

CORROSION INHIBITION OF API5L X60 STEEL IN SULFURIC ACID USING GUM ARABIC

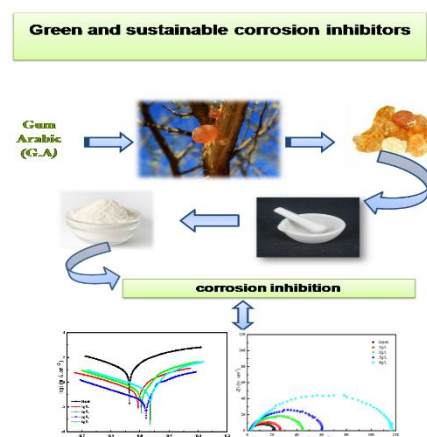
Nour-El-Houda SOBHI^a and Amel BOUKHOUJETE^{b,*}

^aLaboratoire Sciences et Techniques de L'eau et Environnement, Université Mohamed Chérif Messaadia – Souk-Ahras, Algeria

^bLaboratoire de Métallurgie Physique et Propriété des Matériaux, Université Badji-Mokhtar, Annaba, Algeria

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The aim of this research is the evaluation of inhibitory efficiency of Gum Arabic (GA) against the corrosion of API5L X60 pipeline steel in H₂SO₄ (0.5M) media, using mass loss measurement and electrochemical methods. The results show that inhibition efficiency increases with inhibitor concentration to attain 83% at 4 g/L of GA. Polarization curves reveal that GA acts as a mixed-type inhibitor in sulfuric acid. The adsorption of GA on pipeline API 5L X60 steel surface obeyed the Langmuir adsorption isotherm. Gibbs free energy of adsorption indicated that the adsorption process is spontaneous and the molecules adsorbed on the metal surface by the process of physical adsorption.



INTRODUCTION

Corrosion has always been a major industrial problem that affects most industrial sectors and can cause enormous losses.¹⁻⁴ The use of inhibitors is one of the best options of protecting metals against corrosion.⁵⁻⁹ Nevertheless, the use of chemical inhibitors has been limited because of the environmental threat.¹⁰ Recently, non-toxic, ecofriendly, harmless, readily available and renewable natural products are used as inhibitors in order to develop new clean chemicals for green environment.¹¹⁻¹⁹ The purpose of the present work was to study the effect of Gum Arabic (GA) for API 5L X60 steel in sulfuric acid medium.

Gum Arabic (GA) or Acacia gum is an edible biopolymer obtained as exudates of mature trees of Acacia Senegal and Acacia seyal which grow principally in the African region of Sahel in Sudan.²⁰ Chemically, GA is a complex mixture of macromolecules of different size and composition (mainly carbohydrates and proteins). In literature, GA has been fractionated by size exclusion chromatography, hydrophobic affinity chromatography and flow field-flow fractionation where two distinctive components have been characterized; a low molar mass protein-poor arabinogalactan (AG) and a high molar mass protein-rich arabinogalactan-protein complex (AGP).^{21,22} Fig. 1 shows the molecular structure of arabinogalactan (AG).

* Corresponding author: amel.boukhouiete@univ-annaba.dz

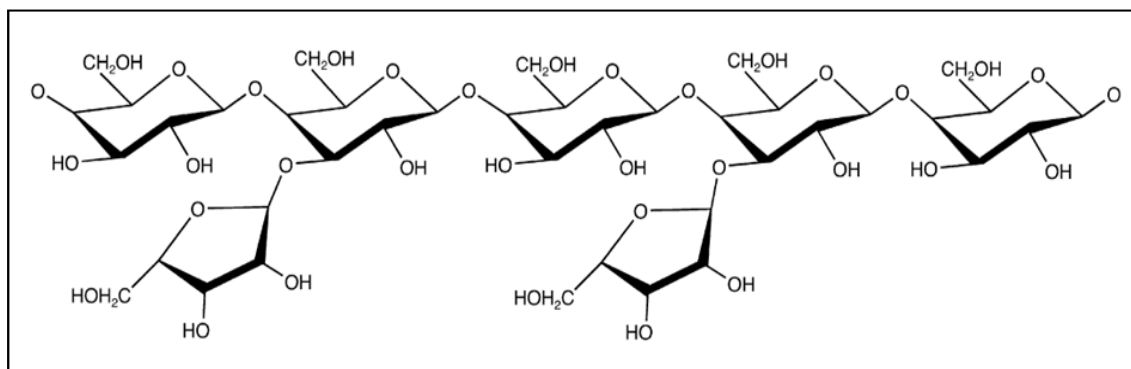


Fig. 1 – The molecular structure of arabinogalactan [22].

Table 1

Chemical composition of API5L X60 steel (wt. %)

Element	C	Mn	Si	S	Cu	Mo	Cr	Ni	Fe
Composition (wt.%)	0.20	1.16	0.36	<0.003	0.18	0.10	0.08	0.10	Balance

The first reports on corrosion inhibition of metals using Gum Arabic were reported by Umoren *et al.*,^{23,24} but the maximum inhibition efficiency was 21.9% to 43.7% at 30° C, with 0.5 g / L of GA as the maximum concentration of inhibitor. This paper aims on demonstrate that GA is an effective inhibitor in sulfuric acid medium at inhibitor concentrations greater than 0.5 g/L.

In this experimental work, inhibitive action of GA as a cheap, eco-friendly and naturally occurring substance, on corrosion behavior of API 5L X60 pipeline steel in 0.5M H₂SO₄ has been studied by weight loss techniques, free potential, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS).

EXPERIMENTAL

Materials

The material used in this study is API5L X60 steel, commonly used in the petroleum industry, and its chemical composition (wt. %) is presented in Table 1.

Medium

The aggressive solution H₂SO₄ (0.5M) was prepared by dilution of analytical grade acid (98% H₂SO₄) with distilled water. The solution tests are freshly prepared before each experiment.

Inhibitor

The inhibitory solution was prepared by dissolving dried Gum Arabic powder directly in 0.5M H₂SO₄ solution.

Gravimetric measurements

The experiments were carried out in solution of 0.5 M H₂SO₄ without and with GA at different concentrations on

API5L X60 steel. The metal steel sheets with dimensions 2 cm x 2 cm x 0.2 cm were abraded successively with different grades of emery papers up 1,200 grades washed with distilled water, degreased with acetone and dried. Afterwards, the samples were weighed accurately before all corrosion tests using an analytical balance. The weighed specimens were immersed in 100 ml of 0.5M H₂SO₄ with the absence and presence of different concentration of gum arabic and at various immersion times. At the end of the experiment, the specimens were removed from the corrosive medium and rinsed with water, cleaned with acetone, dried in hot air and finally weighed in each instance, duplicate experiments were run, and the average weight loss is reported.

Electrochemical measurements

The electrochemical tests were performed on the stable open circuit potential (OCP) using an Autolab 302N potentiostat/galvanostat equipped with Nova 2.0 software, in a conventional three-electrode cell with: a platinum counter electrode (CE), a saturated calomel electrode (SCE) as the reference electrode and API5L X60 steel as a working electrode (WE) with a section of 1 cm². The three electrodes setup was immersed in glass cell, containing 200 ml of the test solution, without and with addition of different concentrations of GA. All electrochemical tests have been performed in aerated solutions at room temperature.

RESULTS AND DISCUSSION

Gravimetric study

The weight loss was taken as the difference in the weight of the steel coupons before and after immersion in the test solutions. The weight loss was used to estimate the Corrosion rate (CR) by following expression:

$$\text{Corrosion rate} = \frac{\text{weight loss}}{\text{density} \times \text{area} \times \text{time}} \quad (1)$$

Table 2

Weight loss results of X60 steel in 0.5M H₂SO₄ without and with different concentrations of GA

[GA] (g/L)	Corrosion rate (mm/h)	E (%)	θ
0	0.901	—	—
1	0.658	27	0.27
2	0.216	76	0.76
3	0.207	77	0.77
4	0.156	83	0.83

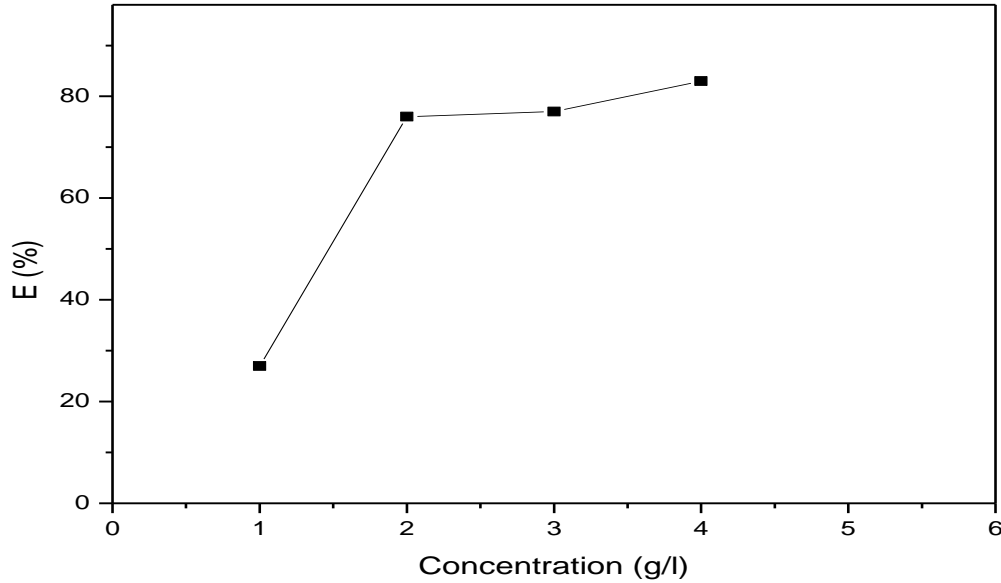


Fig. 2 – Variation of inhibition efficiency (E %) of corrosion of API 5L X60 steel in 0.5M H₂SO₄ with different concentrations of GA.

The degree of surface coverage (θ) and the the inhibitor efficiency (E %) were calculated using equations (2) and (3) respectively:

$$\theta = \frac{CR^{\circ} - CR}{CR^{\circ}} \quad (2)$$

$$E (\%) = \frac{CR^{\circ} - CR}{CR^{\circ}} \cdot 100 \quad (3)$$

where CR° is corrosion rate without inhibitor, and CR is the corrosion with inhibitor

1. Effect of inhibitor concentration

The values of percentage inhibition efficiency E (%) and corrosion rate CR obtained from weight loss method at different concentrations of GA at 298 K are summarized in Table 2 and Fig. 2.

The results obtained in Table 2 and Fig. 2 indicated that the corrosion rate of API 5L X60 steel decreased continuously with increasing the inhibitor concentration, the corrosion of steel is retarded by GA. However, the inhibition efficiency E (%)

increases sharply with increase in concentration of inhibitor reaching a maximum value of 83% at 4 g/L. This behavior may be attributed to the ability of GA to form complexes through its functional groups with metal ions which occupy a large area and by so doing blanket the metal surface from aggressive anions present in solution.²⁵ Therefore, it may be concluded that GA is a good corrosion inhibitor for API 5L X60 steel in 0.5M H₂SO₄ solution.

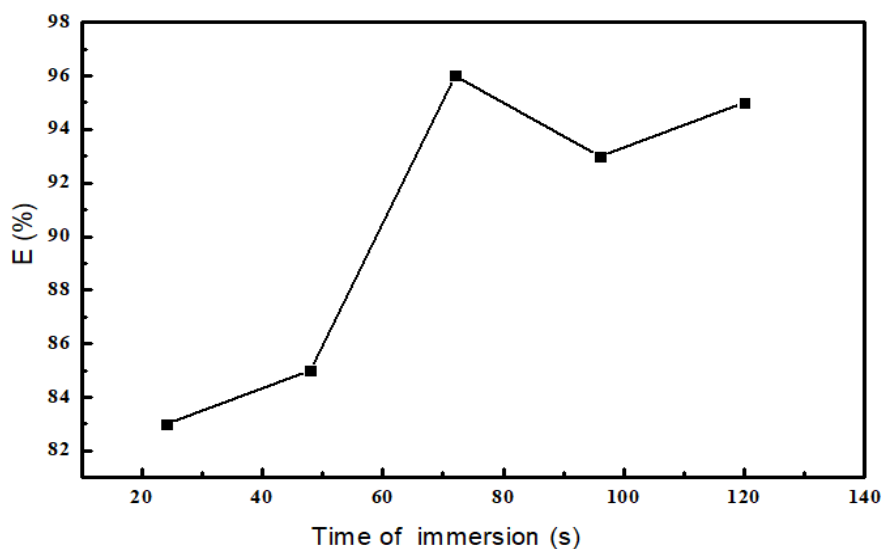
2. Effect of immersion time

According to the results listed in Table 3 and the curve represented in Fig. 3, it can be seen that inhibition efficiency of GA increases with immersion time and achieves a maximum of 96% after 72 hours of immersion, before decreasing to the value of 93% after 96 hours and finally, stabilizing at 95% in the interval (96–120) h. This can be explained by the presence of stable inhibiting film covering the API 5L X60 steel surface.

Table 3

Effect of immersion time on corrosion inhibition of 5L X60 by GA in 0.5M H₂SO₄ solution

Medium	Time (h)	Corrosion rate (mm/h)	E (%)	θ
H ₂ SO ₄ (0.5M)	24	0.961	—	—
	48	0.347	—	—
	72	0.409	—	—
	96	0.345	—	—
	120	0.379	—	—
H ₂ SO ₄ (0.5M) + G.A (4 g/l)	24	0.159	83	0.83
	48	0.050	85	0.85
	72	0.015	96	0.96
	96	0.024	93	0.93
	120	0.018	95	0.95

Fig. 3 – Variation of inhibitory efficacy of GA in 0.5M H₂SO₄ versus immersed time.

Electrochemical measurements

1. Open Circuit Potential measurements

OCP versus immersion time curves of API 5L X60 steel electrodes in H₂SO₄ solutions containing different concentrations (0 to 4 g/L) of GA are indicated in Fig. 4. In an uninhibited solution (0.0GA), the OCP establishes quickly at -0.52 V/SCE after a few seconds of immersion. Addition of GA results in the shifts of OCP curves to more noble potentials. Consequently interactions of inhibitor on the surface of steel and also formation of possible protective layers lead to the prolongation of the time required for stabilization. As increase of GA concentrations lead to the OCP shifts to more noble potentials, its reason might be attributed to the inhibiting effects of GA on steel oxidation and evolution of hydrogen gas in acidic solutions in which GA is preferably adsorbed on anodic and cathodic sites of the steel. The GA can be classified as a mixed type of inhibitor due to the displacement in corrosion potential, which is less than 85 mV.²⁶

2. Potentiodynamic polarization measurements

The polarization curves were drawn using potential range of -700 to -300 mV (vs. OCP) and potential scanning rate of 0.5 mV/s 30 minutes after stabilization of H₂SO₄ solutions. Polarization tests were conducted on the solutions with different concentrations (0 to 4 g/L GA) at room temperature (Fig. 5).

Fig. 5 shows clearly that the anodic and cathodic reactions are affected by the addition of the inhibitor. Indeed, in addition of the displacement of free potential to more noble values, the addition of the natural substance (GA) in H₂SO₄ 0.5 M induces the decrease of the cathodic and anodic current. GA acts as a mixed-type corrosion inhibitor in H₂SO₄ medium, as has already been shown in the OCP study. The cathodic and the anodic currents progressively diminish with an increment in GA concentration that is clearer in anodic current.

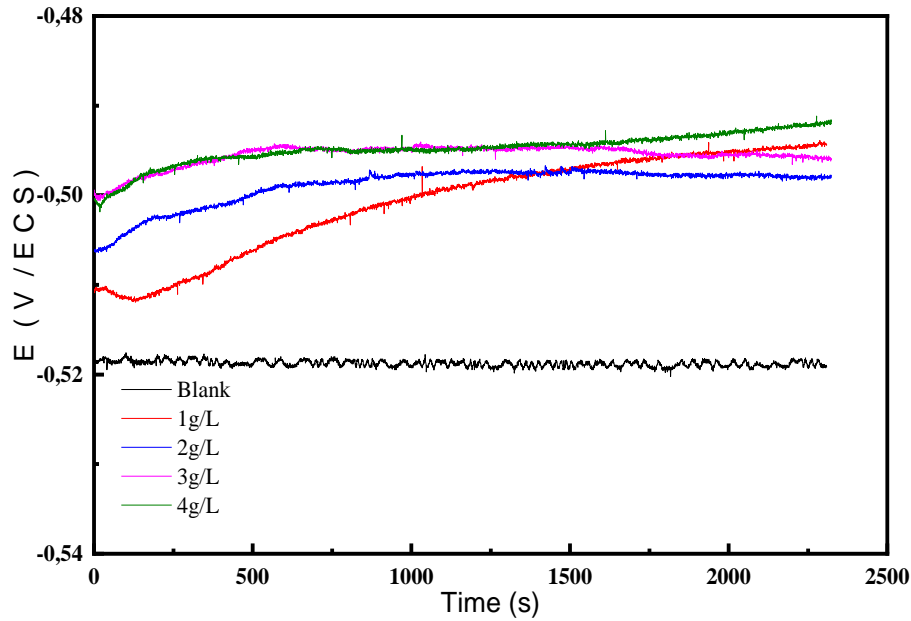


Fig. 4 – Evolution of the free potential for API 5L X60 steel without and with different concentrations of GA in H_2SO_4 (0.5 M).

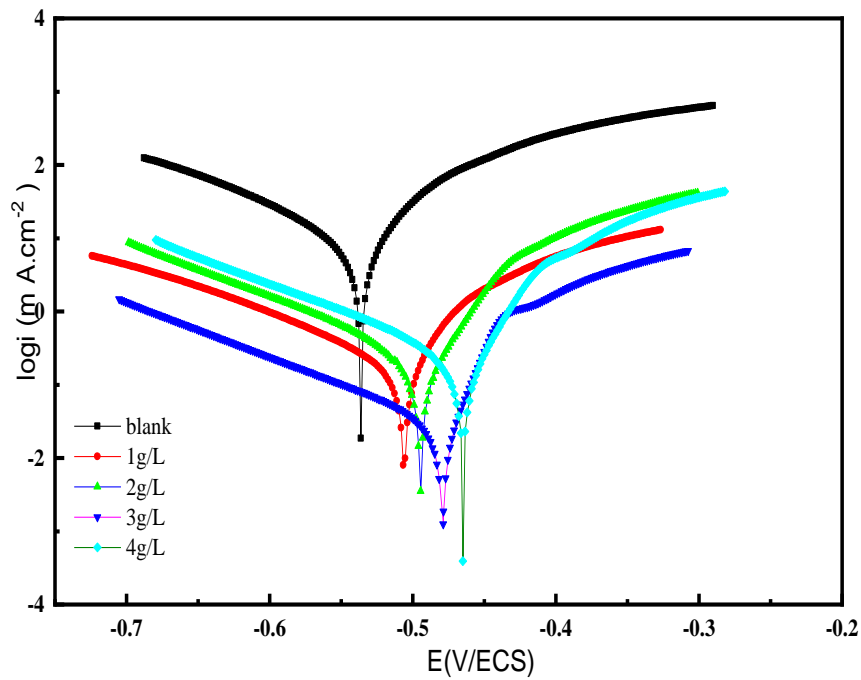


Fig. 5 – Polarization curves of API 5L X60 steel in the absence and in the presence of various concentrations of GA in aerated 0.5 M H_2SO_4 solution.

Table 4

Electrochemical parameters of API 5L X60 steel at various concentrations of GA in 0.5 M H_2SO_4						
C (g/L)	E_{corr} (mV/SCE)	i_{corr} (mA/cm ²)	R_p ($\Omega \cdot \text{cm}^2$)	β_a (m V/dec)	$-\beta_c$ (m V/dec)	E (%)
0	-536	1.7081	7.28	72.0	133.6	—
1	-486	1.1713	10.56	41.1	98.5	31
2	-495	0.8252	15.25	33.6	52.5	52
3	-475	0.6168	20.29	21.1	47.3	64
4	-465	0.2861	43.85	30.7	53.6	83

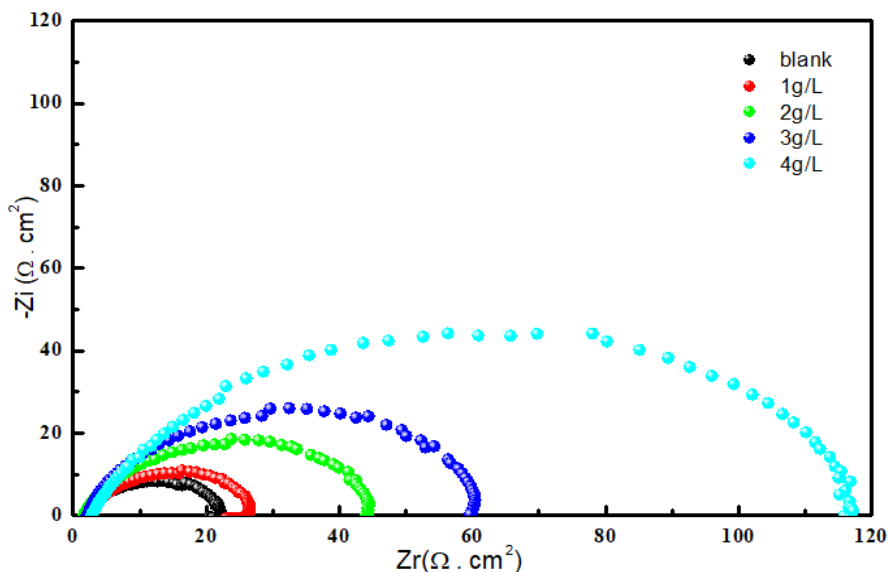


Fig. 6 – Nyquist plots of the corrosion of API 5L X60 pipeline steel in 0.5M H₂SO₄ without and with different concentrations of GA.

Table 5

Impedance parameters and inhibition efficiency for API 5L X60 steel in 0.5 M H₂SO₄ solutions containing various concentrations of GA

GA (g/L)	R _s (Ω.cm ²)	R _t (Ω.cm ²)	C _{dl} (mF.cm ⁻²)	E (%)
0	2.2	20.8	0.71	–
1	0.9	30.9	0.49	32
2	1.3	44.9	0.30	54
3	1.2	60.6	0.22	66
4	1.4	117.1	0.15	82

The corrosion parameters including corrosion current densities (i_{corr}), potential (E_{corr}), anodic and cathodic Tafel slope (β_a and β_c) and inhibition efficiency (E %) are listed in Table 4. In this case, the inhibition efficiency is defined as follows:

$$E\% = \left(\frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \right) \cdot 100 \quad (4)$$

where i_{corr}^0 and i_{corr} are the uninhibited and inhibited corrosion current densities, respectively.

Table 4 shows that the i_{corr} values decreased in the presence of the natural material (GA) and that the inhibition efficiency (E %) increased with the concentration of GA and attained a maximum value of 83% at the maximal concentration (4 g/L), indicating the natural compound being an excellent inhibitor. The change in the values of the Tafel constants (β_a , β_c) with the addition of GA indicates that the inhibitor controlled both reactions (Adding GA to H₂SO₄ solution reduces the anodic

dissolution of API 5L X60 steel and retards the cathodic hydrogen evolution).²⁶ Good agreement between gravimetric and electrochemical measurements was observed.

3. Electrochemical Impedance Spectroscopy measurements

EIS is a well-established and powerful tool in the study of corrosion. Surface properties, electrode kinetics and mechanistic information can be obtained from the impedance diagrams.^{27,28} In order to get more information about the corrosion behavior of the carbon steel, in acidic solution with and without GA, EIS measurements have been carried out at room temperature after 90 min of immersion. The Nyquist plots recorded for the corrosion inhibition of API 5L X60 steel with different concentrations of GA at OCP in 0.5 M H₂SO₄ are shown in Fig. 6.

As it can be seen from Fig. 6, impedance diagrams show a semi-circular appearance, indicating a charge transfer process mainly controls the corrosion of steel.^{29,30} The diameter of the semicircle increases with increasing the concentrations of the GA resulted from the effective surface coverage of the inhibitor on API 5L X60 steel surface. All spectra obtained are similar in shape, which suggests that the geometric blocking effect is the inhibition mode of GA.

Table 5 lists the values of EIS parameters derived from Nyquist plots together with the values of the inhibition efficiency calculated by the following equation:

$$E\% = \frac{(R_t - R_t^0)}{R_t} \cdot 100 \quad (5)$$

where, R_t and R_t^0 are the charge transfer resistances in inhibited and uninhibited solutions respectively. From the impedance data given in Table 5, we conclude that the values of R_t increase while the values of C_{dl} decrease with increase in concentration of GA. The decrease in C_{dl} shows that the adsorption of the inhibitor takes place on the metal surface in acidic solution; which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electric double layer.^{27,29} It also supports the same fact that tested inhibitor has highest adsorption capability due to its higher surface coverage area and a higher number of hetero atoms in its structure.²⁵ Furthermore, we note from Table 5 that inhibition efficiency increases with increase in concentration of GA with the highest value of 82% obtained at inhibitor concentration of 4 g /L. These impedance measurements were in good agreement with the corrosion weight loss and polarization curves tests.

The impedance spectra were fitted to the equivalent circuit model consisting of the charge transfer resistance (R_t) in parallel connection with the capacitance (CPE) connected in series with the solution resistance (R_s). The CPE is used in the equivalent circuit in place of a double-layer capacitor (C_{dl}) to give a more accurate fit. The equivalent circuit is shown in Fig. 7.



Fig. 7 – Electrical equivalent circuit of the metal/electrolyte interface.

Adsorption isotherm

To describe the probable mechanism for the interaction of GA as a green corrosion inhibitor and the surface of metal, isotherms of adsorption are investigated. The adsorption isotherms give useful information on the mechanism of corrosion inhibition. The adsorption isotherm explains the interaction between inhibitor molecules and the carbon steel surface. The values of surface coverage (θ) at different concentrations were calculated from the weight loss method. The data were tested graphically by fitting to different isotherms, and the Langmuir adsorption isotherm was found to provide the best description of the adsorption behavior of the studied inhibitor. Langmuir's adsorption isotherm is defined by the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (6)$$

where C , K_{ads} and θ are the concentration of the inhibitor, equilibrium constant of adsorptive, and the surface coverage, respectively. The plot of C/θ versus C (1 to 4 g/L) at 303 K temperature is represented in Fig. 8.

The linear plot has a slope of 0.0263 and a regression coefficient (R^2) of 0.9995. The plot's y-intercept yields the K_{ads} value where is equal:

$$K_{ads} = (1/\text{intercept}) \quad (7)$$

The equilibrium constant of adsorption obtained from the Langmuir adsorption isotherm is related to the standard free energy of adsorption according to the following equation:

$$\Delta G^{\circ}_{ads} = -R T \ln(55.5 K_{ads}) \quad (8)$$

where R is the universal gas constant and T is the temperature in K (Kelvin), the concentration of water in acidic solution is 55.5 mol/L.

The thermodynamic parameters obtained from the plots are presented in Table 6.

A negative standard Gibbs free energy benefit a steady and spontaneous adsorption process. If G°_{ads} value is less than $-20 \text{ kJ}\cdot\text{mol}^{-1}$, physisorption occurs, which includes a mild electrostatic contact between the charged inhibitor molecules and the charged metal. A value below than $-40 \text{ kJ}\cdot\text{mol}^{-1}$ indicate chemisorption, in which the inhibitor molecule forms a coordinating bond with the metal surface. A G°_{ads} value of -20 to $-40 \text{ kJ}\cdot\text{mol}^{-1}$ confirms the existence of both physisorption and chemisorption.

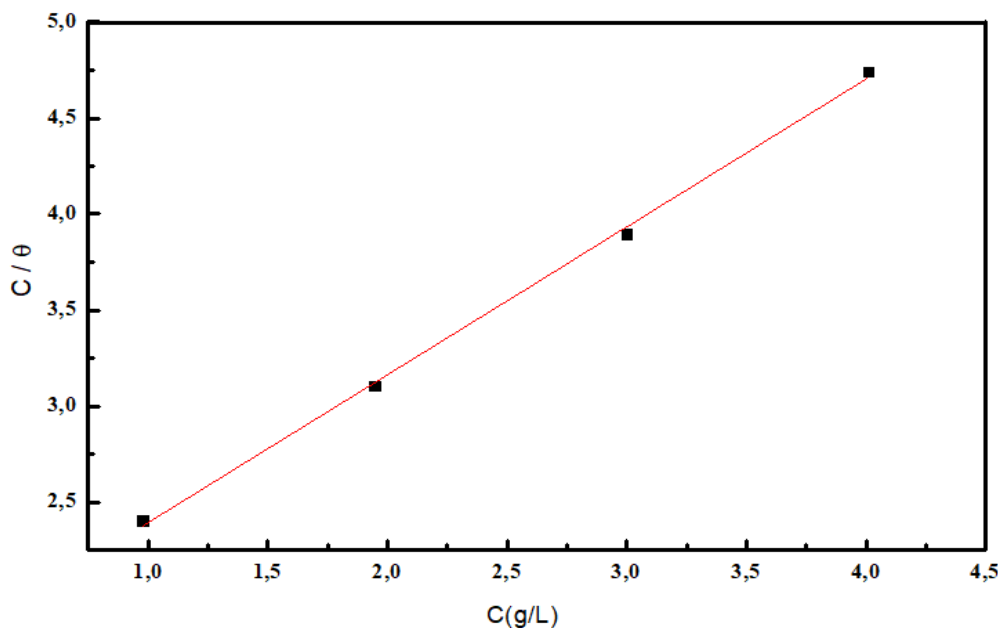


Fig. 8 – Langmuir adsorption isotherm for GA on API5L X60 in 0.5M H₂SO₄ solution at 303 K.

Table 6

The adsorption parameters obtained from Langmuir adsorption isotherm

Isotherme mode	Linear correlation coefficient	Slope	K (L g ⁻¹)	ΔG ^o _{ads} (kJ mol ⁻¹)
Langmuir	0.9995	0.02638	1.6	-19.33

The value of G°_{ads} calculated from the Langmuir isotherm is -19.33 kJ/mol. This is indicative of a physisorption process, which means that there is an electrostatic contact between the charged inhibitor molecules and the charged metal. This shows that the Langmuir isotherm is the optimal adsorption type for this investigation. From this estimation, it can be concluded that the GA is physically adsorbed on the steel surface.

CONCLUSIONS

We have studied the application of GA as environmentally friendly inhibitor for the API 5L X60 pipeline steel in 0.5M H₂SO₄ by using various methods. The results obtained are as follows:

GA has remarkable inhibitory power on API 5L X60 steel in 0.5M H₂SO₄, which increases with the duration of immersion.

The inhibition efficiency increases with increased GA concentration to attain a maximum value of 96% at 4 g/L, after 72 h of immersion.

Potentiodynamic polarization measurements demonstrate that GA acts essentially as a mixed type inhibitor.

The EIS experiments showed that charge transfer resistance (R_t) increased and double layer capacitance (C_{dl}) decreased in the presence of the inhibitor; this indicated the adsorption of the inhibitor at the surface of steel.

The adsorption of GA on the metal surface is a spontaneous process which follows Langmuir adsorption isotherm.

The data obtained from different techniques used in this research are in good agreements

In conclusion, this work has shown that GA is a good corrosion inhibitor for steel in H₂SO₄ solution and can be used to replace toxic chemicals.

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