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# **Calotropis Procera Extract as Corrosion Inhibitor for Copper in Nitric Acidic Environment**

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The corrosion of Cu in 2.0 M HNO<sub>3</sub> using Calotropis Procera (CP) extract as save inhibitor has been conducted utilizing, AC impedance spectroscopy (EIS), Tafel polarization (PP), electrochemical frequency modulation (EFM) and weight loss (WL) tests. Polarization studies proved that, this extract plays as a mixed - kind inhibitor. Inhibition efficiency (IE) of this extract has been found to vary with concentration of CP extract and temperature. The thermodynamic parameters of Cu corrosion in 2.0 M HNO<sub>3</sub> were computed and discussed. The surface analysis of Cu was showed using several techniques. These analyses revealed that CP extract was adsorbed on the Cu surface, preventing the Cu surface from corrosion. Fourier transform infrared (FTIR) results showed that the mechanism of protection was by absorption process, through the functional group's present in the extract. All techniques gave parallel results.

Keywords: Calotropis Procera extract, Copper, Corrosion inhibition, HCl, Temkin isotherm

# **1. INTRODUCTION**

Copper greatly utilized in the manufacture of industrial products because it shows excellent, lowtemperature good characteristics, and shows high resistance against chemicals, and atmospheric factors. However, it can be corroded when exposed to aggressive media such as acids, ammonia, oxygen, or fluids with high sulfur content [1]. Aqueous solutions of acids are utilized, by wide shape, acid cleaning of boilers, descaling, and oil well acidizing [2]. The main problem concerning Cu applications is its relatively low corrosion resistance in acidic solutions, especially in nitric acid solutions [3-7]. A significant way of keeping Cu against deterioration resulting from corrosion is by utilizing of inhibitors. Plant extracts are considered to be good corrosion inhibitors due to they are renewable, facilely obtainable, environmentally safe, and its cost is less [8–11]. Heterocyclic components of extracts (alkaloids, flavonoids, carbohydrates, and proteins) include nitrogen, sulfur or oxygen atoms, and include double bonds in the aromatic rings, that are the senior adsorption positions [12–13]. Up till now, many plant extracts have been used as effective corrosion inhibitors for Cu in an acidic environment, such as: Zenthoxylum alatum [14], Azadirachta Indica [15], caffeine [16] Cannabis [17.

The impact of this paper was to study the inhibitory effect of Calotropis Procera (CP) extract as a green corrosion inhibitor against Cu in 2.0 M HNO<sub>3</sub> utilizing different methods. The temperature influence on the rate of corrosion and thermodynamic parameters were computed and discussed.

# 2. MATERIALS AND SOLUTIONS

The utilized Cu chemical composition in weight %: Fe 0.0297, Ni 0.0103, Si 0.0053, Pb 0.023 and Cu balance. Experiments were achieved using Cu coins 1cm<sup>2</sup> as working electrode mounted in Teflon. The corrosive solution utilized was prepared by dissolution of analytical grade, 70% HNO<sub>3</sub> with bidistilled water. The utilized stock solution (1000 ppm) of CP extract was obtained by liquefaction with bidistilled water. The utilized concentration range of CP extract was 50-300 ppm.

# 2.1 Preparation of plant extract

The roots were shade dried at room temperature for 8–15 days and ground into fine powder in a mixer grinder. 500 gram sample powdered was extracted with methanol 70% for 48 h. Then, the extract supernatant was taken away, filtered and evaporated to remove solvent. The solid was taken and has been put away at 4°C. This stock was used for preparation of different concentrations of the extract by dilution with bidistilled water. Examples of major constituents of CP extract are tannins, flavonoids, steroids, saponins glycosides and are shown below:

Compound	Structure	IUPAC Name
Tannins		1,3,6-Tris-O-(3,4,5-trihydroxybenzoyl) hexopyranose
Flavonoids (Flavanthrone)		Benzo[5,6] acridino[2,1,9,8-klmna] benzo[h]acridine-8,16-dione
Steroids ( Steroid C)	CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> CH <sub>3</sub> H <sub>3</sub> C CH <sub>3</sub> H <sub>3</sub> C CH <sub>3</sub>	Disodium22-(2-isopropyl-3-methyl-2- buten-1-yl)-1,3,7-trimethyl-19,21,23 trioxahexacyclo[18.2.1.02,18.03,16.06, 15.07,12]tricosane-9,10-diyl bisulfate

## 2.2 Methods Utilized for Corrosion Tests

## 2.4.1 Weight Loss (WL) Tests

Seven specimens of Cu with dimensions (2cm x 2cm) were abraded well using emery papers of grades (up to1200) till the surface be shiny, then, all specimens were washed with acetone to remove impurities on metal surface, then washed by bi-distilled water, dried, weighed accurately. One of the specimens has been immersed in 100 ml solution of 2.0 M HNO<sub>3</sub> to act as a blank, and the other six immersed in solutions with different CP extract specimens were concentrations (50,100,150,200,250,300 ppm) for a time of 3h which had been previously adjusted at temperature 25°C, then, all samples were excluded, washed utilizing bi-distilled water, dried gently then weighed accurately.

The average WL of the all Cu sheets could be attained. The (% IE) and ( $\theta$ ) of CP extract for the corrosion of Cu was measured as the next:

$$\% IE = \theta x 100 = [(W^{o} - W)/W^{o}] \times 100$$
<sup>(1)</sup>

Where W<sup>o</sup> and W are the data of the average WL's without and with various concentrations of CP extract, correspondingly.

# 2.4.2 Potentiodynamic Polarization (PP) Test

PP experiments were done in a conventional three-electrode cell. Cu electrode as working electrode, saturated calomel electrode (SCE) as reference electrode and Pt foil as auxiliary electrode. The potential was started from - 600 to + 400 mV vs. OCP with scan rate 0.5 mV/s. All experiments were carried out in freshly prepared solutions at 25°C. % IE and ( $\theta$ ) were measured from the next equation (2):

% IE = 
$$\theta \ge 100 = [(i_{corr} - i_{corr(inh)}) / i_{corr}] \ge 100$$
 (2)

Where  $i_{corr}$  and  $i_{corr(inh)}$  are the unprotected and protected corrosion current densities, correspondingly.

#### 2.4.3 AC Impedance Spectroscopy (EIS) Test

EIS tests were performed, after 30 minutes of dipping of the working electrode in the HNO<sub>3</sub> solution, by employing AC signals have capacity 5 mV peak to peak at the OCP in the frequency domain 100 kHz and 0.2 Hz. The estimations were analyzed and elucidated utilizing the equivalent circuit. The basic parameters from the Nyquist bends are the double layer capacity,  $C_{dl}$ , and the resistance,  $R_{ct}$ , that is the high-frequency loop diameter. % IE and  $\theta$  of EIS tests were computed as follows (3) [18]:

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

where  $R^{\circ}_{ct}$  is the charge transfer resistance with CP extract and  $R_{ct}$  is the charge transfer resistance without CP extract

The larger peaks were used to obtain  $i_{corr}$ , (CF-2 & CF-3) and ( $\beta_c \& \beta_a$ ).  $\theta$  and % IE from EFM measurements were calculated using equation (2) [19-20].

All electrochemical tests were achieved utilizing Gamry instrument utilizing similar manner as earlier with a Gamry framework system rely on ESA400. Gamry apparatus includes software DC105 for polarization, EFM140 for EFM and EIS300 for EIS methods; the computer has used for collecting data. Echem Analyst 5.5 Software was utilized for drawing and fitting data.

#### 2.4.5 Surface Morphology

In order to perform surface investigations, the copper was exposed to the test solutions for 24 h at 25 °C. The investigations of surface topography of the pure Cu and Cu exposed to 2M HNO<sub>3</sub> solution without and with the presence of 300 ppm of the CP extract were utilizing (Scanning Electron Microscope: JOEL 840, Japan) with a magnifying power of (x1500) speed which located in the Faculty of Agriculture, Mansoura university. The surface morphology of Cu coins without and with the presence of 300 ppm of the extract was also investigated using (Atomic Force Microscope: SPM 9600, dynamic (Non-contact) mode, Shimadzu) which located in the atomic force lab, Nanotechnology Center, Mansoura University. And lastly, coins surface was analyzed with IR Affinity (Perkin Elmer) spectrophotometer for recording FTIR spectra for CP extract and CP extract adsorbed on Cu dipping in 2.0 M HNO<sub>3</sub> at the central laboratory in the faculty of pharmacy, Mansoura University.

#### **3. RESULTS AND DISCUSSION**

#### 3.1 Weight Loss (WL) Tests



**Figure 1.** Time-WL curves for the Cu corrosion without and with different concentrations of CP extract at 25°C

Conc., ppm	WL, mg cm <sup>-2</sup>	C.R., mg cm <sup>-2</sup> min <sup>-1</sup>	θ	%IE
blank	1.842	0.02		
50	1.312	0.015	0.285	28.5
100	0.933	0.01	0.493	49.3
150	0.633	0.007	0.656	65.6
200	0.517	0.006	0.719	71.9
250	0.433	0.005	0.765	76.5
300	0.317	0.004	0.828	82.8

**Table 1.** C.R. and %IE values obtained from WL tests for Cu without and with various concentrationsof CP extract at 25°C

WL tests were carried out for Cu in 2M HNO<sub>3</sub> with different concentrations of CP extract and are shown in Figure (1). The (IE %) values measured from Eq. (1) are recorded in Table 1. From this table, the corrosion rate (C.R.) lowered and the IE% rises steadily with improving the concentration of the CP extract. This is due to the formation of adsorbed film from the CP extract on the Cu surface isolating it from the corrosive solution (HNO<sub>3</sub>).

## 3.2 Effect of Temperature

The temperature impact on the C.R. of Cu in corrosive environment and in with various CP extract concentrations was calculated in the temperature range of 25-45<sup>o</sup>C utilizing WL method. As the rise in temperature, the C.R. improved and the %IE of the CP extract lowered as exposed in Table 2 for CP extract. The adsorption performance of CP extract on Cu among adsorption physical.

**Table 2.** Data of WL tests for Cu in corrosive environment and with various CP extract concentrations at 25–45°C

Conc., ppm	Temp., oC	C.R., mg cm <sup>-2</sup> min <sup>-1</sup>	θ	%IE
	25	0.0146	0.285	28.5
	30	0.0221	0.251	25.1
50	35	0.0408	0.191	19.1
	40	0.0582	0.158	15.8
45	45	0.0817	0.095	9.5
	25	0.0100	0.493	49.3
	30	0.0170	0.414	41.4
100	35	0.0320	0.363	36.3
	40	0.0510	0.265	26.5
	45	0.0720	0.204	20.4
	25	0.0070	0.656	65.6
150	30	0.0113	0.618	61.8
150	35	0.0242	0.521	52.1
	40	0.0367	0.469	46.9

	45	0.0525	0.418	41.8
	25	0.0060	0.719	71.9
	30	0.0100	0.665	66.5
200	35	0.0210	0.583	58.3
	40	0.0320	0.539	53.9
	45	0.0520	0.425	42.5
	25	0.0048	0.765	76.5
	30	0.0078	0.737	73.7
250	35	0.0160	0.683	68.3
	40	0.0232	0.664	66.4
	45	0.0473	0.476	47.6
	25	0.0040	0.828	82.8
	30	0.0060	0.784	78.4
300	35	0.0120	0.758	75.8
	40	0.0220	0.685	68.5
	45	0.0300	0.671	67.1

## 3.3 Adsorption Isotherms

The best isotherm for adsorption of any inhibitor on a metal surface is selected by graphically fitting the experimental data to the adsorption equations. After several adsorption isotherms testing contain Temkin, Freundlich, Bockris–Swinkels, Frumkin, Flory–Huggins and Langmuir, the current data were found to obey Temkin isotherm which is presented in Fig. 2 for CP extract, which expressed by:

 $a \Theta = \ln K_{ads}C \tag{4}$ 

where C is the CP extract concentration (ppm). A plot of log C vs.  $\Theta$  should obtain lines straight with slope equal 2.303/a and the intercept =2.303/a log K<sub>ads</sub>. The gotten K<sub>ads</sub> from the Temkin is related to the free energy of adsorption  $\Delta G^{\circ}_{ads}$  utilizing the following equation:

 $K_{ads} = 1/55.5 \exp\left[-\Delta G^{\circ}_{ads}\right] / RT]$ (5)

where R is the universal gas constant and 55.5 is the value of water concentration of the solution bulk (mol/L).

Plotting of  $(\Delta G^{o}_{ads})$  vs T (Fig. 3) gave  $(\Delta H^{o}_{ads})$ .  $(\Delta S^{o}_{ads})$  can be calculated using the basic thermodynamic principle equation as follows:

 $\Delta G^{o}_{ads} = \Delta H^{o}_{ads} - T \Delta S^{o}_{ads}$ 

(6)

Table 3 clearly indicates a best dependence of  $\Delta G^{o}_{ads}$  on T, suggesting the good correlation between thermodynamic parameters. By analyzing the obtained results, we deduced that the sign of  $\Delta G^{\circ}_{ads}$  is negative which indicates a spontaneous reaction. Besides,  $\Delta G^{\circ}_{ads}$  equals -20 kJ/mol or lower are in agreement with physisorption, that includes electrostatic attraction between the charged molecules and the charged metal surface, while  $\Delta G^{\circ}_{ads}$  larger than -40 kJ/mol includes chemisorption,. For the investigated extract,  $\Delta G^{\circ}_{ads}$  variation with temperature in the range from 19.8 to 19 kJ/mol presenting physisorption.



Figure 2. curves fitting of Temkin adsorption for corrosion Cu in 2 M HNO<sub>3</sub> with CP extract at different temperatures

The computed data of  $\Delta H_{ads}^{\circ}$  was 32.3 kJ mol<sup>-1</sup> with a negative sign representing exothermic reaction and as it slightly exceed 40 kJ mol<sup>-1</sup> which assumed to be more physisorption than chemisorption since, it didn't exceed 100 kJ mol<sup>-1</sup> which results in that, physical and chemical adsorptions are both included [21]. The values of entropy of adsorption ( $\Delta S_{ads}^{\circ}$ ) were found to have positive signs, which indicated that adsorption reaction is attended by an increase in the disorder.



Figure 3. Plots of T vs  $\Delta G^{\circ}_{ads}$  for the adsorption of CP extract on Cu in 2.0 M HNO<sub>3</sub>

Temp.	Kads,	a	- $\Delta G^{o}_{ads}$	- $\Delta \mathrm{H}^{\mathrm{o}}$ ads	- $\Delta S^{o}$ ads
K	M-1		kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
298	1.728	3.35	19.8		
303	1.632	3.33	19.6		
308	1.493	3.14	19.2	32.3	42.2
313	1.456	3.20	19.1		
313	1.370	3.37	19.0		

Table 3. Thermodynamic data for the adsorption of CP extract on Cu surface at various temperatures

The activation energies  $(E_a^*)$  of the corrosion processes were obtained by plotting corrosion rates of Cu (k<sub>corr</sub>) vs. temperature (1000/T) (Figure 4). The  $E_a^*$  data were obtain according to the following Arrhenius eq. (7):

 $k_{\rm corr} = A \exp\left(E_a^* / RT\right) \tag{7}$ 

where  $k_{corr}$  is the rate of metal dissolution, and A is the constant Arrhenius pre-exponential.  $\Delta H^*$ and  $\Delta S^*$  of the corrosion reaction can be getting via plotting log  $k_{corr}$  /T against 1000/T as indicated in the next Transition state eq. (8):

 $k_{corr} = (RT/Nh) \exp(\Delta S^*/R) \exp(-\Delta H^*/RT)$ (8)

where h is Planck's constant. The obtained activation parameters are tabulated in Table 4. The increase in  $E_a^*$  with increase in CP extract concentration (Table 4) is typical of physical adsorption. The positive sign of  $\Delta H^*$  indicates endothermic process, that requires more energy to understand the equilibrium. The negative values of  $\Delta S^*$  indicate that the activated complex in the rate determining step proves an association not a dissociation, that indicates the lowering in disorder comes through the moving from the reactants to the activated complex [22,23].



**Figure 4.** 1/T vs. log k<sub>corr</sub> for the dissolution of Cu in corrosive environment and in presence of various CP extract concentrations



Figure 5. 1/ T vs (log  $k_{corr}$  / T) of Cu in corrosive environment and in presence of various CP extract concentrations

Table 4. Kine	tic activation	parameters for	r dissolution	of Cu in	corrosive	environment	and in	presence
of varie	ous CP extrac	et concentration	ns					

Comp	Conc.,	$\mathbf{E}_{\mathbf{a}}^{*}$ ,	$\Delta \mathbf{H}^*$ ,	- $\Delta S^*$
	ppm	kJ mol <sup>-1</sup>	kJ mol <sup>-1</sup>	J mol <sup>-1</sup> K <sup>-1</sup>
Blank	0.0	60.3	57.8	83.2
	50	69.5	67.0	55.2
Calotropis	100	78.0	75.5	42.4
Procera	150	86.6	79.6	18.9
	200	87.9	85.4	11.2
	250	89.2	86.7	10.3
	300	92.4	88.9	9.0

#### 3.5 Potentiodynamic Polarization (PP) Tests

Theoretically, Cu can hardly be oxidized in the deoxygenated acid media, as Cu cannot liberate hydrogen from acid medium discussing to the theories of chemical thermodynamics [24]. PP for corrosion for dissolution of Cu in corrosive environment and in presence of various CP extract concentrations at 25 °C were verified in Figure 6. The ( $\theta$ ) and (%IE) of PP tests were computed utilizing equation (2), then tabulated in Table 5 together with (E<sub>corr</sub>), ( $\beta_c$ ) & ( $\beta_a$ ) and the (C.R) [25].



**Figure 6.** PP curves for dissolution of Cu in corrosive environment and in presence of various CP extract concentrations at 25°C

Table 5. Data from PP of Cu in 2M HNO<sub>3</sub> and in presence of various concentrations of CP extract at  $25^{\circ}C$ 

Conc., ppm	-E <sub>corr</sub> , mVvs SCE	i <sub>corr,</sub> μA cm <sup>-2</sup>	β <sub>c</sub> mV dec <sup>-1</sup>	βa mV dec <sup>-1</sup>	C.R , mpy	θ	% IE
0	5.8	206	218	138	101.6		
50	29.9	150	443	126	72.72	0.272	27.2
100	24.3	106	294	148	52.38	0.485	48.5
150	25.7	76.3	224	141	37.66	0.629	62.9
200	29.1	50.3	240	150	24.83	0.756	75.6
250	36.5	44.3	351	183	21.84	0.785	78.5
300	40.8	39.0	274	160	19.26	0.811	81.1

In the presence of this extract  $E_{corr}$  was enhanced with no definite trend, signifying that this extract acts as mixed-type inhibitor in 2.0 M HNO<sub>3</sub>, forming an adsorbed layer at the Cu/solution interface that lower the available anodic and cathodic sites. The i<sub>corr</sub> lower noticeably after the adding of CP extract in 2.0 M HNO<sub>3</sub> and% IE rises with improving the CP extract concentration.

## 3.6 Electrochemical Impedance Spectroscopy (EIS) Method

Figure (7) shows the Nyquist plots obtained from the Cu electrode at corresponding corrosion potentials after 30 min dipping in 2 M HNO<sub>3</sub> and in presence of various CP extract concentrations at 25°C. The Nyquist diagrams do not display ideal semicircle, this referred to the frequency dispersion [26] which results from the surface roughness. The inductive arc of the diagrams (large capacitive loops

with low frequency dispersion) referred to adsorbed intermediates governing the anodic process [27]. In corrosive solution without and with CP extract, the diagrams show the same capacitive loop, but its diameter rises with rise CP extract concentration. The impedance spectrum was analyzed by using the simple equivalent circuit model displayed in Figure (8). The circuit has  $R_s$  and  $C_{dl}$  that placed parallel to  $R_{ct}$  [28].  $R_{ct}$ , is attained from the diameter of the high-frequency loop, while  $C_{dl}$  is obtained as follows:

$$C_{dl} = Y^0 \omega^{n-1} / \sin[n(\pi/2)]$$
(10)

where  $Y^0$  is the magnitude of the constant phase element (CPE),  $\omega = 2\pi f_{max}$ ,  $f_{max}$  is the frequency at which the imaginary component of the impedance is maximal [29]. In appending, the data of the (C<sub>dl</sub>) lowered by appending inhibitor into corrosive solution. Additionally, C<sub>dl</sub> can be measured with the next eq. (11):

$$C_{dl} = \varepsilon \varepsilon o \left( A/\delta \right) \tag{11}$$

where  $\varepsilon$  is the double-layer dielectric constant,  $\varepsilon$ o the vacuum electrical permittivity, and  $\delta$  the double-layer thickness. Mainly, the lower in C<sub>dl</sub> data is attributed to the replacement of the adsorbed water molecules at the copper surface by the CP extract having minor dielectric constant [30]. The electrochemical data were recorded in Table (6). The % IP was slow from the R<sub>ct</sub> data from eq. (3).



**Figure 7.** EIS Nyquist plots for liquefaction of Cu in corrosive environment and in presence of various concentrations of CP extract at 25°C



Figure 8. Equivalent circuit utilized to EIS data

**Table 6.** EIS data for liquefaction of Cu in corrosive environment and in existence of various CP extract concentrations at 25°C

Comp	Conc., ppm	n	$Y^{0}$ , $\mu\Omega^{-1}s^{n}cm^{-2}$	R <sub>ct</sub> , Ω	Cdl, µFcm <sup>-2</sup>	θ	%IE
Blank	0.0	0.768	563.7	97.2	234		
	50	0.728	537.9	122.6	195	0.207	20.7
CD	100	0.712	432.8	243.5	174	0.601	60.1
CP EXTRACT	150 200	0.687 0.632	320.9 283.7	280.5 364.7	107 75.9	0.653 0.733	65.3 73.3
	250 300	0.589 0.516	242.8 177.9	387.7 635.4	46.8 23.1	0.749 0.847	74.9 84.7

# 3.7 Electrochemical Frequency Modulation (EFM) Tests

EFM for liquefaction of Cu in corrosive environment and in existence of various CP extract concentrations was presented in Figure 9. Data obtained from EFM were listed in Table 7. It is observed that i<sub>corr</sub> lowered by raising the CP extract concentration. Also, CF-2 and CF-3 values were very approach to theoretical data and this agrees with the EFM theory [31], and guarantees the rightness of Tafel slopes and i<sub>corr</sub>.

The inhibition protection  $\%IE_{EFM}$  increase by raising the extract concentrations and was measured as from eq. (12):

$$\% IE_{EFM} = [1 - (i_{corr}/i_{corr}^{0})] \times 100$$
(12)

where  $i^o{}_{corr}$  and  $i_{corr}$  are corrosion current without and with CP extract



**Figure 9.** EFM spectra for dissolution of Cu in corrosive environment and in existence of various CP extract concentrations at 25°C

**Table 7**. EFM data for liquefaction of Cu in corrosive environment and in existence of various CP extract concentrations at 25°C

Comp	Conc., ppm	i <sub>corr</sub> , µAcm	$\beta_{c}, \\ mVdec^{-1}$	βa, mVdec	CF- 2	CF- 3	C.R , mpy	θ	%IE
Blank	0.0	260.00	88	990	1.98	3.57	128.6	-	-
	50	141.20	53	103	1.69	3.32	69.7	0.458	45.8
	100	80.19	109	204	1.81	2.57	39.6	0.689	68.9
	150	56.74	58	110	1.74	3.94	28.0	0.782	78.2
CP	200	32.02	53	90	1.74	2.88	15.8	0.877	87.7
extract	250	30.65	72	109	1.77	2.91	15.1	0.882	88.2
	300	16.00	35	49	1.95	3.28	7.7	0.939	93.9

#### 3.8 Surface Morphology

The SEM micrographs of Cu surface alone and after 24 h dipping in 2.0 M HNO<sub>3</sub> with and without addition of 300 ppm are displayed in Figure (10a-c). As predictable, (Fig.10a) displays metallic surface is clear, while in the nonexistence of CP extract, the Cu is scratched by HNO<sub>3</sub>corrosion (Fig.10b). In comparison, in existence of the extract (Fig. 10c); the metallic surface seems to be almost no affected by corrosion. The creation of a thin film of CP extract detected in SEM micrograph, thus defensive the surface versus corrosion.



**Figure 10.** SEM of Cu surface (a) before of dipping in 2.0 M HNO<sub>3</sub>, (b) after 24 h of dipping in 2.0 M HNO<sub>3</sub>, (c) after 24 h of dipping in 2.0 M HNO<sub>3</sub>+ 300 ppm CP extract at 25°C

## 3.9 FTIR Analysis of the Extract and Corrosion Product

CP extract samples had been detected by FT-IR which do quantitative and qualitative analysis. The chemical bonds in a molecule had been recognized by generating an infrared absorption spectrum. Functional groups and characterizing covalent bonding information had been detected by FT-IR which is an influential analytical device [32]. The characteristic spectra of the CP extract and the copper surface

after dipping in 2.0M  $HNO_3 + 300$  ppm of CP extract for 24 hours was obtained and compared to each other it was obviously clear that the same curve of CP stock extract solution present on Cu surface except the absence of any functional group and it suggested to be due to reaction with  $HNO_3$ . From Figure 11 there are small shifts in the peaks of copper surface from the original peak of the stock CP extract solution, these shifts indicate that there is an interaction between the Cu and CP extract components [33].



**Figure 11.** IR spectra of pure extract and corrosion products of copper after the WL test in existence of 300 ppm of the CP extract at 25°C

3.10 Atomic Force Microscopy (AFM) Analysis



**Figure 12.** AFM 3D images of for Cu (a) free Cu (b) with 2.0M HNO<sub>3</sub> for 4 h (c) with 2.0M HNO<sub>3</sub> containing 300 ppm CP extract for 4 h

Table 8. AFM data for Cu (a) free Cu (b	) with 2.0 M HNO <sub>3</sub> for 4 h (c) with 2.0 M HNO <sub>3</sub> containing 300
ppm CP extract for 4 h	

Parameters	(a)	<b>(b)</b>	(c)
(Sa )	24.87	163.06	104.42
<b>(Sm)</b>	-18.86	-18.49	-15.07
( <b>Sq</b> )	31.62	203.14	139.49
( <b>Sv</b> )	-88.58	-1050.6	-604.13
( <b>Sp</b> )	81.51	598.59	932.96
<b>(Sy)</b>	170.09	1649.2	1537.1

The average roughness data of free Cu surface (Fig. 12a), Cu in 2.0 M HNO<sub>3</sub> and Cu in 2.0M HNO<sub>3</sub> with CP extract (Fig.12 b, c) were documented in Table 8. The roughness rise in the existence of (HNO<sub>3</sub>) because of the corrosion reaction, but in the existence of the CP extract the roughness were lowered due to the adsorption of the extract on the Cu surface, creating a defensive layer, representative that the Cu surface was became more smoothly and the consumption rate was diminished .

## 3.11 Corrosion Inhibition Mechanism

Inhibition of the Cu corrosion in 2.0 M HNO<sub>3</sub> by the investigated CP extract as indicated by "WL, PP, EIS, EFM and other tests were found to be determined by the number of adsorption sites in the molecules that existence in CP extract and their charge densities, molecular size and stability of these additives in acidic solution. "The detected corrosion data in existence of this extract, namely: the lowered of C.R. and corrosion current with rose in concentration of the extract, the linear variation of WL with time, the shift in Tafel lines to higher potential regions. The lowered in IE with improving temperature designates that desorption of the adsorbed extract components occurred, the IE was shown to be depending on the number of adsorption active centers in the extract components and their charge densities. The corrosion protection is due to adsorption of the extract at the electrode/ solution interface. Since, the  $\Delta G^{o}_{ads}$  values are between -19 and -19.8 kJ mol<sup>-1</sup>, - $\Delta H^{o}_{ads}$  is less than 40 kJ mol<sup>-1</sup> and IE lowered by increasing the temperature, so, the adsorption of the extract components on Cu surface is physically. This must be due to the electrostatic interaction between the charged Cu surface and the protonated extract components in acid medium. NO<sub>3</sub><sup>-</sup> anions, first adsorbed on the positively charged Cu surface  $(Cu^{2+})$  [34], it becomes negatively charged, and then the protonated extract components get adsorbed on it, due to electrostatic attraction. Table 9 shows a comparison of some plant extracts used as inhibitors for Cu in nitric acid or in a mixture of nitric and phosphoric acids medium. As shown from the table the CP extract used in this paper can be used as inhibitor for Cu in nitric acid Solution and it will be good inhibitor by increasing its concentration.

Inhibitor (Extract)	Medium	IE %	References
Calotropis Procera (CP) extract	HNO <sub>3</sub>	93.9	Our results
Moringa oleifera plant extract	HNO <sub>3</sub> /H <sub>3</sub> PO <sub>4</sub>	89.2	[35]
Berry Leaves Extract	HNO <sub>3</sub>	90.1	[36]
methanol extract of Eeuphorbia Heterophylla	HNO <sub>3</sub>	90.1	[37]
Aqueous Extract of Lupine Seeds	HNO <sub>3</sub>	68.1	[38]
Ceratonia siliqua extract	HNO <sub>3</sub>	82.8	[39]
Hyoscyamus Muticus Extract	HNO <sub>3</sub>	84.4	[40]

**Table 9.** Comparison between %IE of some plant extracts used as corrosion inhibitors for Cu in 1 M HNO<sub>3</sub> at 25°C

# 4. CONCLUSION

It was found that the percentage IE depends on the concentrations, and temperature and chemical structure of CP extract. The tested CP extract behaves as a mixed type corrosion inhibitor in HNO<sub>3</sub> solutions. The protection acts among adsorption phenomenon and creation of barrier film due to lower in the double layer capacitance with respect to the blank solution when these CP extract are added. The adsorption of investigating CP extract on Cu surface in HNO<sub>3</sub> solution follows Temkin adsorption isotherm. The SEM and AFM images of the copper samples displayed that the copper was protected in the existence of the CP extract. The percentage IE of CP extract obtained from the WL, PP curves, EIS and EFM tests are in best agreement.

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