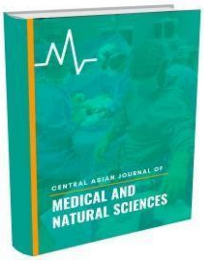

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Article

Corrosion Inhibition of Medium-Carbon Steel Using Oleander Leaf Extracts in Acidic Environments

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Abstract: The research deals with a kinetic and thermodynamic study of using an organic inhibitor extracted from oleander leaves (aqueous extract and alcoholic extract) to inhibit the corrosion of medium carbon steel in an acidic medium (1M) HCL. Several tests were conducted to evaluate the performance of this inhibitor. They included measuring the corrosion rate by weight loss method at different concentrations of the inhibitor (30, 40, 50, 60)% mg, as the inhibition efficiency reached 89.1% when using the aqueous oleander leaf extract at a concentration of (60)% mg and a temperature of 293K and reached 92.2% when using the alcoholic oleander leaf extract at a concentration of (60)% mg and a temperature of 293K. Finally, microscopic examination was conducted and the results showed that the used inhibitors were not only an alternative to traditional inhibitors, but were better than them in all the testing methods conducted to evaluate their performance. It is less expensive because it is natural and widely available in our beloved country. It is more efficient than other common inhibitors is less toxic and does not pollute the environment.

Keywords: oleander tree difference, corrosion, HCl, inhibitors

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1. Introduction

The rapid progress in industrial and engineering technologies constantly creates problems regarding corrosion, so it is necessary to find solutions and methods of protection that are more effective than the available methods. Given the different types of corrosion that can occur and also the different conditions that help these different types to occur, it is not surprising that there are multiple types of corrosion protection methods that have great economic feasibility in choosing a specific method over another. The most important of these methods used to protect against corrosion is choosing the metal material and protecting the metal by covering it with a protective layer against corrosion and treating the environment that causes corrosion in a way that leads to reducing its effectiveness in the corrosion process and the appropriate design for corrosion protection and the use of inhibitors to prevent corrosion [1]. Inhibitors are chemical compounds that react with the metal surface or with the medium to which the metal surface is exposed, so as to give a metal surface protected from corrosion. The basic mechanism of action of inhibitors is the adsorption mechanism on the metal surface itself and works to protect it by forming a film on the metal surface. They work to reduce the corrosion process by controlling the behavior of cathodic polarization or anodic polarization, or what is known as Tafel tendency, by reducing the movement or diffusion of ions to the metal surface and increasing the electrical resistance of the metal surface [2]. Based on this, inhibitors can be divided experimentally into cathodic, anodic, and mixed inhibitors (cathode and anodic). Based on their composition, they are classified into organic inhibitors and inorganic inhibitors [3]. There are several considerations that are taken into account when testing a specific substance for use as a corrosion inhibitor, including cost, toxicity, availability, and non-harm to nature [4]. Organic inhibitors are highly effective due to their relatively low cost and are often non-toxic. Natural inhibitors are a good source for the above-mentioned purposes as they contain aromatic compounds including amides, amino acids, ketones and aldehydes. These compounds are mostly known for their high inhibitory effect [5]. Medium carbon steel is the most widely used material and is very sensitive to various corrosion conditions. It is the most corrosive metal in the normal atmosphere, in addition to the fact that the appearance of the corrosion products of this metal is completely undesirable. Medium carbon steel is corroded by both oxygen and hydrogen ions, and it corrodes violently by hydrogen ions the more acidic the solution in which it is present. It also corrodes in non-oxidizing acids, and hydrochloric acid is the most effective acid in the corrosion of this steel with the release of hydrogen gas. Carbon steel suffers from corrosion in oxidizing acids such as nitric acid by oxygen and hydrogen together, as the corrosion of carbon steel in water and various saline solutions depends on the amount of dissolved oxygen in the solution [6].

The research aims to prepare an extract from the oleander tree (from the leaves of the oleander tree) which is widely spread in our beloved Iraq, and to use these extracts after dissolving them in water as corrosion inhibitors to reduce the corrosion of medium carbon steel in acidic medium.

2. Materials and Methods

2.1 Preparation of the inhibitor

The extract of the leaves of the oleander tree is prepared from the oleander trees and by analyzing the components of the powder of these leaves using the FTIR device, Figure 1 shows the test results for this powder, which shows that it contains many active groups rich in aldehydes, ketones, amines, amides, alcohols and aromatic compounds. All of these compounds have inhibitory properties and electron-rich atoms capable of inhibiting this corrosion [7].

Figure 1. Oleander tree leaves

The corrosion-inhibiting extract of oleander tree leaves was prepared by taking the leaves of the tree, drying them, then cutting and grinding them, then adding a quantity of water, then boiling them on a low heat (aqueous extract) until most of the water evaporates, so we get a paste-like substance close to the liquid, then we take volumetric samples of (30, 40, 50, 60)% mg [8]. As for the alcoholic extract, ethanol alcohol is added to the leaf powder instead of water [9].

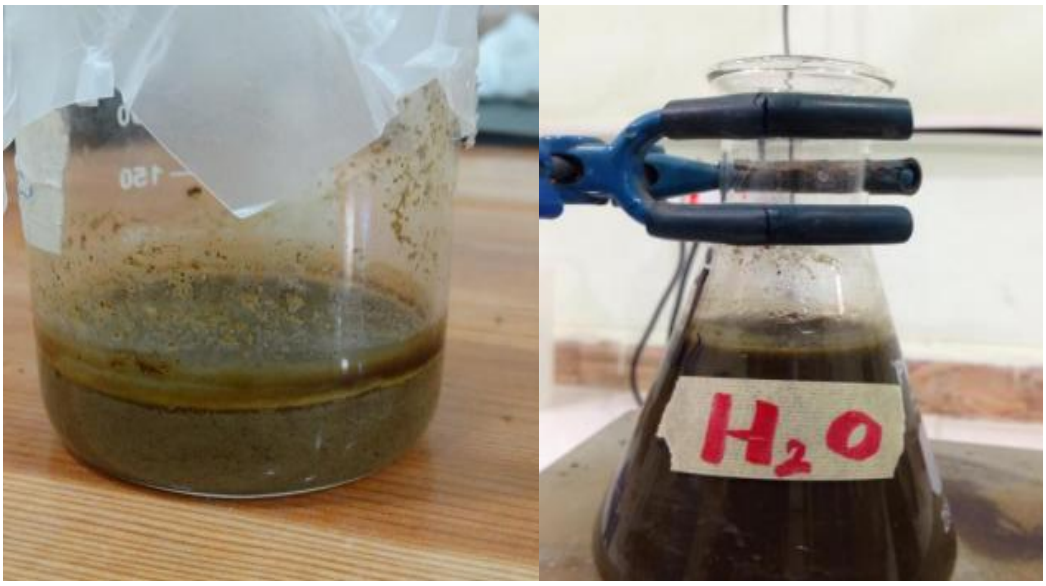

Figure 2. Shows the two extracts of oleander leaves (aqueous and alcoholic)

2.1.1 Infrared spectroscopy

This technique is used to determine the active groups in the plant extract and the analysis is done using the FTIR-8400S device.

2.2 The metal used

The samples were prepared as pieces of medium carbon steel with the chemical composition shown in Table 1, as they were cut into rectangular shapes (cm2 length, cm1 width, cm 0.5 thickness), smoothing papers were used at different degrees (1000, 800, 400, 200) and then polished using a suitable polishing device. After that, the samples were treated with the development solution for two minutes to remove the oxides. After that, the samples were washed with distilled water and alcohol and then dried using an electric dryer. Then they were weighed with a sensitive balance. After recording the weight of the samples, they were kept in a container containing a tight cover to protect them from moisture that causes corrosion [10], see Figure 3.

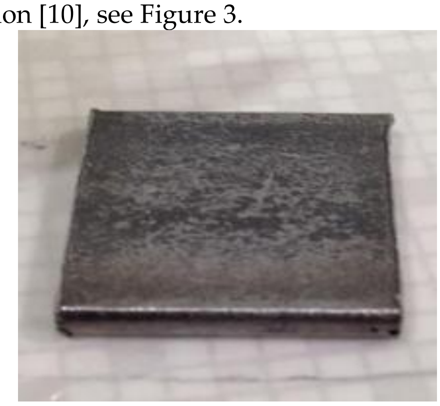

Figure 3. Shows the dimensions of medium carbon steel

2.2.1 Chemical analysis

The medium carbon steel sample is analyzed using an atomic absorption device to determine the percentages of elements present in the sample, which are shown in Table 1.

Table 1. The percentage of elements in the average medium carbon steel

C%	Mo%	Si%	Mn %	P%	S %	Cr%	Al%	Cu %	Ni%	Fe%
0.128	0.002	0.0289	0.437	0.0052	0.0024	0.0028	0.0383	0.0113	0.0148	99.329

2.2.2 Scanning Electron Microscope

The surfaces of the samples are examined by scanning electron microscope before and after corrosion and inhibition experiments.

2.3 Corrosion rate measurement

The metal's resistance to corrosion is measured quantitatively in a specific medium by the corrosion rate, which can be calculated in several ways, including those based on measuring weight loss (used in our research) or the change in tensile strength or measuring the depth of corrosion and microscopic examination of the sample section, and those based on electrochemical methods such as the Tafel completion method and linear polarization.

2.3.1 Weight loss method

In this method, medium carbon steel samples are immersed in an acidic medium with a concentration of (1 M) at room temperature in the presence of (0-24hr) and the absence of the inhibitor (0-250min), using four concentrations of the inhibitor (30,40,50,60) mg%, as the change in weight is measured for different periods of immersion in the solutions.
The corrosion rate is calculated using the following equation [10].

$$C.R = \frac{\Delta W}{A \times t} \quad \ldots\ldots\ldots\ldots\ldots(1)$$

Where: C.R: is the corrosion rate (g/m2day).
ΔW: is the amount of weight difference (g).
A: is the surface area of the sample exposed to the corrosive medium (m^2).
t: time (day).

The inhibition efficiency can be calculated using the following equation [11].

$$IE\% = \frac{CRuninh. - CRinh.}{CRuninh.} \times 100 \quad \ldots\ldots\ldots\ldots(2)$$

The corrosion rate in the absence of an inhibitor is denoted as "CRuninh," while "CRinh" represents the corrosion rate in the presence of an inhibitor. The surface coverage can be determined using the following equation, see Figure 4:

$$\emptyset = \frac{IE\%}{100} \quad \ldots\ldots\ldots\ldots(3)$$

Figure 4. shows the method of weight loss

3. Results

3.1 Study of the structures of inhibitors and infrared rays

The adsorption of inhibitors on the metal surface for the purpose of protecting it, and therefore an infrared spectrum analysis was conducted to obtain an explanation of the possible interactions between the adsorbed inhibitor and the surface of medium carbon steel in an acidic medium [12], and the molecular structure of the inhibitor is what the strength of the inhibitor depends on. The results of the infrared spectrum showed the appearance of a peak at (3298) cm-1, which indicates the vibration of the N-H bond, and the peak at (2920) cm-1 indicates the vibration of the aliphatic CH3 bond, and the peak at absorption at (2853) cm-1 indicates the aliphatic CH2, and the peak at (1739) cm-1 indicates the C=O bond, and the peak at absorption at (1560) cm-1 indicates the aromatic C=C bond, which indicates that the extract contains alkaloids and flavonoids that are adsorbed on The metal surface is formed by a protective layer to protect it from corrosion [13], see Figure 5.

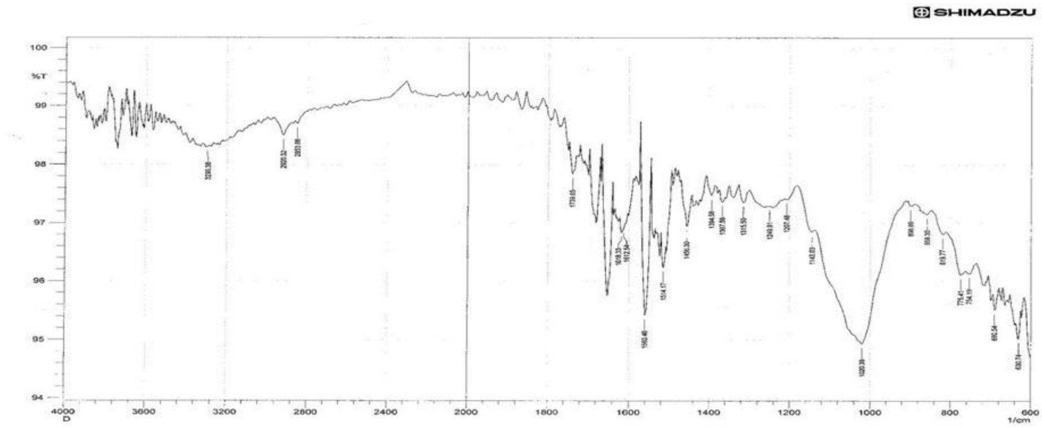

Figure 5. FTIR spectrum of oleander leaf extract.

3.2 Weight loss method

The weight loss test was conducted on medium carbon steel in 1M HCL acid in the absence and presence of two oleander leaf extracts (aqueous and alcoholic) over a period of time. Tables 2 and 3 represent the corrosion rates and efficiency ratio of the studied inhibitors at concentrations of (30, 40, 50, 60)%mg at a range of temperatures (293, 303, 313, 323)K respectively.

It is clear from the tables that the corrosion rate increases with increasing temperature and decreases when inhibitor concentrations are added. This is evidence that the adsorption process occurs on the metal surface as a result of the presence of high molecular weight compounds containing high density electron atoms.

Table 2. Shows the effect of temperature on corrosion rates, inhibition efficiency and surface coverage in the presence and absence of different concentrations of aqueous oleander leaf extract

T (K)	CR (gmd)	%IE	θ	Ci mg
293	0.1081	-	-	
303	0.1198	-	-	
313	0.1245	-	-	%0
323	0.1302	-	-	
293	0.0250	76.8	0.768	
303	0.0345	71.2	0.712	%30
313	0.0399	67.9	0.679	
323	0.0486	62.6	0.626	
293	0.0205	81	0.81	
303	0.0271	77.3	0.773	%40
313	0.0339	72.7	0.727	
323	0.0394	69.7	0.697	
293	0.0156	85.5	0.855	
303	0.0233	80.5	0.805	%50
313	0.0271	78.2	0.782	
323	0.0368	71.7	0.717	
293	0.0117	89.1	0.891	
303	0.0194	83.8	0.838	%60
313	0.0260	79.1	0.791	
323	0.0329	74.7	0.747	

Table 3. Shows the effect of temperature on corrosion rates, inhibition efficiency and surface coverage in the presence and absence of different concentrations of oleander leaf alcoholic extract.

T (K)	CR (mm/y)	%IE	θ	Ci Mg
293	0.1081	-	-	
303	0.1198	-	-	
313	0.1245	-	-	%0
323	0.1302	-	-	
293	0.0153	85.8	0.858	
303	0.0226	81.1	0.811	%30
313	0.0281	77.4	0.774	
323	0.0356	72.6	0.726	
293	0.0143	86.7	0.865	
303	0.0197	83.5	0.835	%40
313	0.0265	78.7	0.787	
323	0.0334	74.3	0.743	
293	0.0115	89.3	0.893	
303	0.0184	84.6	0.846	%50
313	0.0242	80.5	0.805	
323	0.0289	77.8	0.778	
293	0.0084	92.2	0.922	
303	0.0154	87.1	0.871	%60
313	0.0232	81.3	0.813	
323	0.0269	79.3	0.793	

3.3 Inhibitor activities and adsorption study

The adsorption of oleander leaf extract (aqueous and alcoholic) on the metal surface is through the physical or chemical adsorption mechanism or it can be competitive between the two mechanisms (physical and chemical). The surface coverage data play a major role in evaluating the properties of inhibitors and are useful when discussing the adsorption properties. With the help of the adsorption isotherm, the additions of inhibitor molecules that are adsorbed on the metal surface and interact with each other can be described [14]. The Langmuir isotherm is calculated using the equation

$\frac{C}{\theta} = \frac{1}{K_L} + C$ ………….(4)

The C/θ versus C ratio of the inhibitor is plotted in an acidic medium at different temperatures as in Figures 6 and 7.

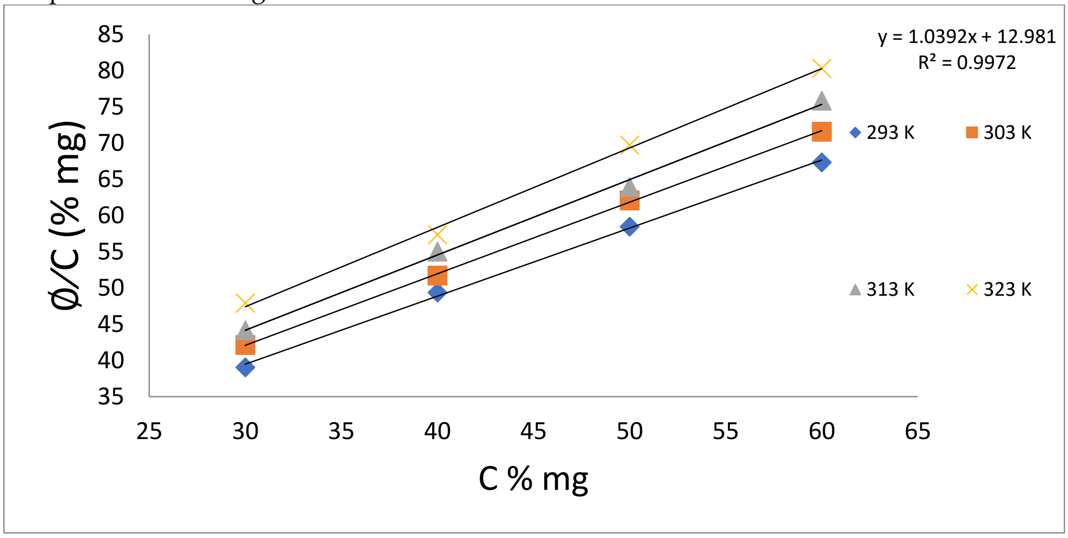

Figure 6. Langmuir equation for the adsorption of aqueous oleander leaf extract onto the surface of medium carbon steel at different temperatures

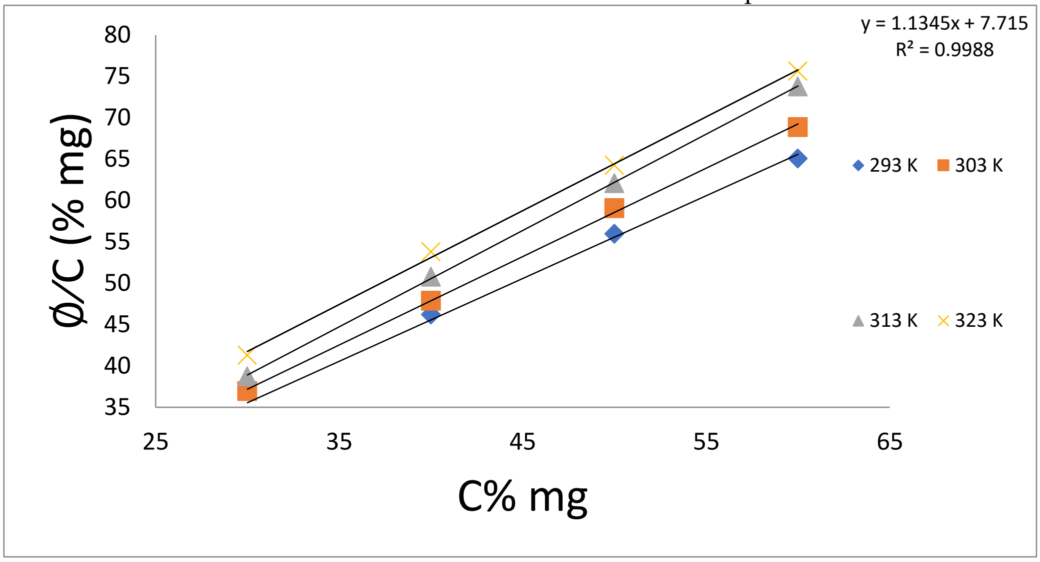

Figure 7. Langmuir equation for the adsorption of oleander leaf extract on medium carbon steel surface at different temperatures.

The data gave straight lines indicating that the adsorption of the inhibitor on the metal surface is done according to the Langmuir adsorption isotherm and that these lines reveal that the main process of inhibition is adsorption, and that the increase in the concentration of the inhibitor leads to an increase in the efficiency of inhibition. This indicates an increase in the inhibitor molecules on the metal surface and the blocking of the active sites from direct attacks by the acidic medium and the protection of the metal [15]. From the graph at the intersection of the straight line on the axis, the values of the Langmuir equilibrium constant KL are given, which can be substituted in the following equation to calculate the free energy of adsorption. It is clear that the Langmuir equilibrium constant increases with increasing temperature [14].

$\Delta G^{\circ}_{ads} = -RT \ln 55.5\, K_L$ …………….(4)

When calculating the free energy section of adsorption, it was found that all its values are negative, which indicates that the inhibitors are automatically adsorbed on the metal surface. All the free energy values of adsorption have values less than (-20) KJ.mol-1, indicating that the prevailing adsorption is chemical adsorption [16], see Table 4 and 5.

Table 4. Langmuir coefficients for the adsorption of aqueous oleander leaf extract at different temperatures

T(K)	Slop	R^2	K_L	ΔG°_{ads}
293	0.9393	0.998	0.0885	-3.877
303	0.9875	0.999	0.0802	-3.761
313	1.0392	0.997	0.0770	-3.780
323	1.0955	0.997	0.0687	-3.596

Table 5. Langmuir coefficients for the absorption of aqueous oleander leaf extract at different temperatures.

T(K)	Slop	R^2	K_L	ΔG°_{ads}
293	1.0008	0.9975	0.180	-5.606
303	1.0687	0.9992	0.195	-5.999
313	1.1644	0.9998	0.251	-6.861
323	1.1345	0.9988	0.129	-5.298

3.4 Effect of temperature

The study of the effect of high temperature on the corrosion rate of medium carbon steel in an acidic medium in the absence and presence of different concentrations of inhibitors in order to know the extent of the effect of these materials as corrosion inhibitors using weight loss measurements.

When referring to Tables 2 and 3, we find that the use of oleander leaf extract (aqueous and alcoholic) reveals an increase in the lost weight and thus an increase in the corrosion rate with increasing temperature. This indicates that increasing temperature reduces the inhibition process and the highest inhibition efficiency is obtained at a temperature of (293) K with a constant concentration of the inhibitor. Temperature has a negative effect as it increases the corrosion rate and also affects the work of the inhibitor. The activation energy Ea for the corrosion process was calculated using the Arrhenius equation.

Log C.R = Log A - $\frac{E_a}{2.303\ RT}$ ……………..(5)

Where: C.R: corrosion rate

A: Arrhenius constant

R: universal gas constant

T: temperature

When plotting between Log C.R versus 1/T as in Figures 8 and 9 to give straight lines and the slope is - $\frac{E_a}{2.303\ R}$. It was found that the activation energy value was (9.536) KJ.mol-1 in the absence of inhibitors and increases to (31.446) KJ.mol-1 at a concentration of (60)% mg of the aqueous oleander leaf extract, while its value when using the alcoholic oleander leaf extract increased to (35.733) KJ.mol-1. Increasing the temperature causes chemical changes in the inhibitor molecules, which leads to an increase in the electronic density in the adsorption centers of the inhibitor molecules and then an improvement in the inhibition efficiency as it increases with the increase in the concentration of this inhibitor, it is clear that the concentration plays a role in increasing the activation energy. The thermodynamic functions were calculated using the following equation (Table 6,7):

$$\ln(\frac{C.R}{T}) = \ln\left(\frac{R}{Nh}\right) + \frac{\Delta S_{act}}{R} - \frac{\Delta H_{act}}{RT} \quad \ldots\ldots\ldots\ldots\ldots..(6)$$

Table 6. Shows the values of activation energies and thermodynamic functions at different concentrations of the aqueous extract of oleander leaves.

C (mg)	**Ea (Kj.mol^{-1})**	**ΔH (Kj.mol^{-1})**	**ΔG (Kj.mol^{-1})**	**ΔS (J.K^{-1}. mol^{-1})**
0%	9.536	7.271	23.84	-56.56
30%	21.798	19.27	27.36	-27.61
40%	22.146	19.65	27.87	-28.05
50%	26.254	23.74	28.51	-16.26
60%	31.446	29.00	29.14	-0.473

Table 7. Shows the values of activation energies and thermodynamic functions at different concentrations of oleander leaf alcoholic extract.

C (mg)	Ea (Kj.mol^{-1})	ΔH (Kj.mol^{-1})	ΔG (Kj.mol^{-1})	ΔS (J.K^{-1}. mol-^{1})
0%	9.536	7.271	23.84	-56.56
30%	26.525	24.079	28.55	-15.28
40%	27.185	24.685	28.78	-13.99
50%	30.411	27.879	29.39	-5.157
60%	35.733	33.179	29.88	11.24

The increase in activation energies in the presence of inhibitors is due to a significant decrease in the adsorption process of the inhibitor on the metal surface with increasing temperatures and a corresponding increase in the reaction rate due to the large area of the metal exposed to the acidic medium.

3.5 Scanning Electron Microscope Studies

Scanning electron microscope images of a medium carbon steel sample were taken to support the results of this current research. In the absence of inhibitors, the sample's microscopic photos following exposure to an acidic medium revealed significant surface damage to the steel as a result of the steel dissolving in the corrosion solution. As seen in Figures 1-4 the surface condition was comparatively better when inhibitors (alcoholic and aqueous) were added. This is dependent on the inhibitor solution's concentration and the inhibitor molecules' adsorption on the metal surface, which resulted in the creation of a protective layer that gave the surface a smooth appearance and prevented corrosion [17], see Figure 8-11

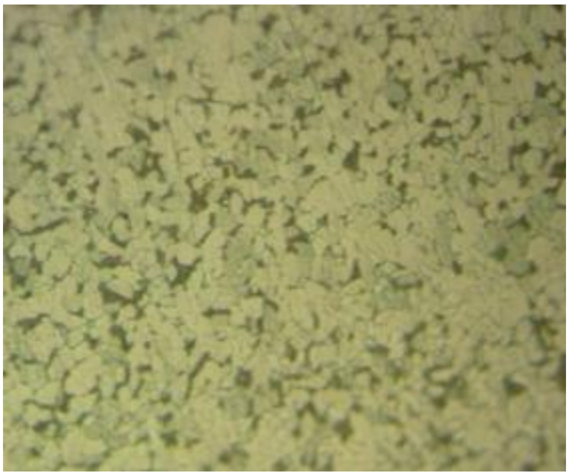

Figure 8. Microscopic image of medium carbon steel before immersion

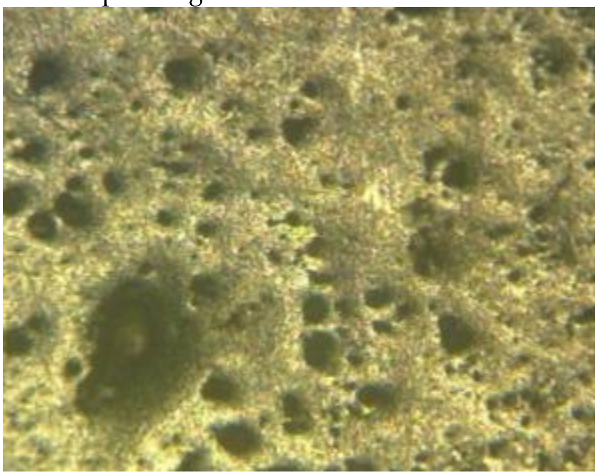

Figure 9. Microscopic image of medium carbon steel after immersion

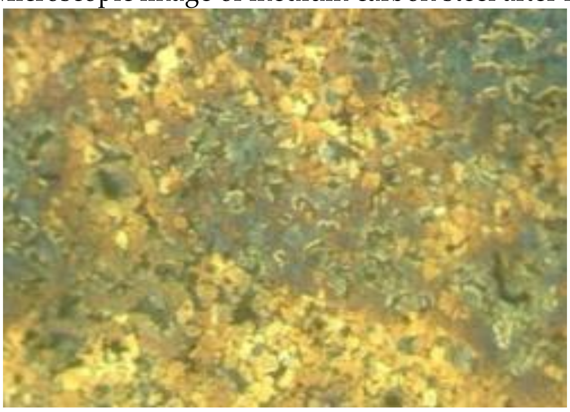

Figure 10. Microscopic image of medium carbon steel after immersion in the presence of

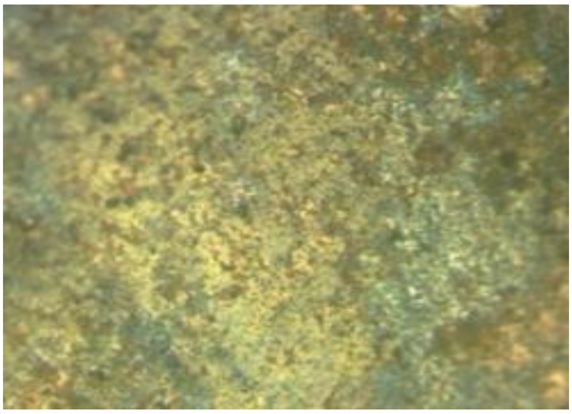

Figure 11. Microscopic image of medium carbon steel after immersion in the presence of oleander leaf alcohol extract

4. Conclusion

This study has confirmed the effectiveness of oleander leaf extract both aqueous and alcoholic as a natural and environmentally friendly corrosion inhibitor for medium-carbon steel in acidic environments. The extracts demonstrated strong inhibition efficiencies, reaching up to 89.1% and 92.2% respectively at a concentration of 60 mg% and a temperature of 293 K. The active organic compounds present in the extracts, such as flavonoids, alkaloids, ketones, and amines, facilitated adsorption onto the steel surface, thereby forming a protective barrier that limited direct contact with corrosive HCl solution. This process significantly reduced the corrosion rate and surface damage.

The inhibition mechanism was shown to follow the Langmuir adsorption isotherm, suggesting a monolayer coverage of the metal surface with minimal lateral interactions between adsorbed molecules. Thermodynamic calculations supported this mechanism, with negative values of Gibbs free energy (ΔG°_{ads}) indicating that the adsorption was spontaneous. Additionally, the increase in activation energy (Ea) in the presence of inhibitors confirmed that the extracts slowed down the corrosion process by increasing the energy required for metal dissolution. Scanning Electron Microscope (SEM) analysis further validated the formation of a smooth, uniform protective layer on the steel surface.

In summary, oleander leaf extract is a highly promising green inhibitor, offering a cost-effective, biodegradable, and non-toxic alternative to conventional corrosion inhibitors. Its local availability, especially in Iraq, adds to its practicality for industrial applications where medium-carbon steel is exposed to aggressive acidic conditions. These findings strongly support the future development and utilization of plant-based inhibitors for sustainable corrosion protection strategies.

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