

## Effect of Some Natural Extracts on the Corrosion of Zinc in 0.5 M NaCl

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The inhibitive effect of Lupine, Hlffabar and Damssisa extracts on the corrosion of zinc in aqueous solution of 0.5 M sodium chloride were investigated at 30 °C by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. Potentiodynamic polarization curves indicated that lupine, hlffabar and damssesa act as mixed type inhibitors. EIS measurements showed that the total resistance and consequently the inhibition efficiency increase with increasing concentration of lupine, hlffabar and damssesa indicating the inhibitive effect of these extracts on zinc corrosion. The inhibition of the extract was assumed to occur via adsorption of active ingredients on the metal surface. Theoretical fitting of different isotherms, Langumir, Florry-Huggins and the Kinetic-Thermodynamic model were tested to clarify the nature of adsorption.

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**Keywords:** Corrosion, zinc, hlffabar, lupine, damssisa, adsorption

### 1. INTRODUCTION

Zinc is considered as one of the most important metals in the world since it is used in different industrial applications. Its uses range from metal products to rubber and medicines. Zinc is consumed as metal, mainly as a coating for iron and steel to protect it from corrosion (galvanized metal), as alloying metal to make bronze and brass, as zinc-based die casting alloy and as rolled zinc [1]. However, zinc is a kind of active metals and can be easily corroded in acid medium. The searching of an effective inhibitor to zinc is significant for the protection during zinc machining [2]. The effect of organic inhibitors [3] such as, sodium benzoate (NaBz) and Sodium N-dodecanoyl sarcosinate (NaDS). S-Octyl-3-thiopropionate (NaOTP), 8-quinolinol (8-QOH) and 1,2,3-benzotriazole (BTAH)

on corrosion of zinc in aerated 0.5 M NaCl solution were investigated by potentiodynamic polarization measurements. Cerium (III) chloride  $\text{CeCl}_3$  and sodium octyl thiopropionate  $\text{C}_8\text{H}_{17}\text{S}(\text{CH}_2)_2\text{COONa}$  (NaOTP) [4] are effective inhibitors for zinc corrosion in 0.5 M NaCl. The inhibition effects of chromate-free[5], environmentally acceptable anion inhibitors were examined on corrosion of zinc in an aerated 0.5 M NaCl solution by polarization measurements, Sodium silicate  $\text{Na}_2\text{Si}_2\text{O}_5$  and phosphate  $\text{Na}_3\text{PO}_4$  were remarkably effective on zinc corrosion. Recently, Plant extracts have again become important as an environmentally acceptable,[6-14] readily available and renewable source for a wide range of needed inhibitors. The aqueous extract of the leaves of henna (lawsonia) [15] was tested as corrosion inhibitor of zinc in neutral solutions, using the polarization technique. It was found that the extract acts as a good corrosion inhibitor in the tested media. The main objectives of this study were to investigate the effect of lupine, hlfabar and damssesa extracts on the mechanism of the corrosion of zinc and to evaluate their inhibition efficiency in preventing the corrosion of zinc metal in 0.5 M NaCl.

## 2. EXPERIMENTAL

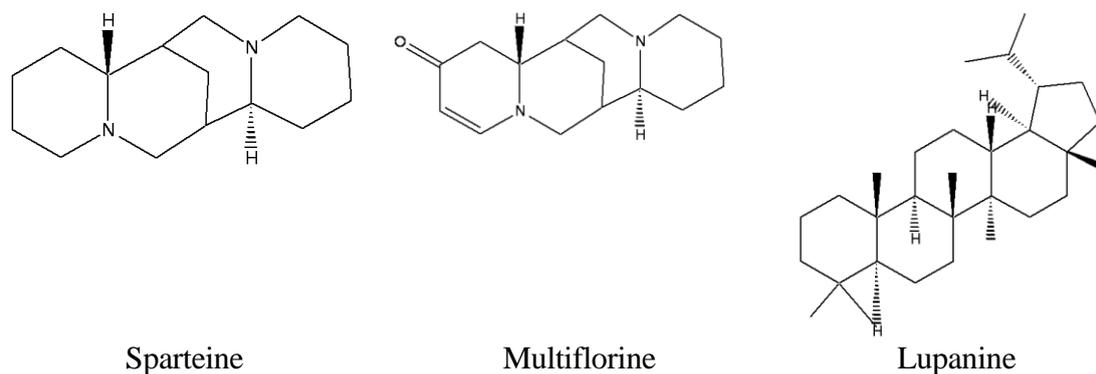
### 2.1. Electrochemical Tests

Electrochemical impedance and polarization curves measurements were achieved using ACM 631 instrument. The frequency range for EIS measurements was  $0.01 \leq f \leq 3 \times 10^4$  Hz with an applied potential signal amplitude of 10 mV around the rest potential. Polarization curves measurements were carried out at scan rate 20 mV/min. The data were obtained in a three electrode mode; graphite rod and saturated calomel electrode were used as counter and reference electrodes. The specimens used for constructing the working electrode were zinc rods that had the following chemical composition (wt %): Zn 98.5; Pb 1.0; Ca 0.4. The zinc samples were fixed in poly tetra fluoro ethylene (PTFE) rods by an epoxy resin in such a way that only one surface was left uncovered. The exposed area ( $0.28 \text{ cm}^2$ ) was mechanically polished with a series of emery papers of variable grades, the samples were then washed thoroughly with distilled water followed with A.R. ethanol and finally with distilled water, just before insertion in the cell. Measurements were done at 30 °C.

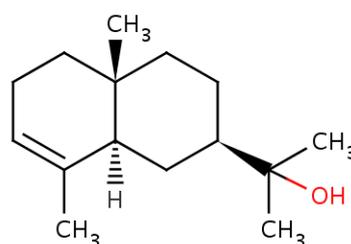
### 2.2. Solution Preparation

Lupine seeds contain up to 5% quinolizidine alkaloids, lupanine was the most abundant, multiflorine and sparteine were also present (figure 1a). Hlfabar contains hydroxyl- $\alpha$ -eudesmol derivatives (figure 1b). Damssisa contain Lactones, damsine, ambrosin and coumarins (figure 1c). The seeds of lupine, hlfabar and damssesa are edible, Lupine used for treatment of anorexia and diabetes while Hlfabar also called Camel-grass, used for medicinal and cosmetic purposes. Damsissa used for treatment to reduce blood sugar and schistosomiasis. The solutions were prepared using double distilled water. Stock solutions of lupine, hlfabar and damssesa seeds were obtained by refluxing 10 g of dry plant seeds in 100 mL of distilled water for 60 min. The refluxed solution was filtered to remove any contamination. The concentration of the stock solution was determined by evaporating 10 mL of

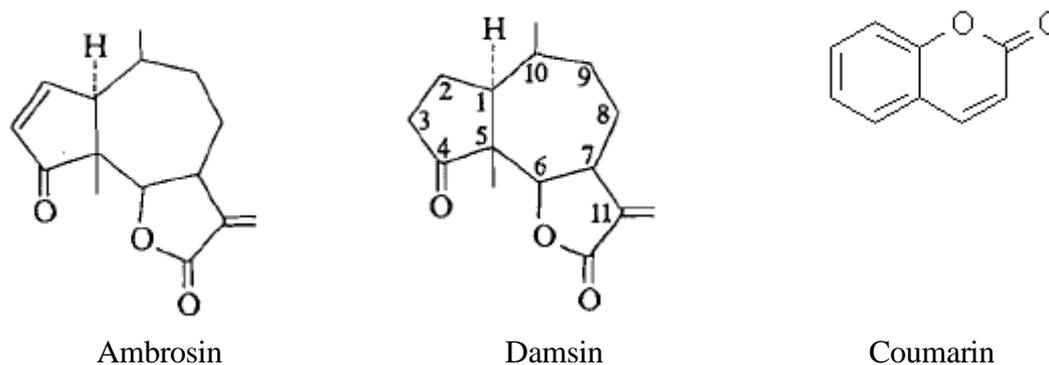
the filtrate and weighing the residue. The concentration of the stock solution was expressed in terms of ppm.



(a): Lupine Chemical Constituents



(b): Hlfbabar Chemical Constituents



(c): Damssesa Chemical Constituents

**Figure 1.** Chemical constituents of Lupine, Halfabar and Damssesa

### 3. RESULTS AND DISCUSSION

Corrosion of zinc in an oxygenated 0.5 M NaCl solution occurs by combination of the anodic zinc dissolution and the cathodic oxygen reduction,[16-18]

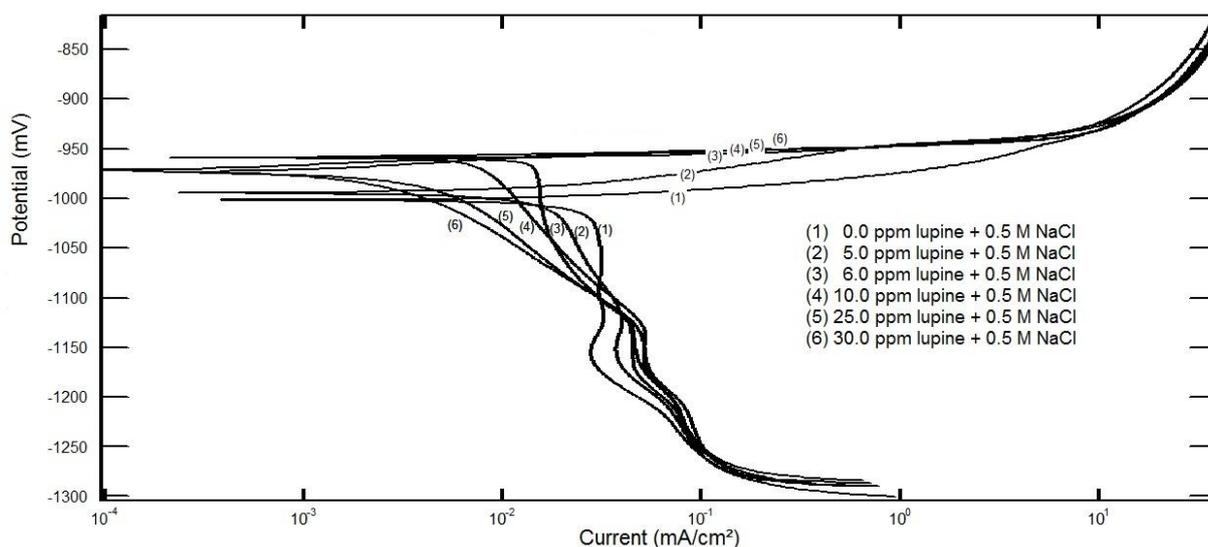


Because of the solubility of zinc hydroxide is markedly low (the solubility product of  $\text{Zn}(\text{OH})_2$ ,  $K_{sp} = 3 \times 10^{-17}$ )[19] zinc hydroxide precipitates on zinc surface and changed gradually to zinc oxide, Thus, a passive film of zinc oxide and hydroxide forms on the surface to prevent zinc corrosion[20].



In the presence of  $\text{Cl}^-$ , the hydroxide reacts with chloride to form soluble  $\text{Zn}^{+2} \cdots \text{Cl}^- \cdots \text{OH}^-$  complexes [21]. Local dissolution of the passive film occurs, resulting in pitting corrosion [22].

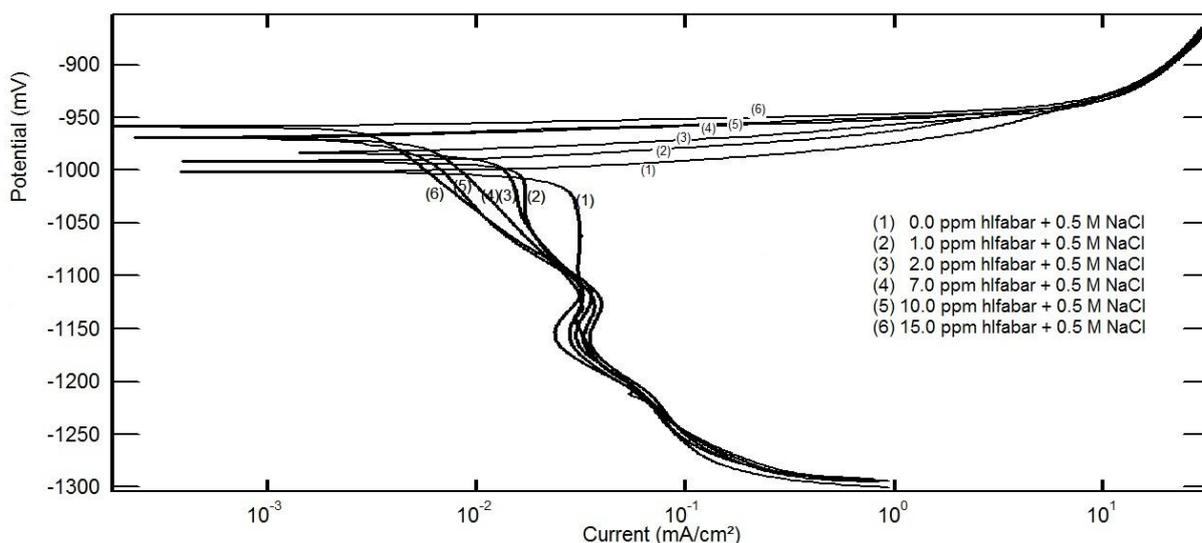
### 3.1. Polarization measurements



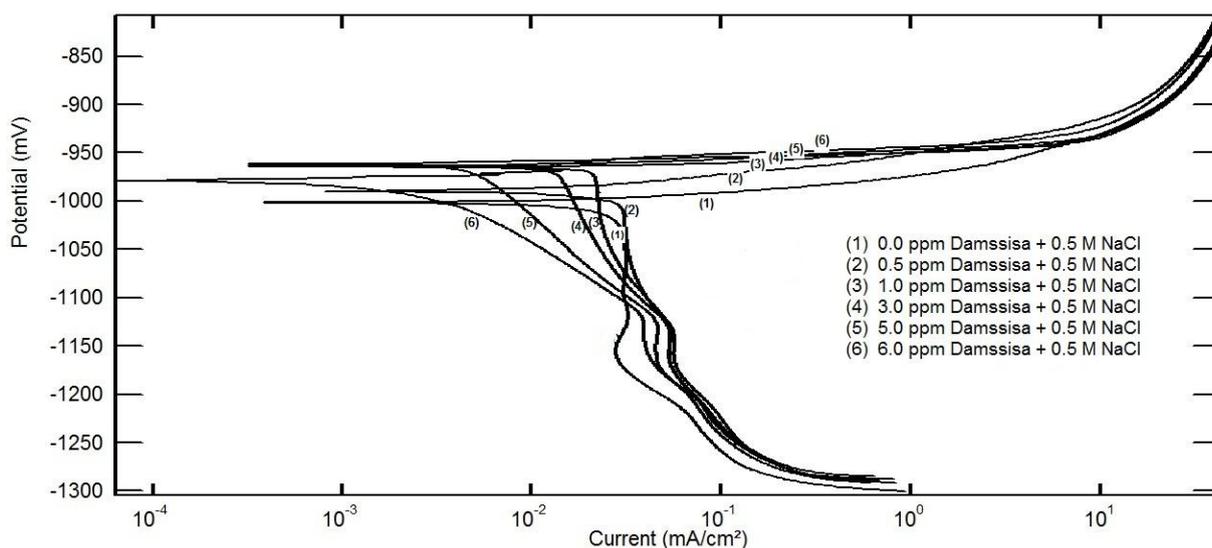
**Figure 2.** The potentiodynamic polarization curves for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of lupine extract.

Figures 2, 3 and 4 show the potentiodynamic polarization curves for zinc in 0.5 M NaCl solution in the absence and presence of different concentrations of lupine, hlfabar and damssesa seeds extracts respectively. Inspection of the figures reveal that the presence of these extracts has little effect on anodic polarization curve and predominate effect on the cathodic one indicating that these extracts act as mixed type inhibitors of zinc metal in 0.5 M NaCl solutions. The cathodic polarization curve in

absence of natural extracts shows limiting current in the range  $10^{-2}$  to  $10^{-1}$  mA this indicates that the cathodic reaction is controlled by diffusion of oxygen from the bulk solution to the zinc surface.



**Figure 3.** The potentiodynamic polarization curves for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of hlafabar extract.



**Figure 4.** The potentiodynamic polarization curves for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of damssesa extract.

It is clear from figures (2-4) that in presence of extracts the plateau of the cathodic polarization curve of zinc splits into two parts which can be discussed on the following bases. Cathodic reduction of oxygen can be expressed either by a direct  $4e^-$  transfer as shown by equation:



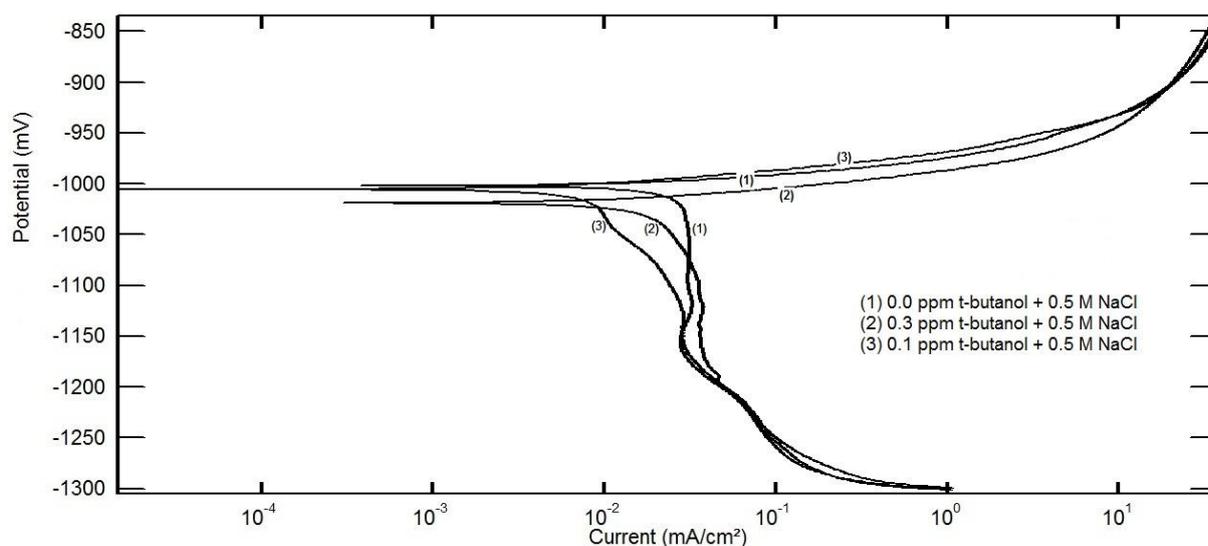
or by two consecutive  $2e^-$  steps involving a reduction to hydrogen peroxide first:



followed by a further reduction:



in absence of the extracts 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 extracts the first step is retarded by the adsorption of the active adsorbable species of the extract at the zinc surface and becomes the rate determining step. To confirm this argument t-butanol as surface active substance[23] is added to zinc in 0.5 M NaCl, the same result of the splitting of the plateau of the cathodic polarization of zinc is attained(Fig 5).

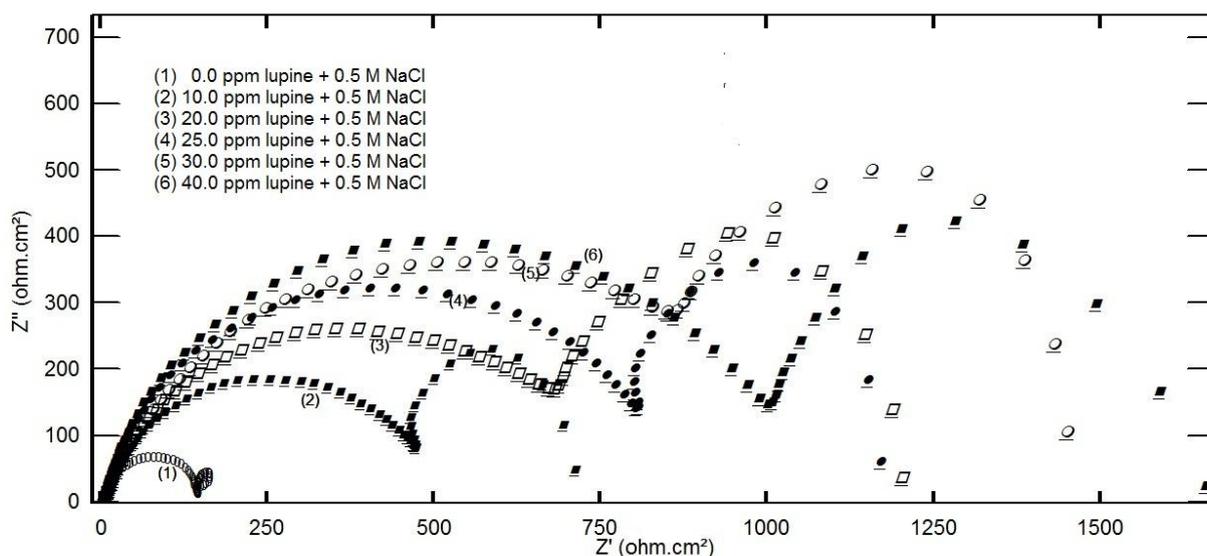


**Figure 5.** The potentiodynamic polarization curves for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of t-butanol.

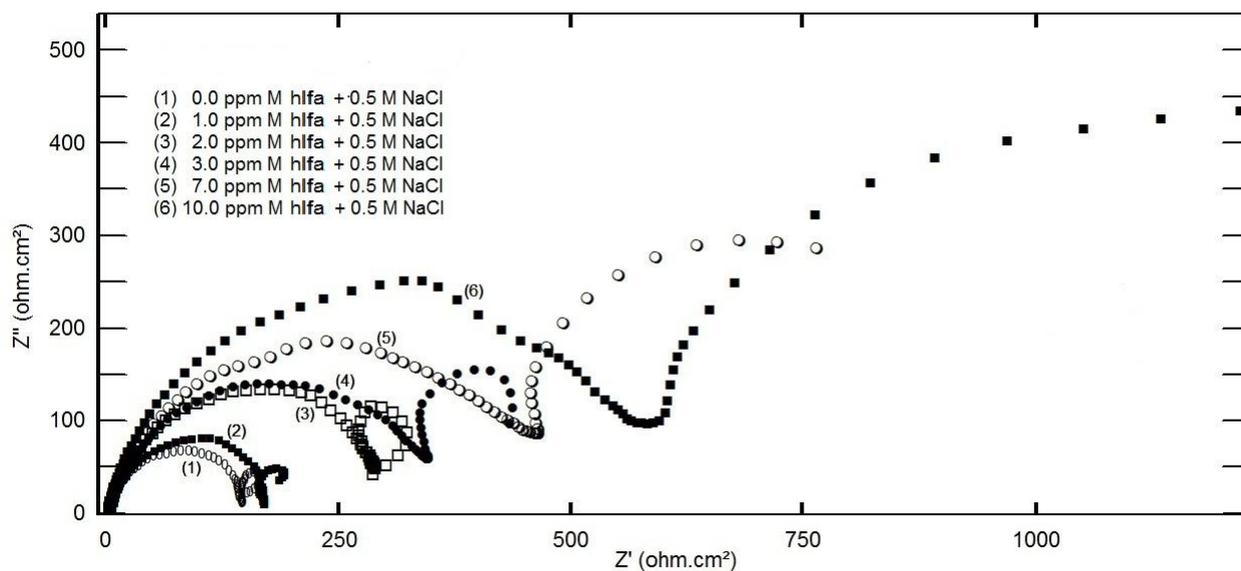
### 3.2. EIS measurements

Electrochemical Impedance Spectroscopy (EIS), have been shown to be an efficient and convincing tool for analyzing the corrosion behavior of metals. Figures 6-8, represent Nyquist plots for zinc metal in 0.5 M NaCl solution in the absence and presence of different concentrations of lupine, hlfabar and damssesa extracts. The figures manifested two depressed capacitive semicircles, at higher and lower frequencies regions. This behavior has been previously reported by several authors [24-27] and discussed on the basis of, the first semicircle (high frequencies) is mainly due to the charge transfer associated with the effect of ionic double-layer capacitance, while the second semicircle (low

frequencies) may indicate a finite thickness layer diffusion process related mainly to oxygen reduction or to diffusion of the oxidation products from the zinc electrode to the bulk solution.



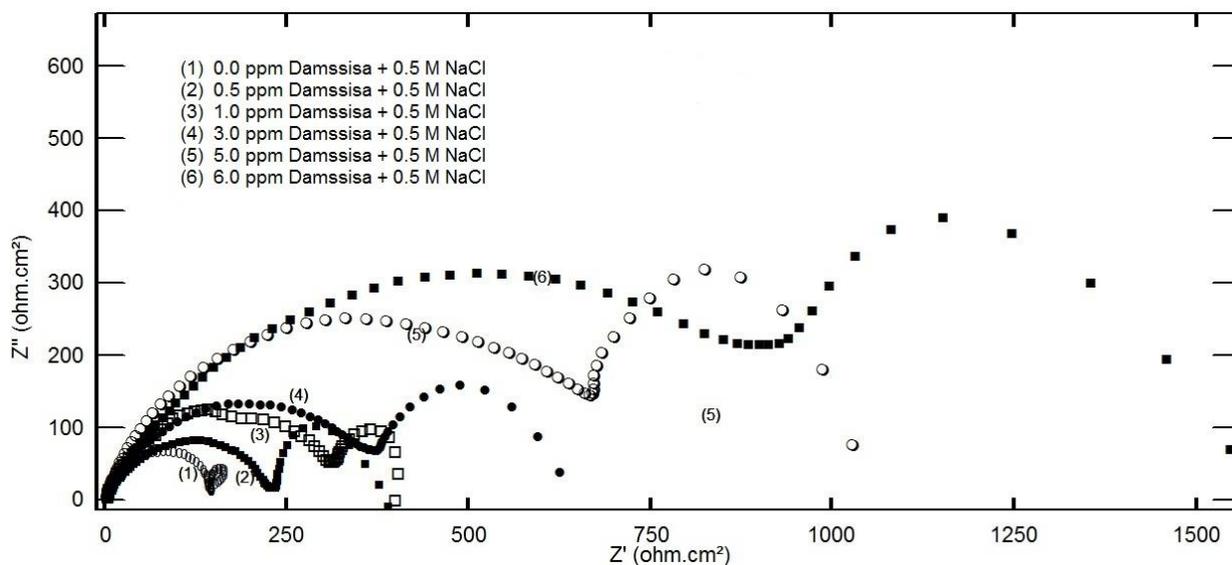
**Figure 6.** Nyquist plots for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of lupine extract



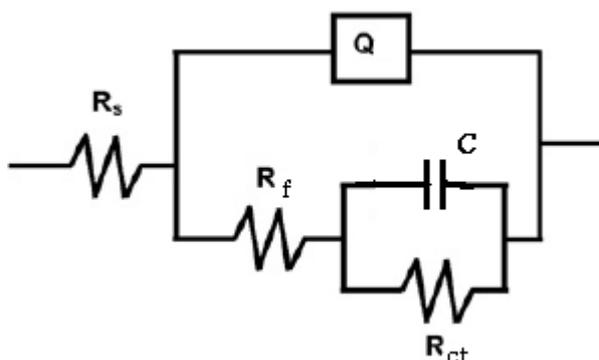
**Figure 7.** Nyquist plots for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of hlfa extract

The impedance spectra for different Nyquist plots were analyzed by fitting the experimental data using Zsimpwin program to a simple equivalent circuit model, figure 9. The equivalent circuit

model includes the solution resistance  $R_s$  and the constant phase element  $Q$  which is placed in parallel to charge transfer resistance element  $R_f$ .



**Figure 8.** Nyquist plots for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of damssesa extract



**Figure 9.** The equivalent circuit model

The low frequency locus displays the characteristics of parallel circuit connected. This circuit includes capacitor  $C$  which is placed in parallel to charge transfer resistance element  $R_{ct}$ . The  $Q$  is used in this model to replace capacitor because it hardly has pure capacitance in real electrochemical process. It is used to compensate for non-homogeneity in the system and is defined by two values,  $C$  and  $n$  where;  $0 \leq n \leq 1$ . Note that for a value of  $n = 1$ , the  $Q$  value corresponds to the capacitance, for  $n = 0$ , a resistance and for  $n = 0.5$  a Warburg element. The values of the electrochemical parameters obtained from EIS for zinc in 0.5 M NaCl solution containing different lupine, hlffabar and damssesa

extracts concentrations and the inhibition efficiency (% inh) are given in tables 1 - 3. The % inhibition were calculated from impedance measurements using the relation

$$\% \text{ inh.} = [(R_T - R_{T0}) / R_T] \times 100$$

Where;  $R_{T0}$  and  $R_T$  are the total resistances in the absence and presence of different seeds extracts.

**Table 1.** The values of the electrochemical impedance parameters for zinc in 0.5 M NaCl solution in the absence and presence of different concentrations of lupine extracts at 30 °C

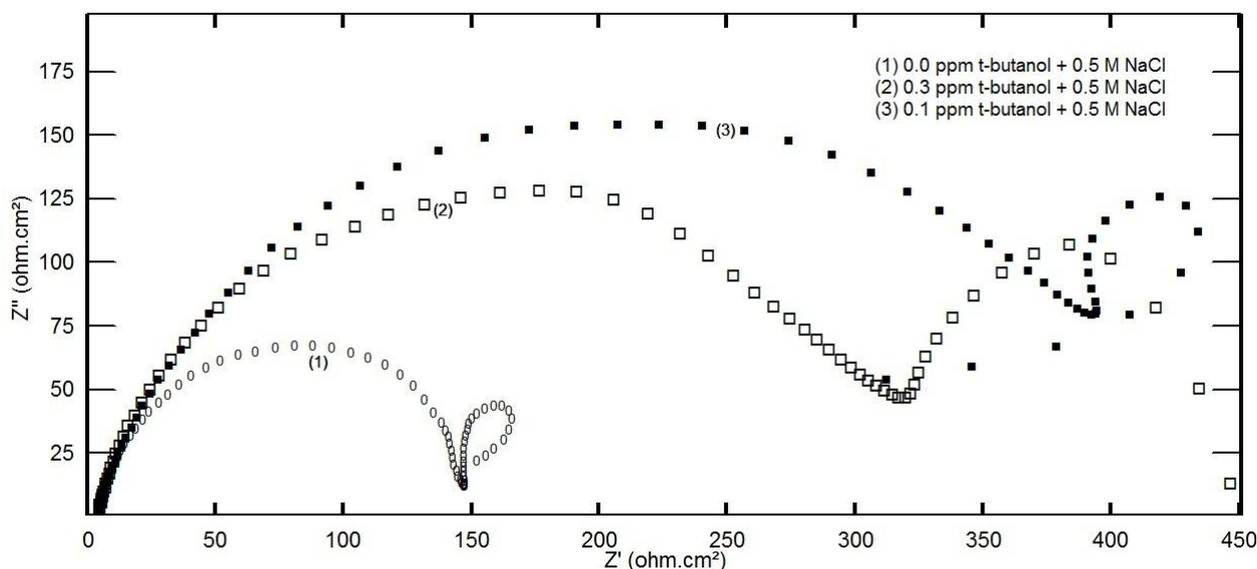
Concn ppm	$R_s$ Ohm.cm <sup>2</sup>	$Q$ F.cm <sup>-1</sup>	$n$	$R_f$ Ohm.cm <sup>2</sup>	$C$ F.cm <sup>-1</sup>	$R_{ct}$ Ohm.cm <sup>2</sup>	$R_T$ Ohm.cm <sup>2</sup>	% inh
0.0	3.9	1.17E-5	0.89	145.4	5.35E-3	45.4	190.8	-
1.0	3.9	1.99E-5	0.84	186.9	5.88E-3	95.0	281.9	32.3
5.0	4.0	1.96E-5	0.84	218.1	5.86E-3	123.0	341.1	44.1
6.0	3.5	1.30E-5	0.87	253.8	3.42E-3	155.2	409.0	53.3
7.5	3.7	1.77E-5	0.83	333.4	3.91E-3	194.7	528.1	63.9
10.0	3.6	1.64E-5	0.84	417.9	1.87E-3	325.3	743.2	74.3
20.0	3.2	2.40E-5	0.82	701.8	9.01E-4	629.4	1331.2	85.7
25.0	3.8	1.28E-5	0.87	808.9	9.36E-4	654.9	1463.8	87.0
30.0	4.6	3.20E-5	0.80	950.4	7.18E-4	700.3	1650.7	88.4
40.0	4.2	1.40E-5	0.87	1007.0	8.22E-4	739.3	1746.3	89.1

**Table 2.** The values of the electrochemical impedance parameters for zinc in 0.5 M NaCl solution in the absence and presence of different concentrations of hlffabar extracts at 30 °C.

Concn ppm	$R_s$ Ohm.cm <sup>2</sup>	$Q$ F.cm <sup>-1</sup>	$n$	$R_f$ Ohm.cm <sup>2</sup>	$C$ F.cm <sup>-1</sup>	$R_{ct}$ Ohm.cm <sup>2</sup>	$R_T$ Ohm.cm <sup>2</sup>	% inh
0.0	3.9	1.17E-5	0.89	145.4	5.35E-3	45.4	190.8	-
1.0	3.9	1.02E-5	0.89	169.9	8.76E-3	79.1	249.0	23.4
2.0	4.0	1.03E-5	0.88	289.8	2.62E-3	112.4	402.2	52.6
3.0	3.7	1.35E-5	0.84	346.0	2.10E-3	231.0	577.0	66.9
7.0	3.7	1.48E-5	0.84	462.4	1.33E-3	561.9	1024.3	81.4
10.0	3.2	8.01E-6	0.87	591.7	6.99E-4	792.3	1384.0	86.2
15.0	3.7	7.17E-6	0.89	718.4	6.72E-4	770.5	1488.9	87.2
17.0	3.7	1.10E-5	0.87	1429	3.94E-4	992.0	2421.0	92.1
30.0	3.9	1.07E-5	0.89	1660	3.19E-4	1252	2912.0	93.4
40.0	3.7	1.21E-5	0.87	2479	4.46E-4	1144	3623.0	94.7

**Table 3.** The values of the electrochemical impedance parameters for zinc in 0.5 M NaCl solution in the absence and presence of different concentrations of damssesa extracts at 30 °C.

Concn ppm	$R_s$ Ohm.cm <sup>2</sup>	$Q$ F.cm <sup>-1</sup>	$n$	$R_f$ Ohm.cm <sup>2</sup>	$C$ F.cm <sup>-1</sup>	$R_{ct}$ Ohm.cm <sup>2</sup>	$R_T$ Ohm.cm <sup>2</sup>	% inh
0.0	3.9	1.17E-5	0.89	145.4	5.35E-3	45.4	190.8	-
0.5	3.4	2.62E-5	0.73	234.7	5.66E-3	153.8	388.5	50.9
1.0	4.0	2.01E-5	0.80	316.7	1.93E-3	122.3	439.0	56.5
3.0	3.2	2.56E-5	0.76	382.3	1.95E-3	260.9	643.2	70.3
4.0	3.8	9.11E-5	0.60	741.9	2.02E-3	364.7	1106.6	82.8
5.0	3.0	1.87E-5	0.80	677.3	1.25E-3	460.4	1137.7	83.2
6.0	2.5	3.90E-5	0.72	980.7	1.43E-3	576.9	1557.6	87.8
7.0	2.8	1.43E-5	0.81	1119	6.23E-4	684.0	1803.0	89.4
10.0	2.5	2.38E-5	0.77	1162	8.96E-4	855.9	2017.9	90.5
15.0	3.2	3.03E-5	0.76	1233	5.34E-4	821.4	2054.8	90.7



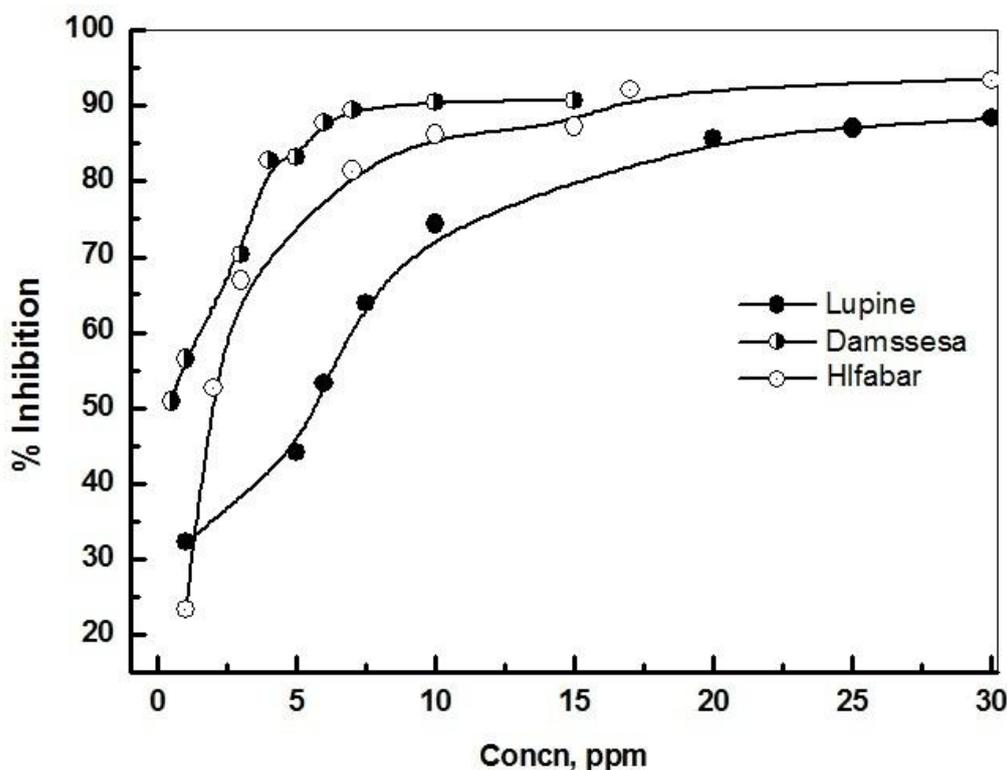
**Figure 10.** Nyquist plots for zinc in 0.5 M NaCl solution in absence and presence of different concentrations of t-butanol.

The data indicate that increasing extract concentration increases the  $R_{ct}$  and the % inhibition and decreases the double layer capacitance which indicate that the lupine, hlfabar and damsissa extracts act as corrosion inhibitors for zinc in neutral medium containing chloride ions. The observed inhibitive action of lupine, hlfabar and damsissa extracts could be due to the adsorption of its molecules on Zinc surface making a barrier for charge and mass transfer between the metal and environment[28]. Figure 10 represents Nyquist plots for 0.5 M NaCl in absence and presence of

different concentrations of t-butanol. The figure manifested two depressed capacitive semicircles indicating similar behavior to that obtained in presence of different plant extracts indicating that this behavior is attributed to the adsorption of t-butanol molecules or the active ingredients at zinc/solution interface.

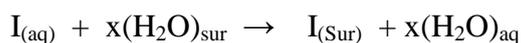
### 3.3. Application of adsorption isotherms

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 is assumed to be due to its adsorption [29] at the metal/solution interface.



**Figure 11.** Variations of percentage inhibition with concentration of lupine, hlfabar and damssesa extracts

This phenomenon 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)  $\pi$ -interaction with the metal, and (iv) a combination of all of the above [30]. The inhibition action was regarded as simple substitution process [31], in which an inhibitor molecule in the aqueous phase substitutes an  $x$  number of water molecules adsorbed on the metal surface, viz.



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. In addition, if one is to realize that the free energy of adsorption is itself a function of surface coverage, lateral interaction effects should be included as well. The degree of surface coverage ( $\theta$ ) of the metal surface by an adsorbed plant extract was calculated using the equation:

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

The variations of percentage inhibition with concentration of different plant extracts were shown in figure 11. These curves are adsorption isotherms that are characterized by an initial steeply rising part indicating the formation of a mono-layer adsorbate films on the zinc surface. At high concentrations, the inhibitory effect was constant or had a maximum suggesting complete saturation of the surface by the inhibitor molecules. The appearance of critical concentration after which the inhibitive effect of extract decreased was also observed.

The Langmuir isotherm is given by [32]

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

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 [33]:

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

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 [34]:

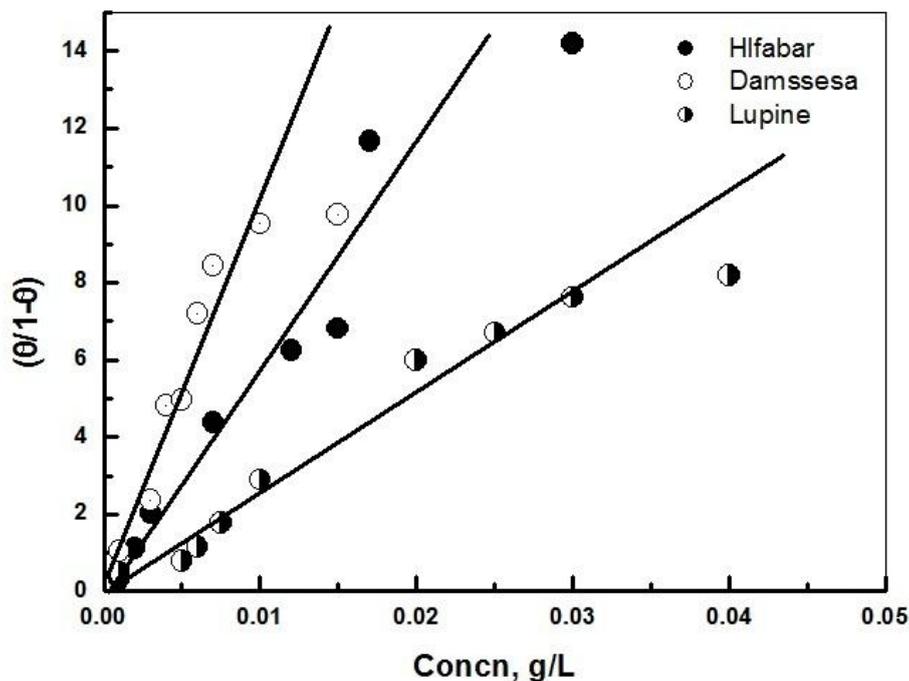
$$\log [\theta / (1 - \theta)] = \log K' + y \log C$$

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

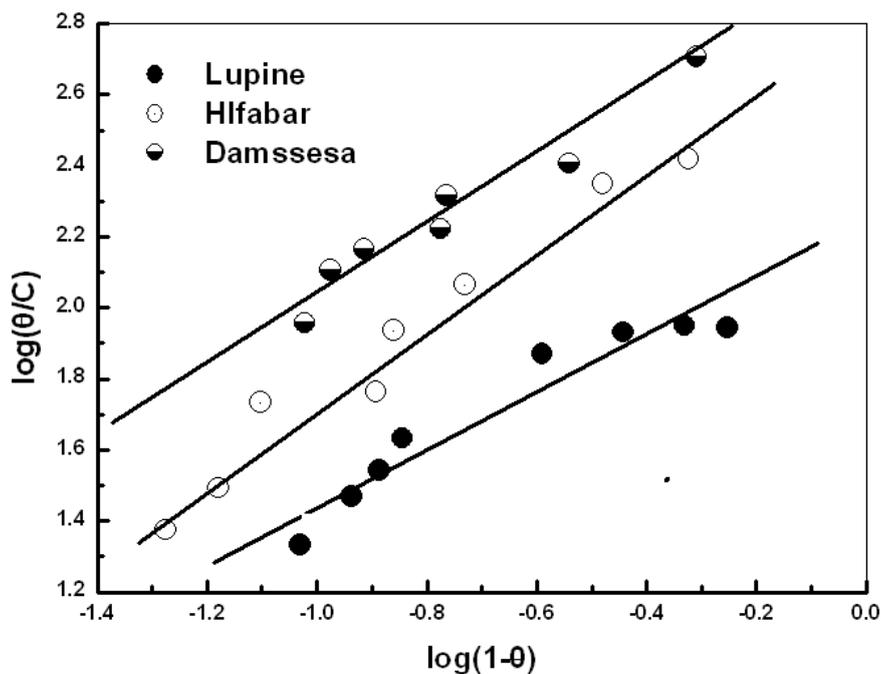
$$K = K' (1/y)$$

The above mentioned isotherms were used to fit the corrosion data of the lupine, hlfabar and damssesa extracts. Figures 12-14 show the application of the above mentioned models to the results of adsorption of these extracts on zinc surface. The parameters obtained from the Figures are depicted in table 4. It is clear that the Langmuir isotherm is applicable to fit the data of Lupine, Halfabar and

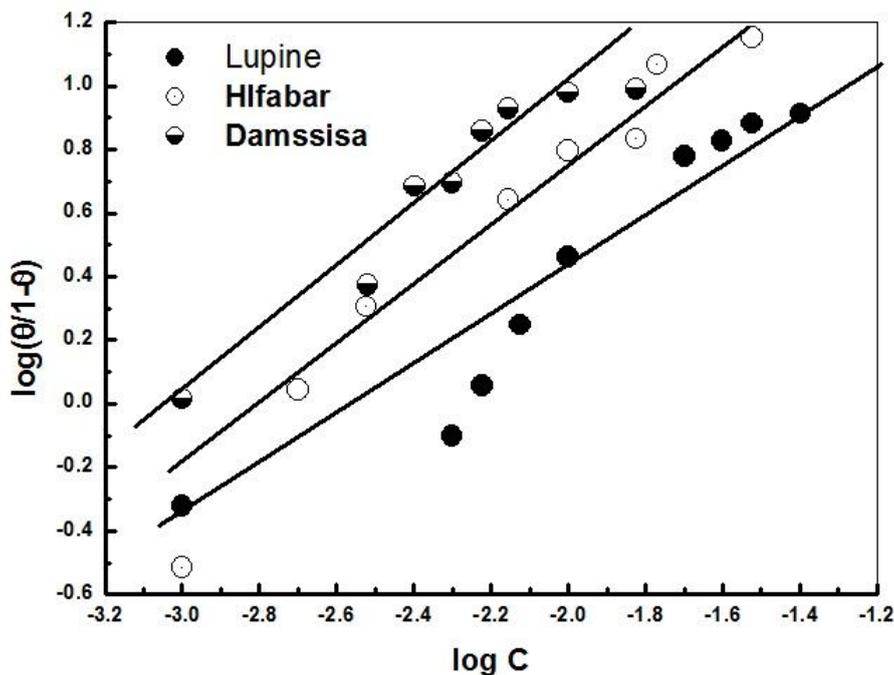
Damssesa indicating ideal behavior in the adsorption processes [35] of these extracts on the zinc surface. On the other hand, Flory-Huggins isotherm is found to be applicable.



**Figure 12.** Application of Langmuir model to the results of adsorption of different extracts on zinc surface.



**Figure 13.** Application of Flory Huggins model to the results of adsorption of different extracts on zinc surface.



**Figure 14.** Application of Kinetic-Thermodynamic model to the results of adsorption of different extracts on zinc surface.

**Table 4.** Linear fitting parameters of Lupine, Halfabar and Damssesa according to the Langmuir, Flory-Huggins and Kinetic-Thermodynamic models.

Plant extracted	Model parameters				
	Langmuir	Flory-Huggins		Kinetic-Thermodynamic	
	K	x	K	1/y	K
Lupine	228.7	1.21	329.0	0.880	203.0
Halfabar	450.5	1.025	757.5	1.104	669.3
Damssesa	1032.8	0.995	1746.2	0.995	1083.5

The values of the size parameter  $x$  for the three extracts indicated that the adsorbed species could displace only one water molecule from the zinc surface [36] in case of Halfabar and Damssesa. Kinetic-Thermodynamic model is also found to fit the data of all plant extracts. The number of active sites occupied by a single inhibitor molecule,  $1/y$  were nearly equal to the size parameter  $x$  for all plant extracts. 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 [37]. Hence, according to the numerical values of  $K$  obtained from the three models, the inhibition efficiency of different plant extracts could be arranged in the order: Damssesa > Halfabar > Lupine

The inhibitive effect could be explained on the basis of the mechanism that suggests adsorption of the plant extract-complex on the surface of the native metal acting as a film forming species decreasing the active area available for the corrosion reaction.

#### 4. CONCLUSIONS

1. The extracts of lupine, hlfabar and damssesa act as a good inhibitors for the corrosion of zinc in 0.5 M NaCl.

2. Lupine, hlfabar, and damssesa extracts are considered as mixed type inhibitors and its molecules are adsorbed on both anodic and cathodic sites at the metal surface and hence can be used as surfactants.

3. The inhibition efficiency was found to increase with increasing extracts concentration up to a maximum value (89.1, 94.7 and 90.7) at 40, 40 and 15 ppm for lupine, hlfabar and damssesa extracts respectively. Above these concentrations, the inhibition efficiency decreased.

4. The inhibition efficiency of different plant extracts is in the order: Damssesa > Halfabar > Lupine.

5. The adsorption of the ingredients of these extracts retarded the first step of the oxygen reduction at the zinc surface causing a split of the plateau of the cathodic polarization curve into two parts.

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