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Evaluation the Inhibition of Steel in Petroleum medium by *Tobacco* Leaves Extract

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Abstract— **This work involves study the corrosion inhibition of steel in petroleum medium using alcoholic extracted of *Tobacco* leaves with four concentrations of extracted (1, 3, 5 and 7mL/L) at four temperatures over the range 50 – 80 ^{o}C. Inhibition efficiency IE% results show that 7 mL/L is the best concentration, which it's gave efficiencies in the range of 72.69 – 76.78%. Polarization curves indicate that *Tobacco* extract is an anodic inhibitor through the values of corrosion potential. The increasing of concentration led to increase the efficiency, while the increasing of temperature results variation in efficiencies due to verity in cathodic and anodic sites on steel surface. Arrhenius relationship shows the increasing of activation energy in presence of *Tobacco* extract and the highest energy was in the presence of 7 mL/L of extract. AFM images illustrate the roughness of steel surface and they showed that the roughness was lower compared with unhibited surface.**

Keywords- ***Tobacco* extract; Activation energy; Roughness of inhibited surface.**

I. INTRODUCTION

There are more than 70 species of tobacco. Further uses of tobacco are in plant bioengineering and as ornamentals, and chemical components of tobacco are used in some pesticides and medications. The addictive alkaloid nicotine is popularly considered the most characteristic constituent of tobacco but the harmful effects of tobacco consumption can also derive from the thousands of different compounds generated in the smoke, including polycyclic aromatic hydrocarbons, formaldehyde, cadmium, nickel, arsenic, tobacco – specific nitrosamines, phenols, and many others. Tobacco also contains beta – carboline alkaloids which inhibit monoamine oxidase. Despite containing enough nicotine and other compounds such as germacrene and anabasine and other piperidine alkaloids.

Alkaloids are a group of naturally occurring chemical compounds that contain mostly basic nitrogen atoms. This group also includes some related compounds with neutral and even weakly acidic properties. Some synthetic compounds of similar structure are also attributed to alkaloids. In addition to carbon, hydrogen and nitrogen, alkaloids may also contain oxygen, sulfur and more rarely other elements such as chlorine, bromine, and phosphorus [1]. Alkaloids are produced by a large variety of organisms, including bacteria, fungi, plants, and animals, and are part of the group of natural products (also called secondary metabolites). Many alkaloids can be purified from crude extracts by acid-base extraction. Organic inhibitors generally have heteroatoms. O, N, and S are found to have higher basicity and electron density and thus act as corrosion inhibitor. O, N, and S are the active centers for the process of adsorption on the metal surface. The inhibition efficiency should follow the sequence O < N < S < P.

Many authors highlighted to use natural products as inhibitors for some of metals and alloys in 0.5 M hydrochloric acid at ambient temperature extracts by *kola* plant and *tobacco* in different concentrations as 'green' inhibitors [2], *Acacia* trees (Gum Acacia) in acidic media [3], and extracts of *centella asiatica* as green corrosion inhibitor for mild steel in 0.5 M H_2SO_4 [4]. Sangeetha et al. used an aqueous extract of asafoetida as a corrosion inhibitor in controlling corrosion of carbon steel. The main constituent of this extract is umbelliferone[5]. Benali et al. studied the corrosion and inhibition behaviors of mild steel in sulfuric acid + 5% EtOH in the presence of *tannin* extract of *Chamaerops humilis* plant and potassium iodide [6]. Fouda et al. studied the inhibiting effect of some quinazoline derivatives on the corrosion of carbon steel in 2M HCl [7]. Rajam et al. evaluated the inhibition efficiency (IE) of an aqueous extract of *garlic* in controlling corrosion of carbon steel in well water in the absence and presence of Zn^{2+} [8]. Iloamaeka et al. studied the use of leaves extract of *Emilia sonchifolia* and *Vitex doniana* as corrosion inhibitors of mild steel in 2.5M HCl medium [9]. Khaled and Ebenso investigated the inhibition performance of cerium sulphate tetrahydrate on the corrosion of steel in 1.0 M HCl solutions [10]. The aim of present work is attempt to inhibit the corrosion of steel in petroleum medium by ethanolic extracted of *Tobacco* leaves in temperatures range 50 – 80^{o}C using electrochemical studies supported by AFM analysis.

II. MATERIALS AND METHODS

Materials and solutions

Steel 37-2 was used in this work (chemical composition wt%: 0.121 C, 0.22 Si, 0.44 Mn, 0.014 P, 0.016 S, 0.041 Cr, 0.002 Mo, 0.022 Ni, 0.02 Al, 0.002 Co, 0.055 Cu and Fe remain) obtained by SpectroMAX. Cubic steel (10x10x3mm) with a square surface area (1cm^2) was used in all experiments. The specimen was mounted by hot mounting using formaldehyde (Bakelite) at 138^{o}C for 8 minutes to insulate all but one side and made a hole on one side for electrical connection and then the mounted specimens has been grinded with SiC emery papers in sequence of 400, 600, 1000, and 2000 grit to get flat and scratch-free surface and polished to mirror finish using polish cloth and alpha alumina 0.5μm and 1μm, and then washed with distilled water, degreased with acetone. The base electrolyte was petroleum medium obtained from Iraqi oil refinery with contents of metals: 48.67% C, 8.73% H, 0.13% N, and 0.71% S. The pH of this medium is 5.25, electrical conductivity is 300 μS/cm, and TDS 296 mg/L.

Extraction of *Tobacco* leaves was achieved by washing the leaves by distilled water and then drayed and grounded and then identified by FTIR spectra Model Shimadzu using KBr. Ethanolic extract obtained by dissolving 5 gm of grounded leaves in 200 mL ethanol and then heated at 45^{o}C. The obtained extract was filtered by using Whatmann filter paper and concentrated to 100 mL and then identified by HPLC analysis with column dimension 25 x 4.6 cm, 75methanol/25water as solvents, λ=280 nm, and flow rate 1.8 m/min.

Four volumes of ethanolic *Tobacco* extract were used as green inhibitor includes 1, 3, 5 and 7 mL/L at four different temperatures 50, 60, 70 and 80^{o}C.

Electrochemical Measurements

Electrochemical cell was composed of platinum counter electrode, prepared steel specimen as working electrode and saturated calomel electrode (SCE) as a reference electrode according to ASTM standard cell G5-94. The electrochemical behavior of steel in inhibiting and uninhibited solution was studied by WINKING M Lab potentiostat by recording anodic and cathodic galvanodynamic polarization curves. Measurements were carried out by changing the electrode current automatically from -15 to +15 mA at scan rate 1 mA.sec^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion parameters.

Atomic Force Microscopy characterization (AFM)

The steel specimen immersed in blank and in the inhibitor solution for a period of 15 days was removed, rinsed with double distilled water, dried and subjected to the surface examination. Atomic force microscopy (Angstrom Advanced Inc.USA, AA3000 220V) was used to observe the sample's 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.

III. RESULTS AND DISCUSSION

Fig. (1) shows FTIR spectrum of *Tobacco* leaves which identify the presence of C—H stretch in vinylic, aromatic and acetylenic hydrocarbons at 2970.48 and 2928.04cm^{-1} conjugated with C—H stretch of aldehyde(—CHO), C═O stretch at 1649.19cm^{-1}. In other hand, can be seen N—H stretch of aromatic secondary amine is strong at 3743.96cm^{-1} which may be corresponding to nicotine that is the main constitute in tobacco, and C—N stretch at 1114.89cm^{-1}. HPLC analysis of *Tobacco* extract is shown in Fig. (2) which indicates the presence of some components such as coumarin at retention time 2.439 min, nicotine at 2.876 [11] and rutin at 1.606 and 1.771 min. Tobacco consists of at least 3,800 chemical constituents. Among them, rutin is an important polyphenolic secondary metabolite in tobacco, which has positive actions such as antiallergic, anti-inflammatory and vasoactive, antitumor, antibacterial, antiviral and anti-protozoal properties [12].

Electrochemical study was carried out to evaluate the inhibition efficiency of *Tobacco* extract as inhibitor using Galvanostatic test at scan rate 1 mA/sec., the data of corrosion were estimated by Tafel extrapolation method and they listed in Table (I). Fig.(3) shows the polarization curves of steel 37-2 in petroleum medium in absence and presence four concentrations of *Tobacco* extract at 50^{o}C which illustrates the cathodic region where the reduction of hydrogen ions take place, and the anodic region represented by oxidation of iron to ferrous ions. Generally, the presence of *Tobacco* extract shifted the corrosion potentials to noble direction, i.e. *Tobacco* extract acts as anodic inhibitor, and the corrosion current densities to lower values.

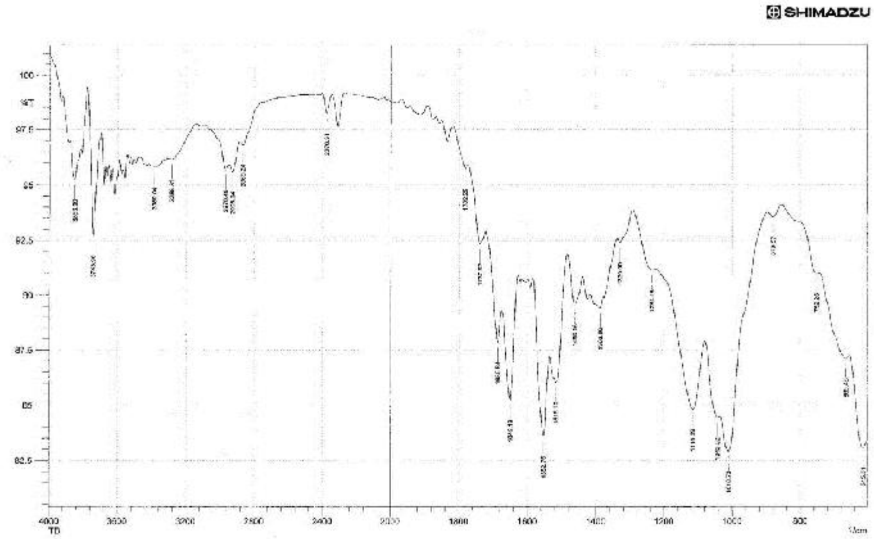


Figure 1. FTIR spectrum of Tobacco leaves.

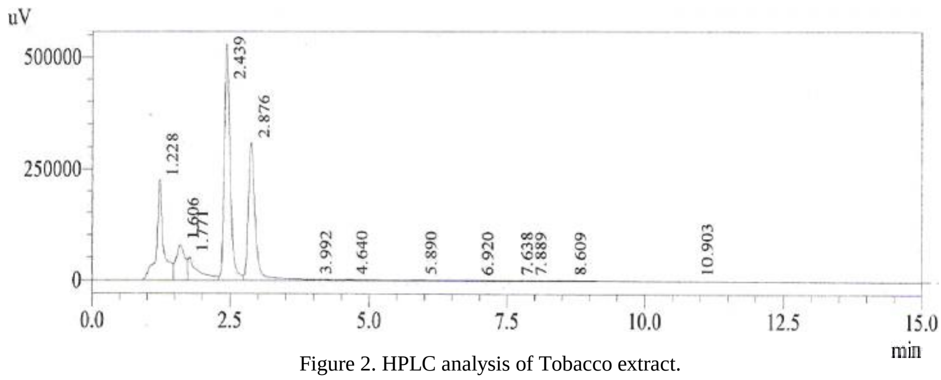


Figure 2. HPLC analysis of Tobacco extract.

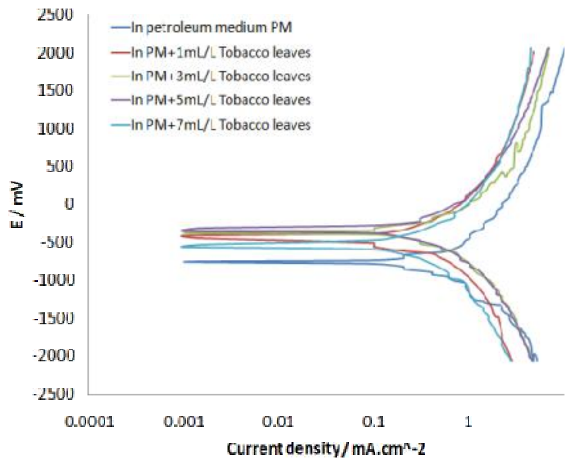


Figure 3. Tafel plots of carbon steel in petroleum medium in the presence of four concentrations of *tobacco* extract at 50^{o}C.

TABLE I. CORROSION PARAMETERS OF STEEL IN PETROLEUM MEDIUM IN ABSENCE AND PRESENCE OF TOBACCO EXTRACT AT FOUR TEMPERATURES.

Conc. of extracted	***Temp.K***	***E_{corr}/mV***	***i_{corr}/μA.cm^{-2}***	***IE%***
0	323	-759.8	497.68	-
	333	-622.0	682.72	-
	343	-550.2	694.09	-
	353	-665.1	719.78	-
1 mL/L	323	-428.6	205.70	58.66822
	333	-435.5	236.26	65.39431
	343	-425.1	211.54	69.52268
	353	-549.3	247.87	65.56309
3 mL/La	323	-375.3	205.89	58.63004
	333	-389.7	222.95	67.34386
	343	-414.8	226.82	67.32124
	353	-428.3	260.09	63.86535
5 mL/L	323	-354.1	165.91	66.66332
	333	-437.2	166.58	**75.60054**
	343	-539.4	199.66	**71.23428**
	353	-509.5	261.68	63.64445
7 mL/L	323	-540.3	120.15	**75.85798**
	333	-388.9	158.54	**76.77818**
	343	-506.3	174.05	**74.92400**
	353	-407.5	196.58	**72.68888**

The latter result can be notice it through the values of inhibition efficiency which calculated according to equation (1), as well as the inhibition increased with increasing the concentration of *Tobacco* extract as shown in Fig. (4).

$$IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \quad .....(1)$$

Where $(i_{corr})_a$ and $(i_{corr})_p$ are the corrosion current density (μA.cm^{-2}) in absence and presence of the inhibitor, respectively. The increasing of temperature led to variation in behavior of efficiency due to vary of cathodic and anodic sites on steel surface.

Langmuir isotherm was tested for its fit to the experimental data. The plots of C/θ against C for the *Tobacco* extract at four temperatures in the range 323 – 353 K were straight lines (Fig. 5) indicating that the extract obeys Langmuir adsorption isotherm which given by the following equation[13]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad ......(2)$$

where, K_{ads} is the equilibrium constant of the adsorption-desorption process, θ is the degree of surface coverage and C is concentration of inhibitor in the bulk solution. The linear regression coefficient close to unity, hence, adsorption of inhibitor followed Langmuir adsorption isotherm. R^2 values were 0.977, 0.996, 0.996 and 0.984 at 323, 333, 343 and 353K respectively. The Langmuir isotherm is based on the assumption that each site of metal surface holds one adsorbed species. Therefore, one adsorbed H_2O molecule is replaced by one molecule of the inhibitor adsorbate on the steel surface. The apparent free energy of adsorption (ΔG^o_{ads}) is calculated from the following relation [13]:

$$\Delta G^o_{ads} = -2.303RT \ log 55.5\ K_{ad} \quad ......(3)$$

The values of K_{ads} and ΔG^o_{ads} are shown in Table (II).

The negative values of ΔG^o_{ads} indicated the spontaneous adsorption of *Tobacco* extracts. The values of K_{ads} are relatively small indicating that the interaction between the adsorbed extract molecules and steel surface is physically adsorbed. This is also supported by lower negative (ΔG^o_{ads}) values.

The activation energies (E_a^*) for the corrosion process in absence and presence of *Tobacco* extract was evaluated from Arrhenius equation [14]:

$$\log C_R = \log A - \left[\frac{E_a^*}{2.303\ RT}\right] \qquad \text{.....(4)}$$

where C_R is the corrosion rate ($g/cm^2.min$), A is the constant frequency factor and E_a^* is the apparent activation energy, R is the gas constant (8.314 $J.mol^{-1}K^{-1}$) and T is the absolute temperature. By plotting of logarithm of the corrosion rate of steel in petroleum medium in absence and presence of *Tobacco* extract versus the reciprocal of absolute temperature range (323 – 353 K), give straight lines with slope equal to ($-E_a^*/2.303R$) as represented in Fig. (6). The data of activation energy are listed in Table (III) which demonstrate that, the presence of *Tobacco* extract in petroleum medium increase the values of E_a^* comparing to its unhibited. Adsorption of the organic molecules occurs as the interaction energy between molecule and metal surface is higher than that between the H_2O molecule and the metal surface. The protection efficiency and the degree of surface coverage θ change with temperature [15]. This change is incorporated in the value of apparent activation energy (E_{app}^*). The more sensitive protection efficiency and the degree of surface coverage to temperature changes, the larger are the differences in activation energy between the inhibited and uninhibited solutions. To eliminate this effect, the activation energy should be determined at a constant surface inhibitor activity, i.e. at a constant degree of surface coverage[16]. Also the apparent activation energy (E_{app}^*) depend on the many factors according to the following equation:

$$E_{app}^* = E_a^* + \beta F(\phi - \psi_2) \qquad \text{.........(5)}$$

where E_a^* the activation energy not depended on the potential of electrode, β the transfer coefficient, F faraday number, the total difference in potential at electrical double layer, and ψ_2 Zeta potential.

Where the adsorbent particles which increase the Zeta potential ψ_2 is decreases the apparent activation energy for corrosion reaction, while the adsorbent particles which decrease the Zeta potential ψ_2 lead to increasing in the apparent activation energy.

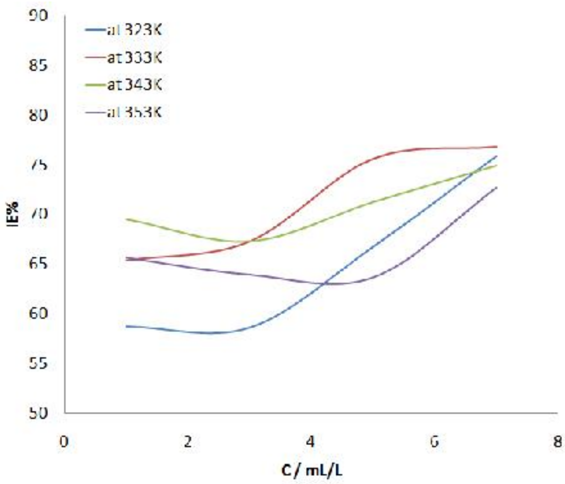


Figure 4. Relationship between inhibition efficiencies and concentrations of *Tobacco* extract at four temperatures.

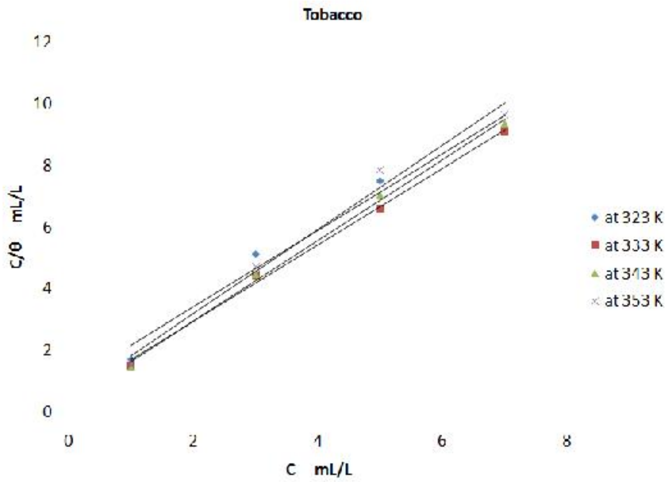


Figure 5. Langmuir adsorption plots for steel in petroleum medium with different concentrations of *Tobacco* extracts at four temperatures.

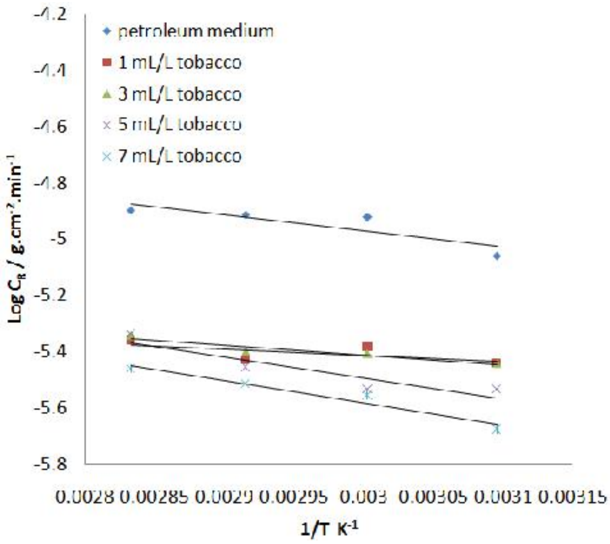


Figure 6. Arrhenius plots of the corrosion rate for steel in petroleum medium in absence and presence of *Tobacco* extract.

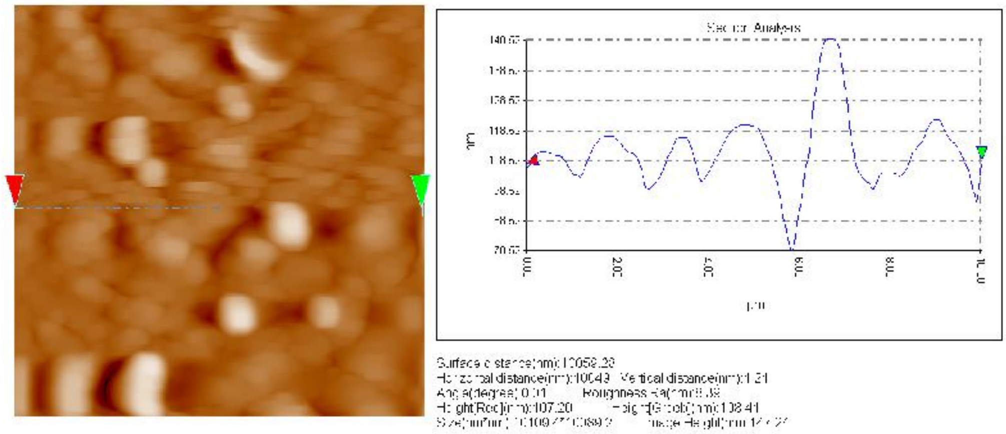
TABLE II. THERMODYNAMIC FUNCTION FOR ADSORPTION OF TOBACCO EXTRACT IN PETROLEUM MEDIUM AT FOUR TEMPERATURES.

Conc.	***Temp. K***	K_{ads}	ΔG^o_{ads}/kJ.mol^{-1}
1 mL/L	323	1.419433	-11.4688
	333	1.889672	-12.5987
	343	2.281163	-13.5022
	353	1.903853	-13.3769
3 mL/L	323	0.472404	-8.57924
	333	0.687408	-9.86052
	343	0.686690	-10.1537
	353	0.589133	-10.0099
5 mL/L	323	0.399934	-8.14184
	333	0.619672	-9.57963
	343	0.495265	-9.24227
	353	0.350116	-8.51618
7 mL/L	323	0.44888	-8.44509
	333	0.472323	-8.84439
	343	0.426749	-8.82698
	353	0.380218	-8.75294

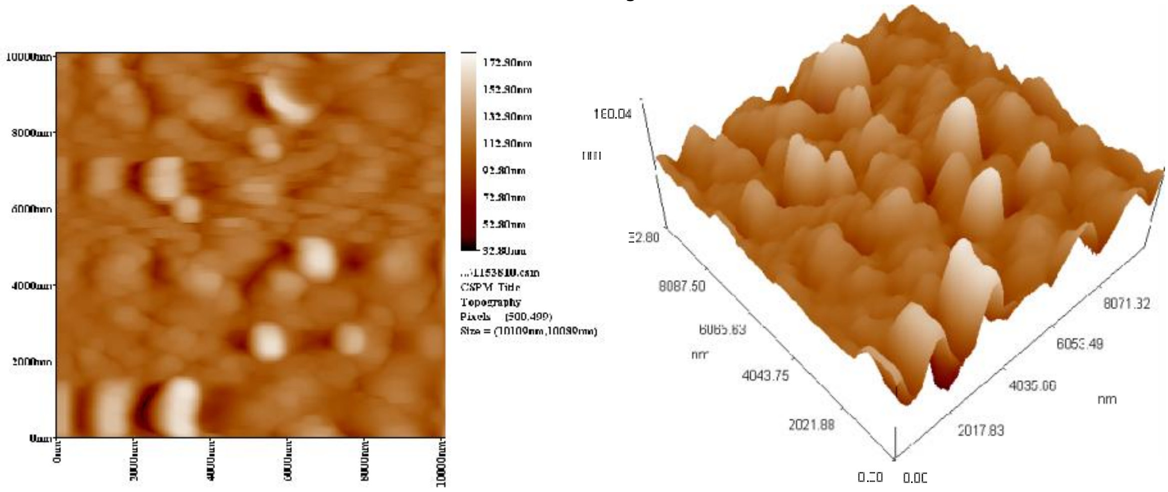
TABLE III. ACTIVATION ENERGIES FOR ADSORPTION OF TOBACCO EXTRACT ON STEEL IN PETROLEUM MEDIUM.

Extract	***Conc./ mL/L***	E_a^*/ kJ.mol^{-1}
Petroleum medium	-	10.57
Tobacco	1	4.15
	3	6.63
	5	14.21
	7	14.65

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 [17-20]. The two dimensional (2D), three dimensional (3D) AFM morphologies and the AFM cross sectional profile for polished steel surface (reference sample), steel surface immersed in petroleum medium (blank sample) and steel surface immersed in petroleum medium containing 7mL/L Tobacco extract (the best concentration) are shown in Figs. (7) to (9). The value of roughness Ra for the polished carbon steel surface is 8.39 nm, the slight roughness observed on the polished steel surface is due to atmospheric corrosion. Figure (8) displays the corroded metal surface with few pits in the absence of the inhibitor immersed in petroleum medium, with Ra 44.7 nm. These data suggests that steel surface immersed in petroleum medium has a greater surface roughness than the polished metal surface, which shows that the unprotected steel surface is rougher and was due to the corrosion of the steel in petroleum medium. Fig. (9) displays the steel surface after immersion in petroleum medium containing 7mL/L *Tobacco* extract, the Ra value is 5.89 nm. This parameter confirms that the surface is smoother. The smoothness of the surface is due to the formation of a compact protective film of Fe^{2+} − Tobacco extract complex thereby inhibiting the corrosion of steel. The results of AFM were agreement with the results of Khaled and Ebenso [10] and Sangeetha et al. [5] when they used the AFM technique for corrosion inhibition measurements.

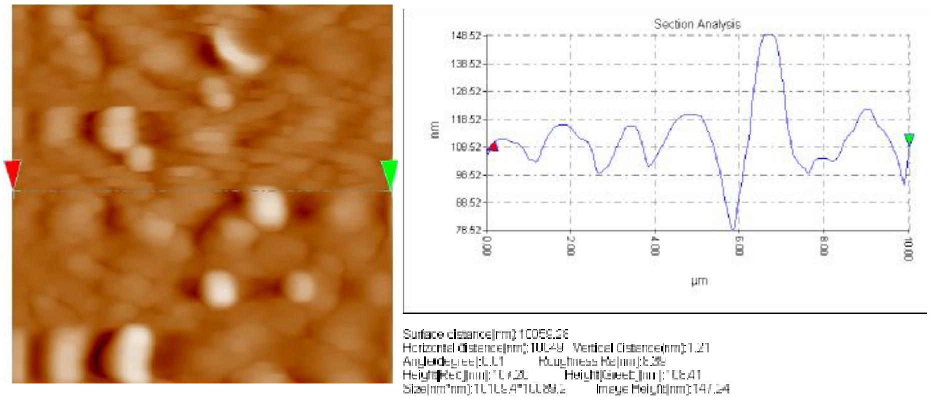


Cross-sectional image

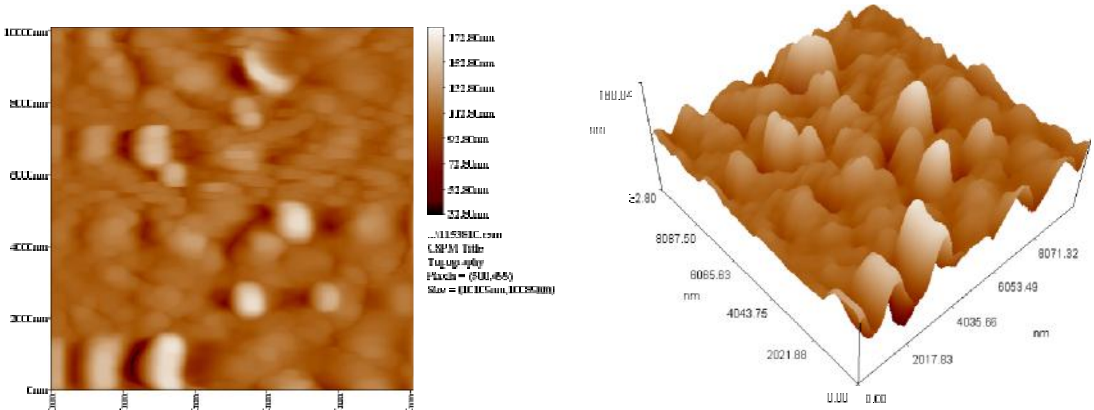


2D ***3D***

Figure 7. AFM images of the surface of as polished steel.

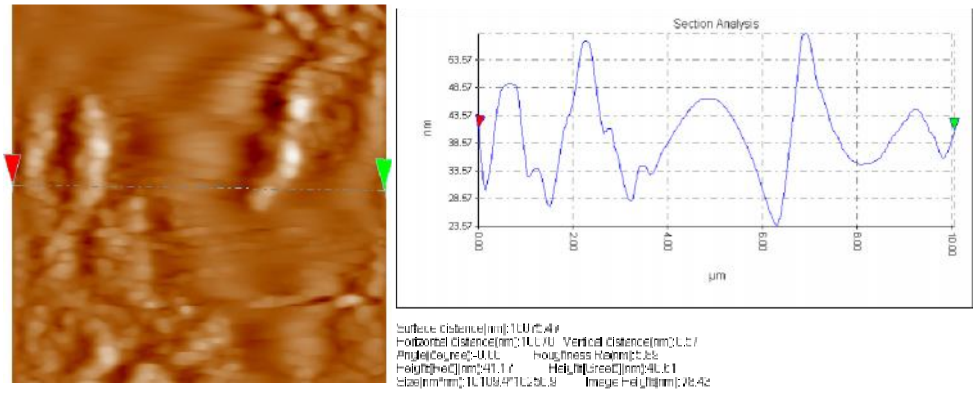


Cross-sectional image

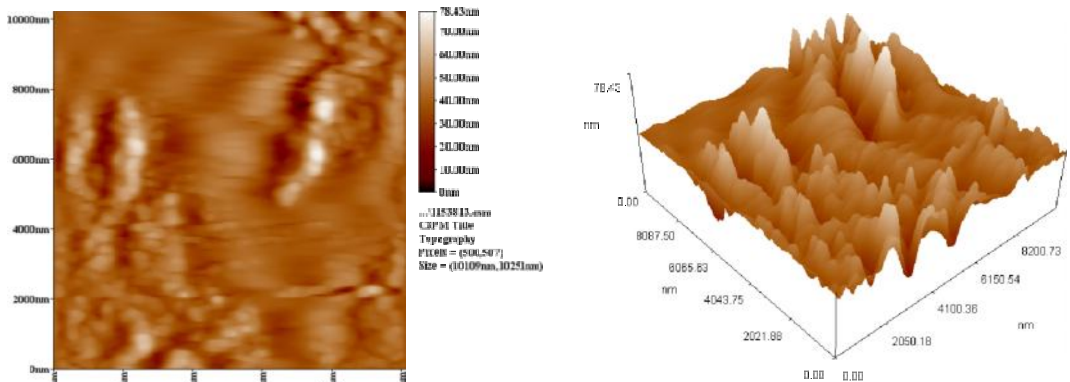


2D ***3D***

Figure 8. AFM images of the surface of steel immersed in petroleum medium (blank).



Cross-sectional image



2D ***3D***

Fig. (9): AFM images of the surface of steel immersed in petroleum medium containing 7mL/L Tobacco extract.

IV. CONCLUSION

Tobacco leaves extract was used to inhibit the corrosion of steel 37-2 in petroleum medium at different temperatures in the range 50 - 80 oC, and gave acceptable efficiencies which increase with increasing the concentration of extract from 1 to 7 mL/L in petroleum medium. 7mL/L of *Tobacco* extract gave inhibition efficiencies from 72.69 to 76.78%. FTIR spectrum shows the most important peaks for components of *Tobacco* leaves, while HPLC analysis indicates the retention times of coumarin, nicotine and rutin in *Tobacco* extract. *Tobacco* extract was obeying Langmuir isotherm with small values of equilibrium constant and the change in free energy of adsorption, i.e., the adsorption of *Tobacco* extract is physically adsorption. Activation energies also calculated which were higher than that for the case of uninhibited medium; this means that the *Tobacco* extract acts as barrier to isolate the metallic surface from aggressive medium. The best concentration of *Tobacco* extract was 7mL/L which gave lower roughness of film formed on steel surface compared with polished and corroded surface.

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