimadzu-AUW320electronic balance (precision±0.0001 g).Weight-loss measurements were carried out in triplicate to ensure the reproducibility of results.The corrosion rate in mpywas obtained from the following equation:

$$\text{Corrosion rate (mpy)} = \frac{\mathbf{KW}}{\mathbf{DAT}} \quad (1)$$

Where, K - 3.45×10^6, T - the exposure time (h), A - the surface area of the test coupon (cm^2), W- the weight loss (g) andD- density of the test specimen (gcm^{-3}).The percentage inhibition efficiency (IE) and the degree of surface coverage ($\boldsymbol{\theta}$) were calculated by the following equations:

$$\%\ \text{IE} = \frac{\mathbf{W_0 - W_1}}{\mathbf{W_0}} \times \mathbf{100} \qquad (2)$$

$$\boldsymbol{\theta} = \frac{\mathbf{W_0 - W_1}}{\mathbf{W_0}} \qquad (3)$$

Where,$w_0$and w_1 are the weight losses of metal couponswithout and with AME, respectively.

2.4 Comparison of AME in conc.HCl with Clarke solution

Pre-weighed mild steel coupons were allowed to corrode in the marine atmosphere at Tuticorin (longitude 78.13° east and latitude 8.8° north) for a week. The corroded mild steel coupons were weighed to determine the mass of corrosion product. The corroded coupons were then exposed to Clarke solution and AME (18 g/L) in Conc.HCl for 5 min. at 25℃. The weight loss due to corrosion product removal was determined. In order to study the base metal loss,the pickled coupons were immersed in Clarke solution and AME (18 g/L) in Conc.HCl for 5 min. at 25℃.

2.5 Electrochemical measurements

The electrochemical measurements were made usingAutolab with PGSTAT30.The electrochemical studies were performed at room temperature (25°C) in 4 N HClwithout and with AME (0.5,1.0,1.5 g/L).A three-electrode cell consistingofmild steel (1 cm^2 exposure area) as the working electrode,saturated silver-silver chloride electrode as reference, and a platinum electrode as auxiliary was used.The working electrode was allowed to stabilize in the electrolyte for 10 min. before the electrochemical measurements.Tafel polarization tests were conducted at the sweep rate of 10 mVs^{-1}. The kinetic parameters were then derived from Tafel slope plots.Electrochemical impedance spectra (EIS) studies were performed using AC signal amplitude of 10 mVat corrosion potentials (E_{corr}) over a frequency range of 10 kHz to 10Hz.

2.6 Surface analysis

The mild steel coupons were immersed in each 100 ml of Conc.HCl, AME (18 g/L) in Conc.HCl andClarke solution at 25℃. After 20 min.exposureperiod,the coupons were washed with double distilled water, dried, and examined underthe Scanning Electron Microscope (SEM) (HITACHI Model S-3000H instruments). The adsorbed molecules on the mild steel surface werecharacterized using FT-IR analysis. After 5 min. exposure in the corresponding solutions at 25℃, the surface topographies were recorded using Atomic Force Microscope (AFM) (Picoscan 2000 model).

3. Results and discussion

3.1 Characterization of AME

The results of the phytochemical analysis revealed the presence of phytochemicals like tannins, phenols, steroids, terpenoids, saponins, and glycosides. CHNS analysis of AME showed the presence of carbon (19.30%), hydrogen (9.26%), nitrogen (1.43%), and sulfur (0.31%).FT-IR analysis of AME was also done to study the presence of major functional groups. The IR bands of the peak and the corresponding functional groups are shown in Table 1.From the CHNS and FT-IR analyses, it is explicit that AME is rich in nitrogen-based compounds. This observation supports the view of Riggs [18], and Raja and Sethuraman [19], who reported that the organic molecules containing heteroatoms such as nitrogen, sulfur, oxygen shows significant inhibition efficiency. The UV-Vis absorption spectra of AME and AME in Conc.HCl are shown in Fig.1. Strong peaks were observed in the regions between 660-670 nm and 605-610 nm in both cases. It could be noticed that UV-Vis absorption spectra of AME and AME in Conc.HCl are identical, indicating the stable nature of AME in Conc.HCl medium.

Table 1:FT-IR peaks of AME and the corresponding functional groups

S.No	**IR band (cm^{-1})**	**Functional groups**
1.	3433	–OH, corresponding to phenols and alcohols
2.	2940	Alkanes
3.	1634	Amines
4.	1069	Aliphatic amines
5.	1512 and 1340	Nitro compounds
6.	1408,603	Aromatics
7.	1261	Alkyl halides

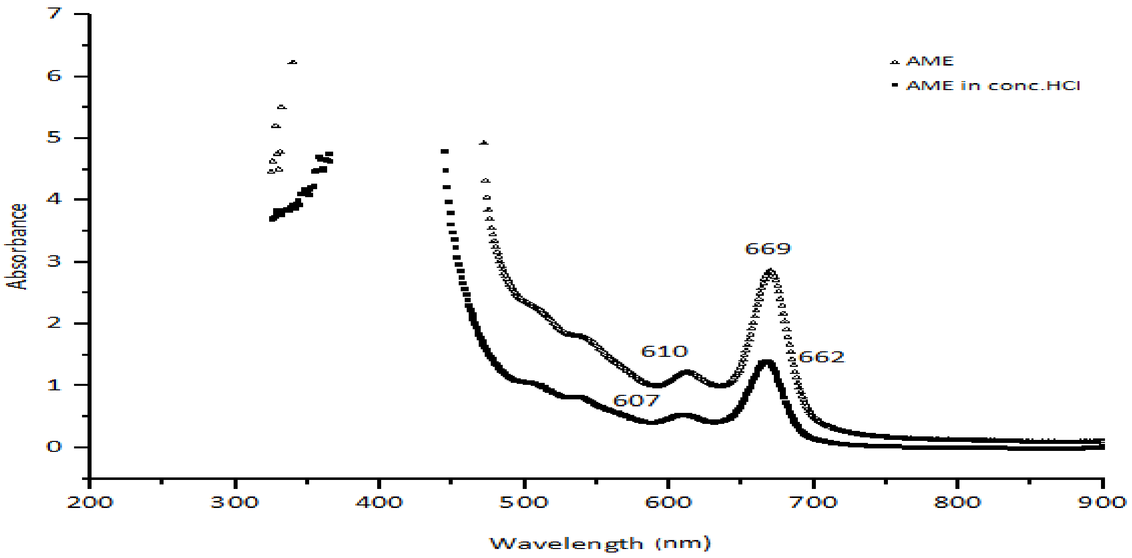

Figure 1:UV-Vis spectra of AME

3.2 Corrosion inhibition efficiency of AME in conc. HCl

It is evident fromTable 2 that the corrosion-inhibition efficiency of AME is found to be concentration dependent. A maximum of 99.3% inhibition was achieved at the concentration of 36 g/L AME in Conc. HCl.However, even at the concentration of 18 g/L,96.7% corrosion-inhibition efficiency was achieved up to 20 min. exposure. Hence,the concentration,18 g/Lwas chosen for surface morphological studies.Also,our earlier reports on *Artemisiapallens*(40 g/L), exhibited 96% inhibition efficiency in Conc.HCl [16].Fig. 2 shows a fivefold decrease in the corrosion rate of mild steel even at 9 g/L of AME in Conc. HCl, when compared to that of the mild steel in Conc. HCl without AME.The active phytochemical compounds present in the AME would have formed a protective film on the metal surface.

Table 2: The corrosion-inhibition efficiency of AME for mild steel in Conc.HCl by weight-loss method.

S.No	**AME in Conc.HCl (g/L)**	**Inhibitionefficiency (%)**			
		5 min	10 min	15 min	20 min
1.	9	95.18072	89.18269	94.22057	77.70398
2.	18	98.56928	96.15385	96.07635	96.76977
3.	36	98.41867	97.05529	99.36373	98.17331

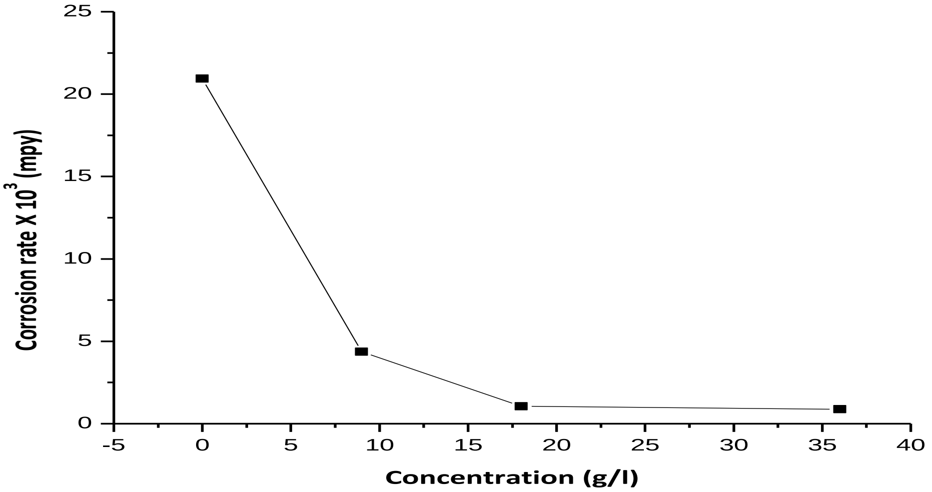

Figure 2: Corrosion rate of mild steel at different concentrations of AME in Conc. HCl for 20 minexposure at 25°C.

3.3 Comparison of AME in Conc.HCl with the Clarke solution.

Table 3 clearly portrays the corrosion-inhibition efficiency of AME in comparison with Clarke solution. It could be noticed that the corrosion product has been completely removed in both cases.However, the base metal losswas found to be 5.6 times lower (0.0008 g) in AME-treated system, when compared to that in Clarke solution(0.0045 g).In our earlier reports on *A.pallens* in Conc.HCl, the corrosion-inhibition efficiency was on par with the Clarke solution[16]. But in the present study,the corrosion-inhibition efficiency of AME in Conc.HCl is better than that ofClarke solution. Hence, the AME (18 g/L) in Conc.HClcould be an alternative to the Clarke solution.

Table 3: Comparison of AME in Conc.HCl with the Clarke solution

S.No	Contents	Weight loss due to corrosion product removal for 5 min (g)	Base metal loss in 5 min (g)	Inhibition Efficiency (%)
1.	Clarke solution	0.0786	0.0045	93.22
2.	AME 18 g/L in Conc.HCl	0.0733	0.0008	98.79

3.4. Electrochemical studies

The potentiodynamic polarization curves for mild steel in 4 N HClsolution with different concentrations of AME at 25°C are shown in Fig 3.The Tafel slope parameters,anodicand cathodicTafel slopes ($b_a$and b_c), corrosion current density (I_{corr}),polarizationresistance (R_p), corrosion potential (E_{corr}), and corrosion-inhibition efficiency is given in Table 4.It could be noticed that the addition of AME caused an appreciablerise in R_p. An order decrease in current density (I_{corr}) with the addition of AME (1 g/L) to the HClmedium is worth mentioning.The b_a and $b_c$values indicate that the addition of AME affects both the anodic andcathodic sitesand hence, the AME is of mixed type inhibitor.The corrosion-inhibition efficiency is calculated using thecurrent density (I_{corr}) values (eq.4) and is found to be concentration dependent.

$$\mathbf{IE}\ (\%) = \frac{I_{corr_0} - I_{corr_{in}}}{I_{corr_0}} \times \mathbf{100} \qquad (4)$$

The effect of AME concentration on the impedance behaviour of mild steel in 4 NHClhas been studied. Nyquist plots are shown in Fig.4. It is clear that the impedance spectra yield adepressed semicircle with increasing diameterwith an increase inAME concentration. Suchbehaviour for solid electrodes are referred to frequency dispersion have been attributed to the roughness and inhomogeneities of the electrode surface [20].Hence, it is evident that corrosion of the mild steel in 4 N HCl is mainly controlled by charge transfer process [21]. The charge transfer resistance (R_t)is the difference between the polarization resistance (R_p) and solution resistance (R_s). $R_t$increases with increase in AME concentration.The corrosion-inhibition efficiency is calculated using the charge transfer resistance (R_t) (eq.5) and the values are given in table 5.

$$\mathbf{IE}\ (\%) = \frac{\mathbf{Rt}_{in} - \mathbf{Rt}_{o}}{\mathbf{Rt}_{in}} \times \mathbf{100} \qquad (5)$$

Table 4: Potentiodynamic polarization parameters for the corrosion of mild steel 4 N HCl Containing different concentrations AME

S.No	**[AME] g/L**	**R_p (Ω cm^2)**	**I_{corr} (A cm $^{-2}$)**	**E $_{corr}$ (V)**	**Tafel slopes**		**Inhibition efficiency (%)**
					β_c(V dec $^{-1}$)	**β_a(V dec $^{-1}$)**	
1.	0	8.823	3.363×10^{-3}	-0.374	0.1532	0.123	-
2.	0.5	22.67	1.267×10^{-3}	-0.342	0.186	0.102	62.3
3.	1	27.30	9.697×10^{-4}	-0.336	0.156	0.108	71.1
4.	1.5	40.47	6.733×10^{-4}	-0.335	0.193	0.101	80

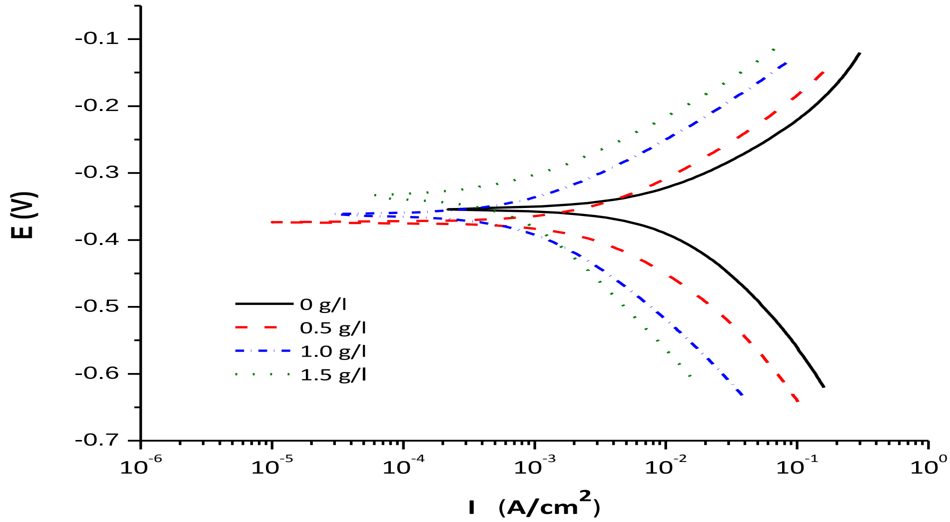

Figure 3: Potentiodynamic polarization curves for mild steel in 4 N HCl in the absence and presence of different concentrations of AME at 25°C

Table 5:EIS parameters for the corrosion of mild steel in 4 N HCl.

S.No	**[AME] g/L**	**R_p (Ω cm^2)**	**R_s (Ω cm^2)**	**R_t (Ω cm^2)**	**Inhibition efficiency (%)**
1.	0	4.2966	0.0862	4.2104	-
2.	0.5	14.5317	-20.82	35.3517	88.09
3.	1	22.2637	-50.93	73.1937	94.24
4.	1.5	44.2573	-31.31	75.5673	94.42

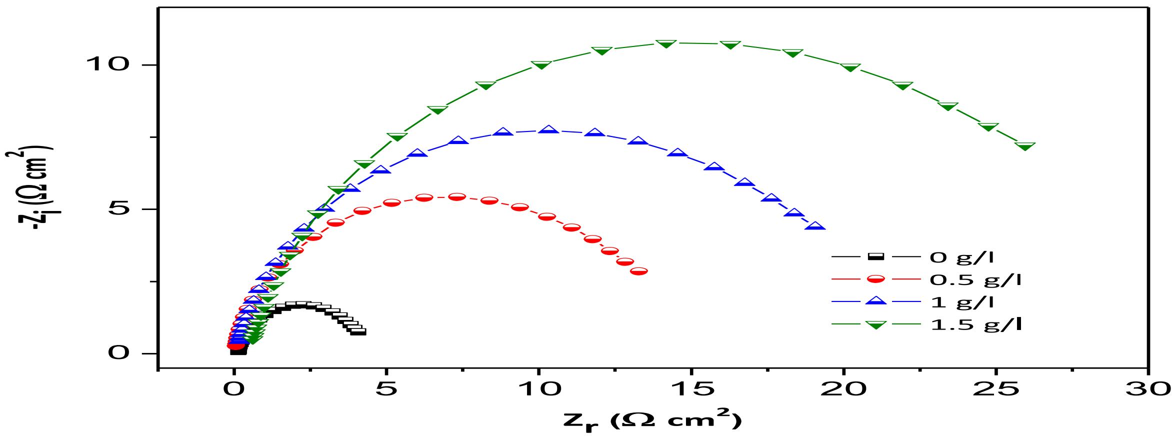

Figure 4: Nyquist plots for the corrosion of mild steel in 4 N HCl in the presence and absence of different concentrations of AME at 25℃

3.5 Adsorption isotherm

Adsorption isotherms are helpful in predicting the corrosion-inhibition process of the inhibitor.The molecules, present in AME render their inhibitory effect by adsorbing onto the metal surface.The adsorption of inhibitors to the metal surface is governed by several factors;charge on the metal surface, type of corrosive media, and chemical structure of the inhibitor [22, 23].The surface coverage parameter described in eq.2 is used to fit the adsorption isotherm.The best fit modelfor adsorption of AME on the metal surface is Langmuir adsorption isotherm;assuming monolayer adsorption and ignoring adsorption between adsorbed molecules.A straight line was obtained by plotting C versus C/***θ*** (Fig.5) with a regression coefficient value of 0.9946 and hence, it is proved that the adsorption process obeys Langmuir isotherm.

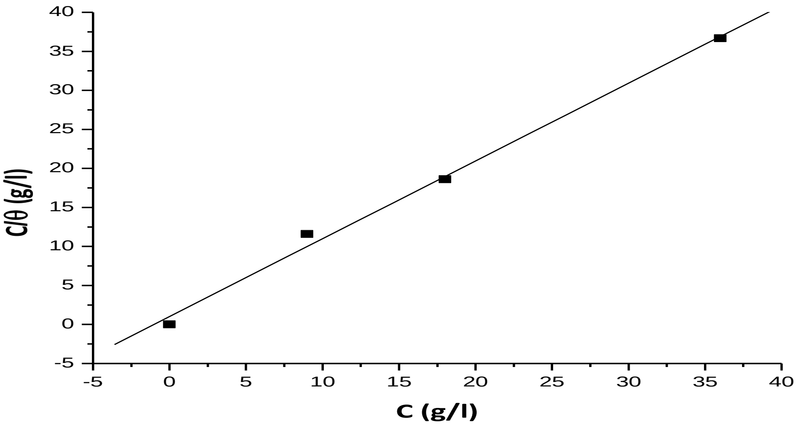

Figure5: The adsorbency plot (C/θ) versus the concentration of AME in Conc.HCl for 20 min exposure at 25℃

3.6 *Thermodynamics parameters*

The mode of adsorption of AME to the metal surface was studied by obtaining standard free energy of adsorption (ΔG_{ads}) value at 25℃(eq.6) from the adsorbency plot [24] (Fig 5).

$$\Delta G_{ads} = -RT\ \ln(55.5K_{ads}) \qquad (6)$$

Where, $K_{ads} = \frac{\theta}{c(1-\theta)}$

According to the equation, one molecule of water is replaced by one molecule of inhibitor [25]. The numerical value ln55.5 in eqn (6) is for molarity of water. So,it is unsafe to determine the value of free energy of adsorption for an extract contains as it contains numerous compounds. All the ingredients and the phytochemicals present in the extract are expected to take a part in the inhibition process. Therefore, it is impossible to define a molarity to be used in the isotherm graph.

3.7 Surface analysis

The SEM images obtained for the mild steel surface after immersion in Conc.HClfor 20 min. in the absence and presence of AME (18 g/L) and in Clarke solution are shown in Fig.6. The mild steel surface immersed in Conc.HCl was subjected to general and pitting corrosion, while the surface of the mild steel immersed in Clarke solution experienced mild corrosion. On the other hand, no general and pitting corrosion was observed in the AME-treated system.

The 3D surface topographies obtained from AFM studies (Fig.7) arefar more encouraging. The roughnesses of the mild steel surface are greatly reduced by the addition of AME (18 g/L). The maximum peak height (R_P) and valley depth (R_V) of the roughness profile for AME-treated surface is approximately threefold lowerthan the roughness profile obtained for Conc.HCl-treated surface (Table 6). The roughness profiles of the coupons in Clarke solution are also less when compared to that in Conc.HCl-treated system. It is worth mentioning that the roughnessprofile of the AME-treated system isbetter than all other systems studied, which could be attributed to the physisorption of biomolecules.

The FT-IR spectra of AME and compounds adsorbed on mild steel surface are shown in Fig.8.From the spectra, it is evident that the compounds having functional groups like amines, aromatics,alkyl halides,and nitro compounds are adsorbed on the mild steel surface. There is a shift in the absorption frequencies of molecules of AME adsorbed on mild steel surface, which strongly supports the interactionbetween the functional groups of AME and metalsurface [16].

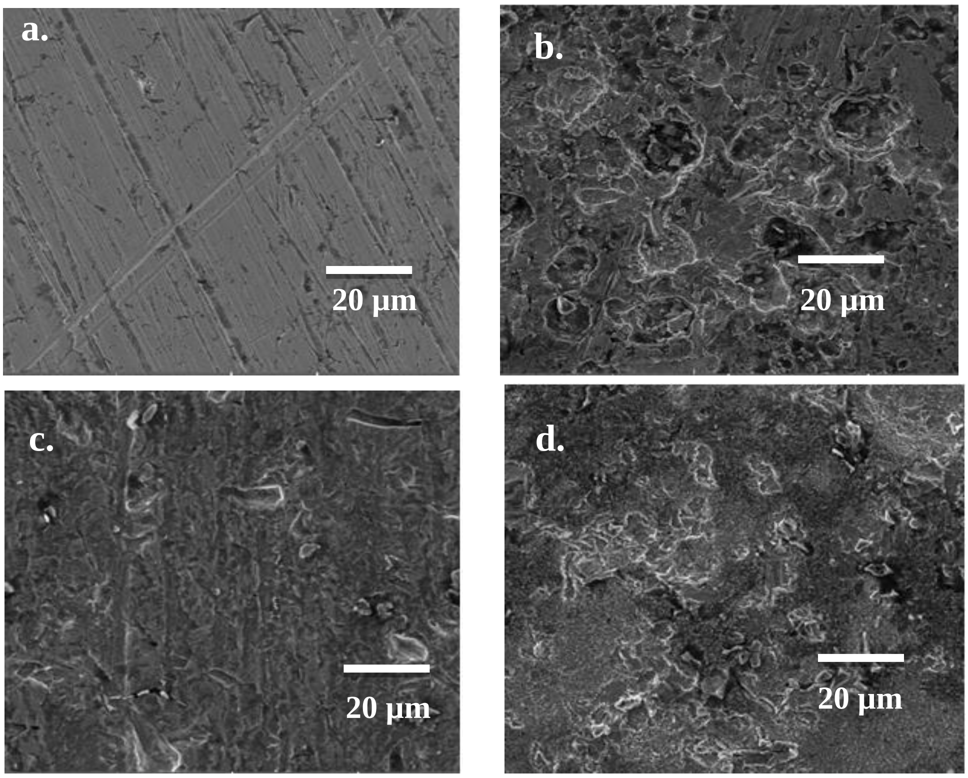

Figure 6: Micrographs of mild steel surface (a) before immersion (b) after immersion for 20 min at 25℃ in Conc.HCl (c) AME (18 g/L) with Conc.HCl (d) Clarke solution

Table 6: Roughness profile of mild steel surface obtained using AFM studies

S.No	**Contents**	**R_P(µm)**	**R_V (µm)**
1.	Polished mild steel	0.485	0.406
2.	Conc.HCl	1.17	0.889
3.	Clarke solution	0.821	0.459
4.	Conc.HCl with AME (18 g/L)	0.359	0.373

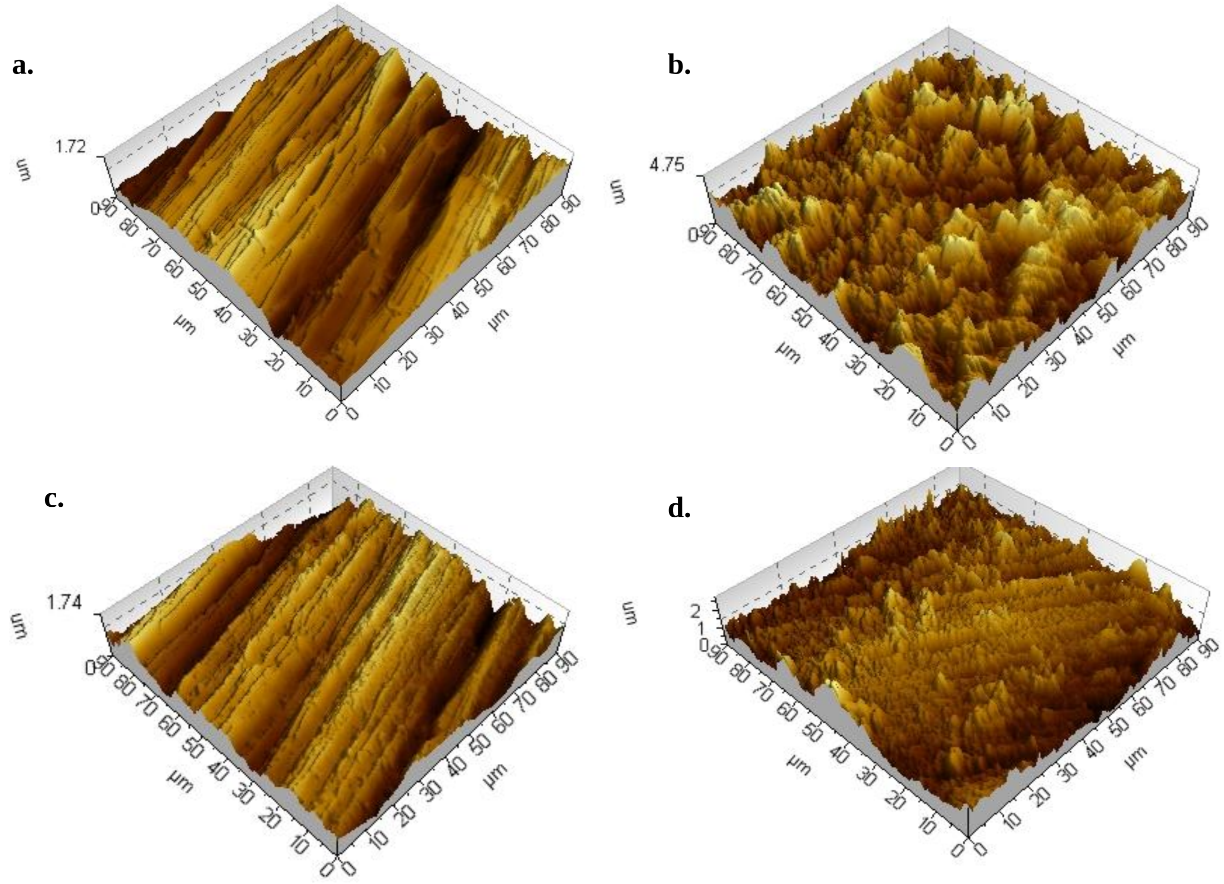

Figure 7: The 3D topographies of mild steel coupons obtained using AFM (a) before immersion (b) after immersion for 20 min at 25℃ in Conc.HCl (c) AME (18 g/L) with Conc. HCl (d) Clarke solution

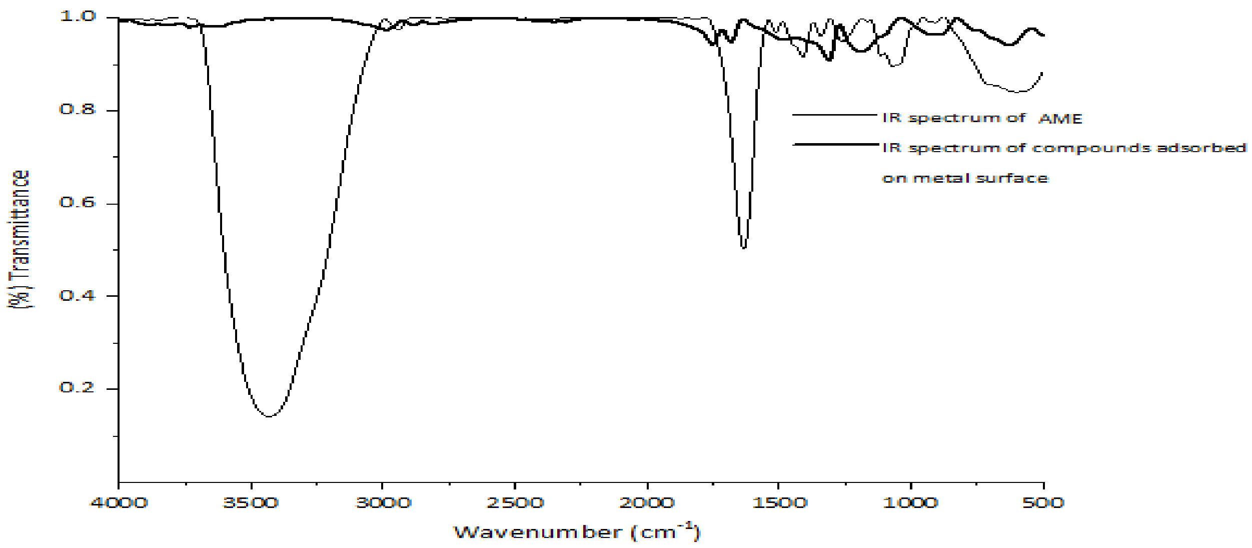

Figure 8: FT-IR Spectra of AME and compounds adsorbed on the mild steel surface.

Conclusions

1. The methanol extract of *A.marina* leaf is rich in nitrogen based compounds.
2. AME proves to be a good corrosion-inhibitor for mild steel in Conc.HCl medium at the concentration of 18 g/L.
3. Negligible base metal loss was recorded in AME-treated system, when compared to that in Clarke solution.
4. The adsorption of AME obeys Langmuir adsorption isotherm.
5. AME acts as a mixed type inhibitor.

6. AME (1 g/L) in 4 N HCl medium decreases the corrosion current by one order.
7. The charge transfer resistance (R_t) increases with increase in AME concentration.
8. The AME molecules adsorb onto the metal surface by physisorption.
9. AFM studies show that the surface roughness profile for AME-treated system is less when compared to other systems studied.
10. This study recommends the AME in Conc.HCl as an alternative to the Clarke solution.

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