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Corrosion Inhibition Effect and Adsorption Activities of methanolic myrrh extract for Cu in 2 M HNO_3

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Myrrh extract was tested as inhibitor on the corrosion of Cu in 2M HNO_3 solution. These Tests were done by several procedures like weight loss procedure (WL), Potentiodynamic polarization (PL), electrochemical frequency modulation (EFM) and AC impedance spectra (EIS). The Cu surface was examined by utilizing atomic force microscope (AFM), scanning electron microscopy (SEM), Fourier transform infra-red (FT-IR) techniques. PL curves give indication that the myrrh acts as mixed type inhibitor. The WL, EIS and EFM results displayed that the inhibition efficiency (%IE) rise with myrrh concentration achieving 91.8% at 300 ppm, while it lowered by raising the temperature. Therefore, the results indicate that Myrrh extract has potential to be a corrosion inhibitor for Cu in acidic environment. The Langmuir adsorption isotherm agreed with the obtained results from WL method. Finally, it was found that the obtained results from several techniques are in approximately agreement.

Keywords: Myrrh extracts, corrosion inhibition, Cu, nitric acid, adsorption

1. INTRODUCTION

Cu is a metal has good advantages, so it used in many important fields. Cu metal enters in many industries like heat exchanger, condenser, electrical wiring, connectors and printed circuit boards. The corrosive solution has bad effect on Cu metal when its concentration increases and also it becomes susceptible for corrosion [1-3]. Nitric acid is used in chemical cleaning and pickling, so it is the best medium to do research on Cu corrosion [4-6]. It is possible to use organic compounds as inhibitors for corrosion due to they contain nitrogen (N), oxygen(O) and sulfur (S) atoms but there is a problem for using these compounds in large quantities due to their toxicity [7,8]. In the present work, the researches aimed to obtain the eco-friendly corrosion inhibitor which has many advantages like low cost, safe on the environment and giving high inhibition efficiency [9]. The presence of plant extracts leads to develop corrosion inhibitors because these natural compounds are non-toxic, acceptable, readily available, renewable and can prepared by easy methods [10-14]. The corrosion inhibitors can be produced from any parts of the plant and this is depending on the way of extracting. Multiple parts of the plant like seeds, flowers and leaves can be used to obtain a lot of green inhibitors to prevent corrosion [15-25]. Many plant extracts were used as inhibitors for Cu in acidic medium such as Fruit [26] Azadirachta Indica [27] Strychnos nuxvomica, Piper longum and Mucuna pruriens seed [28] Ceratonia siliqua [29] Carapichea Ipecacuanha [30]. The good IE of these plant extracts due to the presence of organic compounds and heterocyclic constituents in their molecular structure. These organic compounds have large adsorption centers, and this is due to presence of polar functions with N, O and S atoms [31]. Commiphora Myrrha is a type of the trees which having barbed branches. These trees grow in Oman, Yemen, Somalia, North Africa and Southwest Saudi Arabia. When the leg of this tree was cut, there is a natural resin or gum secretes from the tree and this material is called myrrh [32]. Myrrh was used in medicine as an ingredient in toothpastes and mouthwashes due to its antiseptic properties and also it can be used in perfumes. The chemical composition in myrrh contains compounds from the furano sesquiterpene family. This family includes furanoeudesma-1,3-diene, lindestrene and dihydro pyrocurzerenone, which combined around 19% of the essential oil that can be obtained from the myrrh resin. Finally, the modern researches explained that the myrrh extracts have anti-inflammatory properties, which have pain killing properties [33].

In this study, Myrrh extract was tested for Cu corrosion inhibition in 2 M nitric acid by many techniques such as WL, EIS, PL and EFM techniques. The achieved results have confirmed by utilizing FT-IR spectroscopy and AFM microscope.

2. EXPERIMENTAL

2.1 Preparation of Cu coupon

Cu coupons have the chemical composition in weight %: 0.009 Al, 0.001 Ni, 0.002 Si, 0.004 Mn and balance Cu. The Cu rod was cut to certain dimension for using in WL and electrochemical tests. The appropriate dimension for Cu pieces to use in WL method is (2×2×0.1 cm) x 2 and to use in electrochemical methods is 1×1 cm. The Cu pieces were scraped with 800, 1200 and 2000 grade of emery papers before use in the experiment. The Cu was cleaned with bidistilled water then it was dried. Finally, the perfect weight of the Cu metal was recorded using electronic digital balance.

2.2 Chemical composition of myrrh extract

The myrrh extract is widely studied and its chemical composition is well known before [34, 35].The myrrh extract contains, Caryophyllene, 1,4-Methanoazulene, (3R-trans), Longifolene-(V4), decahydrate-4,8,8-trimethyl-9-methylene-,[1S-(1`a,3a´a,4`a,8a´a)], [s-(E,E)]-, Naphthalene, 1,2,3,5,6,7,8,8a-octahydro-1,8a-dimethyl-7-(1-methyl phenyl)-, [1S-(1`a,7`a,8a`a)], ,decahydrate-1,1,7-trimethyl-4-methylene-, [1aR-(1a`a, 4a´a,7`a,7a´a,7b`a)], meso-Hydrobenzoin,9(1H)-

Phenanthrene,2,3,4,4a,10,10a-hexahydro-4a-methyl-,cis, Benzenemethanol 3-methoxy-a-phenyl, Cyclohexane methanol, 4-ethenyl-`a,`a,4-trimethyl-3-(1-Methylethenyl)-, [1R-(1`a,3`a,4´a)], Testosterone

2.3 Preparation of the plant extract

The dried Commiphora Myrrh was cleaned and crushed to fine powder. The plant samples were dried in oven at 45°C for one day. Fine powdered sample (50 g) was extracted with (250 ml) methanol for 12 h by using Soxhlet apparatus. The extracts that obtained from the previous procedures had filtered then the filtrates had focused under reduced pressure and freeze-dried to yield a solid form. Concentrated solution (1000 ppm) of the myrrh has utilized to prepare different concentrations of the extract and this had done by dilution with bidistilled water. The different concentrations of myrrh extract that used in our tests were in the range between 50 ppm up to 300 ppm. Figure (1) shows the main chemical components in myrrh extract.

2.4 Weight loss (WL) test

Glass beaker of volume 100 ml was used in this method. The temperature of the experiment was controlled by using water bath. The Cu pieces were prepared as previously mentioned in Cu preparation. The solution of 100 ml of 2M nitric acid only and with addition of different concentrations of myrrh extract were prepared for immersion of Cu pieces for 3 hours at temperature range from 25°C to 45°C. After every 30 min of the test the Cu was removed from the corrosive solution, washed with bidistilled water, dried and then weighed carefully by sensitive balance. WL tests were carried out in triplicate to check the reproducibility. The (% IE) could be calculated from the average WL values that obtained according to the following Eq. (1).

$$IE\ \% = \Theta \times 100 = [1 - (W_{inh} / Wi_{free})] \times 100 \quad (1)$$

Where F_{ree} is the average WL of Cu in acid only and W_{inh} of acid in presence of different concentrations of myrrh extract

2.5 Effect of Temperature

The effect of temperature on the Cu corrosion was studied at different temperatures as 25-45°C for 3 hours. The results obtained from this study could be used for calculating the inhibition efficiency (IE %), and some activation and adsorption parameters.

2.6 Electrochemical procedures

The electrochemical techniques have performed using PCI4-G750 Potentiostat/Galvanostat and a personal computer with Gamry PCI4-G750 software for measurements. The utilized electrical circuit include of three electrodes (SCE reference electrode, Pt auxiliary electrode and brass electrode). 1 cm^2 of the Cu electrode is ready, and cleaned as illustrated in WL test. All electrochemical studies were performed at 25 ±1 °C. (PL) is a beneficial method due to they give more information about the corrosion protection and the factors influence the corrosion procedure and hindrance behavior of the myrrh extract. This is done by determining the potential- current appearances of the Cu/ solution system. In PL test, electrode potential from –1000 to 1000 mV was applied at scanning rate 1 mVs^{-1} [36]. The (%IE) and (ϴ) were determined by using (i_{corr}) according to the following mathematical eq. (2).

$$IE\% = \Theta \times 100 = [1 - (i_{corr(inh)} / i_{corr(free)})] \times 100 \qquad (2)$$

Where $i_{corr(free)}$ is the corrosion current density for Cu in HNO_3 and $i_{corr(inh)}$ for Cu in acid with appending of various concentration of the myrrh extract.

EIS technique had utilized frequency range is between 100 kHz and 0.1 Hz and AC signal is 10 mV peak to peak. % IE and θ were obtained by employing the next relation:

$$\% \ IE = 100 \ x \ \theta = 100 \ x \ [1 - (R^{\circ}_{ct} / R_{ct})] \qquad (3)$$

Where R°_{ct} and R_{ct} are the resistances nonexistence and existence inhibitor, separately
Influence EFM tests reached with decision for the frequencies of range 2 and 5Hz by on three contentions [37]. The higher peaks have applied to given i_{corr}, Causality factors (CF-2 & CF-3) and (β_c & β_a).

2.7 Surface analysis

The Cu metal was dipping 2M nitric acid only and in acid with appending of greater concentration of myrrh extract for three hours, detached from acid and dried. The formed protected film on the surface of Cu had analyzed by using three tests such as AFM, SEM and FT-IR spectroscopy. The device (AFM) that used in the materials research was obtained from Nan surf Company, Germany. The type of this device is Flex-Axiom. This device was used to obtain the images for the Cu surface. This image expresses the changes in surface morphology which happen at several hundred nanometers. This changes in surface morphology occurred owing to the creation of film on Cu surface in presence of inhibitors [38]. The scan range XYZ of all AFM images is 100×100×10 µm at a scan speed of 60 ms/line. The type of FTIR device is Thermo scientific Nicolet 10 spectrophotometer. This device was used for analysis of the film on the Cu surface and the inhibitor used. A frequency range 4000 – 400 cm^{-1} was applied in this analysis. The Cu piece after preparing as previously was put in 2M nitric acid in presence of inhibitor for 3 hours, then the Cu was taken away from acid, washed with bidistilled water, dried and the FTIR spectra of the film formed on the Cu surface was recorded.

3. RESULTS AND DISCUSSION

3.1 WL method

Figure (1) shows WL experiments for Cu corrosion in 2M Nitric acid only and also in presence of various concentrations of myrrh. The (% IE) that obtained from this process shown in Tables 1&2. It observed that the IE improves with raising the myrrh concentration and lowered gradually when the temperature increases from 25°- 45°C. The IE and θ were determined as mentioned in Eq. (1). Inhibitory effect against corrosive acid was due to the adsorption of myrrh on the Cu surface. Leads to limit the dissolution of Cu and this happened when the myrrh molecules block the corrosion sites. The adsorption process can be done through the interaction among lone pairs of electrons of the oxygen atom of myrrh components with Cu surface due to existence of low energy d orbital in the Cu. Consequence, the corrosion process was inhibited due to the formation of complexes among vacant d orbital of Cu and free electrons of the extract [39].

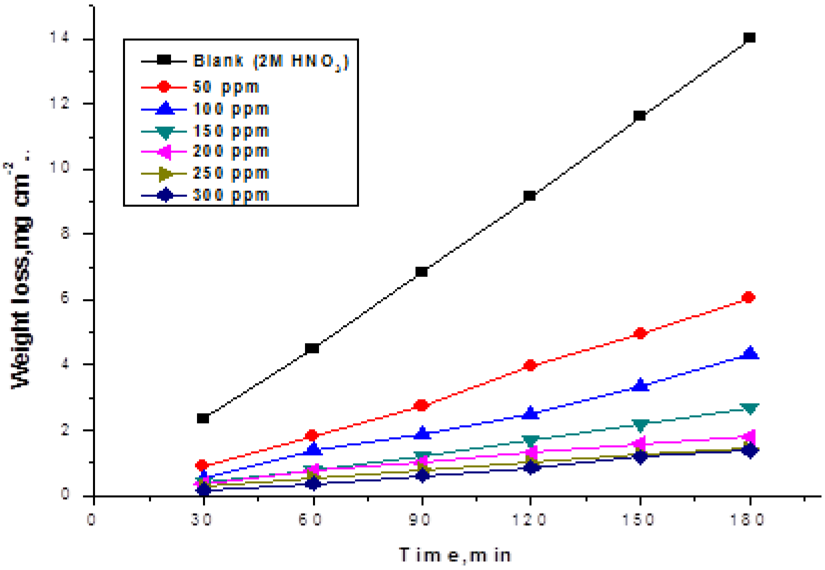


Figure 1. WL-time graph for Cu in 2M nitric acid only and also in presence of various concentrations of myrrh extract at 25°C

3.2 Temperature influence of and activation parameters

The temperature raising leads to increase the degradation of Cu in 2M nitric acid. It was established that the presence of myrrh leads to decrease the corrosion rate than the acid solution without extract. Table 2 shows that by raising the temperature of the medium IE decreases, this is proved that the kind of adsorption of this extract on Cu surface is physical adsorption. From Arrhenius-type equation some activation parameters were calculated such as (E_a^*), (ΔH^*) and (ΔS^*) for Cu corrosion in 2M nitric acid only and also in presence of varying concentrations of the myrrh according to the following mathematical eq.(4):

$$\text{Rate } (k_{corr}) = Ae^{-Ea/RT} \quad (4)$$

The transition state as follows:

$$\text{Rate } (k_{corr}) = \frac{RT}{Nh} e^{\frac{\Delta s^*}{R}} e^{\frac{-\Delta H^*}{RT}} \quad (5)$$

where A is the frequency factor and h is the constant Planck's.

Kinetic parameters were determined from Fig. 2 which is graphs between log k_{corr} and (1/T). Figure 3 displays the diagrams among log (k_{corr}/T) and (1/T) for the myrrh extract. The results of the activation parameters for Cu are shown in Table 3. From Table 3, it was established that the presence of myrrh leads to improve the values for (E_a^*) and (ΔH^*) and in contrast of this, these values are lower in absence of the extract. These results showed that the extract under study has good protection efficiency. There is also a similarity between improve in the data of the IE and raising the data of (E_a^*) and (ΔH^*). The adsorption of this myrrh on the Cu leads to rise the (E_a^*) of Cu degradation and this can be done by creation a barrier to charge and mass transfer. It was found that the increase of (ΔH^*) due to presence of myrrh explains the raising of the height of corrosion reaction to a certain extent and this depends on the type and extract concentration. Also, the existence of the extract leads to increase of the positively of entropy (ΔS^*). The positive sign of entropy designates that improve in disordering happens in transmission process from reactants to the activated complex. This shows that the Cu surface was protected by an ordered stable layer of the extract [40].

Table 1. (k_{corr}), θ and %IE values determined from WL process for Cu corrosion in 2M HNO_3 only and also in presence of varying concentrations of myrrh at 25°C

Concentration [ppm]	k_{corr} x10^{-3} [mg cm^{-2} min^{-1}]	θ	IE [%]
2M Nitric acid	76	-----	----
50	33	0.566	56.6
100	21	0.728	72.8
150	14	0.817	81.7
200	11	0.855	85.5
250	8	0.892	89.2
300	7	0.908	90.8

Table 2. Results obtained from raising the temperature to 45°C on Cu corrosion in 2M nitric acid also in acid in presence of various concentrations of myrrh extract

Con. [ppm]	Temp. °C	k_{corr}, x10^{-3} [mg cm^{-2} min^{-1}]	ϴ	IE %
50	30	76	0.531	53.1
	35	153	0.516	51.6
	40	354	0.461	46.1
	45	878	0.456	45.6
100	30	50	0.692	69.2
	35	103	0.675	67.5
	40	244	0.628	62.8
	45	619	0.617	61.7
150	30	33	0.796	79.6
	35	69	0.782	78.2
	40	171	0.739	73.9
	45	443	0.726	72.6
200	30	27	0.833	83.3
	35	58	0.817	81.7

	40	145	0.779	77.9
	45	387	0.76	76.0
250	30	22	0.864	86.4
	35	48	0.848	84.8
	40	125	0.809	80.9
	45	341	0.789	78.9
300	30	18	0.889	88.9
	35	41	0.87	87.0
	40	107	0.837	83.7
	45	282	0.825	82.5

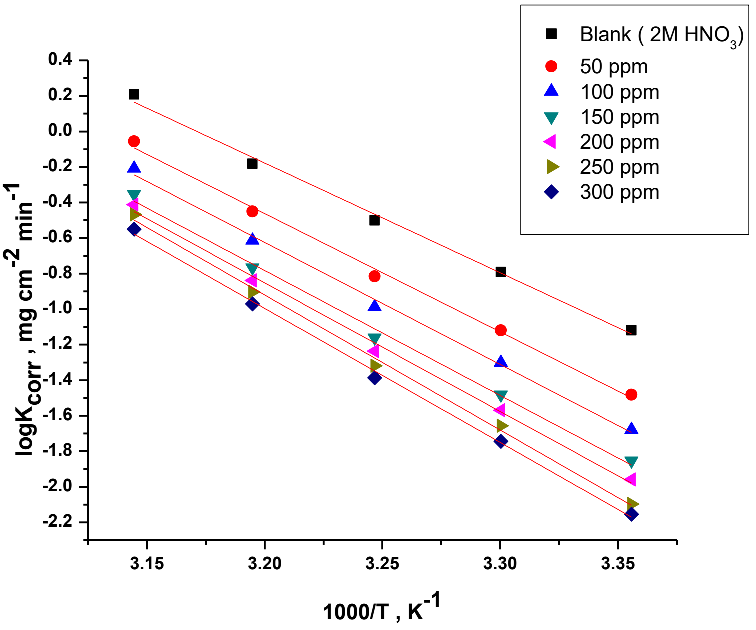


Figure 2. Log k_{corr} vs 1/T graphs for Cu dissolution in 2M nitric acid only (blank) and in presence of different concentrations of myrrh extract

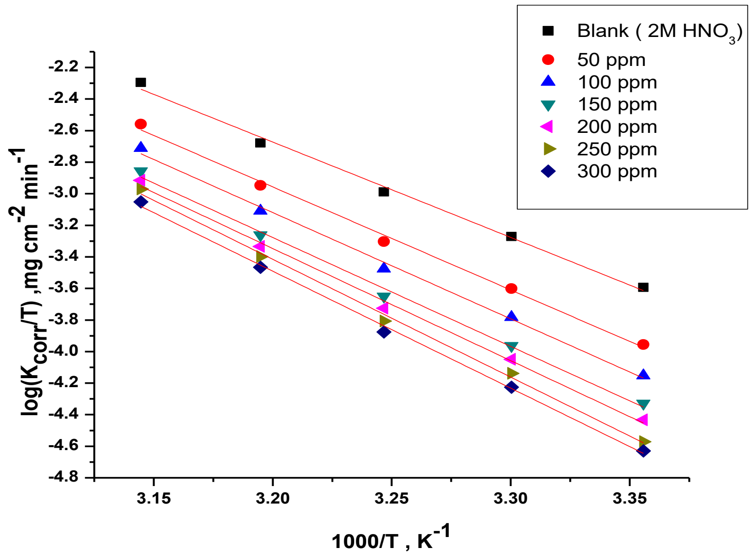


Figure 3. Log (k_{corr} / T) vs 1/T graphs for Cu dissolution in 2M nitric acid (blank) and in presence of varied myrrh extract concentrations

Table 3. Influence of varied concentrations of myrrh extract on the E_a^*, $\Delta S^*$and $\Delta H^*$of Cu dissolution in 2M nitric acid

Con. [ppm]	E_a^*, [kJ mol^{-1}]	ΔH^*, [kJ mol^{-1}]	ΔS^*, [J mol^{-1} K^{-1}]
blank	118.2	115.6	121.4
50	127.5	124.9	145.7
100	131.5	128.9	155.3
150	134.6	132.1	162.3
200	138.5	136.1	173.8
250	145.5	142.9	192.9
300	146.4	143.8	195.1

3.3 Adsorption isotherms

(ϴ) of the adsorbed molecules of the myrrh on the Cu surface was evaluated by %IE ratio. Different isotherms were applied to the obtained data from several curves by fitting these results. Figure 4 shows the graphs between ϴ/1-ϴ and concentration of myrrh extract (C). This diagram shows a straight line and gives the correlation coefficient approximately equals unity. The good value of correlation showed that the type of adsorption of myrrh extract on the Cu surface is obeyed by Langmuir isotherm. The criteria for Langmuir isotherm is: i) assume the surface of Cu is homogeneous, ii) All sites are equivalent iii) each site can hold at most one molecule (mono-layer coverage only) and iv) there is no interaction between the adsorbate molecules on adjacent sites [41]. The standard free energy of adsorption ($\Delta G°_{ads}$) can be determined from the data of the equilibrium constant (K_{ads}). The constant (K_{ads}) of the adsorption can be calculated by the following mathematical eq. (6) [42]:

$$K_{ads}C = \Theta / 1\text{-}\Theta \qquad (6)$$

$$K_{ads} = 1/55.5e^{\frac{-\Delta G°ads}{RT}}, \qquad (7)$$

Where 55.5 expresses to the concentration of water species with the unit (mol L^{-1}) at metal/solution interface. The thermodynamic parameters obtained are shown in Table 4. The results showed that $\Delta G°_{ads}$ has – ve sign .indicating the spontaneousity of the adsorption process. $\Delta G°_{ads}$ values about-20 kJ mol^{-1} or less, the adsorption is due to an electrostatic interaction between the charged Cu and the charged molecules of the extract (physical adsorption). Values of $\Delta G°_{ads}$ are about -40 kJ mol^{-1} or more, due to the transfer of electrons from the extract molecules to the Cu surface (chemisorption) [43].The Van't Hoff equation was used to calculate the heat of adsorption ($\Delta H°_{ads}$) as follows [44]:

$$\ln K_{ads} = -\frac{\Delta H°ads}{RT} + \text{const.} \qquad (8)$$

The graph between log K_{ads} and 1/T for Cu dissolution in 2M nitric acid in presence of myrrh extract appears in Figure 5. From the results in Table 4, it is shown that the adsorption is an exothermic processs due to the negative values of the heat of adsorption $\Delta H°_{ads}$ [45]. The standard adsorption entropy ΔS°_{ads} can be determined from the following mathematical eq.:

$$\Delta S^{\circ}_{ads} = \frac{\Delta H°ads - \Delta G°ads}{T} \qquad (9)$$

From the calculated data in Table 4, it appears that the ΔS°_{ads} values have a negative sign. This negative value proves that the adsorption is an exothermic process [46]. All the thermodynamic parameters determined were listed in the following Table 4.

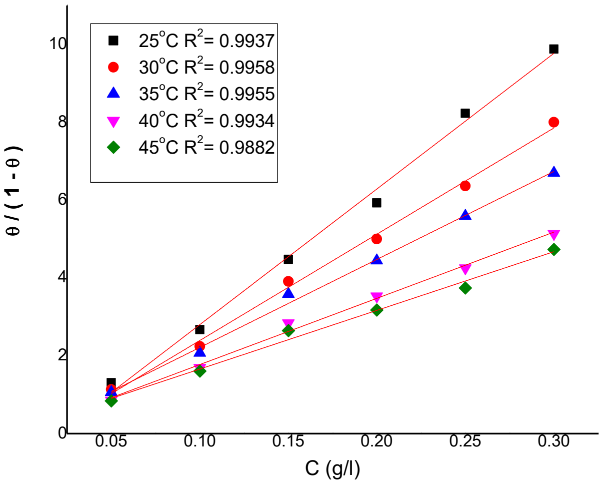


Figure 4. Langmuir adsorption plots for the adsorption of myrrh extract on Cu in 2M nitric acid at varied temperatures

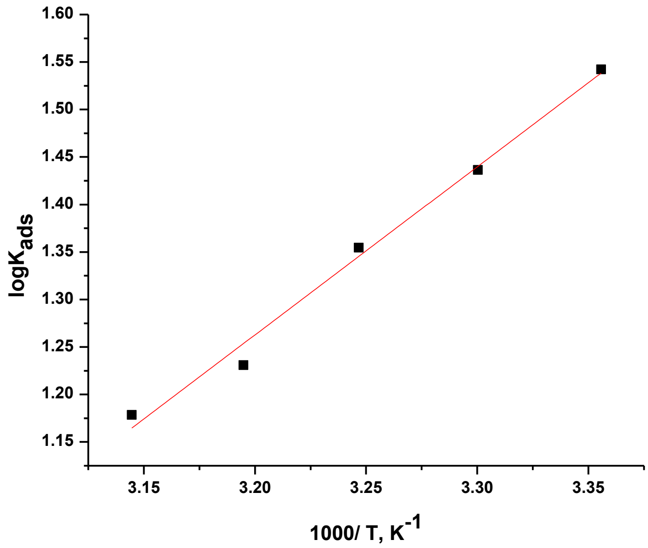


Figure 5. Log K_{ads} vs. 1/T plot for Cu degradation in 2M nitric acid in presence of myrrh extract

Table 4. Parameters for Cu dissolution in 2M HNO_3 in presence of myrrh extract at various temperatures

Temp. [C°]	K_{ads} [g^{-1} l]	- ΔG°_{ads} [kJ mol^{-1}]	- ΔH°_{ads} [kJ mol^{-1}]	- ΔS°_{ads} [J mol^{-1} K^{-1}]
25	34.85	18.8	33.9	50.8
30	27.31	18.5		50.9
35	22.62	18.3		50.7
40	17.02	17.8		51.3
45	15.08	17.8		50.6

3.4 Effect of myrrh on OCP

Figure 6 represents the OCP for Cu corrosion in presence and absence of varying concentrations of myrrh. From the plot, it was observed that the Cu metal is stabilized at positive values compared to the other metals [47]. At the first 300 sec, there was a drop in OCP and this is due to dissolution of the oxide film formed on the surface of Cu. In existence of myrrh, the OCP start at positive region then shifted cathodically according to the increasing the concentrations of extract and this is indicating that the metal has a high ability to resistant corrosion. The inhibitor can be classified as a cathodic or anodic type according to E_{ocp} shift. When the difference in values of E_{ocp} between the first measuring and other measuring is at least ±85 mV, it can be classified as a cathodic or anodic inhibitor. In this study, it was shown that the difference in values of E_{ocp} is about 14 mV indicating that the myrrh extract act as mixed kind inhibitor [48].

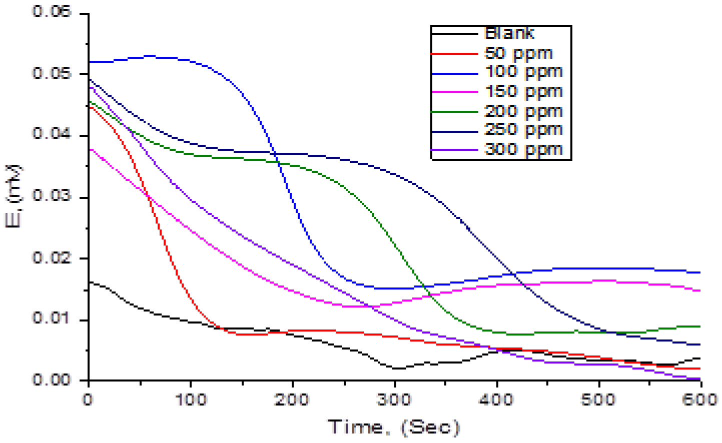


Figure 6. OCP for Cu corrosion in 2M HNO_3 in the presence and absence of various concentrations of myrrh extract

3.5 Effect of myrrh on Tafel polarization (PL) behavior

Figure 7 indicates the outcome data on PL graphs for Cu in 2M nitric acid and 2M nitric acid in presence of varying concentration of the myrrh under study. Parameters obtained from PL that associated to this procedure were record in Table 5 such as (i_{corr}), (E_{corr}), ($ß_a$), ($ß_c$) and (IE %) [49]. From this table, the data of i_{corr} lowered in existence of myrrh extract and hence lowered the C.R. Both cathodic and anodic curves exchange to (i_{corr}) lower in presence of myrrh extract in 2M nitric acid. It was found that the mechanism of Cu dissolution procedure and cathodic oxygen and/or HNO_3 (HNO_3 ---- HNO_2---- H_2O +NO) reduction does not change when adding the myrrh extract and that is owing to the data stability of both cathodic and anodic slopes in presence of myrrh extract. In presence of myrrh extract, (E_{corr}) pass on to negative data but this move is fewer than 85 mV, so myrrh can be categorized as mixed kind inhibitor, but the cathode is more polarized than anode due to cathodic slopes($ß_c$) values are higher than anodic slopes (ß$_a$) values. The %IE values obtained from this technique are in good agreement with the results obtained from the WL technique.

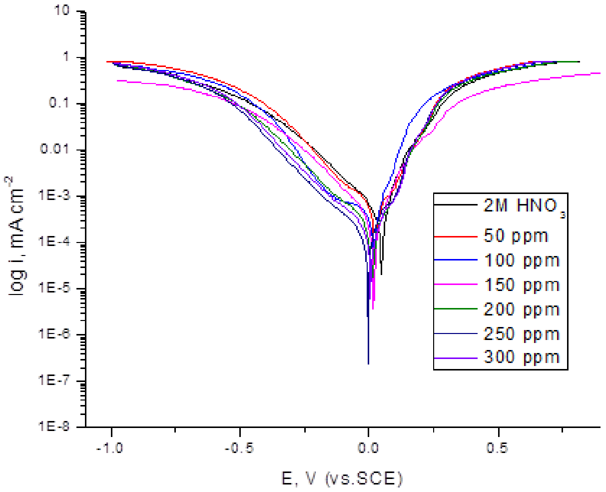


Figure 7. Tafel polarization plots for Cu corrosion in 2M nitric acid and also in presence of various concentrations of myrrh extract

Table 5. Electrochemical parameters at different concentrations of myrrh extract on Cu dissolution in 2 M HNO$_3$ at 25°C

Con. [ppm]	i_{corr} [µA cm^{-2}]	E_{corr} [mV vs. SCE]	β_a [mV dec^{-1}]	β_c [mV dec^{-1}]	k_{corr}. [mpy]	Θ	IE [%]
Blank	766	48	120	254	378.2	-----	-----
50	444	24	107	178	219.2	0.420	42.0
100	228	18	61	205	112.3	0.702	70.2
150	222	19	103	167	109.5	0.710	71.0
200	176	12	96	182	87.04	0.770	77.0
250	140	5.0	113	198	69.07	0.817	81.7
300	132	7.0	90	179	65.01	0.828	82.8

3.6 Effect of myrrh on EIS technique

Figures 9&10 show the Nyquist and Bode plots get for the Cu electrode at corresponding corrosion potentials after half hours dipping in 2M HNO$_3$ without and with various concentrations of myrrh at 25°C. As the myrrh concentration increases, the semi-circle diameter rises. EIS data of the myrrh were analyzed utilized the circuit equivalent, Figure 11, which fits well with our obtained data [50]. The use of CPE for acid-based electrochemical corrosion of metals often yields better approximation [51]. The impedance of the CPE can be represented as:

$$Z_{CPE} = Y_0^{-1}(j\,\omega)^{-n} \qquad (10)$$

Where Y_0 and n signify the CPE constant and exponent, correspondingly, $j = (-1)^{1/2}$.

The double layer capacitance, C_{dl}, for a circuit containing a CPE value (Y^0 and n) were measured from eq. (11) [52]:

$$C_{dl} = 1 / 2 \pi F_{max} R_{ct} \qquad (11)$$

Where f_{max} is the frequency at the maximum altitude of the semicircle [53]. The IE %), the next mathematical balance was applied.

$$IE \% = [1 - (R_{ct(free)}/R_{ct (inh)})] \times 100 \qquad (12)$$

The semi-circle diameter represent the R_{ct}, and inversely proportional to the i_{corr} data. The EIS data was list in Table 6. From the calculated results, it was detected that the R_{ct} data improve with increasing myrrh concentration but C_{dl} values decrease. The adsorption of myrrh on the Cu surface leads to this result. The outcomes data obtained demonstrate that the myrrh works by forming the protective layer on the Cu which modifies the Cu/acid interface.

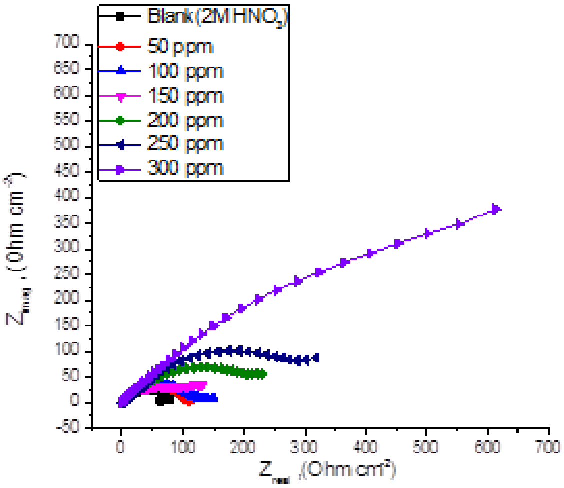


Figure 9. Nyquist plans for Cu in 2M HNO_3 in the presence and absence of different concentrations of myrrh extract

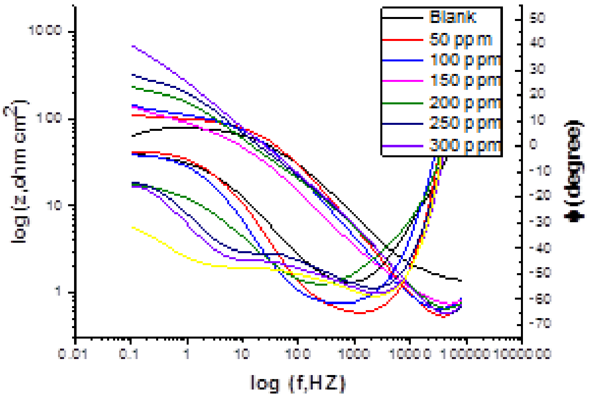


Figure 10. Bode plots for Cu in 2M HNO_3 in the presence and absence of various concentrations of myrrh extract

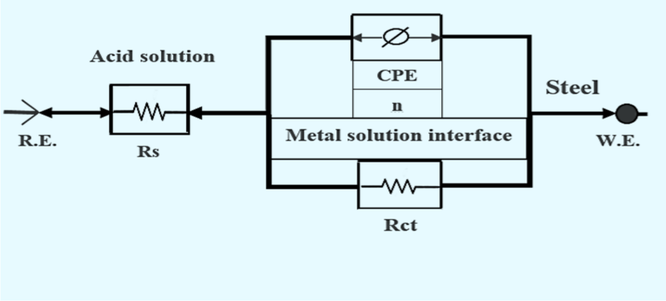


Figure 11. Equivalent circuit used to fit experimental EIS data

Table 6. Parameters from EIS method for Cu corrosion in 2M HNO_3 (blank) with and without different concentrations of myrrh extract

Con. [ppm]	R_{ct} [Ω cm^2]	C_{dl} [μF cm^{-2}]	n	[Θ]	IE [%]
2M HNO_3	75.1	16.3	0.804	-----	-----
50	98.2	7.4	0.810	0.235	23.5
100	115.5	5.7	0.817	0.349	34.9
150	118.0	1.4	0.820	0.364	36.4
200	233.6	0.77	0.825	0.678	67.8
250	327.2	0.65	0.827	0.770	77.0
300	888.2	0.22	0.830	0.915	91.5

3.7 EFM tests

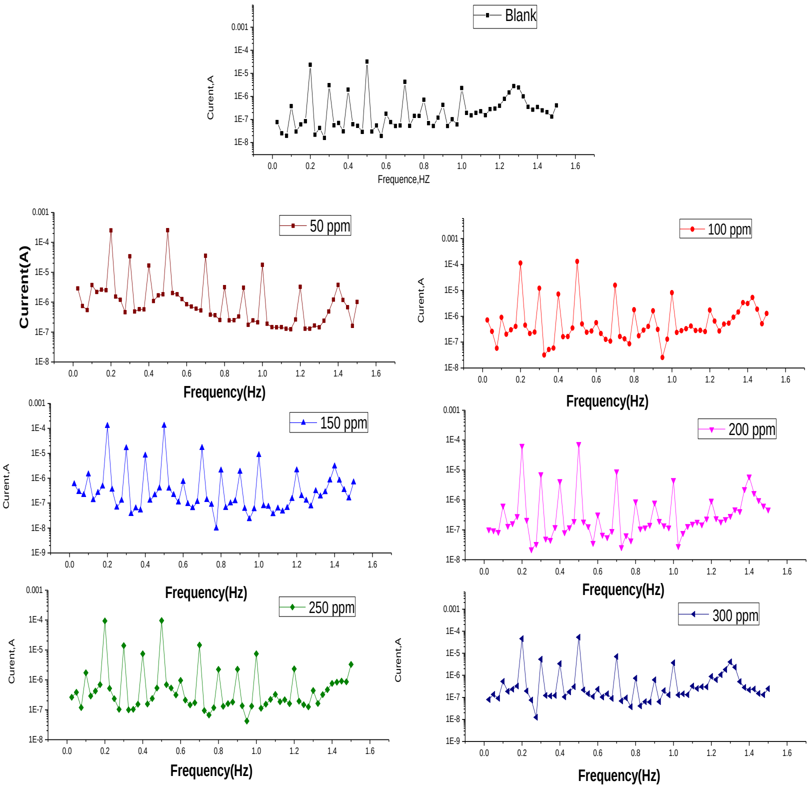


Figure 12. EFM spectra for Cu corrosion in 2M nitric acid alone and also in presence of various concentrations of myrrh extract

EFM for Cu electrode in aggressive medium presence and absence of myrrh extract was draw in Figure 12. Data gotten from EFM were list in Table 7. EFM tests produces varying corrosion parameters such as (IE %), both s (β_a, β_c), (i_{cor}) and (CF-2, CF-3) for Cu liquefaction in 2M HNO_3 in existence of varying concentration of myrrh. It is observed that i_{corr} lowered by raising the myrrh concentration. Also, CF-2 and CF-3 values were very approach to theoretical data and this agrees with the EFM theory [54].

Table 7. EFM data for Cu corrosion in 2M HNO_3 without and with various concentrations of myrrh extract

Conc. [ppm]	i_{corr} [μA cm^{-2}]	β_c [mV dec^{-1}]	β_a [mV dec^{-1}]	CF-2	CF-3	θ	IE_{EFM} [%]
Blank	582.2	403.0	91	2.01	3.53	-----	------
50	251.2	249.4	91	1.82	2.62	0.568	56.8
100	243.9	249.7	83	1.96	2.66	0.581	58.1
150	148.3	282.8	93	1.83	3.05	0.745	74.5
200	140.8	175.7	66	1.93	3.01	0.758	75.8
250	97.34	252.4	85	1.77	2.89	0.832	83.2
300	47.45	203.3	76	1.73	2.64	0.918	91.8

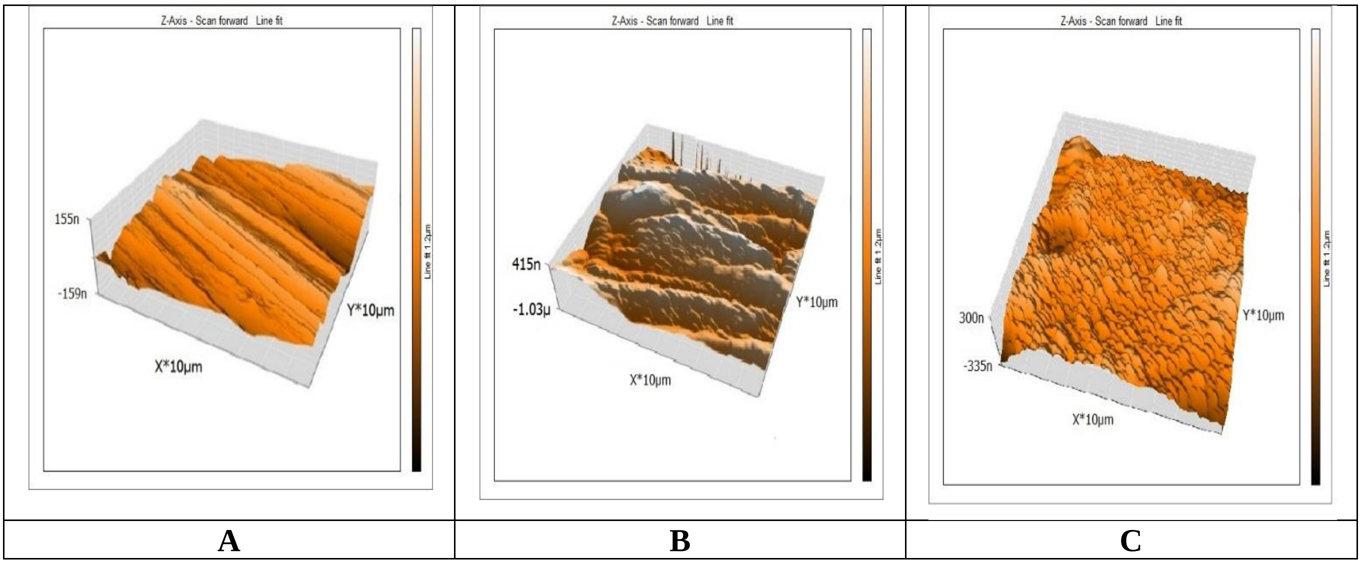
3.8 Analysis surface morphology

3.8.1 AFM technique

AFM is a remarkable technique used for measuring the surface roughness with high resolution [55]. Many details about alpha brass surface morphology can be obtained from AFM tests that help to explain the corrosion procedure. The 3D AFM images represented in Fig (13).The roughness calculated from AFM image has summarized in Table 8. The values showed that the roughness increases with adding 2M HNO_3 due to the corrosion occurs on the Cu surface but lowered with adding the extract.

Table 8. Roughness data obtained for Cu surface by AFM technique

Specimen	Average roughness (R_a), [nm]	RMS roughness (R_q), [nm]
Furbished Cu (standard)	24.87	31.62
Cu in 2M HNO_3	163.06	203.14
Cu in 2M acid and +300 ppm extract	36.03	47.4

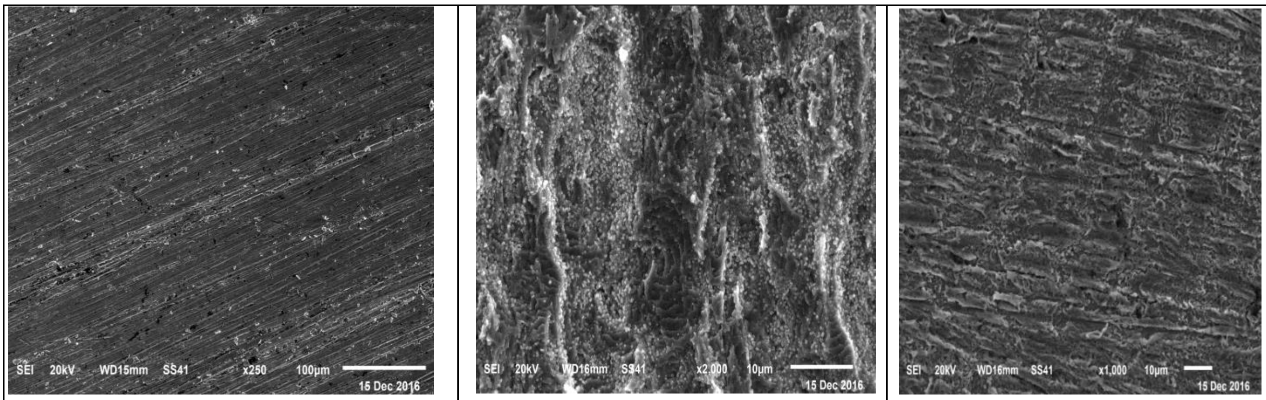


A **B** **C**

Figure 13. Three-dimension AFM images for Cu surface (A) furbished Cu (standard specimen) (B) Cu dipped in 2M nitric acid only (Blank sample) (C) Cu dipped in 2M acid containing 300 ppm of myrrh extract

3.8.2 Scanning electron microscopy (SEM) technique

The adsorption and morphological assessment of Cu in 2M HNO_3 solution was done by SEM without and with 300 ppm examined myrrh extract for 24 h at 298 K. Fig. 14a shows the smooth surface Cu before contact to HNO_3. Fig. 14b demonstrates the Cu surface is intensely corroded in HNO_3, whereas in the existence of the myrrh the Cu is significantly improved (Fig. 14c). This designates the adsorption of myrrh on Cu surface and creates a shield protective to defend from corrosion [56].



(a)Micrograph of pure Cu surface

(b) Micrograph of Cu surface in 2M HNO_3 solution

(c) Micrograph of Cu surface in 2M HNO_3+ 300 ppm myrrh

Figure 14. SEM images of polished Cu (a), Cu dipped in 2 M HNO_3 without extract (b) and Cu dipped in 2 M HNO_3 in presence of Myrrh extract

3.8.3 FT-IR tests

Figure 15 shows the functional groups existing in the myrrh and on the Cu surface. FT-IR technique was used to predict whether inhibitor is adsorbed or not adsorbed on the Cu. The infrared spectrum in myrrh extracts shows in Fig.15a. The spectrum shows a broad band at 3407cm^{-1} which designates the presence of OH group. The peaks at 2969, 2933 cm^{-1} signifies the -CH group. The peak at 1740 cm^{-1} characterizes the C=O group. The peak at 1630 cm^{-1} signifies the C=C group. The peak at 1320 cm^{-1} signifies the -CN group. The peaks at 1248,1023 cm^{-1}represent the -CO group. The examination of the film designed on the Cu is shown in Fig. 15b. It was observed that the -CN group move from 1320 cm^{-1} to 1314 cm^{-1} and -CO group shifted from 1023 cm^{-1} to 1046 cm^{-1}. Also, the C=O shifted from 1740 cm^{-1} to 1764 cm^{-1}. The presence of the peaks lower than 700 cm^{-1} designates the existence of CuO. The disappearance of OH group and appearance CuO indicates the creation of a film on Cu through the oxygen atom [57]. The absence of some peaks of the myrrh approves the myrrh adsorbed of on the surface of Cu.

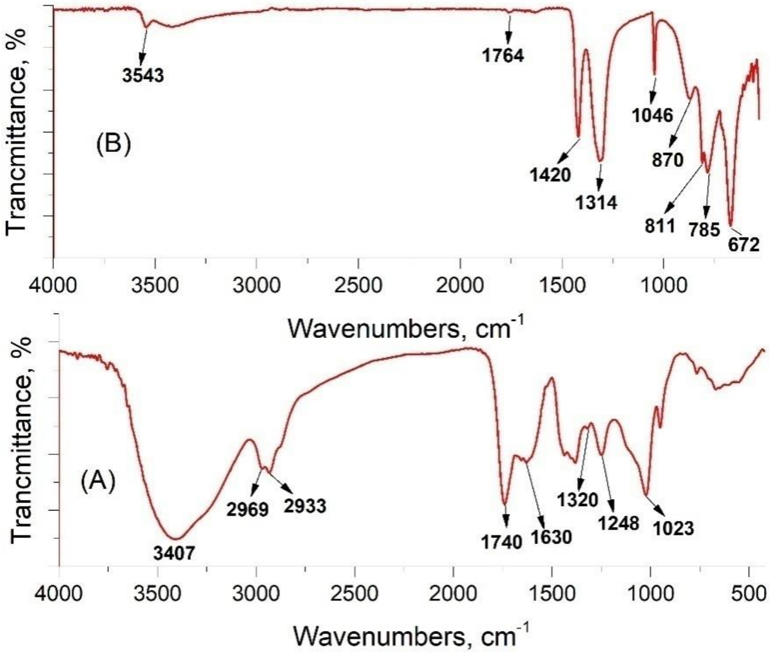


Figure 15. FT-IR spectra for (A) Myrrh extract (crude) and (B) The film formed on the Cu surface after immersion in 2M nitric acid containing 300 ppm of myrrh for 3h

3.9 Mechanism of inhibition

The properties of any inhibition process depend on the electron density at the reaction center. The presence of a polar group with an atom of selenium and phosphorus or sulfur or in some cases nitrogen is very important for the inhibitor [58]. The chemisorption between the metal and inhibitor become stronger with increasing the electron density at the center [59]. The chemical composition of myrrh extract contains many organic composite. The myrrh adsorbed on the Cu surface is the main factor for the inhibition process. Previously, it was found that myrrh composed of photochemical compounds such as furanoeudesma-1,3-diene, lindestrene, and dihydropyrocurzerenone, which combined around 19% of the essential oil. The phyto-chemical compounds characterized by the presence of heteroatom such as oxygen or nitrogen and have to center of the the $\boldsymbol{\pi}$ −eelectron. The properties of these compounds facilitate the adsorption procedure on the Cu surface. Myrrh adsorbed on the Cu surface in HNO_3 could be done in two ways: first, the neutral molecules adsorbed on the metal surface via chemisorption. In this mechanism, water molecules are displaced out of the Cu surface and electrons are shared between the Cu and hetero-atoms of the components of the extract. In addition, adsorption of extract molecules can be done by interactions between donor-acceptor, i.e. among π-electrons of the extract molecules and d-orbital (vacant) of surface atoms. Second, as Cu surface in acid solution has positive charge [60] so the protonated molecules will not come close to the positive Cu surface because of the strong electrostatic repulsion. Also, No_3^- ions cause excess negative charges close to the Cu/solution interface and so, data in more adsorption of positively, the protonated composite adsorb among electrostatic interactions among the positively charged molecules and negatively charged Cu surface. From the data of effect of temperature (IE lowered with temperature raised) and the data of ΔG^o_{ads} (< 20 kJ mol^{-1}) , we can conclude that IE of Cu in 2 M HNO_3 solutions is mostly due to the adsorption on the metal surface via electrostatic interaction.

4. CONCLUSIONS

From the preceding tests, the deductions can be listed as:

Methanolic myrrh extract was effectively utilized as a green corrosion inhibitor (nearly 91.8%) for Cu in 2M HNO_3 solution. The IE of myrrh extracts improve with increasing the concentration and diminutions with temperature raising. The adsorption type of myrrh extract on Cu surface is compatible with Langmuir. Tafel polarization tests prove that the myrrh acts as ma mixed inhibitor type. Surface tests by AFM and SEM confirmed the formation of protective film on surface of Cu. This can be explained due to the adherence of extract molecules on Cu surface and blocking both anodic and cathodic sites. There is somewhat similarity between the obtained data from chemical and electrochemical techniques.

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