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Inhibitive Action of Alhagi Maurorum Plant Extract on the Corrosion of Copper in 0.5 M H_2SO_4

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Abstract The effect of Alhagi Maurorum plant extract on the corrosion of copper in aqueous 0.5M sulphuric acid was investigated by electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, and weight loss techniques. The plant extract act as cathodic-type inhibitor and 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. The thermodynamic parameters of the corrosion reaction of copper in acidic medium in the absence and the presence of the extract have been determined.

Keywords Potentiodynamic Polarization, EIS, Weight Loss, Inhibitor, Copper, H_2SO_4

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 resistant toward the influence of atmosphere and many chemicals, however, it is known that in aggressive media it is susceptible to corrosion. The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected [1]. Inhibitors are widely used in the corrosion protection of metals in several environments. Most of the efficient inhibitors are organic compounds which contain nitrogen, sulphur and/or oxygen atoms in their molecules [2, 3].

Nowadays, the uses of some chemical inhibitors have been limited due to their synthesis is often very expensive and they can be toxic or hazardous for human beings and environment as well. Recently, plant extracts, containing mixture of compounds having oxygen, sulphur and nitrogen elements, are employed as corrosion inhibitors in order to develop cleaning chemicals for green environment. Several studies have been published on the use of plant extracts as corrosion inhibitors in different media [4–10].

The possibility of the copper corrosion prevention in different aqueous solutions has attracted many researchers so until now numerous possible inhibitors have been investigated. [11]. These studies reported that there are a number of organic and inorganic compounds which can do that for the corrosion of copper [12-16]. A previous study [17] used electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques to evaluate the inhibitive efficiency of thioxoprymidinone derivatives on the corrosion of copper in sulphuric acid media. The results obtained show that the thioxoprymidinone derivatives could serve as an effective inhibitor for the corrosion of copper in sulphuric acid media.

In a recent work obtained from our laboratory [11] we studied the effect of extract of cannabis plant on the corrosion of copper in aqueous 0.5M sulphuric acid using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, weight loss and optical micrograph techniques. The corrosion rates of copper and the inhibition efficiencies of the extract were determined. 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. The inhibition mechanism was discussed.

The main objectives of this study were to evaluate the inhibition efficiency of Allhagi Maurorum extract in preventing the acid dissolution of copper metal at different temperatures and to investigate the influence of exposure time on the performance of Allhagi Maurorum extract. Also, the effect of the extract on the mechanism of the corrosion of copper will be taken in consideration.

2. Experimental

2.1. Electrochemical Measurements

Electrochemical impedance and polarization measurements were achieved using frequency response

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analyzer (FRA)/potentiostat supplied from Parstate 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 cell; graphite rod 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 solution and left for 20 min to attain the open circuit potential (OCP) 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} -300 mV) going to anodic direction. All the measurements were done at 30.0 ± 0.1°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.

2.2. Weight Loss Measurements

Coupons with area 2 cm^2 rectangular copper and with the same chemical composition of copper samples used in the electrochemical measurements were used in the experiment. The weight loss coupons were polished, cleaned and suspended in beakers containing 100 ml of the test solutions. After definite time, the coupons were removed from the solution, washed with distilled water, ethanol and then dried by acetone and re weighted. The weight loss was then determined (gm/cm^2) the experiment was then repeated for different time in travels up to 72 hours.

To test the reliability and responsibility of the measurements, duplicate experiments were performed in each case of the same conditions.

2.3. Solution Preparation

The test solutions were prepared from analytical grade reagents and distilled water: 98% H_2SO_4 was purchased from Aldrich chemicals. The plant extract was obtained by drying the plant for 1 h in an oven at 80°C and grinding to powdery form. A 10 g sample of the powder was refluxed in 100 mL double distilled water for 1 h. The refluxed solution was filtered to remove any contamination. The concentration of the plant extract was determined by evaporating 10 mL of the filtrate and weighing the residue. Prior each experiment, 5M H_2SO_4 is added to an appropriate volume of the extract solution and double distilled water to obtain a solution of 0.5M H_2SO_4 and the required concentration of the extract.

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 Alhagi Maurorum extract. As seen from the figure, addition of the Alhagi Maurorum extract affects the cathodic part of the polarization curve for copper rather than the anodic one indicating that the Alhagi Maurorum extract could be classified as cathodic-type inhibitor and retard the reduction of oxygen gas at the cathodic areas. 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 under diffusion control.

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

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

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

$$O_2+2H^+{}_+ 2e^- \rightleftharpoons H_2O_2 \quad (2)$$

Followed by a further reduction [18]

$$H_2O_2+2H^++2e^- \rightleftharpoons 2H_2O \quad (3)$$

In absence of the extract the first step is probably fast reversible and the second one is the rate determining step of the reduction process of oxygen. However, in presence of the extract the first step is retarded by the adsorption of the active adsorbable species of the extract at the copper surface and becomes the rate determining step [18]. 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:

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

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

Where Cu^{+ads} is an adsorbed species at the copper surface and does not diffuse into the bulk solution [14]. Since Alhagi Maurorum extract act as cathodic inhibitor for the acidic dissolution of copper and the reduction process of oxygen gas at the cathodic areas take place under diffusion control, Tafel equation cannot be applied to calculate the electrochemical parameters of the corrosion reaction in this case.

Figure 2 illustrates the chemical constituents of Alhagi Maurorum extract [19] contains oxygen atoms and π-electrons bonds, [20, 21]. Therefore, the adsorption at the metal/solution interface could take place via (i) dipole-type interaction between unshared electron pairs in the inhibitor with the metal, and (ii) the π-electrons bonds interaction with the metal [22].

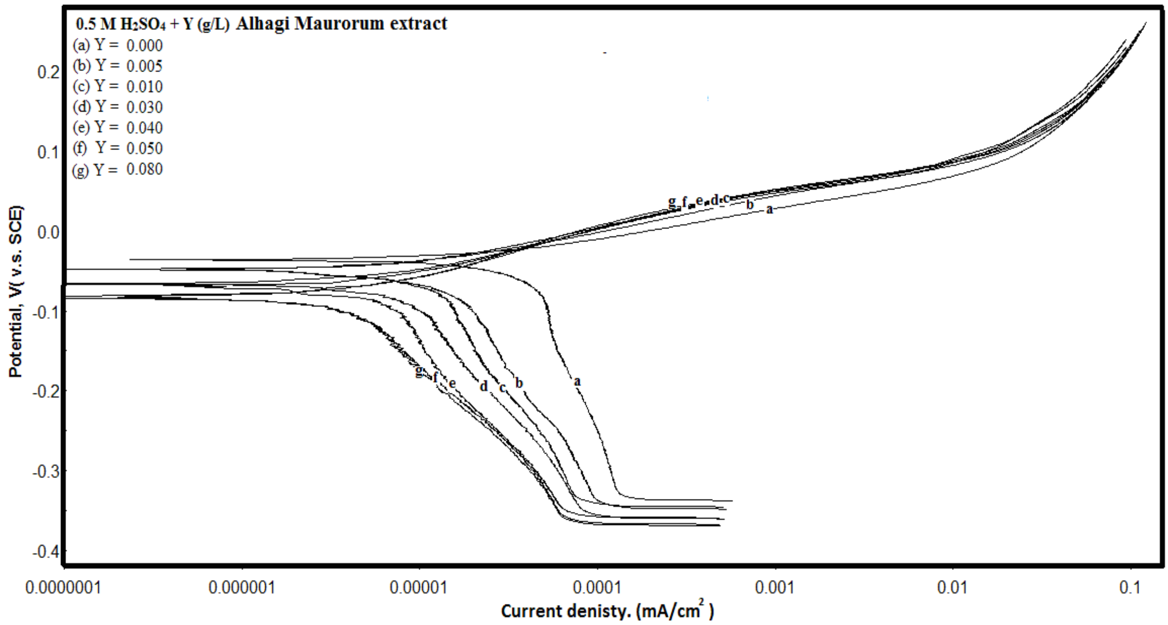

Figure 1. Potentiodynamic polarization curves of copper in 0.5M sulphuric acid, in absence and presence of different Alhagi Maurorum extract concentrations

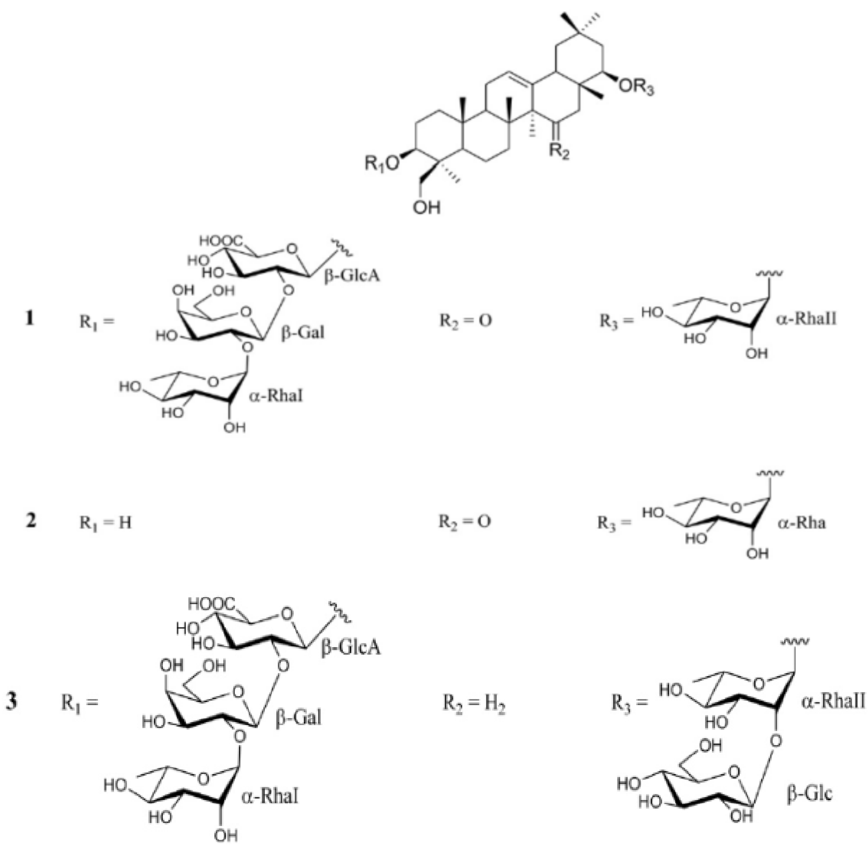

Figure 2. Chemical constituents of Alhagi Maurorum extract

3.2. Electrochemical Impedance Spectroscopy (EIS) Results

Figure 3 shows the Nyquist impedance plots of copper in 0.5M sulphuric acid, in absence and presence of different concentrations of Alhagi Maurorum extract. 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 which confirm the results obtained from the polarization measurements. The increase in the size of the semicircle in presence of the extract indicates that a barrier gradually forms on the copper surface.

The impedance spectra of Nyquist plots for copper in 0.5 M sulphuric acid, in absence and presence of different concentrations of Alhagi Maurorum extract were analyzed by fitting the experimental data to the equivalent circuit model shown in figure 4. In this circuit Rs represents the solution resistance; Rct 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

$$ZCPE=Q^{-1}(i\omega)^{-n} \quad (6)$$

Where, i = (-1)1/2, ω is frequency in rad s-1, ω = 2πf and f is the frequency in Hz. If n equals one, then equation 8 is identical to that of a capacitor, ZC = (iωC)-1 where C is ideal capacitance. For non-homogeneous system, n values ranges 0.9-1 [23].

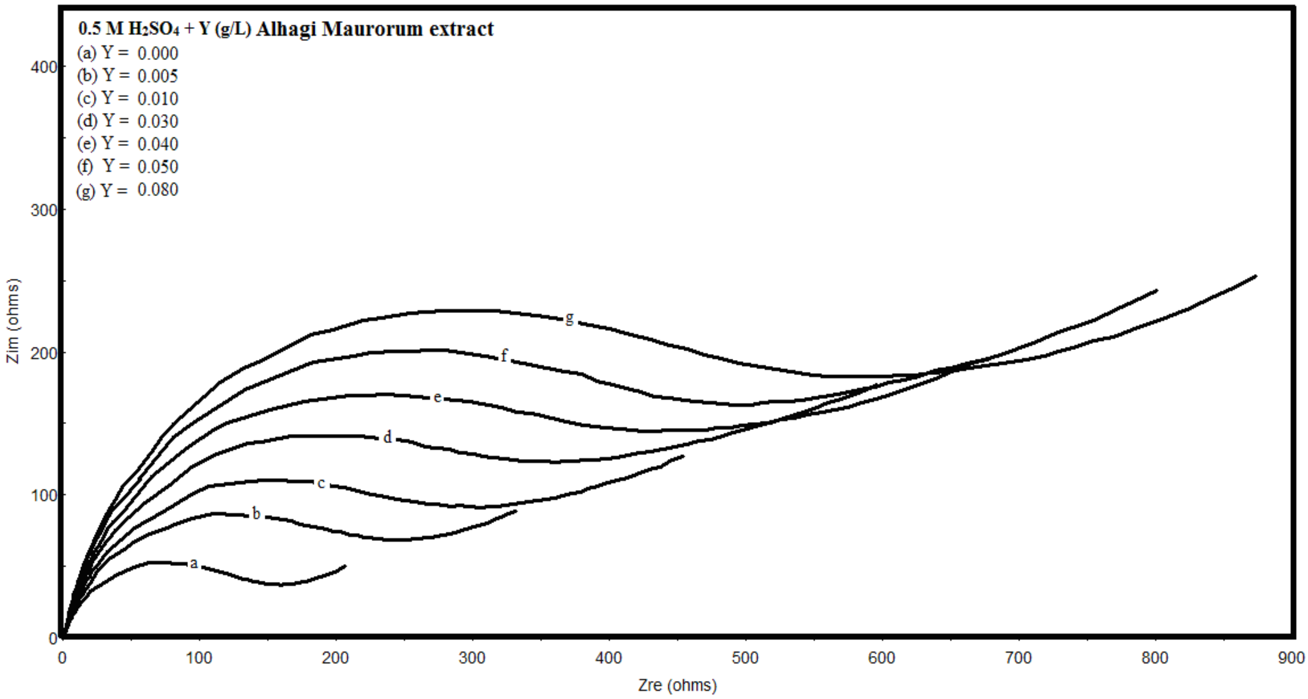

Figure 3. Nyquist plots of copper in 0.5M sulphuric acid, in absence and presence of different concentrations of Alhagi Maurorum extract

Table 1. Electrochemical impedance parameters of copper in 0.5M sulphuric acid containing different Alhagi Maurorum extract concentrations

Conc, (g/L)	R_s	Q_f ($\mu F.cm^{-1}$)	n_1	R_p ($Ohm.cm^2$)	R_{ct} ($Ohm.cm^2$)	Q_{dl} ($\mu F.cm^{-1}$)	n_2	R_2 ($Ohm.cm^2$)	Q_3 ($\mu F.cm^{-1}$)	n_3	% P
0.000	1.0	38	0.9	123	131	1320	0.7	273	4520	0.6	0.0
0.005	1.2	36	0.9	157	196	822	0.7	460	4431	0.4	33.2
0.010	1.1	35	0.9	182	233	651	0.6	682	4328	0.3	43.8
0.020	1.2	34	0.9	198	377	541	0.7	841	4212	0.4	65.3
0.030	1.4	32	0.9	216	482	435	0.7	1021	4154	0.4	72.8
0.040	1.3	31	0.9	247	578	367	0.7	1101	3910	0.4	77.3
0.050	1.7	30	0.9	268	626	321	0.6	1220	3824	0.3	79.1
0.060	1.8	28	0.9	277	672	301	0.7	1398	3621	0.4	80.5
0.080	1.9	26	0.9	362	741	246	0.7	1600	3492	0.4	82.3
0.100	1.9	24	0.9	387	788	227	0.7	1695	3256	0.4	83.4

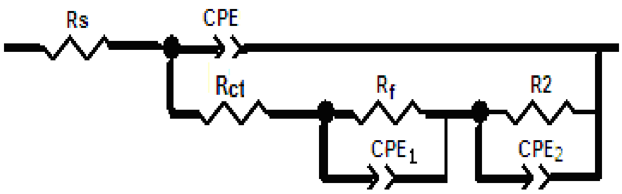

Figure 4. Schematic for the equivalent circuit of copper

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 Alhagi Maurorum extract at the metal surface [23]. The data shown in table (1) 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:

$$\%P=[(R_{ct}-R_{cto})/R_{ct}]x100 \quad (7)$$

Where Rct and Rcto are the charge transfer resistances, in presence and absence of Alhagi Maurorum extract respectively.

3.3. Weight Loss Results

Table 2 shows the variation of weight loss of copper in 0.5M sulphuric acid, in absence and presence of Alhagi Maurorum extract with exposure time up to 72 hours at 30°C. As seen, the weight loss increased with exposure time and decreased by the addition of the extract.

The percentage inhibition efficiency (% p) was calculated from the following equation:

$$\%p = [(w_o-w)/w_o] \text{ x } 100 \quad (8)$$

Where w_o and w are the weight loss in $g.cm^{-2}$, in absence and presence of Alhagi Maurorum extract.

Figure 5 shows the relation between the percentage inhibition efficiency, and concentration of Alhagi Maurorum extract for copper in sulphuric acid solution. This curve represents adsorption isotherm that are characterized by an initial steeply rising part indicating the formation of a mono-layer adsorbate film on copper surface. The figure shows that there is a considerable agreement between the data obtained from impedance technique and weight loss method measured at 12 hours exposure.

Table 2 and Figure 6 show that the inhibitor efficiency of Alhagi Maurorum extract at certain fixed time of immersion increases with increasing the concentration of the extract.

Table 2. Effect of the concentration of the inhibitor and immersion period on the corrosion of copper in 0.5M H_2SO_4 medium

Conc. (g/L)	Immersion period					
	12 h		24 h		36 h	
	W (g cm^{-2})	%P	W (g cm^{-2})	%P	W (g cm^{-2})	%P
0.000	0.487	0.0	0.773	0.0	0.962	0.0
0.005	0.309	36.6	0.578	25.2	0.788	18.1
0.010	0.298	38.8	0.529	31.6	0.682	29.1
0.020	0.211	56.7	0.415	46.3	0.605	37.1
0.030	0.146	70.0	0.358	53.7	0.462	51.9
0.040	0.121	75.2	0.303	60.8	0.388	59.7
0.050	0.108	77.8	0.234	69.7	0.307	68.1
0.060	0.103	78.9	0.177	77.1	0.242	74.8
0.080	0.088	81.9	0.149	80.7	0.194	79.8
Conc. (g/L)	Immersion period					
	48 h		60 h		72 h	
	W (g cm^{-2})	%P	W (g cm^{-2})	%P	W (g cm^{-2})	%P
0.000	1.381	0.0	1.402	0.0	1.817	0.0
0.005	1.158	16.1	1.206	13.9	1.598	12.1
0.010	0.998	27.7	1.047	25.3	1.419	21.9
0.020	0.919	33.5	1.001	28.6	1.318	27.5
0.030	0.689	50.1	0.784	44.1	1.078	40.7
0.040	0.597	56.8	0.632	54.9	0.897	50.6
0.050	0.483	65.0	0.557	60.3	0.762	58.1
0.060	0.391	71.7	0.426	69.6	0.564	68.9
0.080	0.298	78.4	0.309	77.9	0.396	78.2

However, the dependence of the inhibition efficiency of the extract on the immersion time in presence of certain concentration of the extract shows a slight decrease in the efficiency with increasing the immersion time for the solutions containing low concentrations of the extract, but in presence of high concentrations of the extract the efficiency is nearly constant. This behaviour is probably discussed on the basis that in the presence of high concentration of the extract the surface of the metal becomes saturated with inhibitor molecules and the equilibrium between the adsorption and desorption processes of the inhibitor molecules at the metal surface is attained.

3.4. Adsorption of Alhagi Maurorum Extract At Copper/Solution Interface

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.

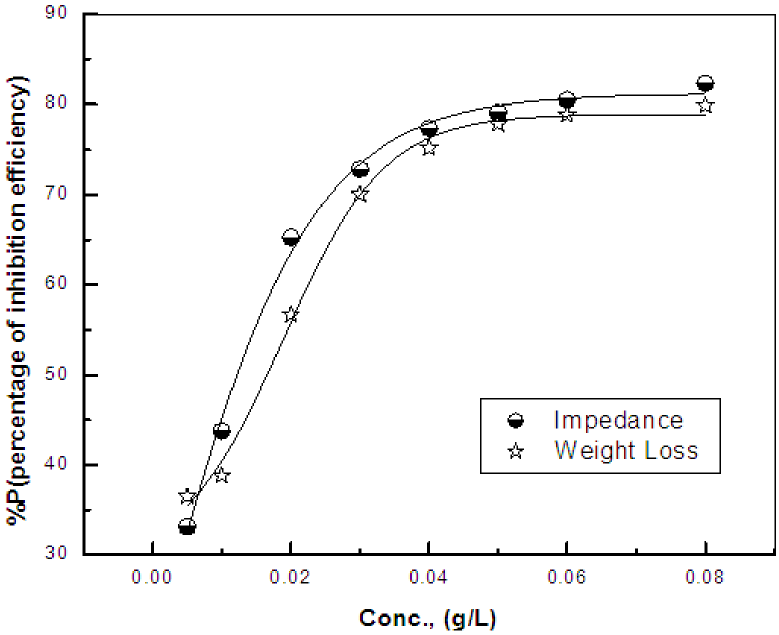

Figure 5. Relation between the percentage inhibition efficiency and concentration of Alhagi Maurorum extract for copper in 0.5M sulphuric acid solution

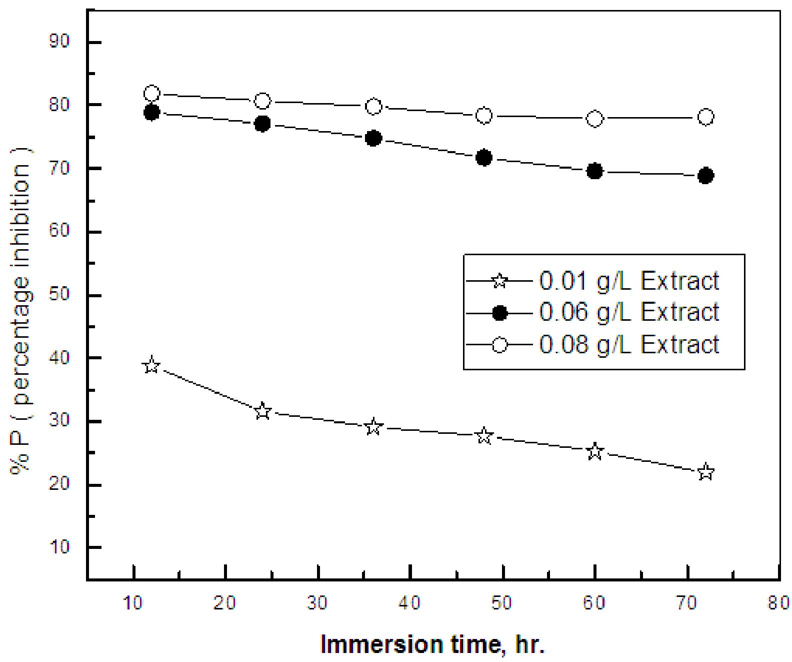

Figure 6. Dependence of the %P of Alhagi Maurorum extract for copper in 0.5M sulphuric acid on the immersion time

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.

$$I_{(aq)} + x(H_2O)_{sur} \rightarrow I_{(Sur)} + x(H_2O)_{aq} \quad (9)$$

Where x is the size ratio (the relative size of the inhibitor molecule to the number of surface–adsorbed water molecules).

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

$$\theta = (R_{ct} - R_{cto}) / R_{ct} \quad (10)$$

Langmuir, Flory Huggins isotherms [25] and Kinetic-Thermodynamic model [26] were used to fit the corrosion data of the Alhagi Maurorum extract.

The Langmuir isotherm is given by

$$[\theta/(1-\theta)]=K[C] \quad (11)$$

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

$$\theta/[x(1-\theta)^x]=K[C] \quad (12)$$

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

$$\log[\theta/(1-\theta)]=\log K' + y \log C \quad (13)$$

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

$$K=K'(1/y) \quad (14)$$

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

Table 3. Linear fitting parameters of the data of Alhagi Maurorum extract to the used models

Langmuir	Flory-Huggins		Kinetic-Thermodynamic	
K	x	K	1/y	K
76.9	1.2	83.0	1.1	92.6

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 Alhagi Maurorum extract on the copper surface and there is a fairly agreement between the values of K obtained using three models. 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 Alhagi Maurorum extract on the surface of the native metal acting as a film forming species decreasing the active area available for acid attack [27].

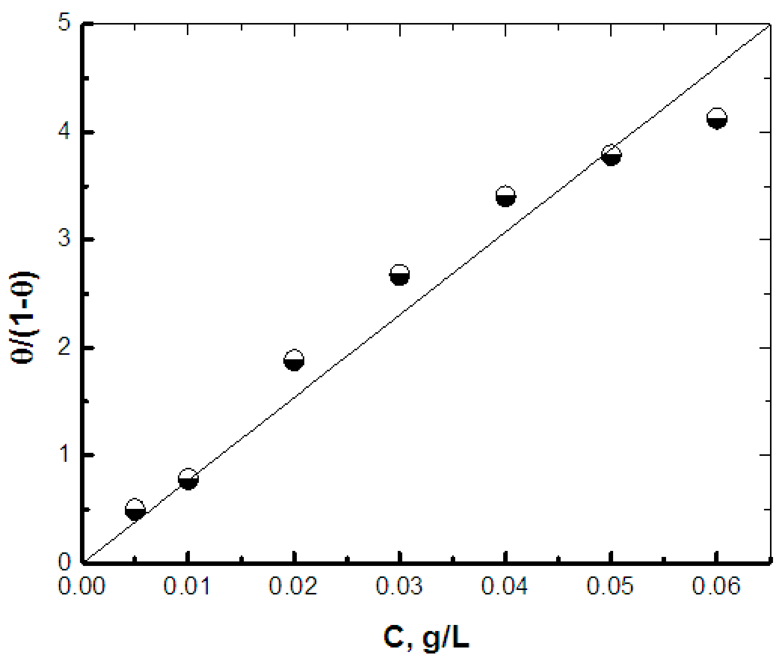

Figure 7. Linear fitting of the data of Alhagi Maurorum extract to Langmuir isotherm for copper

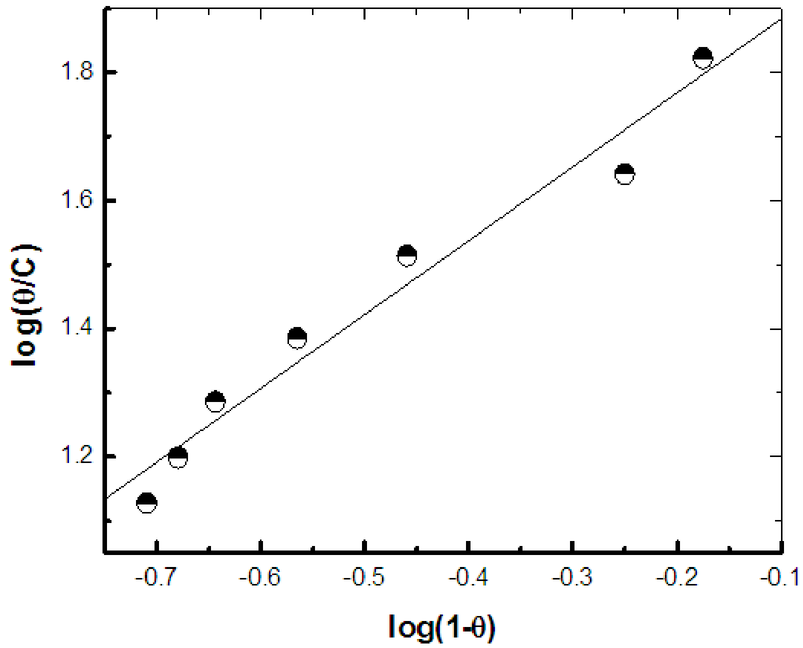

Figure 8. Linear fitting of the data of Alhagi Maurorum extract to Flory Huggins isotherm for copper

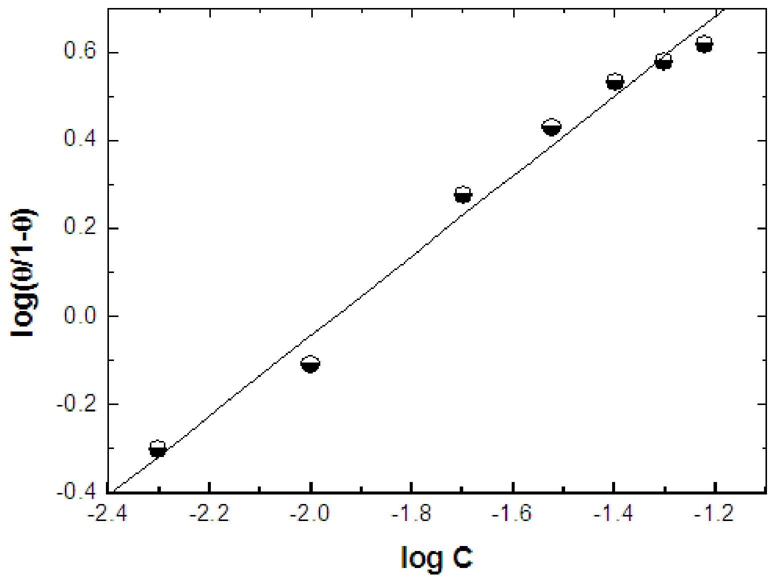

Figure 9. Linear fitting of the data of Alhagi Maurorum extract to Kinetic-Thermodynamic model for copper

3.5. Effect of Temperature on the Corrosion Behaviouer of Copper in 0.5M Sulphuric Acid in Absence and Presence of Alhagi Maurorum Extract

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. Alhagi Maurorum plant was used in this investigation as an example of plant extracts, as a corrosion inhibitor.

Figures 10, 11 show the Nyquist plots of copper in 0.5M sulphuric acid solution, in absence and in presence of Alhagi Maurorum extract at different temperatures. As seen, the size of the capacitive semicircle decreases with rising the temperature of corrosive medium this may be attributed to the acceleration of the corrosive action of the acid. These plots were analyzed by the equivalent circuit that is previously used, Figure 4. The values of Rct and Cdl of copper in 0.5M sulphuric acid, in absence and presence of Alhagi Maurorum 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 Alhagi

Maurorum extract than its absence due to the inhibitive effect of the extract. General trend for increasing Cdl values with rising the temperature are also observed as shown in figure 12, this behaviour is probably attributed to the desorption of the adsorbed ions and the extract ingredients from the copper surface with rising the temperature. Table 4 shows also that the efficiency of Alhagi Maurorum extract for the acidic corrosion of copper is slightly increased from 82 to 88% at temperature 30 to 60°C. This behaviour indicates that Alhagi Maurorum extract act as good corrosion inhibitor for copper in 0.5M H2SO4 and its efficiency is nearly constant and independent on the temperature which means that Alhagi Maurorum act as a good inhibitors for the acidic corrosion of copper.

Determination of the activation parameters

It has been pointed out by many investigators that the logarithm of the charge transfer resistance (ln $(1/R_{ct})$) is a linear function with the reciprocal of the absolute temperature 1/T (Arrhenius equation) [28]:

$$\ln(1/R_{ct}) = -E_a/RT + A \qquad (15)$$

Where Ea 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:

$$1/R_{ct} = (RT/Nh)\exp(\Delta S^*/R)\exp(-\Delta H^*/RT) \qquad (16)$$

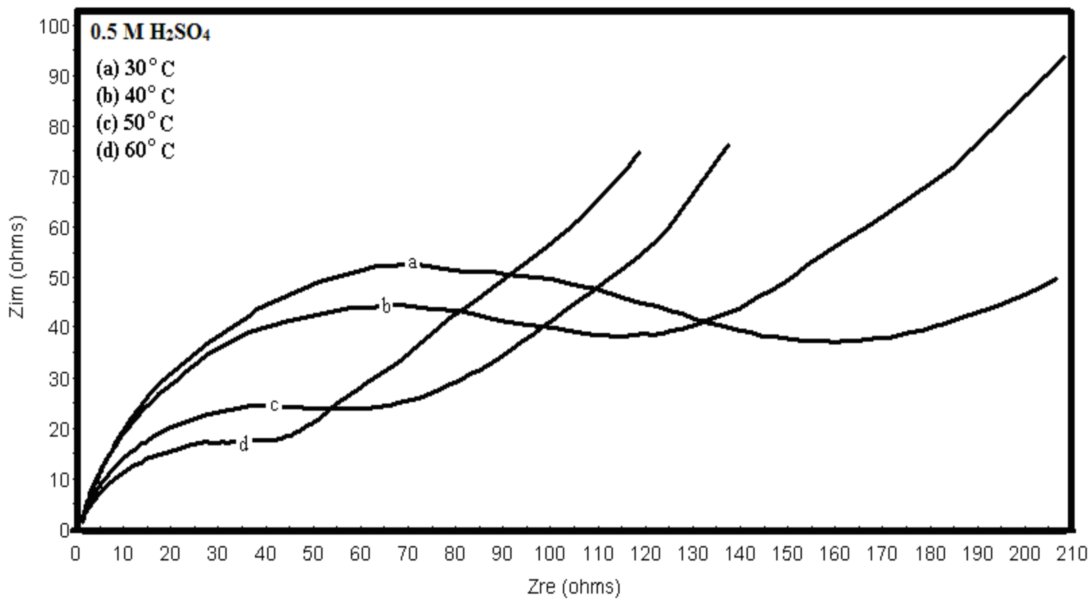

Figure 10. Nyquist plots of copper in 0.5M sulphuric acid at different temperatures

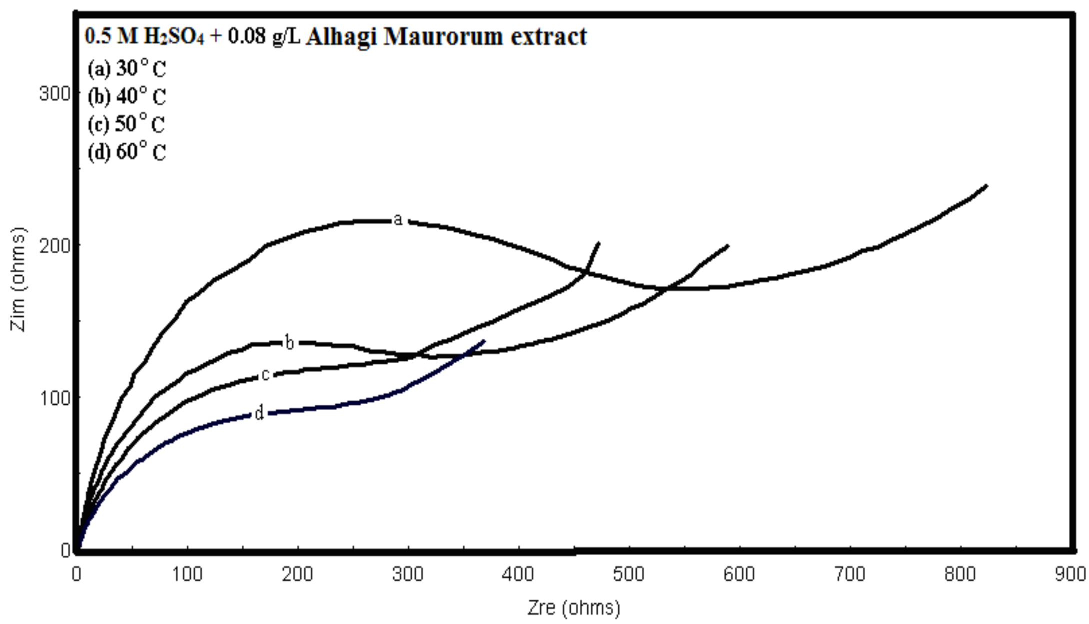

Figure 11. Nyquist plots of copper in 0.5M sulphuric acid, in presence of 0.08 g/L of Alhagi Maurorum extract at different temperatures

Table 4. The electrochemical impedance parameters of copper in 0.5M sulphuric acid solution in absence and presence of 0.08 g/L Alhagi Maurorum extract at different temperatures

Conc.	Temp . °C	Rs	Qf (μF.cm^{-1})	n1	Rp (Ohm.cm^2)	Rct (Ohm.cm^2)	Qdl (μF.cm^{-1})	n2	R2 (Ohm.cm^2)	Q3 (μF.cm^{-1})	n3	%P
Blank	30	1.0	38	0.9	123	131	1320	0.7	273	4520	0.6	--
	40	1.1	39	0.9	117	98	1367	0.7	243	4542	0.6	--
	50	1.2	40	0.9	108	68	1412	0.7	194	4580	0.6	--
	60	1.2	42	0.9	100	36	1432	0.7	167	4599	0.6	--
0.08 g/L Extract	30	1.9	26	0.9	362	741	246	0.7	1600	3492	0.4	82
	40	1.1	25	0.9	240	420	262	0.7	1103	3536	0.4	84
	50	1.2	24	0.9	212	361	287	0.7	742	3842	0.4	86
	60	1.2	24	0.9	197	294	304	0.7	428	3953	0.4	88

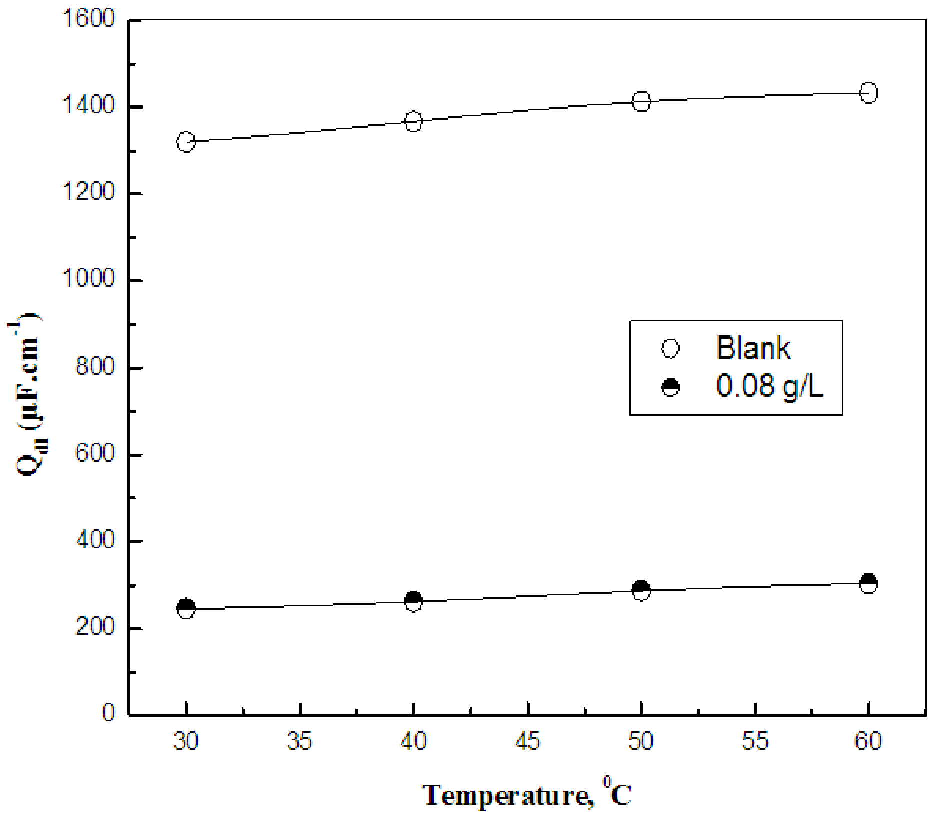

Figure 12. Variation of the C_{dl} values in absence and presence of 0.08 g/L of Alhagi Maurorum extract at different temperatures

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 charge transfer resistance obtained from impedance measurements. The activation parameters of copper in 0.5M sulphuric acid, in absence and presence of Alhagi Maurorum extract were obtained from linear square fits of ln $1/R_{ct}$ and ln $((1/R_{ct})/T)$ data vs. (1/T) as shown in figures (13, 14).

The resulting values of the activation parameters are given in table 5. The values of E_a and ΔH* for copper in sulphuric acid solution are similar to that obtained previously [29-31, 11]. The values of Ea and ΔH* for copper in sulphuric acid solution containing Alhagi Maurorum extract is higher than those free from extract. This behaviour can be discussed on the basis that the adsorption of active ingredients of the extract on the copper metal surface increases the energy barrier of the corrosion reaction. The data in table 5 show a fairly agreement between the values of the activation parameters measured using the weight loss method or the impedance technique.

The negative value of (-ΔS*) implies that the activated complex represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex [32-34]. The increase in (-ΔS*) values in presence of the extract may be attributed to increasing the number of chemical constituents extracted from Alhagi Maurorum extract which are involved in the adsorption process.

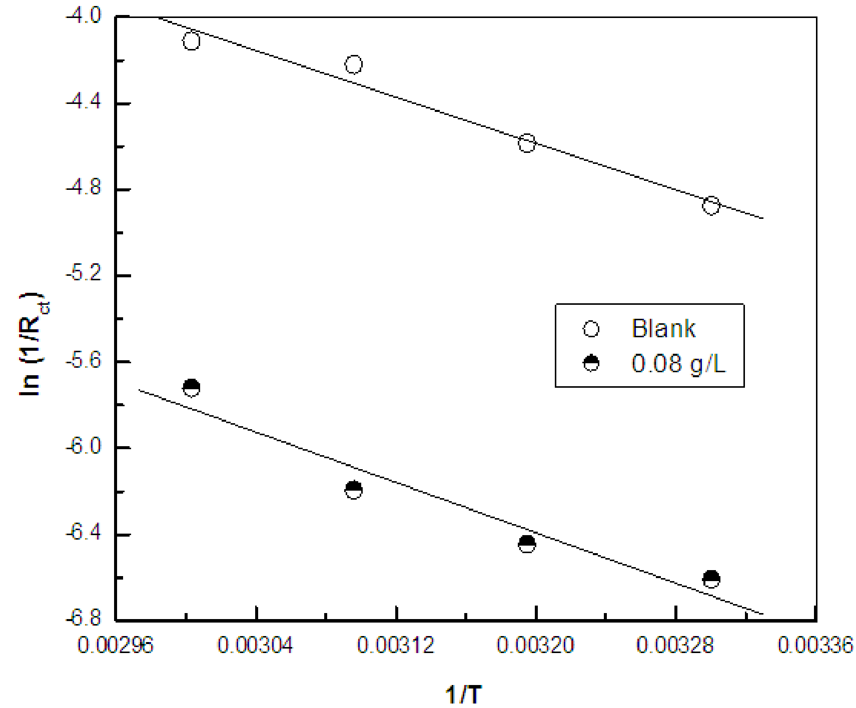

Figure 13a. Linear Square fit for copper of ln $1/R_{ct}$ vs. (1/T)

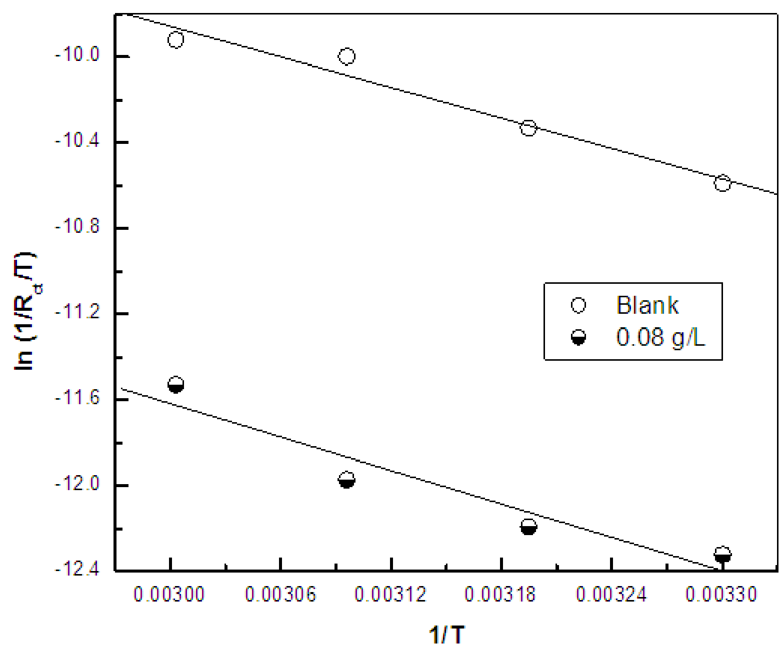

Figure 13b. Linear Square fit for copper of ln((1/Rct)/T) vs. (1/T)

Table 5. The thermodynamic parameters of activation concerning copper corrosion in 0.5M sulphuric acid, in absence and presence of 0.08 g/L of Alhagi Maurorum extract which obtained from impedance and weight loss results

Solution	Activation parameters					
	E_a KJ / mol.		ΔH* KJ / mol.		ΔS* J / mol. K	
	Impedance	Weight loss	Impedance	Weight loss	Impedance	Weight loss
0.5M H_2SO_4	22.38	21.20	19.75	18.56	-220	-189
0.5M H_2SO_4+ 0.08 g/L of extract	24.27	22.46	21.63	19.83	-229	-199

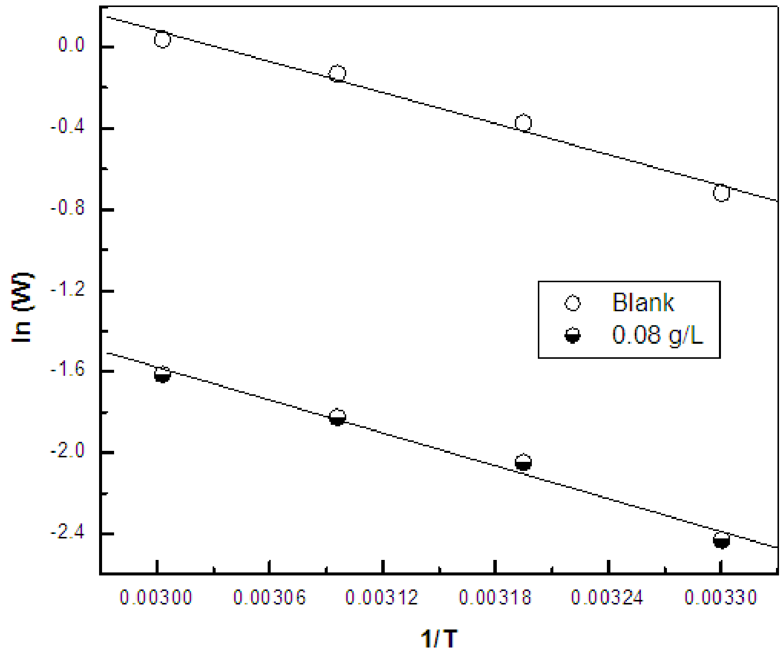

Figure 14a. Linear Square fit for copper of ln W vs. (1/T)

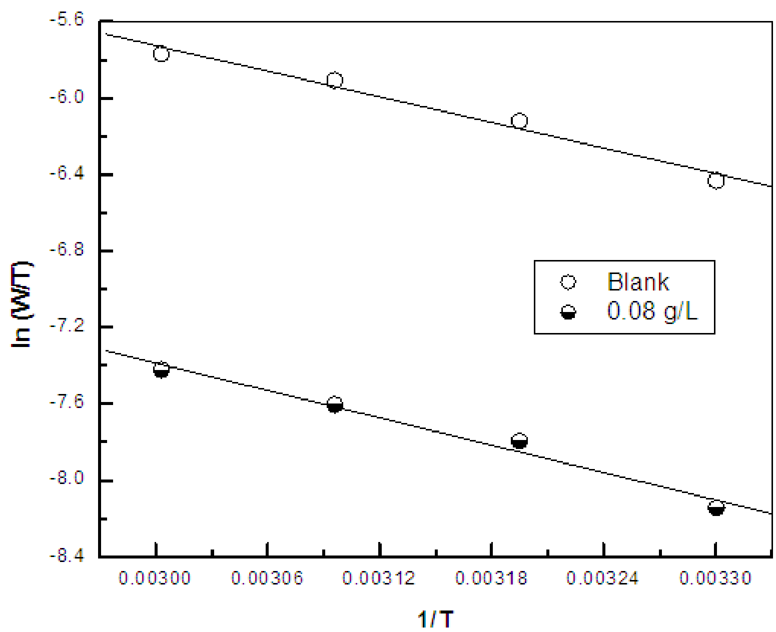

Figure 14b. Linear Square fit for copper of ln((W)/T) vs. (1/T)

3.6. Stability of the Extract

The stock solution of the extract has been stored in refrigerator at 5°C. After certain times of storage, solution of 0.5M H_2SO_4 containing 0.08 g/L extract was prepared and Nyquist plots of copper in these solutions have been recorded (figure 15). As seen, the size of the capacitive semicircle slightly decreases with increasing the storage time. These plots were analyzed by the equivalent circuit that is previously used, Figure 4.

Figure 15 shows the dependence of the percentage inhibition of Alhagi Maurorum extract (0.08 g/L) on the corrosion of copper in 0.5M H_2SO_4 on the storage time of the extract. This curve represents slightly decrease in the percentage inhibition with the storage time up to 40 days indicative of remarkable stability of the extract during the storage period.

4. Conclusions

1. Potentiodynamic polarization results indicated that Alhagi Maurorum extract act as efficient cathodic type inhibitor for the corrosion of copper in 0.5M sulphuric

acid and the efficiency of inhibition was found to increase with increasing the concentration of the extract.

2. EIS results showed that the dissolution process of copper occurs under diffusion control.
3. Weight loss results showed that the inhibition efficiency of Alhagi Maurorum extract for the corrosion of copper in 0.5M sulphuric acid decreases slightly with increasing the immersion time in presence of low concentrations of the extract, but in presence of high concentrations of the extract the inhibition efficiency is nearly constant and independent of immersion time.
4. Langmuir, Flory-Hyggins isotherm, and Kinetic-Thermodynamic model were found to be applicable to fit the data of adsorption of Alhagi Maurorum extract at the copper surface. The data showed that the adsorbed species of Alhagi Maurorum extract are displacing only one water molecule.
5. Impedance measurements at different temperatures showed that the inhibition efficiency of the Alhagi Maurorum extract for the corrosion of copper in 0.5M sulphuric acid increases slightly to 82 - 86% at temperatures 30 - 60°C respectively indicative that Alhagi Maurorum extract is a good inhibitor.
6. The activation parameters of the corrosion reaction of copper in acidic medium are measured using the weight loss method and impedance technique, a fairly good agreement between the values of E_a , ΔH^* and ΔS^* is obtained.

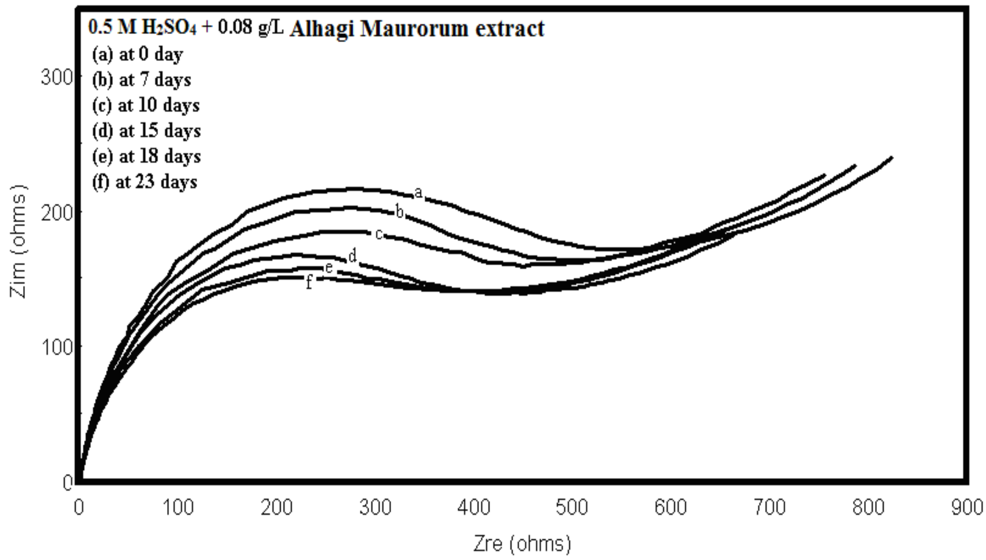

Figure 15. Nyquist plots of copper in 0.5M sulphuric acid, in absence and presence of different concentrations of Alhagi Maurorum extract at different storage time

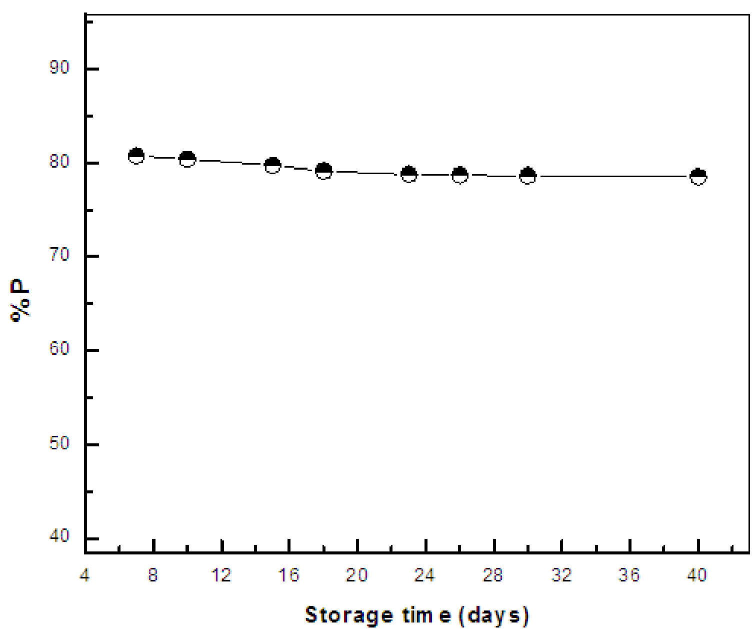

Figure 16. Relation between the percentage inhibition efficiency the storage time of Alhagi Maurorum extract for copper in 0.5M sulphuric acid solution

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