Inhibitive Action of Cannabis Plant Extract on the Corrosion of Copper in 0.5 M H$_2$SO$_4$

B.A. Abd-El-Nabey [1], A.M. Abdel-Gaber[1], M. El. Said Ali[2], E. Khamis[1], S. El-Housseiny [1,*]

[1] Chemistry Department, Faculty of Science, Alexandria University, Office address: Ibrahimia, P.O.
Box 426, Alexandria 21321, EGYPT
[2] Naif Arab University for Security Sciences; Riyadh, Saudi Arabia - (NAUSS).
[*]E-mail: sharif15002004_ali@yahoo.com

The effect of extract of cannabis plant on the corrosion of copper in aqueous 0.5M sulphuric acid was investigated by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, weight loss and optical micrograph techniques. EIS and polarization measurements showed that the dissolution process of copper occurs under diffusion control. Potentiodynamic polarization curves indicated that the plant extract behaves as cathodic-type inhibitor. The corrosion rates of copper and the inhibition efficiencies of the extract were calculated. The results obtained show that the extract solution of the plant could serve as an effective inhibitor for the corrosion of copper in sulphuric acid media. Theoretical fitting of different isotherms, Langmuir, Flory–Huggins, and the kinetic–thermodynamic model, were tested to clarify the nature of adsorption.

Keywords:

1. INTRODUCTION

Copper is metal that has a wide range of applications due to its good thermic conductivity and mechanical properties. It is used in electronics, for production of wires, sheets, tubes, and also to form alloys. Copper is a relatively noble metal. Nevertheless, it reacts easily in ordinary, oxygen containing, environments. However, in some environments containing species such as chloride, sulphate or nitrate passive film breakdown may occur leading to the propagation of pits [1]. The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. The possibility of the copper corrosion prevention in different aqueous solutions has attracted many researchers so until now numerous possible inhibitors have been investigated. These studies reported that there are a number of organic and inorganic compounds which can do that for the corrosion of copper [2-6]. It is noticed that presence of heteroatoms such as nitrogen, sulphur, phosphorous in the

organic compound molecule improves its action as copper corrosion inhibitor. Amongst these organic compounds and their derivatives such as azoles [7, 8], amino acids [9] and many others, but these compounds are highly toxic. Recently, the research is oriented to the development of green corrosion inhibitors, compounds with good inhibition efficiency but low risk of environmental pollution [10]. Plant extracts have attracted attention in the field of corrosion inhibition for many decades. As natural products, they are a source of non-toxic, eco-friendly, readily available and renewable inhibitors for preventing metal corrosion [11].

In a recent work obtained from our laboratory [12] we studied the effect of cannabis extract on the corrosion of nickel in aqueous 0.5M H_2SO_4. Electrochemical impedance spectroscopy measurements showed that the dissolution process of nickel occurs under activation control, however, potentiodynamic polarization curves indicated that the plant extract behaves as mixed-type inhibitor. The corrosion rates of nickel and the inhibition efficiencies of the extract were calculated and the results obtained show that the cannabis extract could serve as an effective inhibitor for the corrosion of nickel in sulphuric acid media.

The aim of present work is to test extract of cannabis plant as inhibitor for the acidic corrosion of copper and discuss their inhibition mechanism.

2. EXPERIMENTAL

Electrochemical impedance and polarization measurements were achieved using frequency response analyzer (FRA)/potentiostat supplied from prostate instrument. The frequency range for EIS measurements was 0.1×10^4 Hz with applied potential signal amplitude of 10 mV around the rest potential. The data were obtained in a three- electrode mode; platinum sheet and saturated calomel electrodes (SCE) were used as counter and reference electrode. The material used for constructing the working electrode was copper that had the following chemical composition (% wt) 0.5% Ca, 99.5% Cu was used for the electrochemical corrosion studies in aqueous solutions. The working electrode was fabricated by cutting and shaping them in cylindrical forms. A long screw fastened to one end of the test cylinder for electrical connection. The Teflon gasket thereby forms a water-tight seal with the specimen electrode that prevents ingress of any electrolyte and thus avoiding crevice effect. The leak-proof assembly exposes only glass, only one side of rod was left uncovered as constant surface area in contact with the solution. The sample was wet hand-polished using different grade emery papers 320, 400, 600, and 800 grit finishes starting with a coarse one and proceeding in steps to the fine grit up to a mirror finish, washed thoroughly with double-distilled water and finally dried by absolute ethanol, just before immersion in the solution. Each experiment was carried out with newly polished electrode.

Before polarization and EIS measurements, the working electrode was introduced into the test of solution and left for 10 min to attain the corrosion potential ($E_{corr.}$) at which the change of ocp with time is 2 mV/min, i.e., the system had been stabilized.

The polarization curve measurements were obtained at scan rate of 20mV/min starting from cathodic potential (E_{corr} -250 mV) going to anodic direction. The measurements were done at 30.0 ± 0.1 ^{o}C in solutions open to the atmosphere under unstirred conditions.

To test the reliability and reproducibility of the measurements, duplicate experiments were performed in each case of the same conditions. The results were consist within 2%.

Weight loss and optical micrograph studies:

Wight loss studies were carried out at (30°C). The copper coupons were weighed and surface area of all the samples were calculated before the weight loss studies. The copper coupons were immersed in 100 ml test solutions of different concentrations. The weight loss studies were carried out for 6 hours. Corrosion rates (weight loss per cm^2 per hour) were calculated.

Optical micrographs were taken by using Euromex optical microscope, with colour video camera that is connected to a personal computer.

Solution preparation

The test solutions were prepared from analytical grade reagent and distilled water: 98% H_2SO_4 was purchased from Aldrich chemicals. Stock solution of plant extracts was obtained by the flowering tops of plants. A 100 g of dry cannabis plant (the flowering tops of plants), that was obtained by permission from public prosecutor, was minced into very small pieces. The minced plant was boiled with water for 5 minutes to remove chlorophyll and water soluble compounds. The solution was filtered and boiled water was discarded. The process was repeated several times until the final discarded boiled water becomes clear. The minced plant was left to dry in fresh air at room temperature. The dry minced plant was refluxed with 100 ml of petroleum ether. The minced plant solution was then filtered through number 1 Watman filter paper. The extract was evaporated to obtain cannabis residue [12] . This residue was dissolved in 100ml ethanol giving the stock solution of cannabis plant. The concentration of the stock solution was determined by evaporating 10ml and weight the residue [13]. The concentration of the stock solution was expressed in terms of gram per liter. For corrosion measurements in aqueous 0.5 M sulphuric acid, the cannabis residue was used to prepare different concentrations of cannabis extract in presence of 20% ethyl alcohol.

3. RESULTS AND DISCUSSIONS

3.1. Potentiodynamic polarization results

Figure 1 shows the potentiodynamic polarization curves of copper in 0.5M sulphuric acid, in absence and presence of different concentrations of cannabis extracts. As seen from the figure, addition of the cannabis extract affects the cathodic part of the polarization curve for copper rather than the anodic one indicating that the cannabis extract could be classified as cathodic-type inhibitor for copper. Also, the cathodic polarization curves of copper in absence and in presence of the extract show a limiting current, indicating that the cathodic reduction of oxygen gas at the copper surface takes

place through a diffusion control (i_l). Table 1 shows dependence of each of corrosion potential (E_{corr}) and limiting current (i_l) on the concentration of cannabis extract.

In general, copper can hardly be corroded in the deoxygenated dilute sulfuric acid [15], as copper cannot displace hydrogen from acid solutions according to theories of chemical thermodynamics. However, this situation will change in aerated sulfuric acid. Dissolved oxygen may be reduced on copper surface and this will enable some corrosion to take place [16]. It is a good approximation to ignore the hydrogen evolution reaction and only consider oxygen reduction in the aerated sulfuric acid solutions at potentials near the corrosion potential, according to Smyrl [17].

Cathodic reduction of oxygen can be expressed either by a direct $4e^-$ transfer as shown by equation.

$$O_2 + 4H^+ + 4e^- \rightleftharpoons 2H_2O \qquad\qquad (1)$$

Or by two consecutive $2e^-$ steps involving a reduction to hydrogen peroxide first

$$O_2 + 2H^+ + 2e^- \rightleftharpoons H_2O_2 \qquad\qquad (2)$$

Followed by a further reduction [18]

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O \qquad\qquad (3)$$
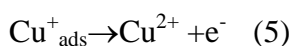
The transfer of oxygen from the bulk solution to the copper/solution interface will strongly affect rate of oxygen reduction reaction despite how oxygen reduction takes place, either in $4e^-$ transfer or two consecutive $2e^-$ transfer step:

Dissolution of copper in sulfuric acid is described by the following two consecutive steps:

$$Cu \rightleftharpoons Cu^+_{ads} + e^- \qquad\qquad (4)$$

$$Cu^+_{ads} \rightarrow Cu^{2+} + e^- \quad (5)$$

Where Cu^+_{ads} is an adsorbed species at the copper surface and does not diffuse into the bulk solution[19]. Since cannabis extract affect the cathodic part of polarization curves for copper in acid solution, it could be concluded that the cannabis extract retard the corrosion of copper by controlling the oxygen reduction process.
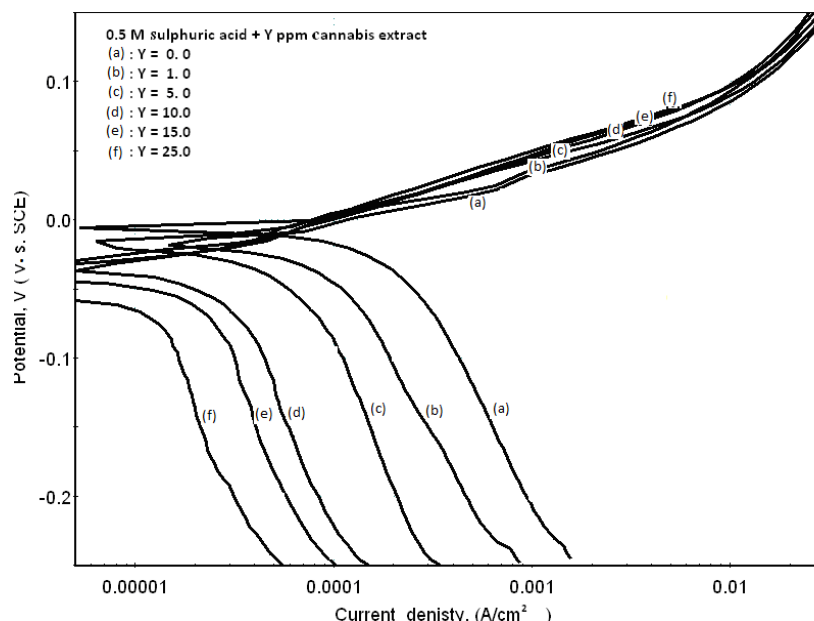
Figure 1. Potentiodynamic polarization curves of copper in 0.5M sulphuric acid, in absence and presence of different cannabis extract concentrations.

The percentage of inhibition efficiency (% P) was calculated from the limiting current density at certain cathodic potential (-0.15 V) using the relation:

$$\%P = [((i_o)_l - (i)_l) / (i_o)_l] \times 100 \qquad (6)$$

Where $(i_o)_l$ and $(i)_l$ are the limiting current densities at -0.15 V (vs. SCE), in absence and presence of cannabis extract.

Table 1. Dependence of the corrosion potential, the limiting current of cathodic polarization curves of copper in 0.5M sulphuric acid and the percentage inhibition effeciency on the concentration of cannabis extract.

Conc. (ppm)	$-E_{corr}$ (mV vs. SCE)	I_L (mA.cm^{-2})	% P
0.0	7	0.637	0
1.0	20	0.305	52
5.0	24	0.150	76
10.0	39	0.055	86
15.0	45	0.039	93
25.0	51	**0.023**	**96**

Figure 2 shows the relation between the percentage inhibition efficiency, and concentration of cannabis extract for copper in sulphuric acid solution.
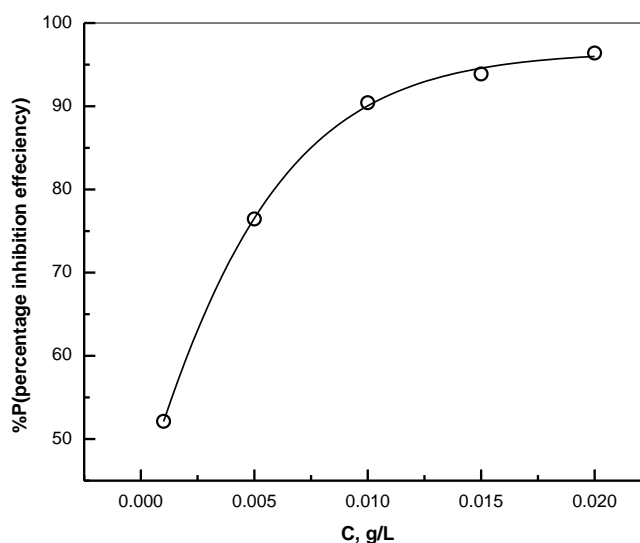
Figure 2. Relation between the percentage inhibition efficiency and concentration of cannabis extract for copper in 0.5M sulphuric acid solution.

The chemical constituents of cannabis extract [12] (cannabidiol-type (CBD) and cannabinol, endogenous cannabinoids anandamide (AEA), 2- arachidonoyl glycerol (2-AG)) contain oxygen, nitrogen atoms and π-electrons bonds, [20, 21]. Therefore, the adsorption at the metal/solution interface could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules (ii) dipole-type interaction between unshared electron pairs in the inhibitor with the metal, (iii) the π-electrons bonds interaction with the metal, and (iv) a combination of all of the above [22].

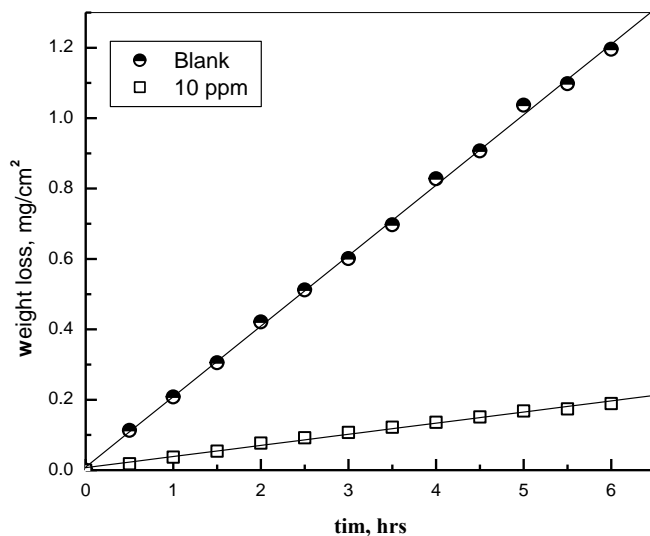### 3.2. Mass loss & Optical micrograph results

a- Mass loss results:-

Figure 3 shows the variations of weight loss of copper in 0.5M sulphuric acid, in absence and presence of 10 ppm cannabis extract with exposure time up to 6 hours at room temperature. The plot has helped to explain the kinetics of the corrosion of metals and check the stability of cannabis extracts in pickling processes. As seen, the weight loss increased with exposure time. Moreover, the rate of corrosion, the slopes of the obtained lines, decreased sharply by the addition of the extract. The percentage inhibition efficiency (% p) was calculated using the relation:

$$\% \ p = [(w_o - w) / w_o] \ x100 \quad (7)$$

Where w_o and w are the weight loss in $g.cm^{-2}.hr^{-1}$, in absence and presence of 10 ppm cannabis extract. The data clarify that cannabis extract acts as a good corrosion inhibitor for the acid corrosion

of copper. The solution containing 10 ppm cannabis gives 84.4% P which is in a good agreement with the data obtained from the polarization (86.0% P) and impedance (83.0% P) measurements (tables 1, 2).

Figure 3. Variation of weight loss of the copper in 0.5M sulphuric acid, in absence and presence of 10 ppm cannabis extract with exposure time.

b- Optical micrograph results:-

The optical micrographic photos of the copper sample were captured using optical microscope with magnification power of 40X.


Figure 4. Optical micrographic photos (40X) of copper in 0.5M sulphuric acid, in absence and presence of cannabis extract.

Figure 4 shows optical micrographic photo of copper in 0.5M sulphuric acid free from or containing cannabis extract after 6 hours. As seen from the micrographic photos, the scratch mark of the emery paper still viewed within the experimental exposure time for copper that was immersed in the acid solution containing cannabis extract whereas in the medium free from the extract, the scratch marks of copper disappeared due to severe uniform corrosion.

3.3. Electrochemical impedance spectroscopy (EIS) results

Figure 5 shows the Nyquist impedance plots of copper in 0.5M sulphuric acid, in absence and presence of different concentrations of cannabis extract. This figure shows that the Nyquist plots of copper in acidic medium consist of distorted semicircles followed by diffusion tail indicative that the corrosion process occurs under diffusion control. This behaviour confirm the results obtained from the polarization measurements witch indicates that the reduction process is controlled by diffusion of oxygen from the bulk solution to the copper surface. The increase in the size of the semicircle in presence of the extract indicates that a barrier gradually forms on the copper surface.
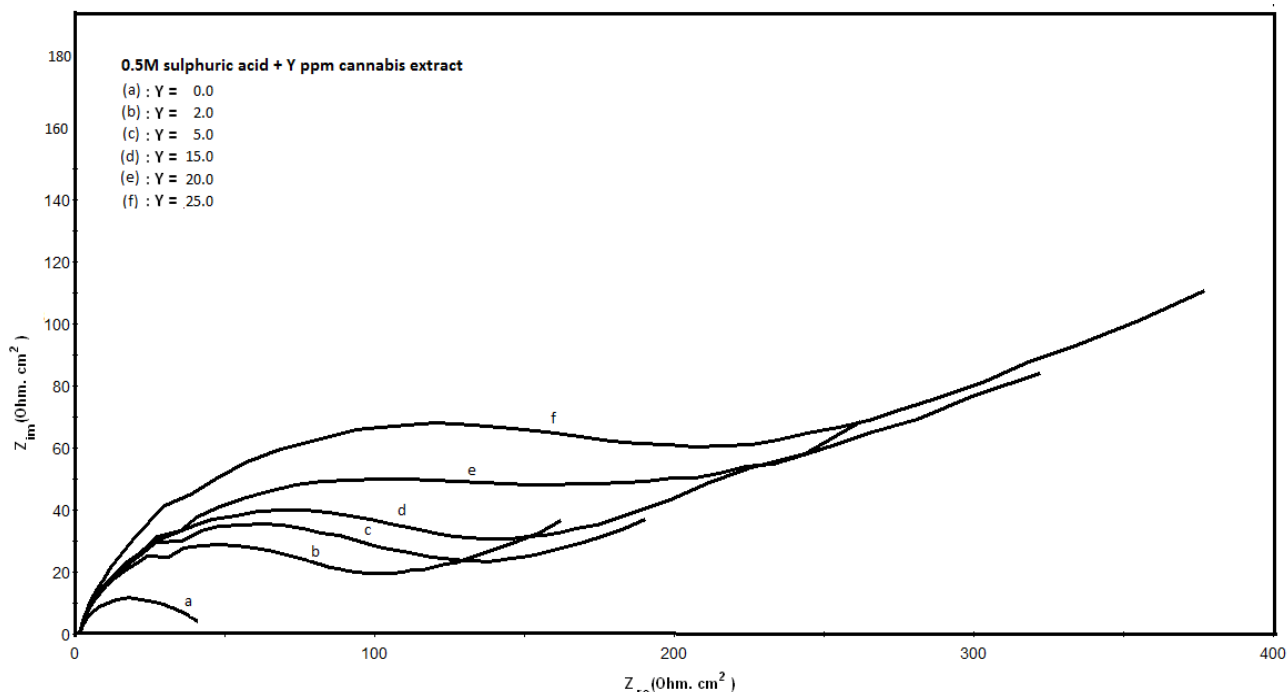
Figure 5. Nyquist plots of copper in 0.5M sulphuric acid, in absence and presence of different concentrations of cannabis extract.

The impedance spectra of Nyquist plots for copper in 0.5 M sulphuric acid, in absence and presence of different concentrations of cannabis extract were analyzed by fitting the experimental data to the equivalent circuit model shown in Figure 6. In this circuit R_s represents the solution resistance; R_{ct} is the charge transfer resistance and CPE is constant phase element related to the double-layer

capacitance. The parallel combination of CPE_2 and R_2 could be equivalent to Warburg diffusion element which describes the diffusion behaviour.

It is noted that, the capacitances were implemented as constant phase element (CPE) during analysis of the impedance plots. Two values, Q and n define the CPE. The impedance, Z, of CPE is presented by

$$Z_{CPE} = Q^{-1} (i\omega)^{-n} \quad (8)$$

Where, $i = (-1)^{1/2}$, ω is frequency in rad s^{-1}, $\omega = 2\pi f$ and f is the frequency in Hz. If n equals one, then equation 34 is identical to that of a capacitor, $Z_C = (i\omega C)^{-1}$ where C is ideal capacitance. For non-homogeneous system, n values ranges 0.9-1 [23].
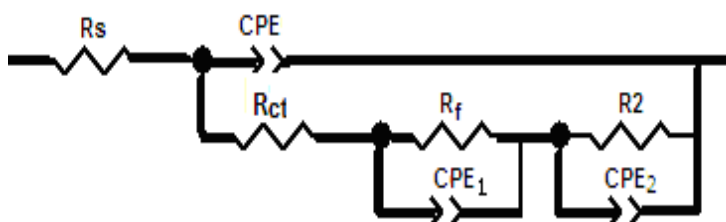

Figure 6. Schematic for the equivalent circuit of copper.

Increasing R_{ct} values with the concentration of the extract, suggesting decrease of the corrosion rate since the R_{ct} value, is a measure of electron transfer across the surface, and inversely proportional to the corrosion rate. The decrease in the Q_{dl} values could be attributed to the adsorption of the chemical constituents of the cannabis extract at the metal surface [23]. The data shown in table (2) indicate that the increase in the extract concentration leads to increase of the charge transfer resistance which is associated with a decrease in the none-ideal double layer capacitance. The percentage of inhibition efficiency (% P) was calculated from the impedance measurements using the relation:

$$\%P = [(R_{ct} - R_{cto}) / R_{ct}] \times 100 \quad (9)$$

Where $\mathbf{R_{ct}}$ and $\mathbf{R_{cto}}$ are the charge transfer resistances, in presence and absence of cannabis extract respectively. The values of %P are in a fair agreement with that obtained from polarization and mass loss measurements.

Table 2. Electrochemical impedance parameters of copper in 0.5M sulphuric acid containing different cannabis extract concentrations.

Conc, (ppm)	R_s	Q_f ($\mu F.cm^-$)	n_1	R_p ($Ohm.cm^2$)	R_{ct} ($Ohm.cm^2$)	Q_{dl} ($\mu F.cm^-$)	n_2	R_2 ($Ohm.cm^2$)	Q_3 ($\mu F.cm^-$)	n_3	%P
0.0	5.3	40	0.9	117	34	1745	0.6	322	4536	1.2	0
2.0	5.7	36	0.9	132	79	692	0.7	946	4582	0.3	57
5.0	6.0	33	0.9	181	139	520	0.6	998	4548	0.3	76
10.0	5.8	35	0.9	185	195	350	0.7	1020	3053	0.4	83
15.0	5.5	34	0.9	242	230	416	0.6	1427	3885	0.4	85
20.0	4.9	33	0.9	251	244	282	0.6	1859	1956	0.3	86
25.0	6.0	32	0.9	318	391	280	0.6	2790	2265	0.4	91

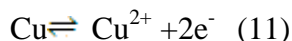## 4. MECHANISM OF CORROSION OF COPPER IN AERATED 0.5M H_2SO_4

a- The cathodic reaction (oxygen reduction):

The cathodic potentiodynamic curves of copper in 0.5M H_2SO_4 in absence and presence of cannabis extract show a limiting current indicating that the cathodic reaction is controlled by diffusion of oxygen gas from the bulk solution to the copper surface. The cathodic reaction can be represented as:

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O \quad (10)$$
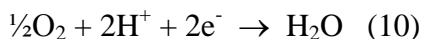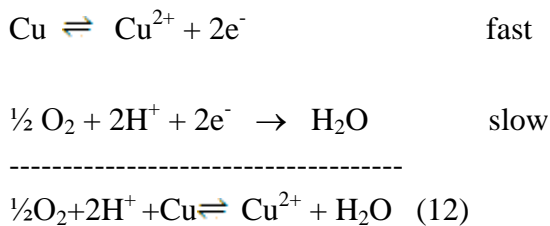
b- The anodic reaction:

The anodic polarization curves of copper in 0.5M H_2SO_4 in absence and presence of cannabis extract show Tafel behaviour indicating that the oxidation reaction of copper is controlled by charge transfer and given by :

$$Cu \rightleftharpoons Cu^+_{ads} + e^- \qquad (4)$$

$$Cu^+_{ads} \rightarrow Cu^{2+} + e^- \qquad (5)$$

$$Cu \rightleftharpoons Cu^{2+} + 2e^- \quad (11)$$

c- The overall corrosion reaction:

The impedance spectroscopy data of copper in 0.5M H_2SO_4 in absence and presence of cannabis extract measured at the equilibrium potential indicated that the corrosion of copper is controlled by diffusion. This means that the reduction of O_2 gas at the cathodic areas is the slow step of

the corrosion reaction of copper. The equation corresponding to the overall reaction of corrosion of copper in aerated 0.5M H_2SO_4 can be obtained by adding equation (10) and (11):

$$Cu \rightleftharpoons Cu^{2+} + 2e^- \qquad\qquad fast$$

$$\tfrac{1}{2} O_2 + 2H^+ + 2e^- \rightarrow H_2O \qquad\qquad slow$$

$$\tfrac{1}{2}O_2 + 2H^+ + Cu \rightleftharpoons Cu^{2+} + H_2O \quad (12)$$

5. APPLICATION OF ADSORPTION ISOTHERMS:

The understanding of the nature of the adsorption process of various kinds of extracts on metal surfaces was essential to our knowledge of their inhibition action on corrosion. The action of an inhibitor in the presence of aggressive acid media is assumed to be due to its adsorption [24] at the metal/solution interface.

The inhibition action was regarded as simple substitutional process, in which an inhibitor molecule in the aqueous phase substitutes an x number of water molecules adsorbed on the metal surface, viz.

$$I_{(aq)} + x(H_2O)_{sur} \rightarrow I_{(Sur)} + x(H_2O)_{aq} \qquad\qquad (13)$$
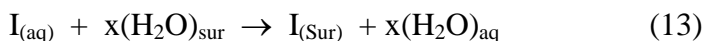
Where x is the size ratio (the relative size of the inhibitor molecule to the number of surface–adsorbed water molecules) this indicates that the number of adsorbed water molecules displaced depends on the size of the adsorbate.

The degree of surface coverage (θ) of the metal surface by an adsorbed cannabis extract was calculated from impedance from the equation:

$$\theta = (R_{ct} - R_{cto}) / R_{ct} \qquad\qquad (14)$$

Langmuir, Flory Huggins isotherms [25] and Kinetic-Thermodynamic model [26] were used to fit the corrosion data of the cannabis extracts.
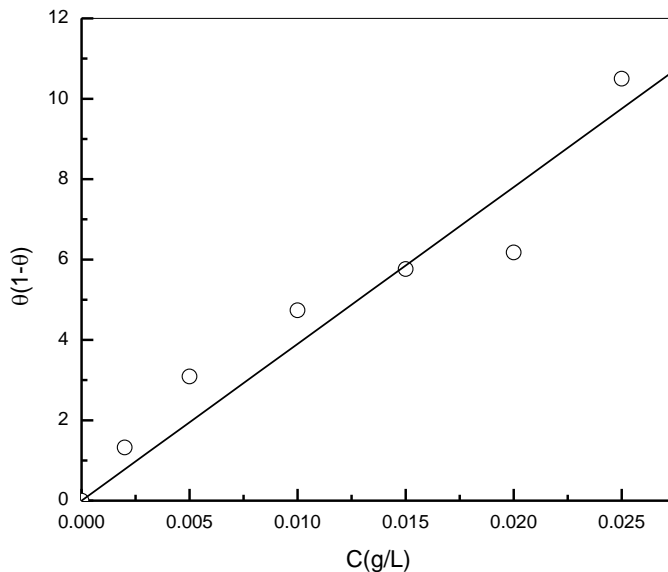
The Langmuir isotherm is given by

$$[\theta/(1-\theta)] = K[C] \qquad\qquad (15)$$

Where K is the binding constant representing the interaction of the additives with metal surface and C is the concentration of the additives.
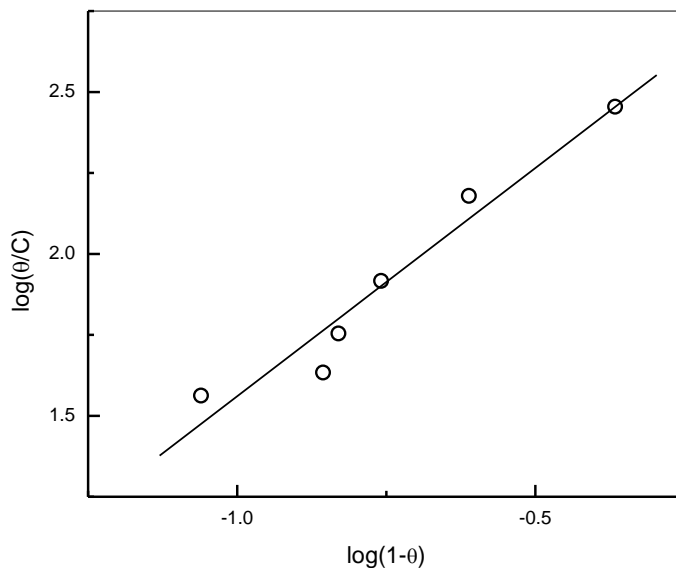
Flory-Huggins isotherm is given by

$$\theta/[x(1-\theta)^x]=K[C] \qquad\qquad (16)$$

Where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.

Figure 7. Linear fitting of the data of cannabis extract to Langmuir isotherm for copper.

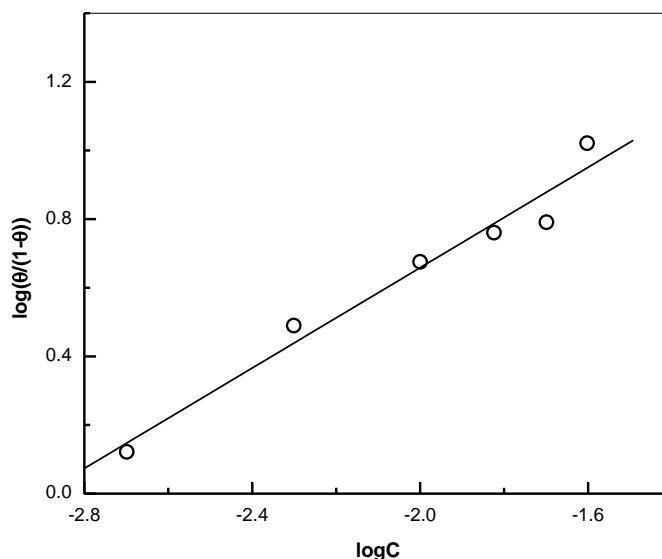**Figure 8.** Linear fitting of the data of cannabis extract to Flory Huggins isotherm for copper.

And the kinetic - thermodynamic model is given by

$$\log[\theta/(1-\theta)]=\log K' + y \, \text{Log} \, C \qquad\qquad (17)$$

Where y is the number of inhibitor molecules occupying one active site. The binding constant K is given by:

$$K = K'^{(1/y)} \quad (18)$$

Figures (7-9) show the application of the above mentioned models to the data of cannabis extract obtained from impedance measurements for copper surface. The parameters obtained from the figures are depicted in table 3.

Figure 9. Linear fitting of the data of cannabis extract to Kinetic-Thermodynamic model for copper.

Table 3. Linear fitting parameters of cannabis according to the used models

Langmuir	Flory-Huggins		Kinetic-Thermodynamic	
K	K	x	K	1/y
490	528	1.3	730	1.4

It is clear that the Langmuir, Flory-Huggins isotherms and Kinetic-Thermodynamic model are found to be applicable to fit the data of absorption of the cannabis extract on the copper surface. The values of the size parameter and the number of active sites occupied by a single inhibitor molecule, 1/y were nearly equal one. This indicated that the adsorbed species could displace only one water molecule. Since the efficiency of a given inhibitor was essentially a function of the magnitude of its binding constant K, large values of K indicate better and stronger interaction, whereas small values of K mean that the interaction between the inhibitor molecules and the metal is weaker . Hence, according to the numerical values of K obtained from the three models, therefore, the inhibitive effect could be explained on the basis of the mechanism that suggests adsorption of the cannabis extract on

the surface of the native metal acting as a film forming species decreasing the active area available for acid attack.

6. CONCLUSIONS

1. Cannabis extract act as highly efficient cathodic type inhibitor for the corrosion of copper in aerated 0.5M H_2SO_4 and the inhibition was found to increase with increasing concentration of the cannabis extract.

2. EIS measurements showed that the dissolution process of copper in aerated 0.5M H_2SO_4 occurs under diffusion control.

3. Langmiur, Flory-Huggins isotherms and Kinetic-Thermodynamic model were found to be applicable to fit the data of adsorption of cannabis at the copper surface. The data showed that only one water molecule was displaced by each cannabis species.

4. A mechanism for the corrosion of copper in aerated 0.5M H_2SO_4 has been proposed.

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