

Full Paper

Inhibition of API 5L Gr.B Carbon Steel Corrosion using Licorice Extract in CO₂ Environment

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Abstract- The corrosion inhibition effect of Licorice hydroalcoholic extract (Licorice extract) was investigated as a green corrosion inhibitor for API 5L Gr.B carbon steel in CO₂ environment, using Tafel polarization and electrochemical impedance spectroscopy (EIS) methods. The results showed that Licorice extract can be effective corrosion inhibitor in the CO₂ environment and act as an anodic inhibitor. The measurement data revealed that inhibition efficiency increased with the increase of Licorice extract concentration. Thermodynamic calculations indicated that adsorption behavior of Licorice extract on the steel surface obeys Langmuir adsorption isotherm and Licorice extract physically-chemically adsorbed on the steel surface in which adsorption process was spontaneous.

Keywords- Carbon steel, CO₂ corrosion, Green inhibitor, Licorice extract, Langmuir

1. INTRODUCTION

One of the most important problems in the petroleum industries is the corrosion, in particular, corrosion of carbon steels. Carbon steel plays an important role in the petroleum industry and many of the pipes and equipment are made of carbon steels because they are cheap and high strength [1-6].

Products of petroleum industry can contain various corrosive agents such as water, carbon dioxide, hydrogen sulfide, chlorides, oxygen, organic acids, and bacteria. All impurities can

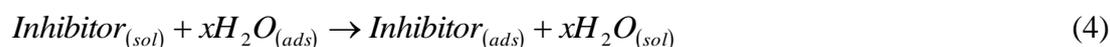
affect the corrosion of carbon steels [6-11]. More than half the corrosion failures in the petroleum industry are related to CO₂ and H₂S corrosion [12]. These gasses are corrosive in presence of moisture. Corrosion caused by CO₂ and H₂S gasses is known as sweet and sour corrosion, respectively [13].

In a solution containing CO₂, a fraction of dissolved CO₂ hydrated and carbonic acid is formed as well as solution pH decreases according to the following reactions [14,15]:



Produced carbonic acid decrease pH and lead to accelerated corrosion processes. Several factors such as water composition, pressure, and temperature can affect the solubility of carbon dioxide. Often, corrosion of carbon steel in a solution containing CO₂ leads to the formation of FeCO₃ protective film as the corrosion product [16,17].

The use of inhibitors is remarkable and most economical method for control and reduces internal corrosion of pipelines in the petroleum industries [18-20]. Often, organic compounds including oxygen, nitrogen, sulfur heteroatoms, and aromatic rings are used as inhibitor. These compounds through adsorption on the metal surface can change the corrosion rate [21-23]. In the first step of adsorption of organic compounds as inhibitor, water molecules adsorbed on the metal surface replacement by the inhibitor molecules [24-27]:



However, the organic inhibitor can be efficient but most of these compounds are toxic and harmful to human and its environments.

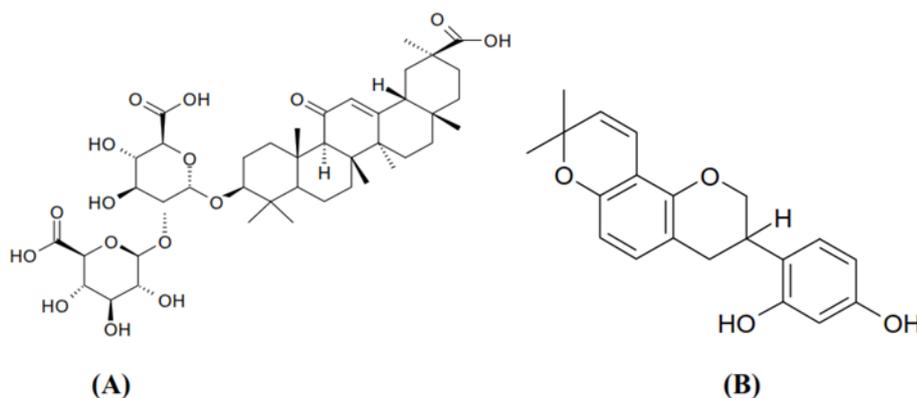


Fig. 1. Molecular structures of (A) glycyrrhizic acid and (B) glabridin

For this reason, recently used plant extracts as green inhibitor instead of organic inhibitors since they are non-toxic and environmental- friendly. Already, some authors have examined the inhibition function of some plant extracts against corrosion of steel, as most of these studies have been carried out in acidic environments [28-31].

In this study, the inhibition effect of Licorice extract was investigated against corrosion of API 5L Gr.B carbon steel in CO₂ environment by Tafel polarization and EIS. Usually, this plant extract used for medical purposes. Licorice extract can have many species. Glycyrrhizic acid and glabridin are the two major active species and molecular structure of them are shown in Fig. 1 [32]. The extraction method to obtain these two species is given below.

2. EXPERIMENTAL PROCEDURE

2.1. Inhibitor

In the present study, we used dipping extraction method. In the first stage, the licorice root powder was prepared. The powder was mixed with 100 ml ethanol/water with the composition of 30/70 v/v and then prepared mixture was stirred for 3600 s at 50 °C [32,33].

2.2. Specimen and Solution Preparation

The test specimen was selected from an API 5L Gr.B carbon steel with a chemical composition (wt. %) C 0.28%, Mn 1.2%, P_{max} 0.03%, S_{max} 0.03%, Ti 0.04% and Fe balance. The sample mounted in a polyester resin with an exposed area of 1 cm². Before each test, the specimen abraded with emery paper up to 1200 grit then rinsed with distilled water and dried with air.

The desired corrosive solution, according to the NACE 1D196 standard, consists of the following compounds: 3.5 wt. % NaCl, 0.305 wt. % CaCl₂ and 0.186 wt. % MgCl₂.6H₂O, These compounds are the most important factors in the simulation of corrosive environments in the oil industry. This solution was deoxygenated for 1 h by using bubbling carbon dioxide (CO₂) gas with the pressure of 1 atm. Then, the solution pH was measured that was approximately 4, which is consistent with NACE standard [7,34,35].

2.2. Electrochemical Measurements

All electrochemical measurements were conducted in a conventional three-electrode glass cell which contained a working electrode as mentioned above and saturated silver/silver-chloride (Ag/AgCl) and a platinum wire served as reference and counter electrode, respectively. We used the μ Autolab Type III/FRA2 system to execute all electrochemical measurements. The working electrode to achieved steady state of open circuit potential was immersed in the solution for 900 s. Tafel polarization was accomplished with a scan rate of 1 mV/s in a potential range ± 250 mV with respect to corrosion potential. The impedance

measurements were conducted using AC signals with the amplitude of 10 mV and normally a frequency range from 100 KHz to 10 MHz at the corrosion potential. The NOVA impedance software was used to EIS data modeling and fit the experimental results using the appropriate equivalent circuit.

3. RESULTS AND DISCUSSION

3.1. Tafel Polarization

Fig. 2 shows polarization curves acquired for API 5L Gr.B carbon steel in the CO₂ environment in absence and presence of different concentration of Licorice extract as corrosion inhibitor at room temperature.

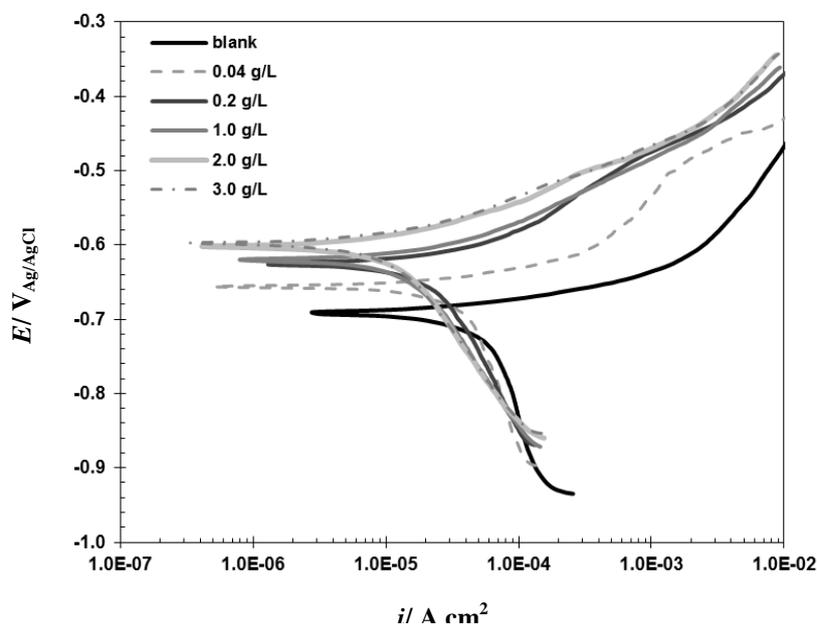


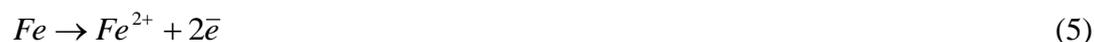
Fig. 2. Tafel polarization curves for corrosion of API 5 L Gr.B in CO₂ environment at 298 K in the absence and presence of various concentration of Licorice extract

Also, corrosion parameters determined from polarization curves are given in Table 1. Considering results indicates that by the addition of the inhibitor, maximum displacement in corrosion potential (E_{corr}) was 88 mV toward positive potentials which shows that Licorice extract act as an anodic inhibitor [36]. As can be seen, the addition of Licorice extract into the aggressive environment shifted polarization curves to the left and therefore, corrosion current density have been reduced. The changes in the corrosion potential toward positive potentials and reduction in corrosion current density can be due to the interaction of corrosion inhibitor with active anodic sites which indicates that inhibitor molecules adsorbed on the metal surface and blocking active anodic sites [37,38].

Table 1. Tafel polarization parameters for corrosion of API 5L Gr.B in CO₂ environment in the absence and presence various concentration of Licorice extract.

Concentration (g/L)	E_{corr} (V _{Ag/AgCl})	i_{corr} ($\mu\text{A}/\text{cm}^2$)	β_a (mV/decade)	$-\beta_c$ (mV/decade)	Θ
-	-0.688	55	50	320	-
0.04	-0.670	33	70	315	0.40
0.2	-0.630	22	75	302	0.60
1.0	-0.622	16	76	265	0.71
2.0	-0.608	12	79	241	0.78
3.0	-0.600	9.9	79	240	0.82

In addition, the results show that in presence various concentration of inhibitor, the anodic and cathodic Tafel slopes slightly changed which indicates that corrosion mechanism has not changed [39-41]. Adsorption of inhibitor molecules on the metal surface can be attributed to the presence of oxygen heteroatoms and/or aromatic rings and electron donating groups in molecule structure of inhibitor [33]. Dissolution of iron is the anodic reaction in CO₂ environment [14]:



Inhibition effect of inhibitor in CO₂ environment also can be associated with formation of iron carbonate film (FeCO₃) on metal surface as follows [17,42]:



The Tafel extrapolation method was used to calculate the corrosion current densities (i_{corr}). The values of surface coverage (Θ) and inhibition efficiency ($\eta\%$) were calculated using data obtained from the polarization test, according to the following equations [33]:

$$\theta = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \quad (7)$$

$$\eta\% = \theta \times 100 \quad (8)$$

Where i_{corr}^0 and i_{corr} are the corrosion current densities in absence and presence of Licorice extract, respectively. Fig. 3a and b show the corrosion current density and inhibition efficiency as a function of inhibitor concentration, respectively. As can be seen, increasing

the concentration of the inhibitor reduced the corrosion current density values and thus increased the inhibition efficiency.

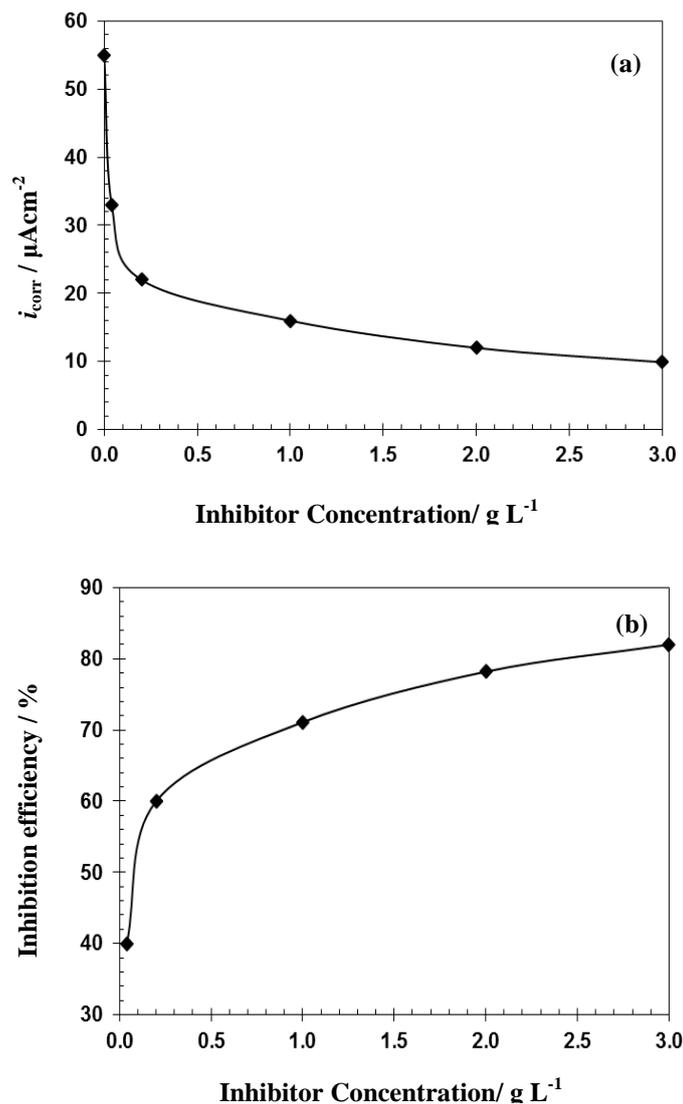


Fig. 3. Variation of the (a) corrosion current density and (b) inhibition efficiency obtained from polarization measurements with various concentration of Licorice extract in CO₂ environment

3.2. EIS Measurements

The results of impedance measurements for carbon steel electrodes in CO₂ environment containing different concentration of Licorice extract at the open-circuit potentials in the form of Nyquist and Bode plots are shown in Fig. 4 a and b.

The corrosion mechanism in blank solution is described with one constant phase element related to the double layer at high-frequency region and an inductive loop at low frequencies. This inductive loop can be interpreted to the two-step dissolution process [4,43]. By the addition of Licorice extract to the blank solution, Nyquist plot shows an incomplete inductive

loop at low frequencies which in according to some previous studies it can be ignored and only adsorption process investigated in data fitting [44–46].

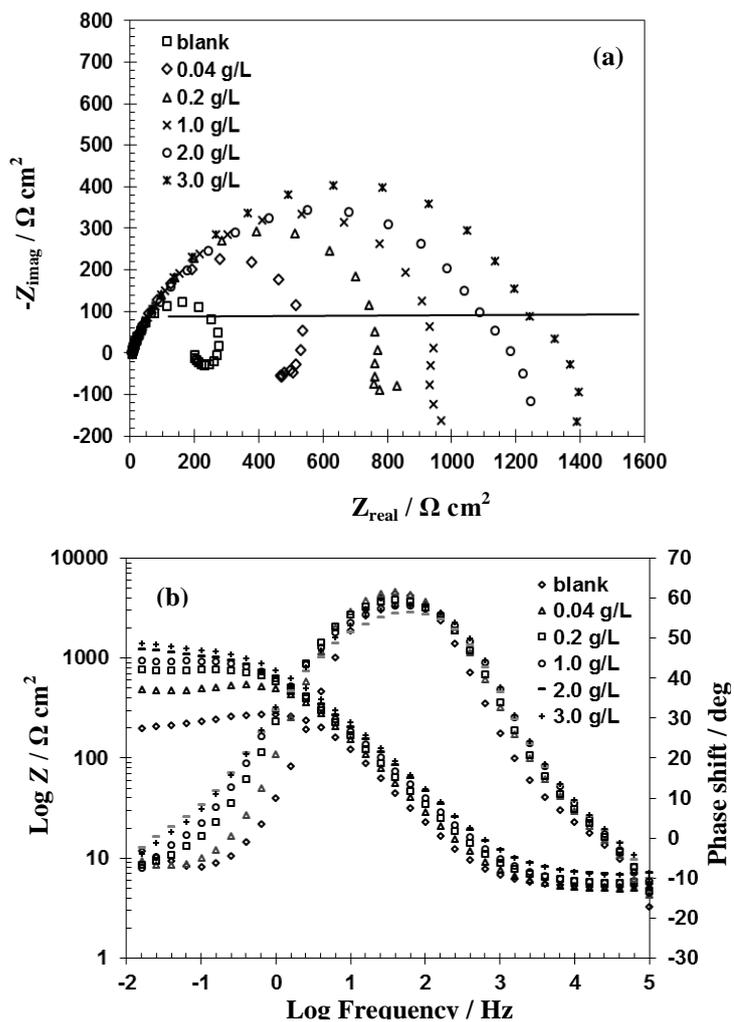


Fig. 4. (a) Nyquist and (b) Bode plots obtained from impedance measurement for API 5L Gr.B in CO_2 environment at 298 K in the absence and presence of various concentration of Licorice extract

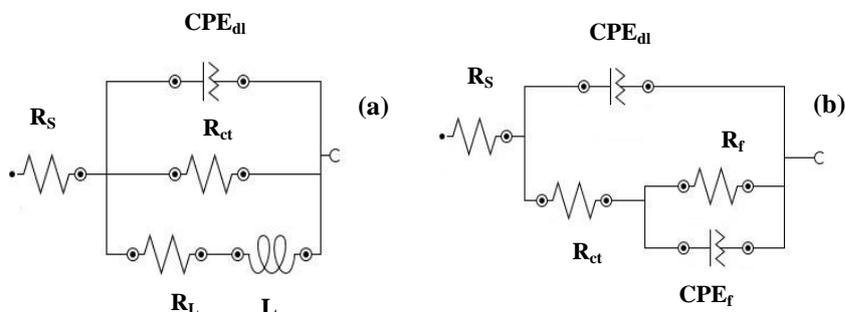


Fig.5. Electrochemical equivalent circuits used for fit the experimental EIS data in (a) blank and (b) inhibited solution

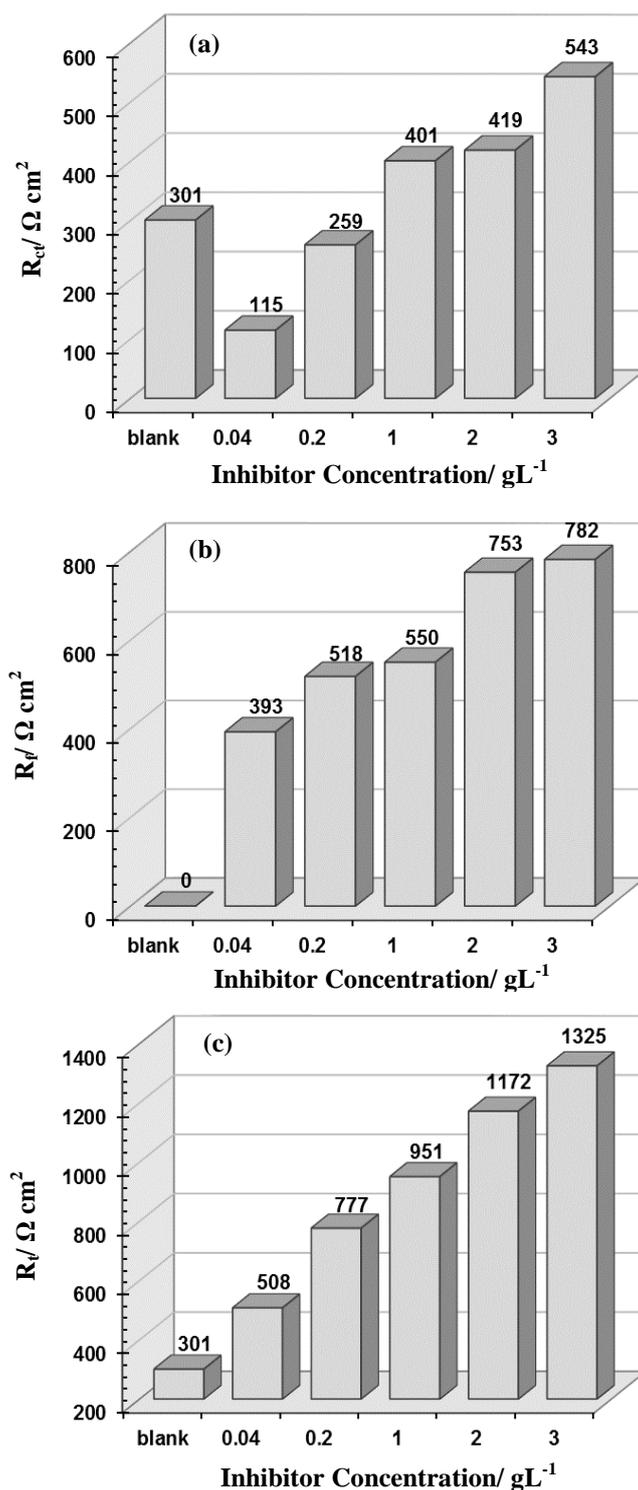


Fig. 6. Effect of increase of Licorice extract concentration on the (a) charge transfer resistance (R_{ct}), (b) protective film resistance (R_f) and (c) total resistance (R_t)

The equivalent circuits suggested to fit spectra obtained for uninhibited and inhibited solution are shown in Fig. 5. In the suggested equivalent circuits, R_s is the solution resistance,

R_{ct} is the charge transfer resistance, L represents the inductance and R_L is the inductance resistance, R_f is the protective film resistance, CPE_{dl} represents the constant phase element of the double layer and CPE_f the constant phase element of the protective film.

Fig. 6 shows the charge transfer resistance (R_{ct}), the protective film resistance (R_f) and the total resistance values (R_t) as a function of the inhibitor concentration.

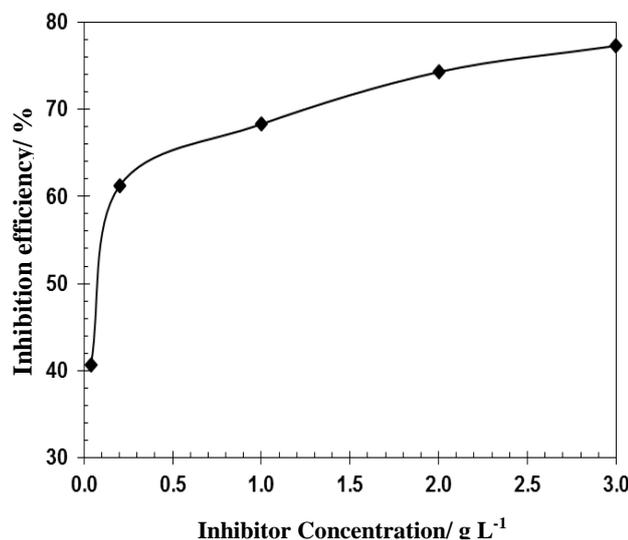


Fig. 7. Variation of the inhibition efficiency obtained from EIS measurements with various concentration of Licorice extract in CO₂ environment

The total resistance in the presence of inhibitor is the sum of the charge transfer resistance and the protective film resistance values but in the absence of inhibitor, only the charge transfer resistance values are considered. As can be seen, all three resistance increases with the increase of Licorice extract concentration that is correspond to increase of the diameter of semicircles in Nyquist plots. This can be interpreted to the reinforcement of protective film and charge transfer layer by addition of Licorice extract to the solution. The inhibitor efficiencies for the various concentration of Licorice extract were calculated using the total resistance of the system as follows [47]:

$$\% \eta = \frac{R - R^0}{R} \times 100 \quad (9)$$

Where R^0 and R indicate the total resistance in absence and presence of Licorice extract, respectively. Fig. 7 shows the inhibition efficiency obtained from impedance measurement which increases with the increase of Licorice extract concentration.

Fig. 3b and 7 show that the inhibition efficiency values obtained from polarization and impedance measurement are close together. In equivalent circuits suggested to fit the experimental results, for reasons such as roughness and surface defects, CPEs were used

instead of capacitors to enhance the fitted data [43,48]. A CPE consist of two components, Y_0 (the base admittance of corresponding CPE) and n that represent the extent of the depression of semicircles [43,46,48]. Capacitance related to the constant phase element of double layer (CPE_{dl}) was calculated according to the following equation [46,49]:

$$C_{dl} = (Y_0 R_{ct}^{1-n})^{1/n} \quad (10)$$

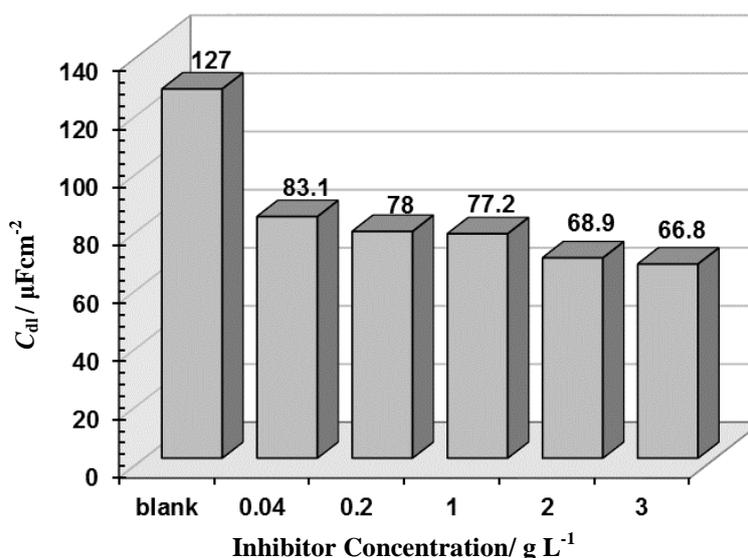


Fig. 8. Variation of capacitance of double layer with different concentration of Licorice extract.

As can be seen in Fig. 8, C_{dl} values decreased with increasing of inhibitor concentration, the formation or augmentation of the protective film on the metal surface could have caused this decline in C_{dl} values [50,51].

3.3. Adsorption Isotherm

Adsorption isotherms provide useful information about the mechanism of corrosion inhibition and investigation of adsorption of inhibitors on the electrode surface [52]. After fitting the obtained experimental data with conventional adsorption isotherms including Langmuir, Temkin, and Frumkin, Was found that the most appropriate isotherm is the Langmuir isotherm. According to the Langmuir isotherm, all sites on the metal surface are equal for adsorbing of particles [19]. The relationship between surface coverage (θ) and inhibitor concentration (C_{inh}) in this isotherm is as follows [53]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \quad (11)$$

In this equation, K_{ads} is the equilibrium constant. Fig. 9 illustrates the expected linear relationship between $\frac{C_{inh}}{\theta}$ and C_{inh} for different concentration of Licorice extract, by using surface coverage values obtained from impedance measurements. The standard free energy of adsorption (ΔG_{ads}^0) is related to the equilibrium constant (K_{ads}) obtained from the Langmuir adsorption isotherm as follows [26]:

$$K_{ads} = \frac{1}{1000} \exp\left(\frac{-\Delta G_{ads}^0}{RT}\right) \quad (12)$$

Where R is the universal gas constant ($8.314 \text{ J.K}^{-1} \text{ mol}^{-1}$), T is the absolute temperature (K) and value of 1000 represent the concentration of water in the solution (g/L) [54]. Ordinarily, the values lower than 20 KJ.mol^{-1} for $-\Delta G_{ads}^0$ indicates physisorption and electrostatic interaction between the charge molecules and charged metal surface, while the values around 40 KJ.mol^{-1} or higher shows chemisorption and formation of a covalent bond by charge sharing or charge transfer from inhibitor species to the metal surface. The values between 20 KJ.mol^{-1} and 40 KJ.mol^{-1} indicate physical-chemical adsorption [54–56]. The calculated value of ΔG_{ads}^0 for different concentration of Licorice extract was -22.9 ; therefore, the adsorption of Licorice extract on the steel surface in CO_2 environment is physical-chemical adsorption. The negative sign of ΔG_{ads}^0 shows that the adsorption process of Licorice extract on steel surface occurs spontaneously [19].

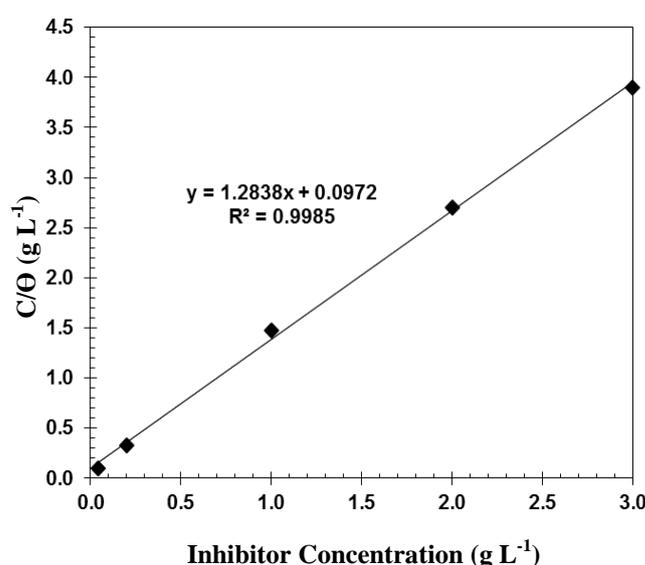


Fig. 9. Langmuir adsorption isotherm for API 5L Gr.B in CO_2 environment at 298 K

4. CONCLUSIONS

Licorice extract is an effective corrosion inhibitor for corrosion of API 5L Gr.B carbon steel in the CO₂ environment. By the addition of Licorice extract to the solution, the corrosion current density reduces and the inhibition efficiency increases that, this is due to the absorption of Licorice extract on the steel surface. The inhibition efficiency increases with the increase of Licorice extract concentration. The results obtained from polarization measurements revealed that the Licorice extract acts as an anodic inhibitor. The results of impedance measurement are in good agreement with the obtained data from polarization measurements that, the diameter of semicircles in Nyquist plot and therefore the total resistance increases with the increase of Licorice extract concentration which represents an increase of inhibition efficiency. The adsorption behavior of Licorice extract obeys Langmuir adsorption isotherm and the thermodynamic measurements revealed that the adsorption of Licorice extract on the steel surface is both physically and chemically but mainly as physically adsorption.

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