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Der Pharma Chemica, 2013, 5(5):68-76
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Analysis of protective (Nano) film of *Ocimum tenuiflorum* (tulsi) extract by surface examination study

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ABSTRACT

Tulsi was evaluated as corrosion inhibitor of steel in molar hydrochloric acid in sea water using weight loss measurements, electrochemical polarization and EIS methods. The tulsi (eugenol) was found to retard the corrosion rate of steel. Tulsi 10g / 100mL(8mL / 100 mL) gives 90% inhibition efficiency. The surface morphology of the protective film on the metal surface was characterized by using Scanning Electron Microscopy (SEM) and atomic force microscopy (AFM),

Key words: Tulsi; protective film; SEM; AFM.

INTRODUCTION

Iron is a widely used metal with extensive industrial application, metals and their alloys are exposed to the action of acid in industrial processes where acids play important roles such as in oil well, acidizing, acid pickling, acid cleaning and acid desealing. Corrosion inhibitors [1-3] are usually added to the acid solutions to minimize metal loss and reduce acid consumption. However some of these corrosion inhibitors are toxic to the environment [2, 3]. Considerable efforts are deployed to find suitable compounds to be used as corrosion inhibitors in various corrosive media to stop or delay to the maximum the attack of a metal. Nevertheless, the known hazard effects of the most synthetic inhibitors and the need to develop environmentally friendly processes, researches are focused on the use of natural products, investigation of natural inhibitors is particularly interesting because they are non – expensive, ecologically friendly acceptable and possess no threat to the environment. Electrochemical studies confirm the formation of a protective film on the metal surface by spirulina solution, this offers 90% corrosion inhibition efficiency[4] Recently aqueous extract of Cocos nucifera - Coconut Palm – Petiole [5]. Fennel (Foeniculum Vulgare) Essential Oil [6]. Pericarp of the Fruit of Garcinia Mangostana [7]. Natural Fenugreek [8]. Ethanol extract of Vernonia Amygdalina[9] and Ipomoea involcrata [10] have been used as corrosion inhibitors.Ginger [11], Eugenol and acethyleugenol [12] have been found to be very efficient corrosion inhibitors for iron and steel in acid media.

The encouraging results obtained by Inhibitory effects of *Ocimum tenuiflorum* (tulsi) [13] in sulphuric acid, Comparative Study of Corrosion Inhibition Efficiency of Holy Basil (Tulsi) for Tin in HNO_3 Solution [14], Combating Aluminium Alloy Dissolution by *Ocimum tenuiflorum* leaves extract[15] leads as to chose tulsi as corrosion inhibitor.

In this paper, electrochemical polarization, EIS techniques are applied to study the ability of *Ocimum tenuiflorum* to inhibit the corrosion oe steel in 1M HCl. The protective film formed on the metal surface characterized with the help of surface analytical techniques such as SEM and atomic force microscopy.

MATERIALS AND METHODS

Corrosion tests were performed using mild steel specimens from the same sheet of the following composition 0.1% C, 0.026% S, 0.06%P, 0.4% Mn and the balance Fe. Mild steel specimens of the dimensions 1.0X4.0X0.2 cm were polished to mirror finish degreased with trichloroethylene and used for weight loss and surface examination studies. The aggressive solution (1M HCl) is prepared by dilution of analytical grade 37% HCl with double distilled water. The initial inhibitory solution is prepared from dissolution of the natural Tulsi in 1M HCl solution. This later is obtained as described elsewhere [16]. It has been shown that Eugenol (Fig:1) s the principal constituent of Tulsi.

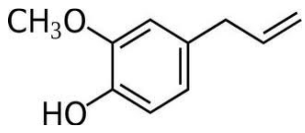


Fig:1 Eugenol

Weight loss is measured on polished sheets, degreased with trichloroethylene and dried before being weighed and immersed in 100 mL of the corrosive medium (in sea water) at room temperature 298 K, corrosion rate was determined by hanging the steel in acid solution with and without inhibitor

The percent inhibition efficiency (IE%) for the weight loss method is calculated as follows.

$IE = 100\ [1-(W_{corr} / W^{o}_{corr})]\ \%$

Where W_{corr} is the weight loss value in the absence of inhibitor and W^{o}_{corr} is the weight loss value in the presence of inhibitor.

Electrochemical studies are carried out
Polarization studies were carried out in a CHI- electrochemical work station with impedance model 660A. It was provided with iR compensation facility. A three electrode cell assembly was used. The working electrode was carbon steel. A SCE was the reference electrode. Platinum was the counter electrode. From polarisation study, corrosion parameters such as corrosion potential (E_{corr}), corrosion current (I_{corr}), Tafel slopes anodic = b_a and cathodic = b_c were calculated and polarization study was done. The scan rate (V/S) was 0.01. Hold time at (Efcs) was zero and quiet time (s) was two.

In the case of polarization method the relation determines the inhibition efficiency (IE%)

$IE = 100\ [I^{o}_{corr} - I_{corr} / I^{o}_{corr})]\ \%$

I^{o}_{corr} and I_{corr} are the uninhibited and inhibited corrosion current densities,

Electrochemical impedance spectroscopy was carried out by CHI 660A electrochemical impedance analyzer model was used to record AC impedance measurements. The cell set up was the same as that used for polarization measurements. The real part (Z') and imaginary part (Z") of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

$C_{dl} = 1/ 2 \times 3.14 \times R_t \times f_{max}$

Scanning Electron Microscopic studies (SEM)
The carbon steel immersed in blank solution 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 carbon steel were examined using JEOL MODEL6390

computer controlled scanning electron microscope. The elemental analysis of the carbon steel surface at the same condition was carried out using an energy dispersive X-ray analyzer (EDAX) unit attached to the SEM machine.

Atomic Force Microscopy characterization (AFM)
The carbon 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 subjected to the surface examination. Atomic force microscopy (Veeco dinnova model) was used to observe the samples' surface in tapping mode, using cantilever with linear tips. The scanning area in the images was 5 μm × 5 μm and the scan rate was 0.6 HZ /second.

RESULTS AND DISCUSSION

The substrates were characterized using EIS which is a very effective means of determining films protective properties by measuring the resistive and capacitive characteristics of the coating. Polarization behavior of steel in 1M HCl in the presence and absence of the inhibitors is shown in fig: 2 from the weight loss study it shows that Tulsi 10g / 100mL(8mL / 100 mL) gives 90% IE.

Polarization study has been used to detect the formation of protective film on the metal surface [17-24].When a protective film is formed on the metal surface, the linear polarization resistance (LPR) increases and the corrosion current (Icorr) decreases. The potentiodynamic polarization curves of carbon steel immersed in various test solutions are shown in Fig:2(a) and (b). The corrosion parameters namely, corrosion potential (Ecorr), Tafel slopes (bc=cathodic; ba=anodic), linear polarization resistance (LPR) and corrosion current (Icorr) are given in Table: 1. When carbon steel is immersed in sea water, the corrosion potential is -771mV vs SCE. The formulation consisting of 8 ml of Tulsi (TUL) in 1M HCl shifts the corrosion potential to -765 mV vs SCE. The shift is very small this suggests that this formulation controls the anodic reaction and cathodic reaction to an equal extant. So we can conclude that this inhibitor acts as mixed type of inhibitor. The LPR value increases from 2378 ohm cm^2 to 5664 ohm cm^2. This suggests that a protective film is formed on the metal surface. Further the corrosion current decreases from 1.579 x 10^{-5} A/cm^2 to 0.6832 x 10^{-5} A/cm^2. The IE calculated from corrosion current is 57%. This value is lower than the IE obtained by weight loss method (90%). The discrepancy may be explained by the fact that in electrochemical process, the instantaneous corrosion current is measured. However, in the case of the weight loss method, IE is calculated after a long time. The protective film formed is strengthened as the duration of immersion increases [25-32].

In presence of inhibitors, the cathodic and anodic Tafel slopes are more or less equal. This indicates that the formulation consisting of Tulsi functions as mixed type inhibitor controlling the cathodic reaction and anodic reaction to an equal extend. However the anodic Tafel slope is slightly higher. This is reflected in the shift of corrosion potential to the anodic side.

Table: 1 Corrosion parameters of carbon steel immersed in tulsi extract obtained from polarization study

System	E_{corr} mV vs SCE	b_c mV/decade	b_a mV/decade	LPR ohm cm^2	I_{corr} A/cm^2
Sea water(blank)	-771	160	186	2378	$1.579x10^{-5}$
TUL(10g / 100mL) (8mL / 100 mL)	-765	148	222	5664	$0.6832x10^{-5}$

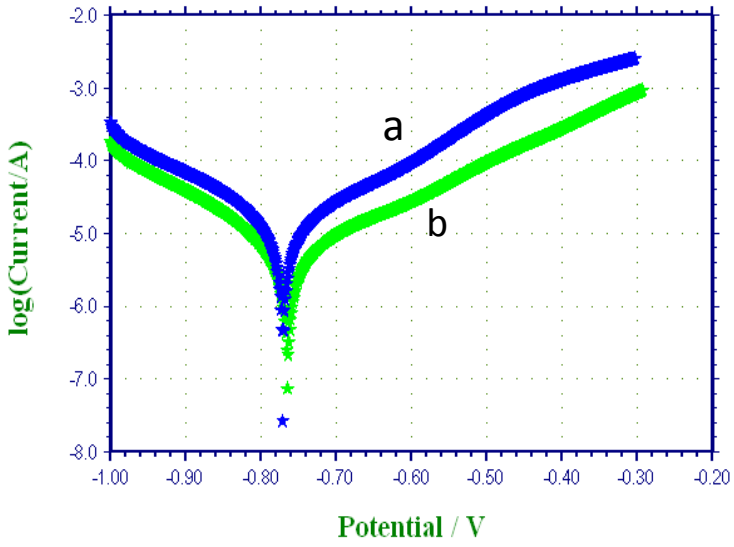


Fig: 2 Polarization curves of carbon steel immersed in various test solutions
(a)Sea water (blank) (b) TUL (8ml)

Impedance fig:3(a),(b) show Nyquist plots for mild steel in 1M HCl without and with inhibitor respectively. Nyquist plots of iron in 1M HCl solutions display one capacitive arc, it shows that the electrode reaction is controlled by charge transfer process; the diameter of the semicircle represents the charge transfer resistance R_t [33]. The mild steel in 1M HCl solutions has small charge transfer resistance 90.32 ohm cm^2 because iron react quickly in acid solution, while on addition of inhibitor (Tulsi extract) its R_t value increased remarkably 175.25 ohm cm^2, values of double layer capacitance are also brought down to the maximum extent in the presence of inhibitor and the decreases in the values of C_{dl} follows the order similar to that obtained for I_{corr} in this study. The decrease in C_{dl}

Means that the adsorption of this Eugenol takes place on the metal surface in acidic solution fig: 3, we also note the increase of the value of R_t with the inhibitor concentration leading to an increase in the corrosion inhibition efficiency [34-38].

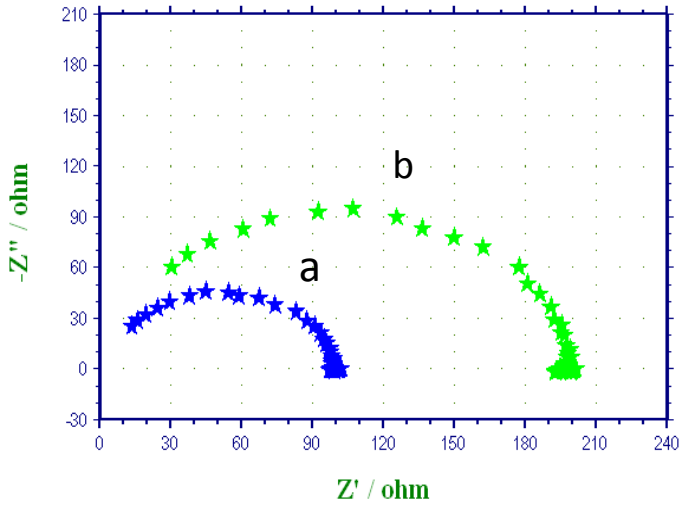


Fig: 3 AC impedance spectra of carbon steel immersed in various test solutions (Nyquist plots). (a) Sea water (blank) ; (b) TUL (8mL)

The SEM images of different magnifications (X 500, X 1000) of carbon steel specimen immersed in sea water for 1 day in the absence and presence of inhibitor system are shown in Fig: 4 images (a,b,c,d,e and f) respectively.

The SEM is used to understand the nature of the surface film; SEM provides a pictorial representation of the surface [39-41]. The SEM micrographs of polished carbon steel surface (control) in Fig: 4(a,b) illustrate the smooth surface of the metal. This shows the absence of any corrosion products formed on the metal surface.

The SEM micrographs of carbon steel surface immersed in sea water in Fig: 4(c,d) shows the roughness of the metal surface which indicates the corrosion of carbon steel in sea water. Fig: 4(e,f) indicates that in presence of tulsi in 1M HCl mixture in sea water, the surface coverage increases which in turn results in the formation of insoluble complex on the surface of the metal (ASF inhibitor complex) and the surface is covered by a thin layer of inhibitors which control the dissolution of carbon steel. Such results have been reported earlier [42].

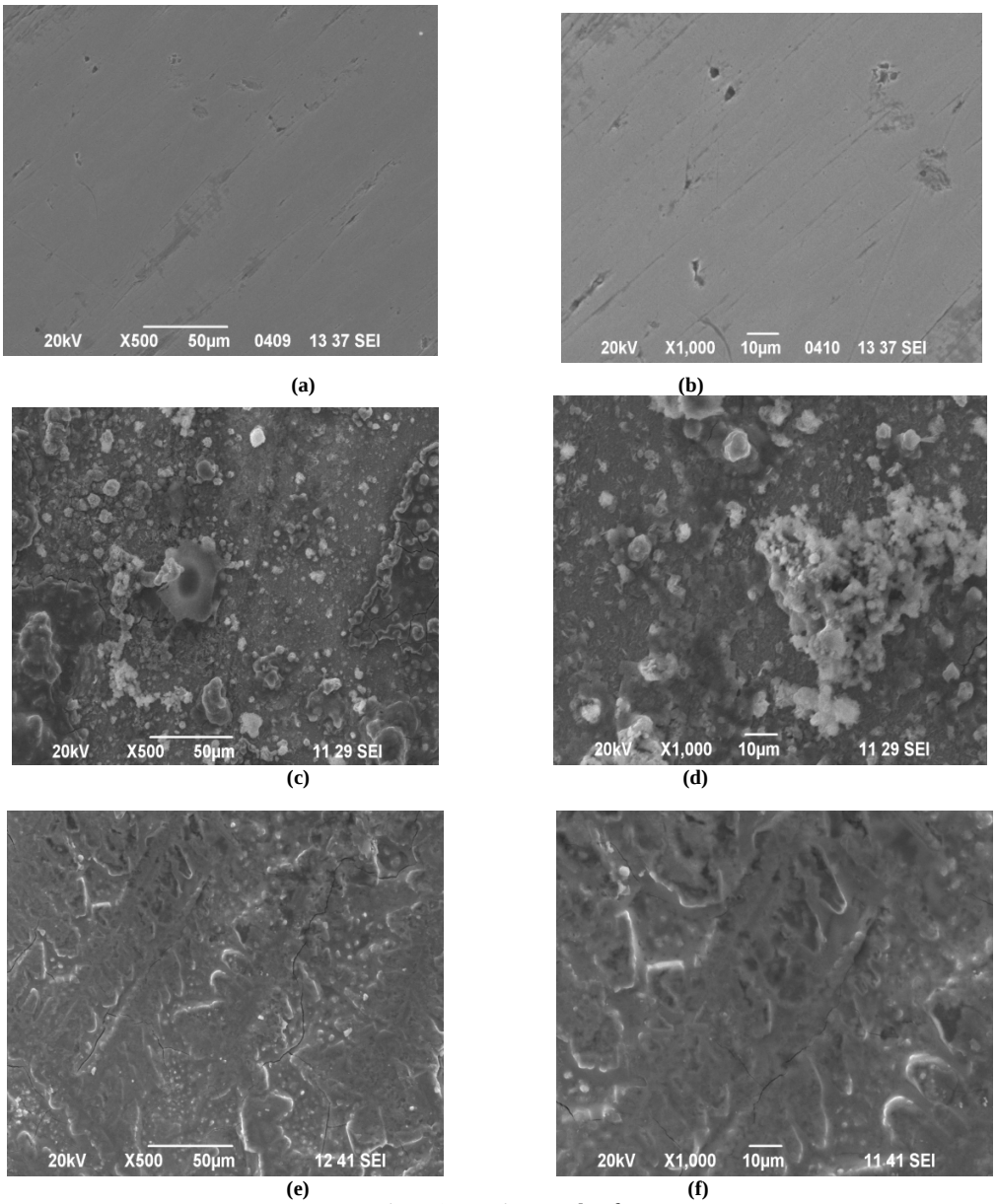
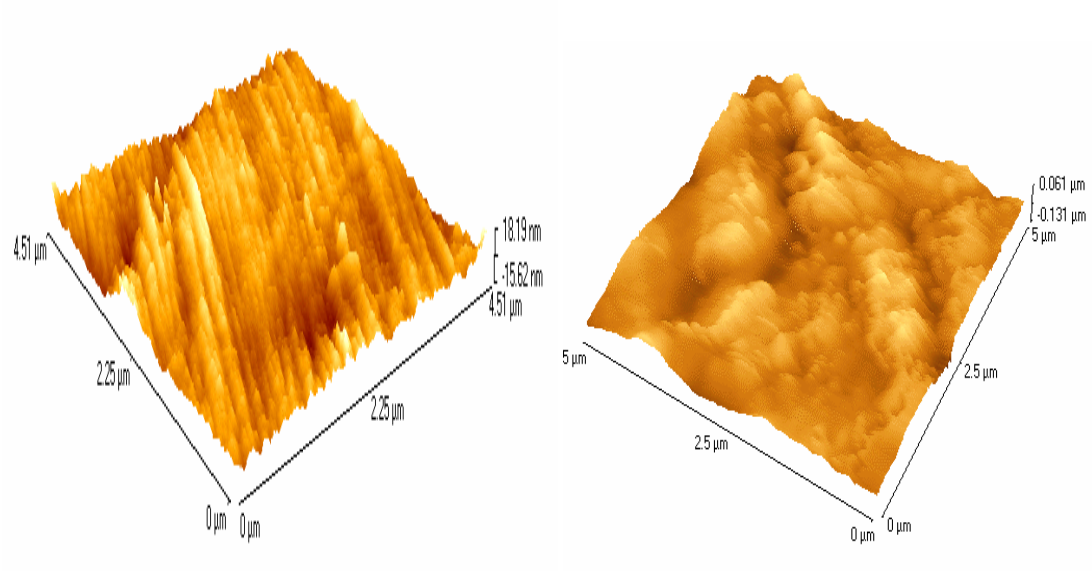


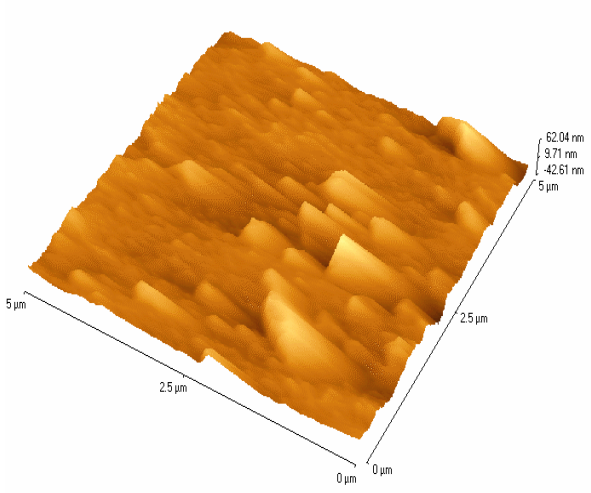
Fig : 4 SEM micrographs of
a),b) polished Carbon steel (control) - Magnifications-X 500,X 1000
c),d) Carbon steel immersed in sea water - Magnifications-X 500, X 1000
e),f) Carbon steel immersed in sea water containing 8mL of TUL- Magnifications -X 500 X 1000.

AFM is a powerful technique to investigative the surface morphology at nano- to micro-scale and has become a new choice to study the influence of inhibitor on the generation and the progress of the corrosion at the metal/solution interface [43-46]. The three dimensional (3D) AFM morphologies and the AFM cross-sectional profile for polished carbon steel surface (reference sample), carbon steel surface immersed in sea water (blank sample) and carbon steel surface immersed in sea water containing the formulation of 8ml of TUL in 1M HCl are shown as Fig:5 images (a, d,), (b, e,), (c, f,) respectively. Root– mean-square roughness, average roughness and peak-to-valley value AFM image analysis was performed to obtain the average roughness, Ra (the average deviation of all points roughness profile from a mean line over the evaluation length), root-mean-square roughness, Rq (the average of the measured height deviations taken within the evaluation length and measured from the mean line) and the maximum peak-to-valley (P-V) height values (largest single peak-to-valley height in five adjoining sampling heights) [44]. Fig:5 (a, d,) displays the surface topography of un-corroded metal surface. The value of Rq, Ra and P-V height for the polished carbon steel surface (reference sample) are 4.5 nm, 3.6nm and 35.58 nm respectively. The slight roughness observed on the polished carbon steel surface is due to atmospheric corrosion.

Fig: 5 (b, e,) displays the corroded metal surface with few pits in the absence of the inhibitor immersed in sea water. The (Rq), (Ra), (P-V) height values for the carbon steel surface are 28.2nm, 19.8nm and 92.6 nm respectively. These data suggests that carbon steel surface immersed in sea water has a greater surface roughness than the polished metal surface, which shows that the unprotected carbon steel surface is rougher and was due to the corrosion of the carbon steel in sea water environment. Fig:5 (c, f,) displays the steel surface after immersion in sea water containing 8ml of TUL . The (Rq), (Ra), (P-V) height values for the carbon steel surface are 11.19nm, 8.40nm and 67.60nm respectively The (Rq), (Ra), (P-V) height values are considerably less in the inhibited environment compared to the uninhibited environment. These parameters confirm that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} - TUL (Eugenol) complex thereby inhibiting the corrosion of carbon steel [44].

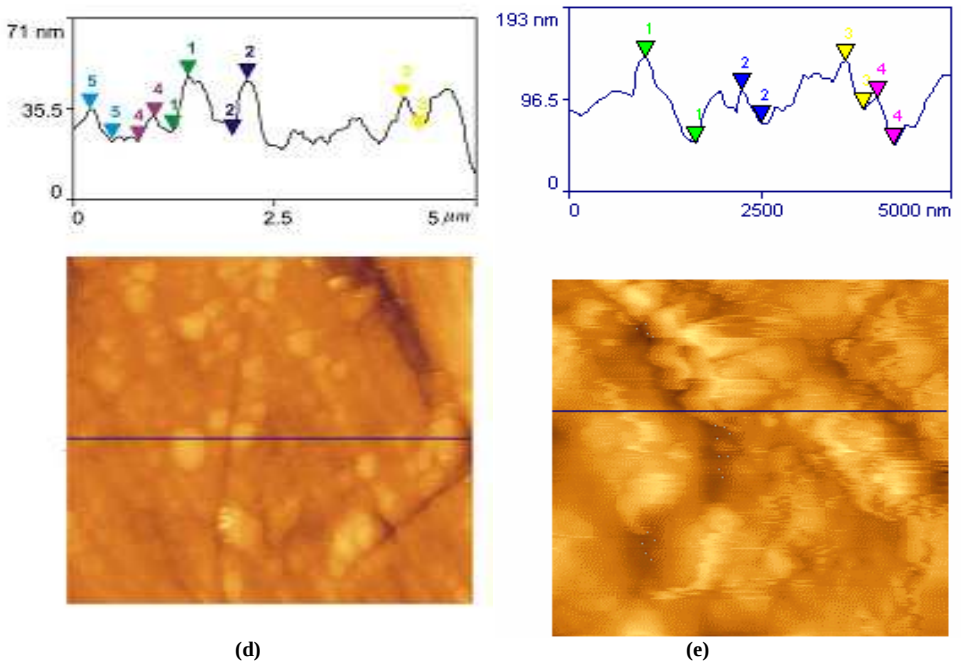


(a) **(b)**

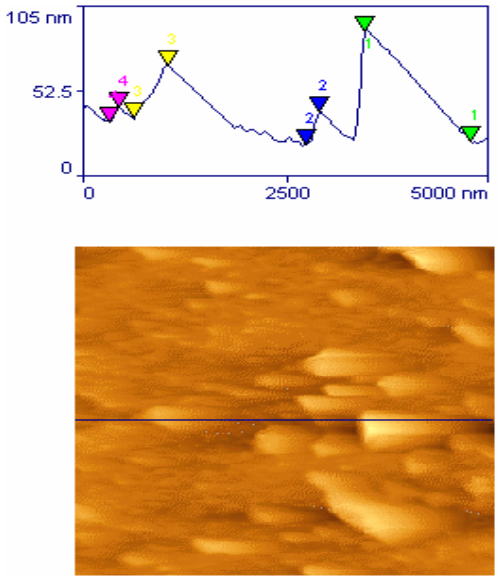


(c)

Fig: 5 Three dimensional AFM images of the surface of
a) As polished carbon steel (control)
b) Carbon steel immersed in sea water (blank)
c) Carbon steel immersed in sea water containing TUL (8 ml)



(d) **(e)**



(f)

Fig: 5 AFM cross-sectional images of the surface of
d) As polished carbon steel (control)
e) Carbon steel immersed in sea water (blank)
f) Carbon steel immersed in sea water containing ASF (4ml) + Zn^{2+} (25ppm).

CONCLUSION

From the overall experimental results the following conclusions can be deduced

- Tulsi acts as a good inhibitor for corrosion of steel in 1M HCl.
- Tulsi 10g / 100mL(8mL / 100 mL) gives 90% inhibition efficiency.
- Polarization study reveals that the formulation functions as mixed inhibitor.
- AC impedance spectra reveal that a protective film is formed on the metal surface.
- The SEM micrographs and AFM images confirm the formation of protective (nano) layer on the metal surface.

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