Cannabis Plant Extract as Inhibitor for the Corrosion of Nickel in 0.5 M H₂SO₄

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The effect of extract of cannabis plant on the corrosion of nickel in aqueous 0.5M sulphuric acid was investigated by electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques. EIS measurements showed that the dissolution process of nickel occurs under activation control. Potentiodynamic polarization curves indicated that the plant extract behaves as mixed-type inhibitor. The corrosion rates of nickel and the inhibition efficiencies of the extracts were calculated. The results obtained show that the extract solution of the plant could serve as an effective inhibitor for the corrosion of nickel in sulphuric acid media. Inhibition was found to increase with increasing concentration of the plant extract Theoretical fitting of different adsorption isotherms, Langmuir, Flory–Huggins, and the kinetic–thermodynamic model, were tested to clarify the nature of adsorption. Effect of temperature on the inhibitive action of cannabis extract for the corrosion of nickel in 0.5M sulphuric acid was investigated and the activation parameters of the corrosion process in absence and presence of cannabis extract were calculated.

Keywords: A. corrosion; B. inhibitors; C. thermodynamic.

1. INTRODUCTION

Many parts of new machines are made of pure nickel [1]. Nickel electrodes are important materials for electrochemical technology and energy conversion devices. In aqueous environments, nickel electrodes are usually covered by electrochemically active Ni(OH)₂ layers, although in acid solution nickel corrosion and passivation take place[2]. Many studies have been carried out to find suitable compounds to be used as corrosion inhibitors for nickel in different aqueous solutions. These studies reported that there are a number of organic and inorganic compounds which can do that for the corrosion of nickel [3, 4]. Many works were conducted to examine some naturally occurring

substances as corrosion inhibitors for different metals in various environments [5-16]. 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 [17–38].

Earlier, Barannik and Putivlova [39] showed that the actual inhibitors in the plant extracts are usually alkaloids and other organic nitrogen bases, as well as carbohydrates, proteins and their acid hydrolysis products. The existing data show that most organic inhibitors act by adsorption at the metal/solution interface. This phenomenon could take place via (i) electrostatic attraction between the charged metal and the charged inhibitor molecules, (ii) dipole-type interaction between uncharged 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 [40]. The adsorption process depends on the electronic characteristics of the inhibitor, the nature of the surface, the temperature and pressure of reaction, steric effect, multilayer adsorption and a varying degree of surface site activity. The aim of present work is to test extract of cannabis plant as inhibitor for the acidic corrosion of nickel 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 electrodes. The material used for constructing the working electrode was nickel that had the following chemical composition (% wt) 0.3% Ca, 99.7% Ni 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 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 the open circuit potential (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. Mainly the measurements were done at 30.0 ± 0.1 ^{o}C in solutions open to the atmosphere under unstirred conditions. , however, there are some experiments were done at 40, 50, 60 to study the effect of temperature on the corrosion of nickel and its inhibition.

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

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

2.1. 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 for one hour. The minced plant solution was then filtered through number 1 Watman filter paper. The extract was evaporated to obtain cannabis residue [41] . 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 [42]. The concentration of the stock solution was expressed in terms of gram per liter. For corrosion measurement in aqueous 0.5 M sulphuric acid solution, the stock solution of 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 nickel in 0.5M sulphuric acid, in absence and presence of different concentrations of cannabis extract. As seen from the figure addition of the cannabis extract affect both anodic and cathodic polarization curves indicating that the cannabis extract could be classified as mixed-type inhibitor for nickel in acidic medium. The anodic dissolution mechanism of nickel in sulphuric acid solution was suggested by De Gromoboy [43]. The first step in the suggested mechanism was attributed to the formation of the unstable adsorbed intermediate according to the following equation:
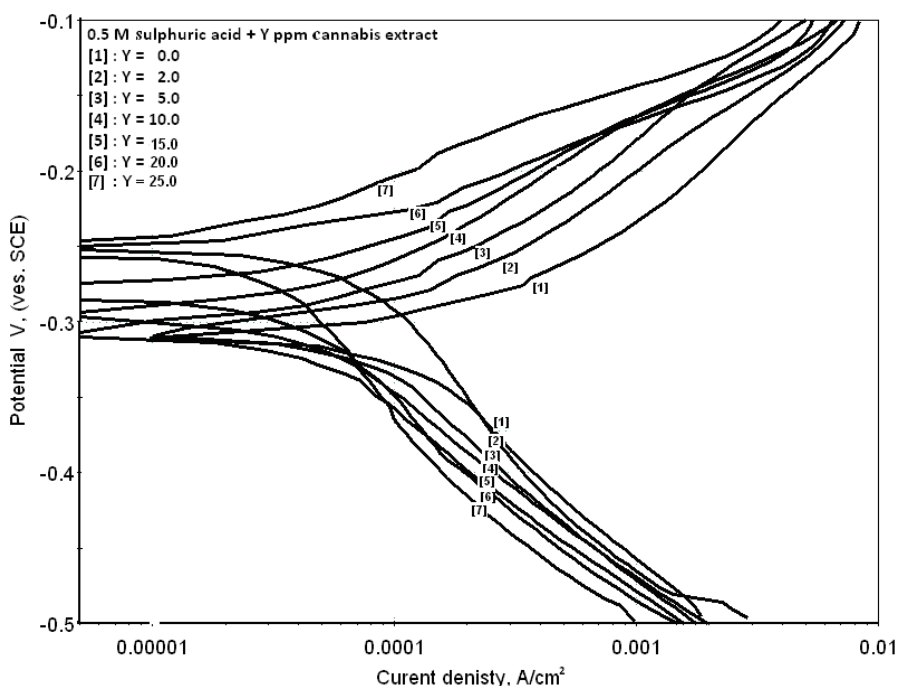
$$Ni+H_2O \rightarrow NiOH+H^+ +e^- \tag{1}$$

This intermediate can further react in two different ways. On the one hand, oxidation and protonation of the intermediate to Ni^{2+}, unable to passivate the metal, leads to the active corrosion of Ni according to the following equation:

$$NiOH + H^+ \rightarrow Ni^{2+} + e^- + H_2O \qquad (2)$$

On the other hand, oxidation and deprotonation of the same intermediate leads directly to passivation according to the equation:

$$NiOH \rightarrow NiO + H^+ + e^- \qquad (3)$$

The surface NiO film constitutes only the first step in Ni passivation. With polarization of the electrode towards more positive potential values, higher oxides of Ni can be formed once the equilibrium potential values are exceeded. The presence of NiO_x imparts stable passivity to the metal [44].

Figure 1. Potentiodynamic polarization curves of nickel in 0.5M sulphuric acid, in absence and presence of different cannabis extract concentrations.

The corrosion current density, (i_{corr}), was calculated from the intersection of anodic and cathodic Tafel lines. The values of the electrochemical polarization parameters, corrosion potential (E_{corr}), corrosion current density, anodic and cathodic Tafel line slope (β_a, and β_c) for different concentrations of cannabis extract are given in table 1. The data revealed that, the corrosion current density that is directly proportional to corrosion rate decreases with increasing the cannabis extract concentration. The values of Ecorr (mV vs. SCE) shifted to less negative values with increasing the concentration of the cannabis extract. The higher values of anodic Tafel line slope of nickel suggests the formation of adsorbed intermediate in the anodic dissolution process[44]. The percentage of inhibition efficiency (% P) was calculated using the relation:
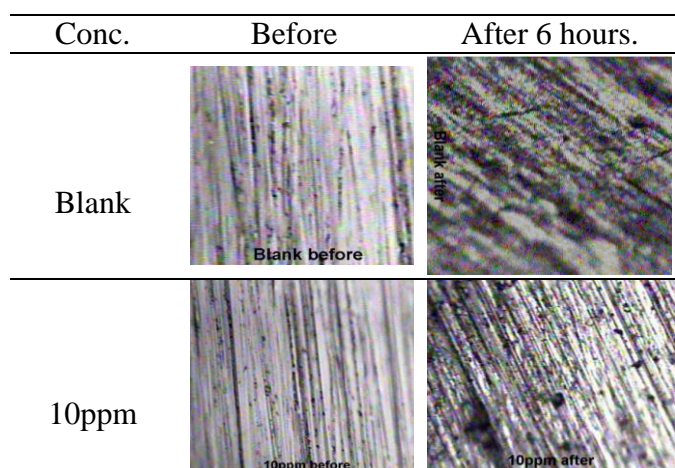
$$\%P=[(i_o-i)/i_o]x100 \tag{4}$$

Where i_o and i are the corrosion current density's in absence and presence of cannabis extract.

Table 1. Electrochemical polarization parameters of nickel in 0.5M sulphuric acid containing different cannabis extract concentrations.

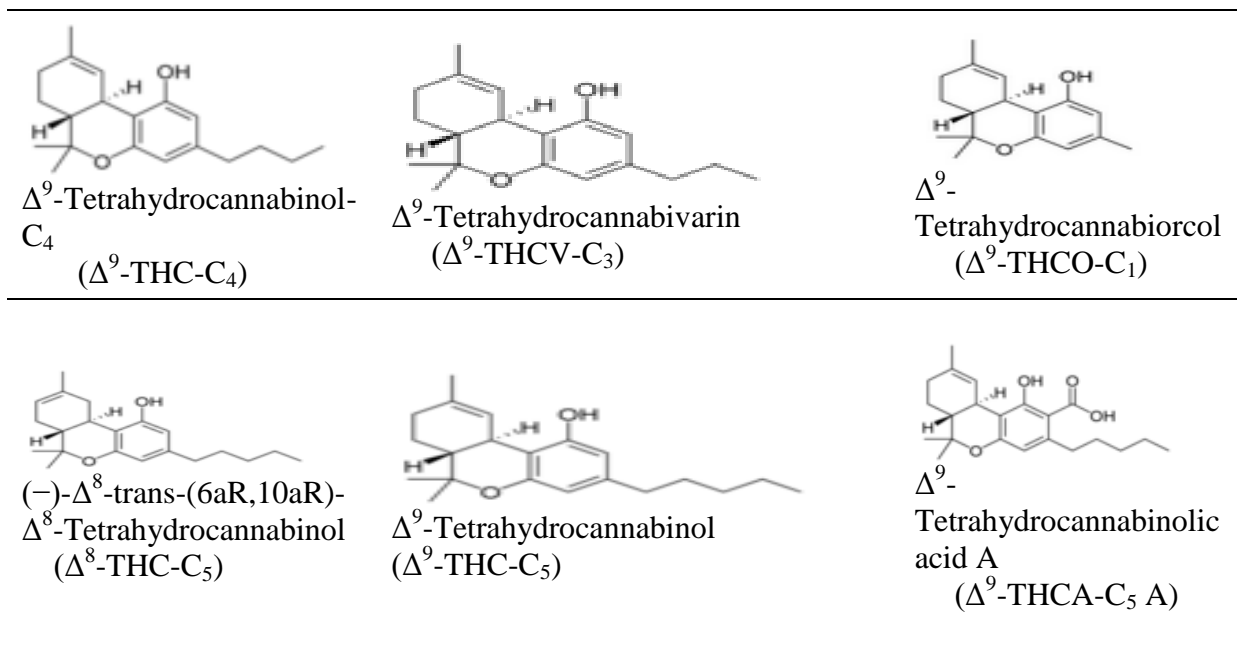| Conc. (ppm)	-E_{corr} (mV vs. SCE)	β_a	β_c	i_{corr} (mA.cm^{-2})	% P
		(mV.decade^{-1})			
0.0	329	106	136	0.120	0
2.0	323	107	130	0.075	37
5.0	327	114	116	0.051	58
10.0	303	91	117	0.039	67
15.0	302	92	118	0.037	69
20.0	300	93	121	0.034	72
25.0	259	82	119	0.033	73

3.2. Optical micrograph results

The optical micrographic photos of the nickel sample were captured using optical microscope with magnification power of 40X. Figure 2 shows optical micrographic photo of nickel in 0.5M sulphuric acid free from or containing 10ppm cannabis extract after 6 hours immersion. As seen from the micrographic photos, the scratch mark of the emery paper still viewed within the exposure time for nickel that was immersed in the acid solution containing cannabis extract whereas in the medium free from the extract, the scratch marks of nickel disappeared due to severe uniform corrosion.

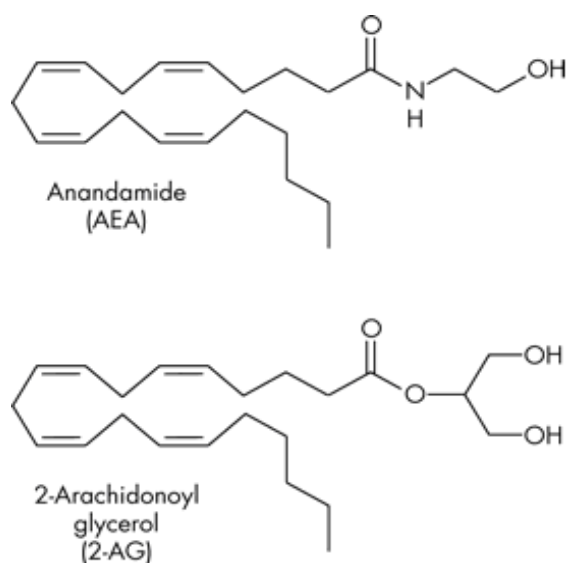| Conc.	Before	After 6 hours.
Blank	Blank before	Blank after
10ppm	10ppm before	10ppm after

Figure 2. Optical micrographic photos (40X) of nickel in 0.5M sulphuric acid, in absence and presence of cannabis extract.

The chemical constituents of cannabis extract (cannabidiol-type (CBD) and cannabinol, endogenous cannabinoids anandamide (AEA), 2- arachidonoyl glycerol (2-AG) contain oxygen, nitrogen atoms and π-electrons bonds figures (3, 4). 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 [40].
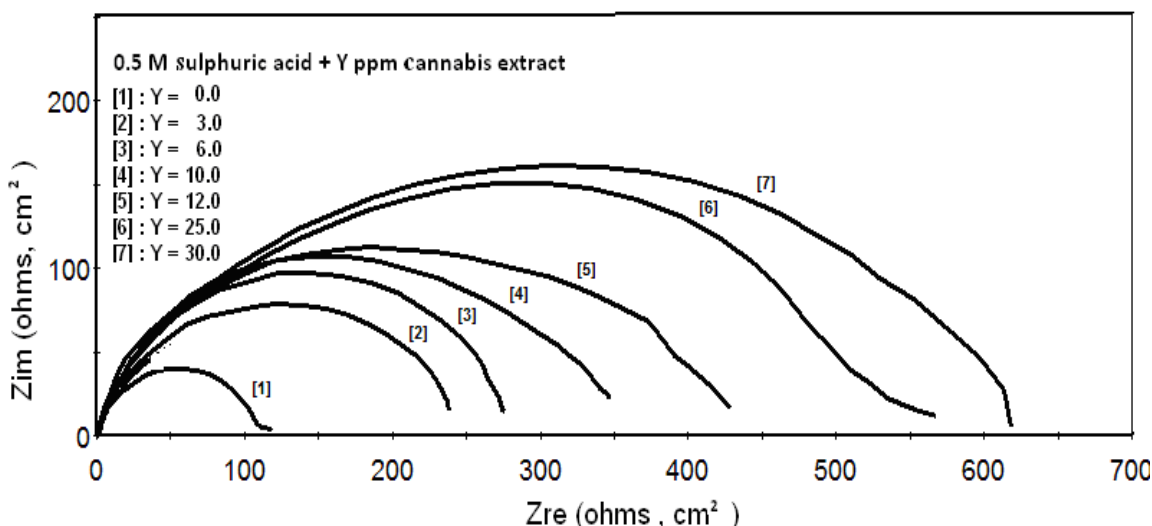

Δ^9-Tetrahydrocannabinol-C_4
(Δ^9-THC-C_4)

Δ^9-Tetrahydrocannabivarin
(Δ^9-THCV-C_3)

Δ^9-Tetrahydrocannabiorcol
(Δ^9-THCO-C_1)

($-$)-Δ^8-trans-(6aR,10aR)-Δ^8-Tetrahydrocannabinol
(Δ^8-THC-C_5)

Δ^9-Tetrahydrocannabinol
(Δ^9-THC-C_5)

Δ^9-Tetrahydrocannabinolic acid A
(Δ^9-THCA-C_5 A)

Figure 3. Chemical structures of cannabidiol-type (CBD) and cannabinol.

Anandamide
(AEA)

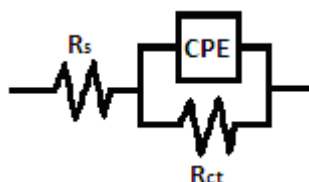2-Arachidonoyl glycerol
(2-AG)

Figure 4. Chemical structure of endogenous cannabinoids anandamide (AEA), 2- arachidonoyl glycerol (2-AG).

3.3. Electrochemical impedance spectroscopy (EIS) results

Figure 5 shows the Nyquist impedance plots of nickel in 0.5M sulphuric acid, in absence and presence of different concentrations of cannabis extract. The Nyquist impedance plots of nickel metal shown in this figure consists of distorted semicircle indicating that the dissolution process occurs under activation control. As seen, the size of the semicircle, increases with increasing cannabis extract concentration. The Nyquist plots for nickel 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**.**

Figure 5. Nyquist plots of nickel in 0.5M sulphuric acid, in absence and presence of different concentrations of cannabis extract.

Figure 6. Schematic for the equivalent circuit of nickel.

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

$$Z_{CPE} = Q^{-1}(i\omega)^{-n} \tag{5}$$

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 5 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 [45].

The electrochemical impedance parameters of Ni in 0.5 M H_2SO_4 containing different concentrations of contains extract are given in table 2.

Increasing R_{ct} values with the concentration of the extract, for nickel metal, suggesting a 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 [46]. The percentage of inhibition efficiency (% P) was calculated from the impedance measurements using the relation:

$$\%P = [(R_{ct} - R_{cto})/R_{ct}] \times 100 \tag{6}$$

Where $\mathbf{R_{ct}}$ and $\mathbf{R_{cto}}$ are the charge transfer resistance, in presence and absence of cannabis extract respectively. The values of %P are in a fair agreement with that obtained from polarization measurements.
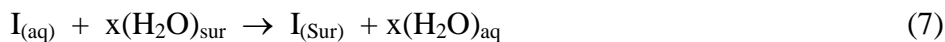
Table 2. Electrochemical impedance parameters of nickel in 0.5M sulphuric acid containing different cannabis extract concentrations.

Conc, (ppm)	R_s (Ohm.cm^2)	Q_{dl} (μF.cm^{-1})	n	R_{ct} (Ohm.cm^2)	% P
0.0	0.68	266	0.8	125	0
2.0	0.74	282	0.8	225	44
3.0	0.37	288	0.8	228	45
4.0	0.69	354	0.8	242	48
6.0	0.75	247	0.8	266	53
8.0	0.54	367	0.8	302	59
10.0	0.79	206	0.8	317	61
12.0	1.49	287	0.8	380	67
25.0	0.64	237	0.8	491	75
30.0	0.67	218	0.8	543	77

3.4. 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 of the chemical constituents of cannabis extract [47] at the metal/solution interface. The inhibition action was regarded as simple substitutional process [48], in which an inhibitor molecule in the aqueous phase substitutes an x number of water molecules adsorbed on the metal surface, viz.

$$I_{(aq)} + x(H_2O)_{sur} \rightarrow I_{(Sur)} + x(H_2O)_{aq} \tag{7}$$
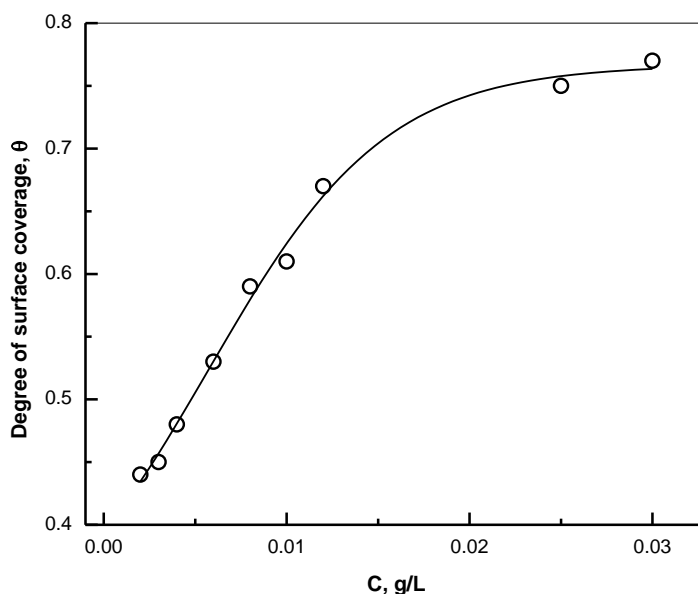
Where x is the size ratio (the relative size of the inhibitor molecule to the number of surface–adsorbed water molecules) this indicates that the number of adsorbed water molecules displaced depends on the size of the adsorbate.

The degree of surface coverage (θ) of the metal surface by an adsorbed cannabis extract was calculated from impedance measurements and the variation of surface coverage with concentration of cannabis extract is shown in figure 7. This curve represens adsorption isotherm that characterized by an initial steeply rising part indicating the formation of a mono-layer adsorbate film on nickel surface. At high concentrations, the inhibitory effect was constant suggesting complete saturation of the surface by the inhibitor molecules.

Langmuir, Flory Huggins isotherms and Kinetic-thermodynamic model were used to fit the inhibition data of the cannabis extract.

Figure 7. Variations of surface coverage with different concentrations of cannabis extract for nickel.

The Langmuir isotherm is given by [49]

$$[\theta/(1-\theta)]=K[C] \tag{8}$$

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 [50]

$$\theta/[x(1-\theta)^x]=K[C] \tag{9}$$

Where x is the size parameter and is a measure of the number of adsorbed water molecules substituted by a given inhibitor molecule.
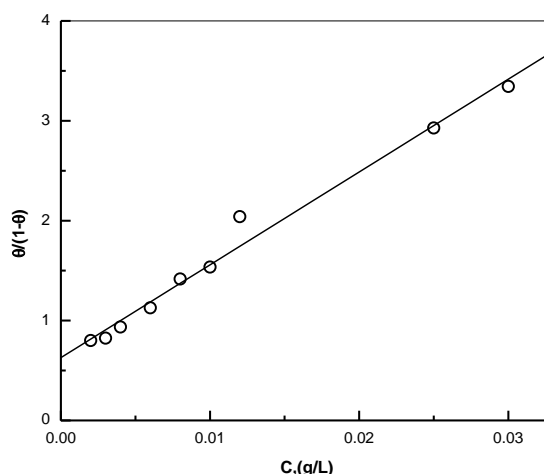
And the kinetic - thermodynamic model is given by [51]
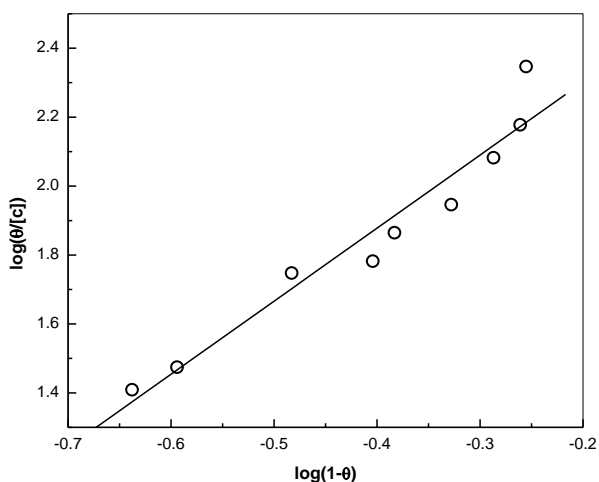
$$Log[\theta/(1-\theta)]=LogK'+yLogC \qquad (10)$$

Where y is the number of inhibitor molecules occupying one active site. The binding constant K is given by:
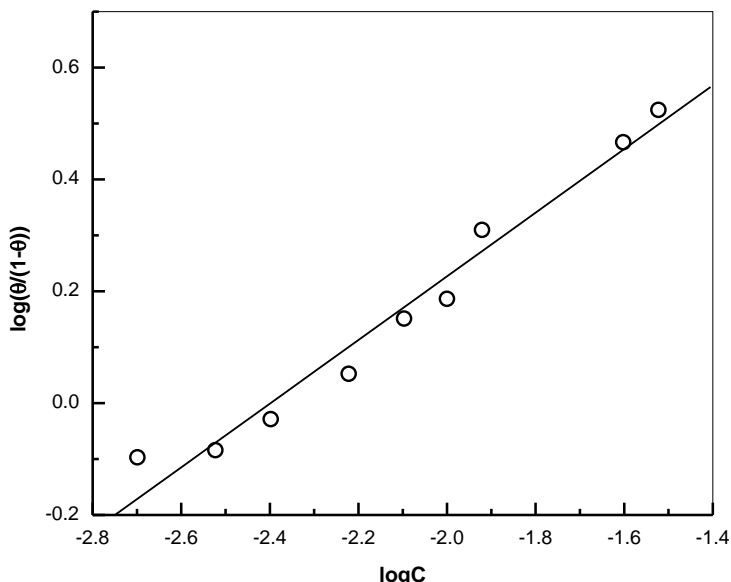
$$K=K'^{(1/y)} \qquad (11)$$

Figures (8-10) show the application of the above mentioned models to the data of cannabis extract obtained from impedance measurements for nickel surface. The parameters obtained from the figure are depicted in table 3.

Figure 8. Linear fitting of the data of cannabis extract to Langmuir isotherm.

Figure 9. Linear fitting of the data of cannabis extract to Flory Huggins isotherm.

Figure 10. Linear fitting of the data of cannabis extract to Kinetic-thermodynamic model.

Table 3. Linear fitting parameters of the adsorption of chemical constituent of cannabis on the nickel surface according to the used models

Langmuir	Flory-Huggins		Kinetic-thermodynamic	
-	K	x	K	1/y
-	248	2.1	245	1.8

It is clear that Langmuir isotherm is unsuitable to fit the data indicating that there might be non-ideal behavior in the adsorption processes [52] of cannabis extract on nickel surface. On the other hand, Flory-Huggins isotherm and Kinetic-thermodynamic model are found to be applicable. The values of the size parameter x for nickel indicates that the adsorbed species of cannabis extract is bulky [53] and two adsorbed water molecules were displaced by each species, the number of active sites occupied by a single inhibitor molecule, 1/y, were nearly equal to the size parameter x for the metal. 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 [54]. Hence, according to the numerical values of K obtained from Flory-Huggins or Kinetic-thermodynamic model, the higher inhibition efficiency of cannabis extract for nickel could be explained on the basis of the mechanism that suggests adsorption of the cannabis extract on the surface of metal acting as a film forming species decreasing the active area available for acid attack.

3.5. Effect of temperature on the inhibitive action of cannabis extract for the corrosion of nickel in 0.5M sulphuric acid.

Many industrial processes take place at high temperatures so, it is particularly important to study the variation of the inhibition efficiency with temperature. When temperature is raised, corrosive action is usually accelerated, particularly in media where evolution of hydrogen accompanies corrosion. Raising the temperature will decrease the inhibitor adsorption on the metal surface; consequently, it will lose its protective action. Cannabis was used in this investigation as an example of plant extracts, as a corrosion inhibitor.

Figures 11, 12 show the Nyquist plots of nickel in 0.5M sulphuric acid solution, in absence and in presence of cannabis extract at different temperatures. As seen, the size of the capacitive semicircle decreases with increasing the temperature of corrosive medium. These plots were analyzed by the equivalent circuit that is previously used, Figure 4. It is evident that the decrease in the charge transfer resistance indicates enhancement of the corrosion rate with temperature.
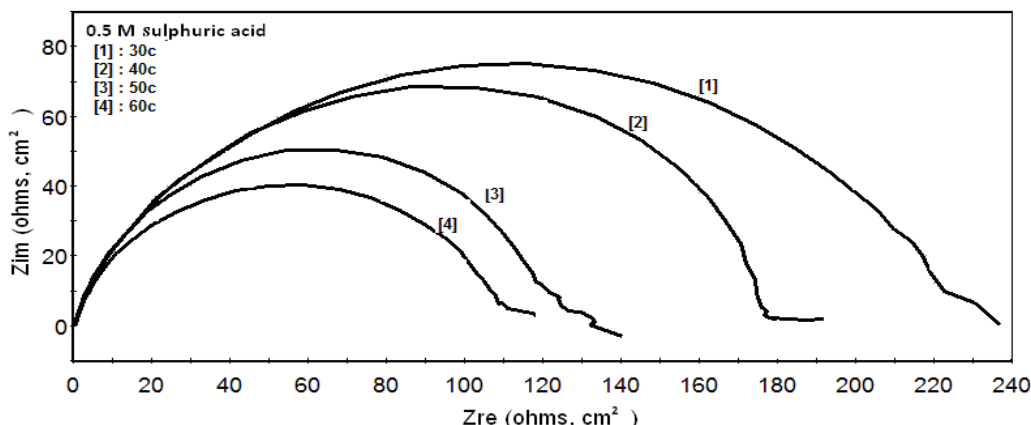

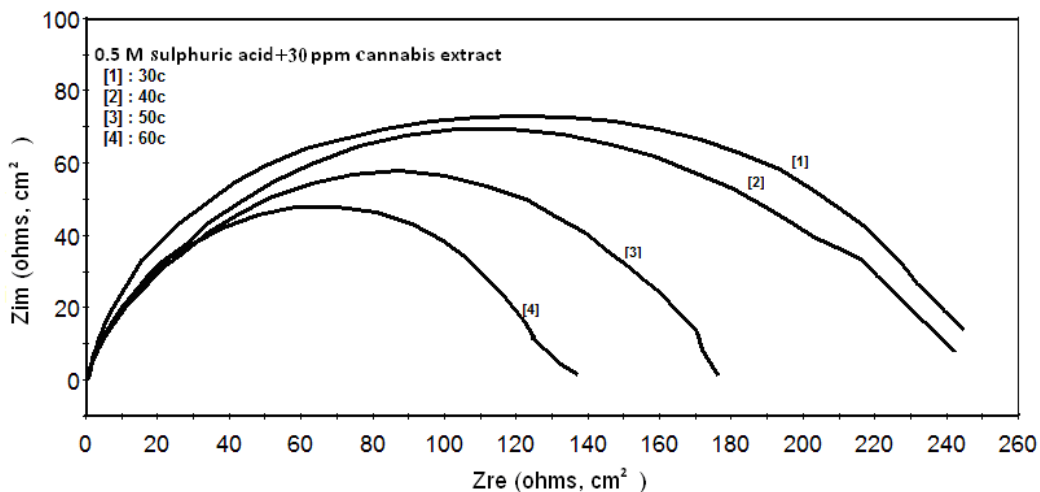**Figure 11.** Nyquist plots of nickel in 0.5M sulphuric acid at different temperatures.

Figure 12. Nyquist plots of nickel in 0.5M sulphuric acid, in presence of 30ppm of cannabis extract at different temperatures.

The values of R_{ct} and C_{dl} of nickel in 0.5M sulphuric acid, in presence of cannabis extract at different temperatures are also given in table 4. It is evident that, at given temperature, the charge transfer resistance is higher in presence of cannabis extract than its absence. On the other hand, increasing the temperature leads to decreasing the R_{ct} values. General trend for increasing C_{dl} values are also observed.

Table 4. The electrochemical impedance parameters of nickel in 0.5M sulphuric acid solution in absence and presence of cannabis extract at different temperatures.

Conc. (ppm)	Temp. °C	R_s (Ohm.cm^2)	Q_{dl} (µF.cm^{-1})	n	R_{ct} (Ohm.cm^2)
Blank	30	0.75	198	0.8	185
	40	0.62	271	0.8	148
	50	0.42	354	0.8	127
	60	0.40	409	0.8	109
30ppm	30	0.67	210	0.8	252
	40	0.58	256	0.8	198
	50	0.52	298	0.8	166
	60	0.48	226	0.8	128

3.6. Determination of the activation parameters

It has been pointed out by many investigators that the logarithm corrosion current density (ln i_{corr}) is a linear function with the reciprocal of the absolute temperature 1/T (Arrhenius equation) [55]:
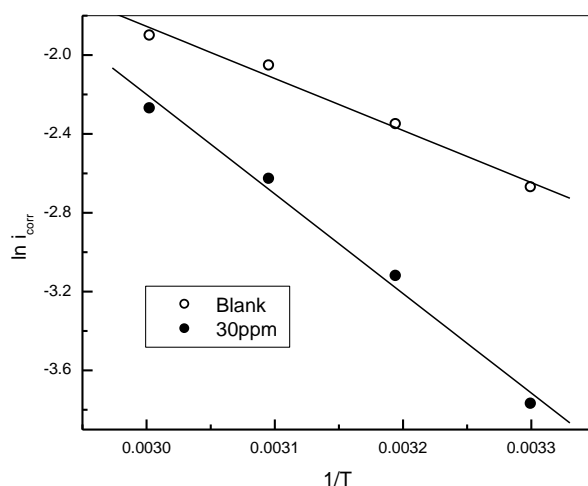
$$\ln i_{corr} = -E_a/R|T + A \qquad (12)$$

Where E_a is the apparent effective activation energy, T is the absolute temperature, R is the universal gas constant, and *A* is Arrhenius pre-exponential factor. An alternative formulation of the Arrhenius equation is the thermodynamic formulation of the transition state theory:
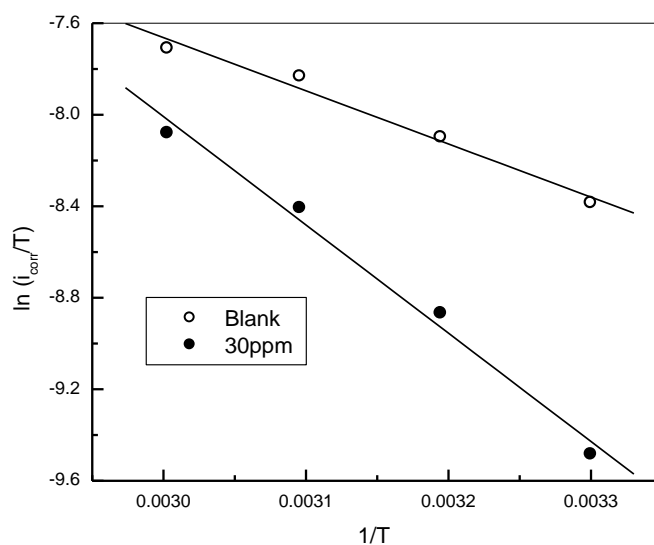
$$i_{corr} = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (13)$$

Where, N is the Avogadro's number, h is the Plank's constant, ΔH^* is the enthalpy of activation, and ΔS^* is the entropy of activation. The corrosion current density (i_{corr}) obtained from polarization measurements. The activation parameters of nickel in 0.5M sulphuric acid, in absence and presence of cannabis extract were obtained from linear square fit of ln i_{corr} and ln (i_{corr} /T) data *vs.* (1/T) as shown in figures(13,14).

The resulting values of the activation parameters are given in table 5. The value of E_a for nickel in sulphuric acid solution is similar to that obtained previously [56-59]. The values of E_a and ΔH^* for nickel in sulphuric acid solution containing cannabis extract are higher than those free from extract. This indicates that the adsorption of cannabis extract constituents at the metal surface retarded corrosion of nickel and the efficiency of the extract, which retarded corrosion at low temperature, is slightly reduced at higher temperatures. This decrease in efficiency may be attributed to the decrease of adsorption of the extract with increasing the temperature [49] which suggests a physical type of adsorption for cannabis extract over nickel surface. The negative value of ΔS^* implies a decrease in the disorder of the system. The decrease in $(-\Delta S^*)$ values in presence of the extract may be explained on the basis of increasing the number of chemical constituents extracted from cannabis which are not involved in the adsorption process.

Figure 13. Linear Square fit for nickel of ln i_{corr} *vs.* (1/T).

Figure 14. Linear Square fit for nickel of ln (i_{corr}/T) *vs.* (1/T).

Table 5. The thermodynamic parameters of activation concerning nickel corrosion in 0.5M sulphuric acid, in absence and presence of 30 ppm of cannabis extract.

Solution	Activation parameters		
	E_a J / mol.	ΔH^* J / mol.	ΔS^* J / mol. K
0.5M sulphuric acid	21948	19313	-203
0.5M sulphuric acid + 30ppm of cannabis extract	41994	39350	-146

4. CONCLUSIONS

1. Cannabis extract act as efficient mixed type inhibitor for the corrosion of nickel in 0.5M sulphuric acid.

2. Inhibition was found to increase with increasing concentration of the cannabis extract.

3. EIS measurements showed that the dissolution process of nickel occurs under activation control.

4. Flory-Hyggins isotherm and Kinitic-Thermodynamic model were found to be applicable to fit the data of adsorption of cannabis at the nickel surface. The data showed that the adsorbed species of cannabis extract are bulky and two adsorbed water molecules were displaced by each species.

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