Anal. Bioanal. Electrochem., Vol. 11, No. 10, 2019, 1289-1303

Analytical & Bioanalytical Electrochemistry

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Full Paper

Lepidium sativum Seeds as Green Inhibitor for Carbon Steel Corrosion in 1.0 M Hydrochloric Acid Solution

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Received: 31 July 2019 / Received in revised form: 30 September 2019 / Accepted: 2 October 2019 / Published online: 31 October 2019

Abstract- In this work, we are interested in studying the effect of the addition *Lepidium sativum seeds (LSS)* on the inhibition of the corrosion of carbon steel in acidic medium 1.0 M HCl. The inhibition of the corrosion reaction of carbon steel (CS) was performed using (*LSS*) in a 1.0 M hydrochloric acid medium using impedance spectroscopy (*EIS*) and potentiodynamic polarization (*PDP*). The phytochemical study revealed the existence of flavonoids, saponosides, tannins, alkaloids, sterols and polyterpenoids compounds. Inhibitory efficiency increases with increasing inhibitor concentration and decreases with increasing temperature. The experimental results show that *Lepidium sativum seeds (LSS)* is a good corrosion inhibitor where the maximum inhibition is around 90% at 2 g/L. PDP studies show that the *Lepidium sativum seeds (LSS)* act as mixed inhibitor. Corrosion current density decreased from 729 µAcm^{-2} (blank) to 125 µAcm^{-2} at 2 g/L *(LSS)*. The studied inhibitor is adsorbed on the metal surface according to the model of the Langmuir adsorption isotherm.

Keywords- Lepidium sativum seeds (LSS), Screening phytochemical, Carbon Steel, HCl, Corrosion inhibition

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1. INTRODUCTION

The plant used in our study is *Lepidium sativum L*, a plant belonging to the *brassicaceae* family. It is an fast annual growing plant, also called garden cress or garden pepperpot, called hab rchad in Morocco. Indigenous to Egypt and western Asia, but grown in temperate regions. CS is an extensively used carbon steel in different fields as a construction material due to its mechanical characteristics and cost. Its use can lead to its dissolution in acidic environments [1]. Generally, the use of inhibitors is a key technique in lowering corrosion rates in this environment [2]. The reduction of this metal corrosion was achieved by particularly economical processes by exploiting inhibitors [3]. The protection against corrosion of carbon steel in acidic solutions, has attracted a great deal of attention by studying various organic inhibitors in recent times [4-9]. Several studies were focused on the use of natural inhibitors originating from aromatic, medicinal plants and spices. Their use as corrosion inhibitors has been encouraged for economic and environmental purposes [10-15]. The bibliographical data available to date shows that little to no studies were performed on the corrosion inhibition properties of the Moroccan *Lepidium sativum* methanol extract.

The novelty of this work is the presentation of the MeOH extract (*LSS*) as eco friendly corrosion inhibitor for the carbon steel in hydrochloric acid medium, using electrochemical methods such as potentiodynamic polarization (*PDP*) and spectroscopy, electrochemical impedance (*EIS*).

2. EXPERIMENTAL

2.1. Plant collections

The seeds were harvested in June 2014 in Tafraout, in the Souss Massa region of Morocco, then dehydrated in the sun and stored at a temperature of 4 °C.

2.2. Methanol extraction from (LSS)

Following a previously described method [16]; 150 g of (*LS*S) was collected, oven dried at 70 °C, for 4 h and then grounded. It was macerated in methanol and allowed to stand for 72 h and then decanted. The filtrates were then evaporated under reduced pressure and rotary dried at 55 °C. The extracts were stored in sterile labeled tubes in a screw cap and at 5 °C in the refrigerator.

2.3. Materials

The type of electrode used in our study is a carbon steel, type (European standard: carbon steel C35 E and US specification: SAE 1035). The composition of this metal is displayed in Table 1.

Table 1. Chemical composition (in % by weight) of CS

C	Si	Mn	S	Cr	Ti	Ni	Co	Cu
0.370	0.230	0.680	0.016	0.077	0.011	0.059	0.009	0.160

The exposed CS carbon zone was mechanically rubbed with 180, 320, 600, 800, 1500 and 2000 emery paper grades. The substrates were washed with bi-distilled water, degreased and ethanol dried.

2.4. Phytochemical Screening of (LSS)

The bio-active methanolic extracts of (*LS*S) were identified according to standard procedures [17].

2.4.1. Flavonoids

The lipid fraction was removed from the extract (0.5 g) with petroleum ether by stirring. The defatted residue was dissolved in 20 mL of 80% ethanol and decanted. The filtrate was used for further applications. Briefly, the filtrate was mixed with 5 mL of ammonia solution, then concentrated H_2SO_4 was added to the whole. A yellow coloration is indicative of the presence of flavonoids.

2.4.2. Sterols, polyterpenes

The identification was made by the use of the LIEBERMANN reagent, a pink-purple ring indicates the presence of terpenes and a blue-green ring between the layers indicates the presence of steroids

2.4.3. Polyphenols

2 mL of distilled water was added to 1 mL of solvent extract from of the sample. Afterwards, a few drops of a 10% aqueous solution of ferric chloride, was added. A color formation (green or blue) indicates the presence of phenols.

2.4.4. Tannins

The identification of the catechin tannins was performed using the Stiasny reagent. Briefly, a mixture of 5 mL of extract, was added to 15 mL of Stiasny reagent and put in a bath at 80 °C for 30 min. A positive revelation would be the apparition of a precipitate in large flakes. Sodium acetate was used to saturate the filtrate obtained. A few drops of $FeCl_3$ indicate the presence of gallic tannins, by showing an intense blue-black coloration

2.4.5. Alkaloids

Two reagents were used, Bouchardat (iodine-iodine reagent) and Dragendorff (potassium iodobismuthate reagent)

2.4.6. Saponosides

A test tube containing 10 mL aqueous extract, is vortexed for 15 seconds and allowed to stand for approximately 15 min. The apparition of a foam, of more than 1 cm in thickness shows the existence of saponins in the sample.

2.5. Corrosion tests

2.5.1. Preparation of solutions

The aggressive solution (1 M HCl) was prepared by dilution of Analytical Grade 37% HCl with double-distilled water. The concentration range of *LSS* employed was varied from 0.25 to 2.0 g/L.

2.5.2. Electrochemical Method

2.5.2.1 Electrochemical Impedance Spectroscopy (EIS)

The electrochemical results were processed using a Volab lab potentiostate apparatus (Tacussel-Radiometer PGZ 100) and verified by the Tacussel corrosion analysis software model (Voltamaster 4). The corrosion cell is presented by a saturated calomel electrode, a reference electrode and the working electrode was carbon steel with a surface area of 0.27 cm^2. All the potentials exposed in this test were resorted to this reference electrode. The test starts with the Eocp measurement. The working electrode was immersed in the solution for 30 min to put the open circuit potential at steady state. The electrochemical tests were carried out completely in 303 K±2 aerated solutions.

EIS processes were performed in a frequency range of (100 kHz-10 mHz), with 10 points at rest potential per decade. The electrode was immersed in the medium under study for approximately 30 min at 10 mV alternating current. Equation 1 calculates the effectiveness of anticorrosion [18]:

$$E_{R_p}(\%) = \frac{R_p^i - R_p^\circ}{R_p^i} \times 100 \quad (1)$$

where R_p and R_p° are polarization resistance of CS in the presence and absence of *LSS*, respectively.

2.5.2.2. Potentiodynamic polarization

Various concentrations of our inhibitor were used for this study, that were added to the corrosive medium studied (1.0 M HCl). And that the electrode potential varies from -800 to 00 mV compared to that of corrosion at a drainage rate of 0.5 mVs^{-1}. The ability to judge the anticorrosion characteristic of a CS sample in a protective solution by plotting the polarization curves. The Tafel curves obtained were used to obtain the current densities (i_{corr}) which allows evaluation of the inhibition efficiency using the relation:

$$E_{i_{corr}}(\%) = \frac{i^{\circ}_{corr} - i^{i}_{corr}}{i^{\circ}_{corr}} \times 100 \quad (2)$$

where i°_{corr} and i^{i}_{corr} are the current densities in the presence and the absence of *LS*S, respectively.

3. RESULTS AND DISCUSSION

3.1. Phytochemical study

Active ingredients revealed in the crude methanolic extract (*LS*S) are revealed in Table 2.

Table 2. Identification of Lepidium sativum seed extract

Identified chemicals groups		*Extract of the Lepidium sativum seeds Methanol*
Flavonoid		+
Alkaloid	*Mayer*	+++
	Bouchardat	++
	Dragendorff	+
Stereol and polyterpenes		+
Tannin	*Catechic*	++
	Gallic	+
Saponiside		+

The chemical screening test of the methanolic extract inhibitor (*LS*S) showed the existence of various medically active components, such as alkaloids, saponins, sterols, tannins, flavonoids and terpenoids (Table 2). Alkaloids are the majority. The presence of alkaloids, saponins, sterols, tannins, flavonoids and terpenoids in (*LS*S) methanol extract has also been reported previously by George et al. [19].

3.2. Polarization curves

3.2.1. Concentration effect

The potentiodynamic polarization behavior of CS in 1.0 M HCl solution in the presence and absence of [*LSS*] is shown in Fig. 1. The related electrochemical parameters such as corrosion potential (E_{corr}), Tafel cathodic and anodic constants (b_c and b_a ,respectively) and corrosion current density (i_{corr}) were listed in Table 3.

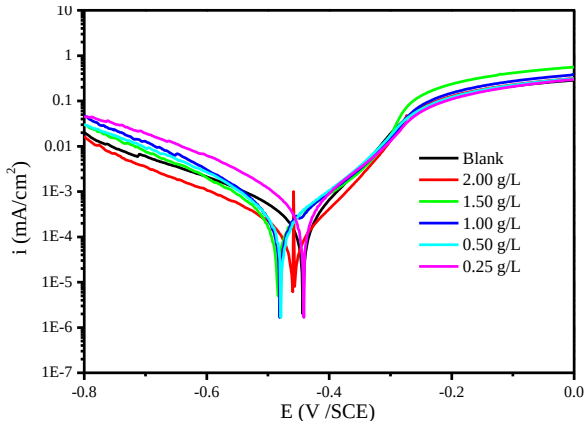

Fig. 1. Tafel of CS to 1.0 M HCl solution at various concentrations of 303 K±2 MeOH extract inhibitor (LSS)

Table 3. Value parameters of the CS substrate in protective solution (1.0 M HCl) with and without the addition of the MeOH extract inhibitor (LSS) at 303 K±2

Inhibitor (g/L)	*-E_{corr} (mV/SCE)*	*i_{corr} (μA/cm^2)*	*-b_c (mV/dec)*	*b_a (mV/dec)*	*E_{icorr} (%)*
Blank	447.6	779.0	93.3	85.0	—
2.00	461.5	125.0	62.0	59.9	84
1.50	485.0	187.0	100.7	128.1	76
1.00	479.5	188.5	82.1	103.9	76
0.50	481.4	199.4	76.7	76.0	74
0.25	441.2	328.7	80.7	67.8	58

According to Figure 1, the presence of the MeOH extract (*LSS*) causes a prominent decrease of current densities for anodic and cathodic Tafel curves. This decrease indicates the inhibition of anodic metal dissolution and the cathodic hydrogen evolution reaction. In addition to this, the increase in the concentration of inhibitor influences the inhibition of these reactions, that is to say when the adsorption increases, the efficiency increases.

When the concentration of the inhibitor studied increases, the E_{corr} values for CS in 1.0 M HCl shifts slightly in the positive direction compared to the uninhibited sample (Figure 1 and Table 3). It can be said that the inhibitor is anodic or cathodic, if the variation of the E_{corr} value is greater than 85 mV. In our case, the difference between the E_{corr} values is 37.4 mV towards the anodic direction, which suggests that the corrosion mode is mixed nature. The values of b_a and b_c are slightly transformed with the addition of anticorrosive, suggesting that our protector acts by stopping the cathode and anode sites of the CS substrate [20].

The recorded values show that the augmentation of the concentration of MeOH extract *LS*S and reduction of i_{corr}, results by achieving a 84% efficiency at 2 g/L, and also affecting the potential values, suggesting that it acts as an effective corrosion inhibitor [21].

3.2.2. Effect of temperature

The character of anticorrosive in an aggressive environment can be changed by changing the temperature [22]. Organic compounds can be more easily spoiled when the temperature increases, leading in turn to a less effective corrosion resistance of the steel [23,24]. For this purpose, we performed stationary electrochemical data in potentiodynamic made in a temperature range between 303 K±2 and 333 K±2. Then, we recorded the polarization curves of the carbon steel at 1.0 M HCl with and without the inhibitor at 2 g/L (Figures 2 and 3).

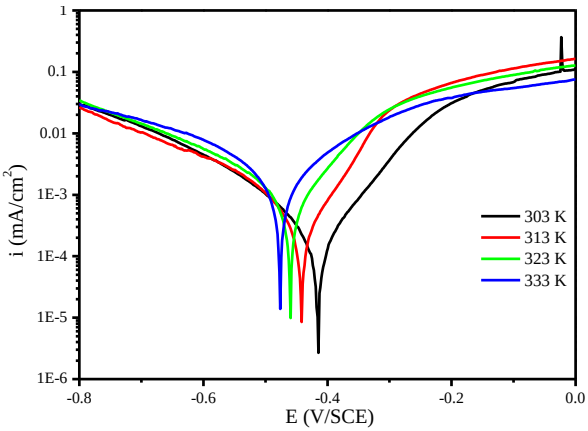

Fig. 2. Temperature effect on the polarization assay of CS in the HCl 1.0 M study medium in the absence of MeOH extract inhibitor (*LSS*)

Assay data for the Tafel of substrate in 1.0 M HCl as a function of temperature with the MeOH extract inhibitor (*LS*S) at the concentration of 2 g/L are summarized in Table 4.
It is remarked that these curves exhibited the Tafel regions. It is noted also that the anodic and cathodic branches increased with increasing of temperature. The curves in the cathodic part are parallel, indicating that the reduction of H^+ ions on the steel surface is done according to the same pure activation mechanism in all temperature range. It is clear that the i_{corr} increase with

increasing temperature in 1.0 M HCl solution without and with 2 g/L of *LSS* inhibitor. These results could be attributed to the acceleration of chemical process as the temperature is increased such as electrochemical, chemical, transport.

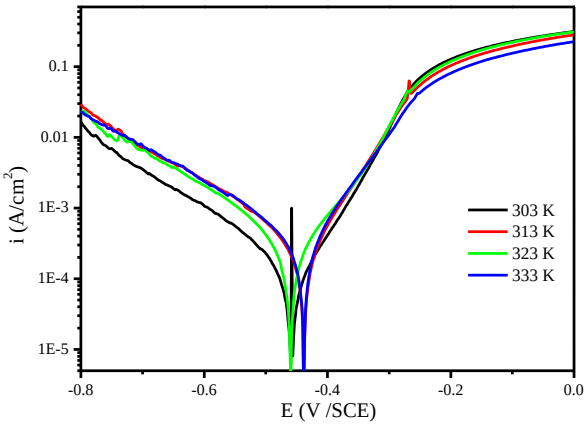

Fig. 3. Effect of temperature on the polarization curves of carbon steel in HCl medium in the presence of MeOH extract inhibitor (*LSS*) at 2 g/L

Table 4. Influence of the temperature on the electrochemical properties of the CS in 1.0 M HCl in the absence and in the presence of 2 g/L of the methanolic extract inhibitor (*LSS*)

Medium	*T* (*K*)	*-E*$_{corr}$ (*mV/SCE*)	*i*$_{corr}$ (*μA/cm*^{2})	*-bc* (*mV/dec*)	*b*$_a$ (*mV/dec*)	*E*$_{icorr}$ (*%*)
1.0 M HCl	303	447	779	93.3	85.0	—
	313	444	1100	125.5	115.3	—
	323	451	1500	111.1	111.5	—
	333	443	2118	200.3	161.8	—
LSS	303	461	125	62.0	59.9	84
	313	440	191	115.7	75.3	75
	323	459	222	115.2	99.5	71
	333	438	242	140.1	83.3	68

The Arrhenius type plot was used for activations value calculation, according to following equations [25,26]:

$$i_{corr} = A\exp\left(\frac{-E_a}{RT}\right) \quad (3)$$

$$i_{corr} = \frac{RT}{Nh}\exp\left(\frac{\Delta S_a}{R}\right)\exp\left(\frac{\Delta H_a}{RT}\right) \quad (4)$$

where the activation energy is E_a, the gas constant is R, the Planck constant is h, the absolute temperature is T, the pre-exponential factor of Arrhenius is A, the enthalpy ΔH_a, the number of Avogadro is N and the entropy is ΔS_a.

The apparent E_a of the inhibitor was measured by drawing the figure $Ln\ i_{corr}$ and 1/T (Fig. 4); the parameters stored in the Table 5 demonstrate an increase in activation energies with the addition of inhibitor. The elevation of E_a can be explained by physical adsorption. Thus, the molecules studied create a closure at the charge and mass transfer. The increase in a E_a value is related to the increase in thickness of the double layer [27].

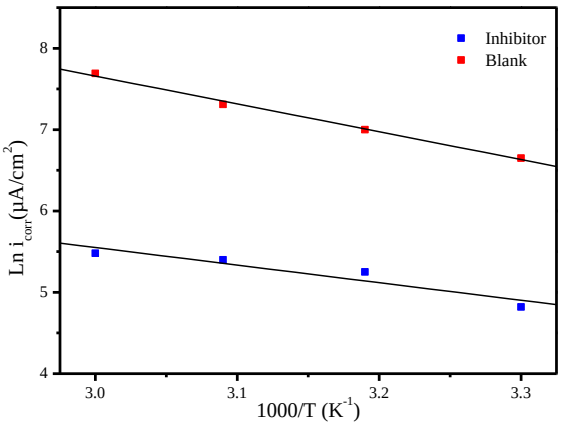

Fig. 4. Arrhenius plots the CS substrate in 1.0 M HCl with or without the methanolic inhibitor (*LSS*) at 2 g/L

The ratio between $Ln\ i_{corr}/T$ and $/T$ is recorded in Figure 5. Lines are obtained with a slope ($-\Delta H_a/R$) and a junction of [$Ln\ (R/Nh)+(\Delta S_a/R)$], from which the data of ΔH_a and ΔS_a are listed and shown in Table 5.

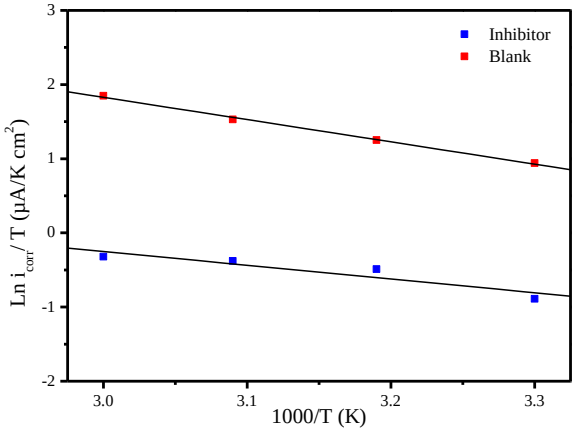

Fig. 5. Transition state plots for the CS substrate in 1.0 M HCl with or without the methanolic extract inhibitor (*LSS*) at 2 g/L

Table 5. Activation parameters for the CS substrate in 1.0 M HCl medium without and with the addition of the inhibitor at optimum concentration

	ΔH_a (kJ/mol)	ΔS_a (J/mol K)	E_a (kJ/mol)
Blank	24.94	-107.48	28.43
2 g/L LSS	15.38	-153.47	17.95

It can be concluded from the positive values of the enthalpy the process in question is in fact of an endothermic nature. Also, E_a and ΔH_a values are varying in the same way (Table 5).

This result makes it possible to examine the known thermodynamic reaction between E_a and ΔH_a as indicated in Table 5 [28]. By examining the activation entropy data (ΔS_a) shown in Table 5, the entropy value is negatively increased with the addition of the MeOH extract inhibitor (*LSS*) relative to the control solution, indicating the formation of a stable protective layer on the surface [29]. This modification is related to the fact of the order and disorder of the inhibitory atoms on the surface of the CS steel. The increased entropy of activation in the presence of the MeOH extract inhibitor (*LSS*) shows that the disorder is increased during the passage of the reactive complex to the activated complex. We can deduct that a slight replacement of the H_2O on the electrode surface takes place, from the increase in entropy values. Fixation of the inhibitor on the metal substrate is always followed by loosening of the atoms (H_2O). Thus, the entropy increase is attributed to the entropy of the solvent (H_2O) represented by the following equilibrium [30-32]:

$$Org_{sol} + xH_2O_{ads} \rightarrow Org_{ads} + xH_2O_{sol}$$

where the number of water molecules replaced by an organic molecule is x.

3.3. Electrochemical impedance spectroscopy measurements

The study of the protective properties of inhibitors of metals by the *EIS* method allows obtaining more reliable results, at the interface metal/solution [33]. The impedance curves for carbon steel in the corrosive media without and with the addition of various concentrations of MeOH extract inhibitor (*LSS*) at 303 K±2 are shown in Fig. 6.

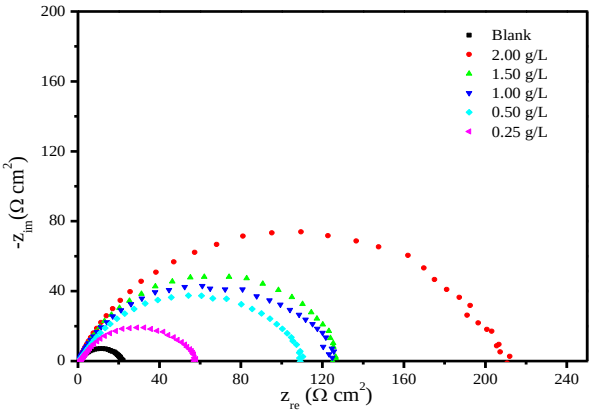

Fig. 6. Nyquist diagrams for the CS substrate electrode with and without MeOH extract inhibitor (*LSS*) after 30 min of immersion at 303 K±2

Figure 6 reveals a single capacitive half-circle depressed over the frequency range studied, shows that there is a link in between the charge transfer and the dissolution [27]. This phenomena is due to the non-homogeneity on the metal surface, called the frequency dispersion [34,35]. Again, the capacitive loop diameters strongly believe in the increasing concentration of the MeOH extract inhibitor (*LSS*) and the shape of the loops does not change.

The calculated parameters from the impedance plots are exhibited in Table 6. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximum ($-Z_{max}$) are shown in the equation:

$$C_{dl} = \frac{1}{2\pi f_{\max} R_p} \tag{6}$$

Table 6. Electrochemical parameters of carbon steel in 1.0 M HCl without and with addition MeOH extract inhibitor (*LSS*) at 303 K±2

Medium	*Conc (g/L)*	R_P *(Ω cm²)*	f_{max} *(Hz)*	C_{dl} *(μF/cm²)*	E_{Rp} *(%)*	θ
Blank	—	20.3	70.2	111.9	—	—
MeOH extract (*LSS*)	2.00	210.7	10.0	0.75	90	0.90
	1.50	125.7	6.3	2.00	83	0.83
	1.00	125.8	7.9	1.59	83	0.83
	0.50	109.6	7.9	1.83	81	0.81
	0.25	57.1	10.0	2.79	64	0.64

The measurements obtained in Table 6 demonstrate an augmentation in R_p value with more MeOH extract inhibitor (*LS*S). On the other hand, the appearance of a defensive layer on the interface leads to an increase in R_p. Decreasing the local dielectric value and / or increasing the size of the double layer are responsible for the decrease in C_{dl}, also showing the absorption of the inhibitor on the surface of the metal, thus affecting the metal/solution interface [36]. The change in the inhibitory efficacy of our inhibitor follows the increase in concentration. We find that there is a good agreement between the values of the inhibitory efficiency determined by impedance measurements and also of *EIS*, knowing that the concentrations of (*LS*S) methanolic extract.

3.4. Adsorption isotherm

Herein, the surface coverage (θ) data were obtained from EIS measurements, corresponding to different inhibitor concentrations in 1.0 M HCl at 303 K±2 and got by the following eq.:

$$\theta = \frac{E_{R_p}}{100} \tag{7}$$

where E_{R_p} is the inhibition efficiency of the inhibitor.

Isotherms of adsorption are handy to comprehend the electrochemical behavior of the inhibitor [37]. Flory-Huggins, Temkin, Frumkin, Parsons, Langmiur, Boer Hill, and Bockris-Swinkel are the most used isotherms for this purpose.

But, the best fit is acquired from the Langmuir isotherm (Figure 7). All these isotherms are of the general form: C_{inh}

$$\int(\theta, x)\, \exp(2a\theta) = K\, C_{inh} \tag{8}$$

where ∫ (θ, x) is the configuration factor from the physical model and the assumptions underlying the derivation of the isotherm. "θ" is the degree of coverage of the surface, "C" is the concentration of inhibitor in the mass of the solution, "a" is the lateral interaction related to the molecular interactions in the adsorption layer and the Heterogeneity of the "K" surface is the adsorption-desorption equilibrium constant. The surface coverage θ for different concentrations of the MeOH extract inhibitor (*LS*S) in 1.0 M HCl at 303 K±2 was assessed from the EIS measurements. The values have been graphically tested see Figure 7, adjusting the Langmuir isotherm that is given by an equation.

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{9}$$

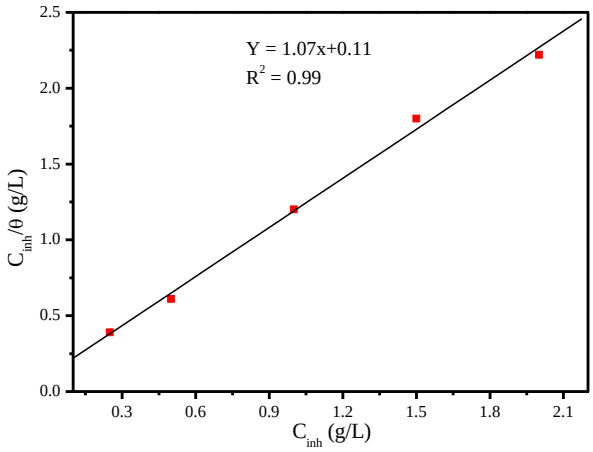

Fig. 8. Langmuir plots of (C_{inh}/θ) versus C_{inh} for MeOH extract inhibitor (LSS)

From the intercepts of the straight lines C/θ-axis, the K value was calculated; K_{ads}=9.09 L/g. K_{ads} is related to the standard Gibbs free energy of adsorption ΔG°_{ads}, according to:

$$\Delta G^{\circ}_{ads} = -RT\,Ln\left(C_{sol} \times K_{ads}\right) \tag{10}$$

where R is the universal gas constant, T the thermodynamic temperature and the water concentration in the solution are 1000 g/L. In general, for ΔG°_{ads} data for -20 kJ mol^{-1} or less, is related to physisorption; those around -40 kJ mol^{-1} and greater are related to chemisorptions [38,39]. However, chemisorption and physisorption are hard to distinguish based on these observations. Even without any chemical bonds forming, Gibbs energy can increase due to Coulomb interactions between the adsorbed cations and the adsorbed anions [40]. However, calculation of the extract value ΔG°_{ads} of the MeOH extract inhibitor (*LSS*) is not feasible because the molecular weight of the extract components is not known. Some authors note this limitation for the use of plant based inhibitors in an acidic medium [41-44].

4. CONCLUSION

Methanol extract of *Lepidium sativum* seeds (*LSS*) has a considerable inhibition effect on the corrosion of steel in 1.0 M HCl solution. The inhibition efficiency of the MeOH extract inhibitor (*LSS*) increases with increasing inhibitor concentration but decreases with increasing temperature. The potentiodynamic polarization tests revealed that the anticorrosive studied is a mixed type inhibitor. The EIS measurements have shown that the polarization resistance (R_p) increases and that the capacity of the double layer (C_{dl}) decreases in the presence of inhibitor, leads the adsorption of inhibitor molecules on the surface of the steel carbon. The adsorption of the inhibitor tested follows the adsorption of the Langmuir isotherm.

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