Article

Corrosion inhibition of carbon steel by malva Sylvestris leaves extract in saline solution.

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Abstract

Researchers used scanning electron microscopy (SEM) as well as potentiodynamic polarization to examine the effectiveness of an extract from Malva Sylvestris (MS) leaves in inhibiting the corrosion of a low-carbon steel saline solution (0.6 M NaCl). The test extract significantly reduced the corrosion rate of carbon steel in a saltwater environment. With 800 ppm of drug on a carbon steel surface, the malva leaf extract exhibited an 86.5% inhibition efficiency; this efficiency rose with increasing inhibitor concentration but fell with rising temperature. Adsorbing MS molecules onto a metal surface stands for a mechanism by which inhibition occurs, according to the results, which followed the Langmuir adsorption isotherm. In order to explain how corrosion inhibition works, certain thermodynamic parameters ΔG_{ads} and activation energy (E_a) were determined. Extract from malva sylvestris leaves was found to be of mixed type according to the polarization measurements. Using SEM, we compared the surface properties of inhibited and uninhibited metal samples.

Keywords: Corrosion inhibition, carbon steel, malva Sylvestris leaves extract, thermodynamic parameters, Adsorption Mechanism.

1. Introduction

The natural occurrence which impacts our lives and degrades household devices, vehicles, aircraft, public roads, bridges, and distribution systems, corrosion is an avoided problem encountered by nearly all industries and is thus one of the worst technological problems of our time [1,2]. Corrosion occurs mostly because metals have an inherent inclination to revert to their initial state when they reach equilibrium. Some metal alloys are brittle and require atmospheric interaction to produce tiny amounts of energy in the form of metal complexes [3]. It is possible to think of corrosion as an outcome of electrochemical or chemical reactions with the environment. The importance of studying corrosion has grown as people have become more conscious of the need to preserve the world's metal supplies. Due to the increasing usage of metals in all domains of technology, there has been a recent uptick in efforts to limit metallic corrosion.

There are a number of methods for regulating the corrosion of metals, but using corrosion inhibitors has shown to be one of the most effective and widely used in both business and research [4]. When used sparingly, corrosion inhibitors stand for compounds in which

corrosive solutions can adsorb on metal surfaces and prevent corrosion by reducing the metals' interaction with the corrosive environment and other connections [5]. Review articles written by multiple authors show that plant extracts have been studied for a while as potential corrosion inhibitors[6,7]. Among the many appealing aspects of natural inhibitors are their low cost, lack of environmental impact, abundance, and sustainability (renewable sources of supply) [8-18] In this study, we use the electrochemical polarization method to investigate the efficacy of (MS) extract as a novel, eco-friendly corrosion inhibitor against CS corrosion in a 0.6 M NaCl solution. MS extract is readily available, inexpensive, and contains numerous organic compounds that are perfect for protecting metals.

2. Experimental methods

2.1 Materials and chemicals

A working electrode carbon steel was a rod with circular shape (2 cm diameter and 2 mm thickness) which previously were grinded with emery papers of variety graded (200,400,800,1200, and 2000) . Then they were polished mechanically with diamond paste using smooth cloth to surface mirror , after which they were degreased with acetone .

Table (1) : A chemical carbon steel composition

C%	Si%	Mn%	P%	S%	Cr%	Mo%	Ni%	AL%	Cu%	Fe%
0.477	0.227	0.628	0.0193	0.008	0.0293	0.0028	0.0095	0.0239	0.0154	Bal.

2.2. Preparing plant extract

The Malva Sylvestris (MS) leaves had gathered from Iraq's western region, cleaned, and dried in an oven set at 70 °C for three days. To make a fine powder, the dried leaves are ground to a powder using an electric grinder. The 90 µm × 17 cm sieves were used to sift the powder. Next, combine 25 grams of (MS) powder with 400 milliliters of distilled water. Heat a mixture for ten minutes, let it cool at room temperature, away from light. After passing a mixture through a filter, add stock solutions of several concentrations (200 ,400 ,and 800) ppm [17].

2.3. Solution

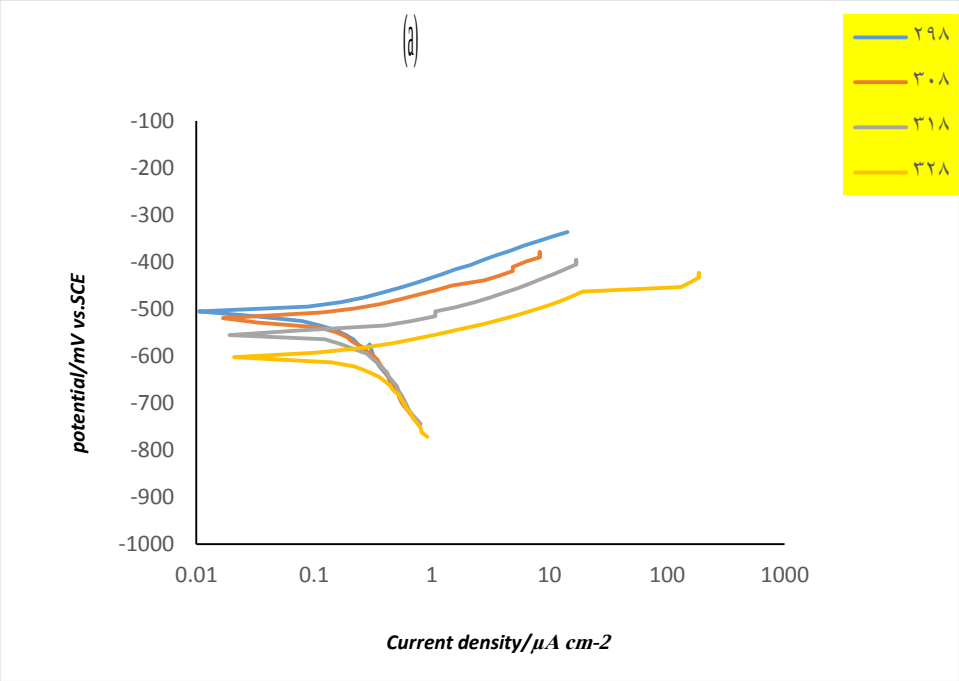
Corrosive solution was prepared of 0.6 M NaCl solution by dissolving calculated mass of NaCl in distilled water . For each experiment a freshly solution was made to study corrosion behaviour of CSin saline solution . Three concentrations of MS leaves extract were used (200 ,400, and 800) ppm to study the inhibition effect of MS leaf extract .

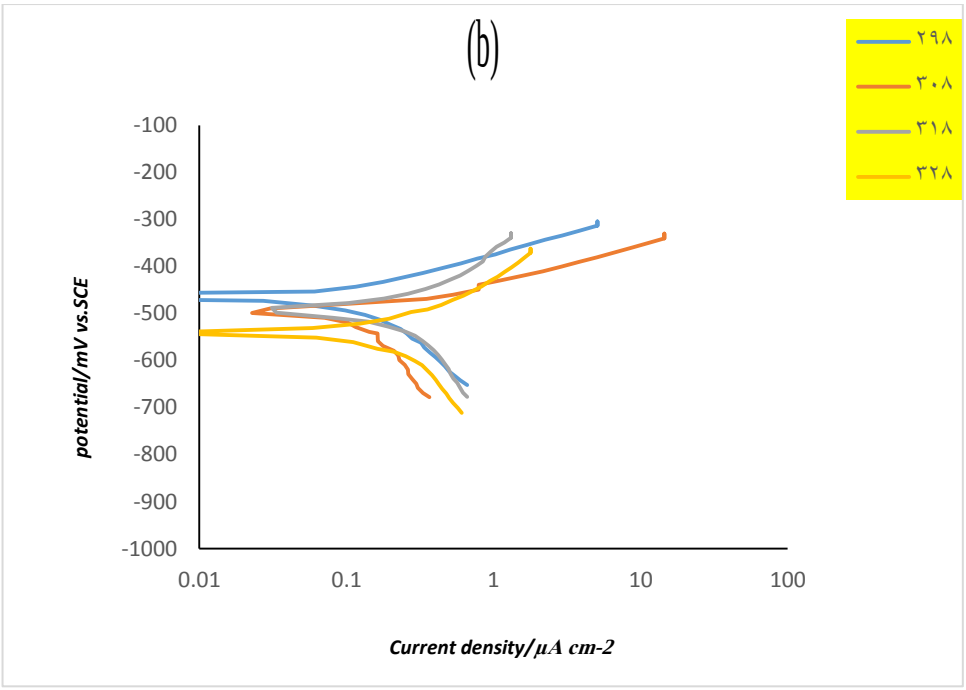
3. Results and Discussion:

3.1.The potentiodynamic polarization:

At varying concentrations of MS extract, potentiodynamic polarization graphs of carbon steel alloy in a 0.6 M sodium chloride solution are displayed in Figure (1). After analyzing the

polarization curves, the corrosion parameters (E_{corr}), (i_{corr}), (b_c), and (b_a) were calculated using the Tafel extrapolation method.
According to Table (2), which displays the reset data, the corrosion current density (i_{corr}) decreased as the extract concentration increased.
The resetting data were displayed in Table (2) and these data show that corrosion current density (i_{corr}) decreased with increasing extract concentration , the addition of MS leave extract affect both anodic and cathodic processes , thus corrosion potential values is a little affected , this means that this inhibitor act as mixed- type inhibitor




(b)
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٣١٨
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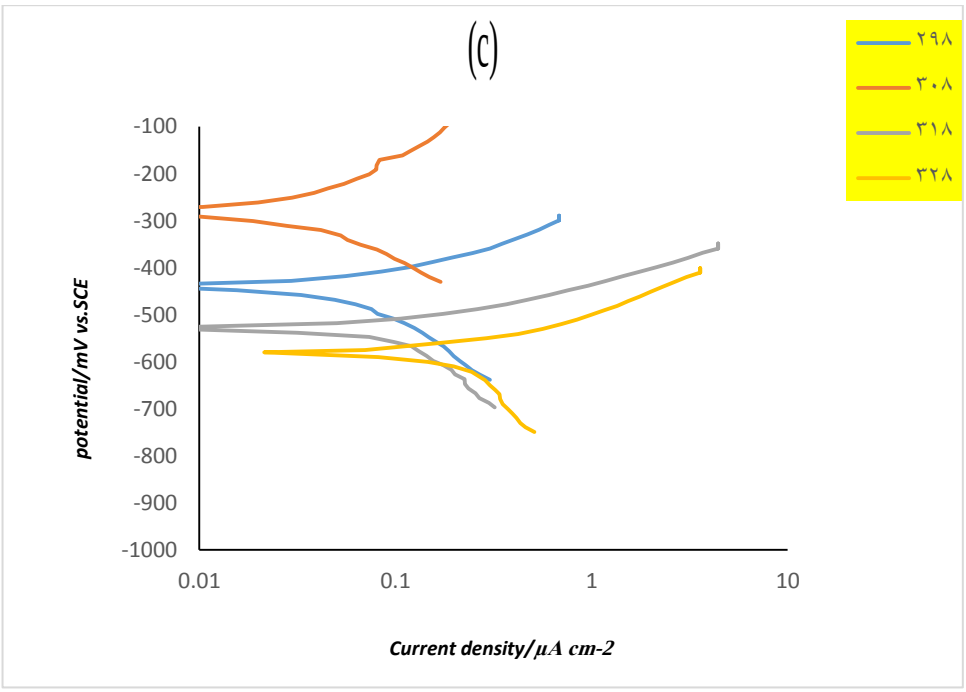
-100
-200
-300
-400
-500
-600
-700
-800
-900
-1000
potential/mV vs.SCE
0.01
0.1
1
10
100
Current density/μA cm-2


(c)
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-100
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-300
-400
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-800
-900
-1000
potential/mV vs.SCE
0.01
0.1
1
10
Current density/μA cm-2

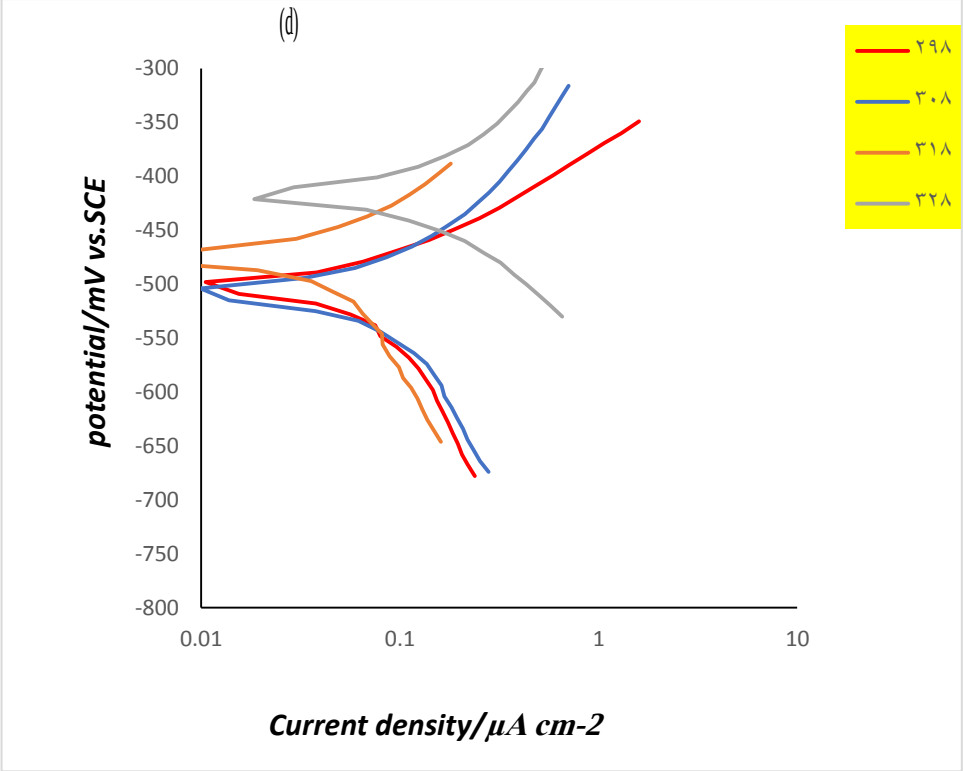

Figure (1): Polarization curves of carbon steel corrosion sodium chloride solution at four temperature (298-328)K,with and without varying amounts of MS leaves extract(a) in 0.6M NaCl (b) in 0.6 NaCl with 200 ppm MS (c)) in 0.6 NaCl with 400 ppm MS (d)) in 0.6 NaCl with 800 ppm MS.

Table (2): Carbon steel corrosion tests in a sodium chloride solution at temperatures ranging from 298 to 323 K using MS leaves extract at varying concentrations and Temperatures.

C inh ppm	T(K)	i_{corr} (µA/cm²)	- E_{corr} (mV)	$+b_a$ (mV.dec^{-1})	$-b_c$ (mV.dec^{-1})	CR. (g.m^{-2}.d^{-1})	PR. mmy
Blank	298	104	−505	72.8	−190.6	3.2×10^{1}	1.21
	308	137	−518.5	65.8	−227.6	3.43×10^{1}	1.59
	318	153	−552.7	52.6	−192.4	3.82×10^{1}	1.78
	328	171	−599	52.4	−166.4	4.25×10^{1}	1.97
200	298	31	−552	49.2	−60.3	7.55	3.51×10^{-1}
	308	47	−488	21.9	−103.5	1.18×10^{1}	5.47×10^{-1}
	318	56	−495.6	57.7	−61.6	1.38×10^{1}	6.4×10^{-1}
	328	65.2	−541	69.6	−81.6	1.63×10^{1}	7.58×10^{-1}
400	298	20	−437	48.5	−84.4	8.87	4.12×10^{-1}
	308	27.5	−282	207.6	−177.8	6.79	3.15×10^{-1}
	318	37	−525	42.1	−101	9.28	4.31×10^{-1}
	328	80.8	−537.7	49.9	−86.6	6.07	2.82×10^{-1}
800	298	14	−176	76.9	−95.4	3.57	1.66×10^{-1}
	308	24	−503	54.8	−83.4	6.03	2.80×10^{-1}
	318	33	−478	118.7	−166.7	8.16	3.79
	328	43.5	−560	89.3	−721	1.08×10^{1}	5.02×10^{-1}

3.2.Effect of temperature:

By means of Arrhenius equation, the activation energy for a corrosion of carbon steel was determined in sodium chloride both in the presence and absence of inhibitors [18].According to the equation:

$$\log i_{corr} = \frac{-Ea}{2.303RT} + \log A \qquad (1)$$

Here, (Ea) symbolizes an activation energy, (R) symbolizes a gas constant (8.314), and (A) stands for Arrhenius constant. Eq.(1) predicts that ln (i_{corr}) plotting in contradiction of $\frac{1}{T}$ should be experimentally linear. The line slope offers $\frac{-E^*a}{RT}$, whereas the intercept for extrapolated line to $\frac{1}{T} = o$ has the particulars of ln A.

Through using alternative formula for Arrhenius relationship [19] (ΔH*) and (ΔS *) has been gotten via:

$$\ln\left(\frac{i_{corr}}{T}\right) = \ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S*act}{R}\right) - \left(\frac{\Delta H\ *act}{RT}\right) \qquad (2)$$

At this point, (h) denotes "planks constant"(6.626*10^{-34} J.S), (N) denotes "Avogadro's number" (6.022*10^{23} mol^{-1}), it denotes possible to draw (ln $\frac{i_{corr}}{T}$) vs. $(\frac{1}{T})$. Here, a straight line slope depicts its magnitude $(-\frac{\Delta H_{act}}{R})$ and the intersection depicts its magnitude $(ln\frac{R}{Nh} + \frac{\Delta S_{act}}{R})$.The consequences depicted in table (3).

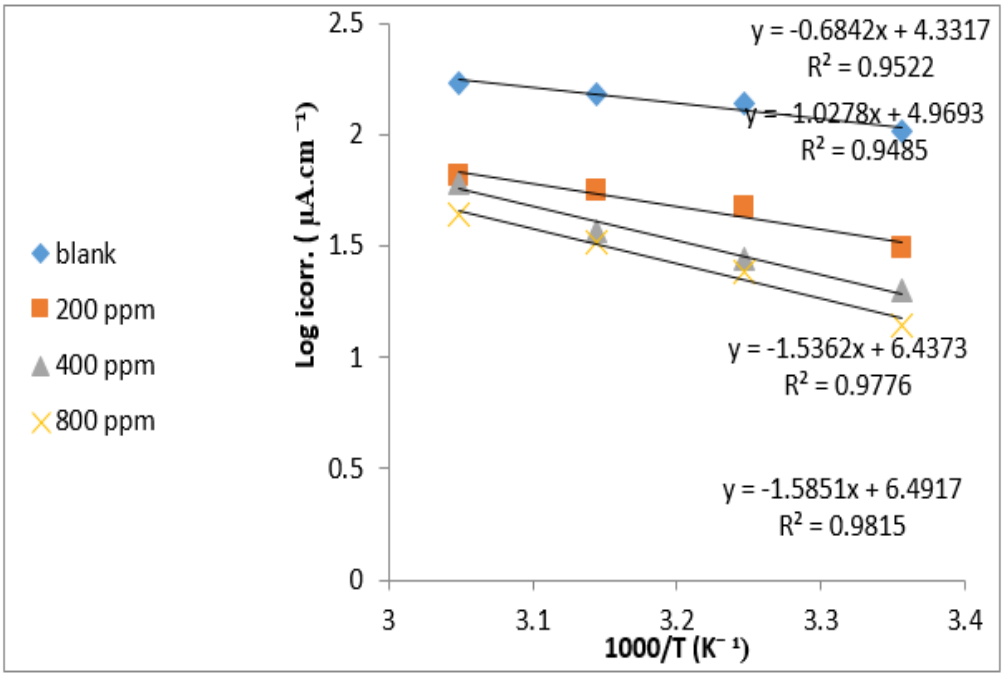

Figure (2) log icorr. Arrhenius against 1/T for corrosions of CS in 0.6 M NaCl with and devoid of diverse concentration of MS leaves extract .

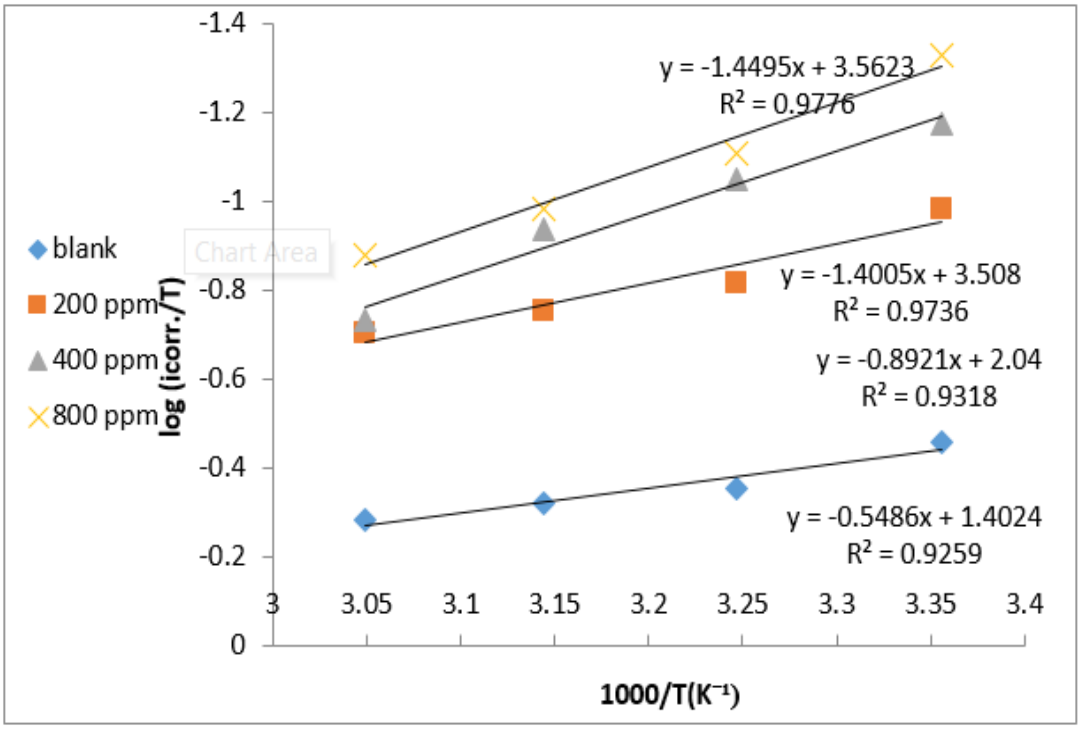

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Figure (3) log (CR/T) against 1/T for the CS corrosion in 0.6 M NaCl with different concentrations for MS leaves extract

Table (3): Activation energy (Ea), activation enthalpy (ΔH*), in addition to an activation entropy (ΔS*) based on a corrosion of carbon steel in 0.6 M NaCl and in an inhibitor existence.

Conc. (ppm)	**E_a (KJ. mol^{-1})**	**$-\Delta S^*$ ($J.K^{-1}.mol^{-1}$)**	**ΔH^* (KJ. mol^{-1})**	**R^2**
Blank	13	170	10.51	0.9776
200	19.68	158	17.35	0.9736
400	29	130	26.8	0.9318
800	30.5	129	27.76	0.9259

A high reaction rate is indicated by an increase in the activation energy (Ea), whereas the low reaction rate has been indicated by an activation energy reduction. Activation energy values increased in an existence of variable MS concentrations, as seen below:Inhibitors were shown to have greater activation energies than those without them; that is, adding MS to a sodium chloride solution increases the energy barrier for carbon steel corrosion [20,21].

In the presence of MS, the activation enthalpy values are negative, suggesting that the association step, and not the dissociation step, determines the rate of the activated complex. Additionally, there is an increase in entropy during the adsorption process, which is what drives the adsorption of MS onto the carbon steel surface [22].

3.3 Inhibition Efficiency (IE %) in addition to surface coverage (θ) :

An inhibition efficiency (IE %) have considered by [23]

$$\text{IE\%} = \left[1 - \frac{i^{\circ}}{i}\right] \times 100 \qquad (3)$$

The values of i besides $i\circ$ characterize the corrosion current densities in a corrosion medium when inhibitors are not present and in the presence of inhibitors, respectively. The method employed for determining a surface coverage (θ) is the relation [24]. Referring to the data presented in table (3).

$$\theta = \frac{\text{IE\%}}{100} \qquad (4)$$

Table (3): Various concentrations of LS in 0.6M NaCl were tested to determine inhibition efficiency (IE %) and surface coverages (θ) throughout a temperature range of 298-323 K.

T. (K)	MS Conc. ppm					
	200		400		800	
	IE%	θ	IE%	θ	IE%	θ
298	76.15	0.7615	85.69	0.8569	89.05	0.8905
303	74.45	0.7445	81.02	0.8102	86.13	0.8613
308	71.89	0.7189	79.08	0.7908	82.35	0.8235
313	66.47	0.6647	67.61	0.6761	77.78	0.7778

The results showed that the IE% values went up as the inhibitor concentration went up and down when the temperature went up. As the temperature increase, a corrosion process accelerates and the inhibition efficiency drops. In contrast, the higher concentration of inhibitors raises a density of electrons in adsorption centers for molecules, leading to an improvement in inhibition efficiency [25].

3.4 The adsorption isotherm:

Because it shows the presence of inhibitor molecules on the metal surface and how they interact, surface coverage data is useful for studying adsorption qualities using isotherm adsorption.

Adsorption isotherms are employed to examine the impact of the inhibitors MS on the surface coverage (θ) for employed electrode (CS) and the concentrations of the inhibitor solutions . We may find the ideal Langmuir isotherm using the following equation [25].

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{adc}} + C_{inh} \ldots\ldots (6)$$

Here, K_{ads} is equilibrium constants for adsorption and desorption suggest in which inhibitor molecules have been approaching the surface adsorption positions.

Then measured K_{ads} stands for computing Gibbs free energies for adsorption through [26,27]

$$\Delta G°_{ads} = -RTln\,(55.5K_{ads}) \ldots\ldots\ldots (7)$$

The standard enthalpies and entropies of adsorption are determined using the Gibbs formula [28]. Gas constants are represented by R, absolute temperatures by T, and molar water concentrations in mol./L by the (55.5) value.

$$\Delta G°_{ads} = \Delta H°_{ads} - T\Delta S°_{ads} \ldots\ldots\ldots (8)$$

Equation(8) predicts that plotting of $\Delta G°_{ads}$ in competition with T must be linear as we experimentally observed a line slope gives - $\Delta S°_{ads}$ whereas the intercept of the line is $\Delta H°_{ads}$

Negative $\Delta H°$ magnitudes clarifies the adsorption for MS molecules as exothermic .An $\Delta G°_{ads}$negative magnitudes with the inhibitor have been based on exothermic adsorption processes.

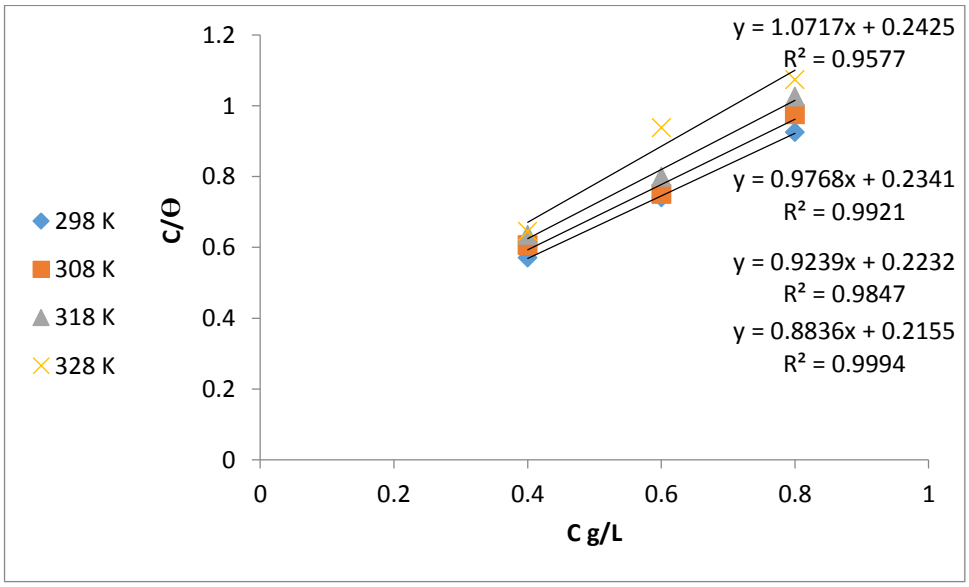


Figure (3) Langmuir Isotherm depiction MS leaves extract adsorptions on CS in 0.6M NaCl.

The above consequences depicted in table (4):

Table 4 : Thermodynamic Parameters for adsorptions of MS leaves extract adsorptions on carbon steel in 0.6M NaCl.

T (K)	K_{ads} ($g.L^{-1}$)	$-\Delta G°_{ads}$ ($kJ.mol^{-1}$)	$\Delta S°_{ads}$ ($J.K^{-1}.mol^{-1}$)	$-\Delta H°_{ads}$ ($kJ.mol^{-1}$)
298	6.779661	14.6928		

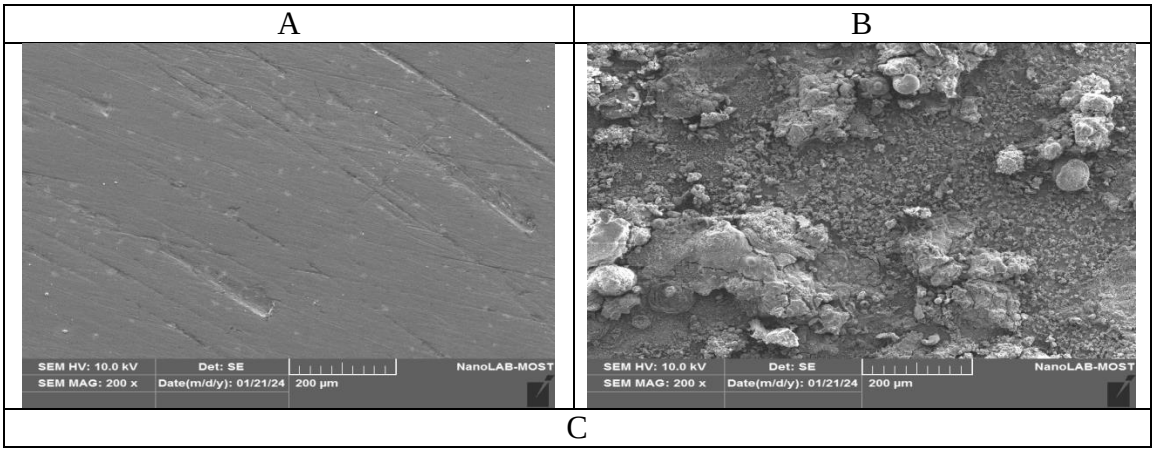
308	6.666667	15.1428	38	2.431
318	5.7	15.2203		
328	5.022602	15.3539		

Based on charged molecules interacting with exterior metal layers (physisorption), the ΔGads values can reach -20 kJ/mol when measured electrostatically. Charging from inhibitor molecules to metal surfaces or the formation of coordinate covalent bonds (chemisorption) causes the ΔGads values to be higher than -40 kJ/mol. The fact that the magnitudes of ΔGads varied from 14.6 to 15.3 Kj mol $^{-1}$suggests that inhibitors physically adsorb onto the surfaces of carbon steel alloys [29].

Negative values of (ΔH∘) suggest that the adsorption for inhibitor compounds is exothermic. Adsorption may be either physical or chemical; nonetheless, the positive magnitude indicates a chemical process due to its endothermic nature [30]. The process of MS leaves extract molecules being adsorbed onto carbon steel surfaces is referred to as "physisorption" in this article.

3.5 Scanning electron microscopy (SEM) analysis

The use of scanning electron microscopy (SEM) on carbon steel surfaces verified that the molecules that had been removed had actually adsorbed onto the carbon steel alloy surfaces, as opposed to being just peeled off. In order to determine the optimal concentrations of LS leaves extract, carbon steel alloy surfaces were scanned using a SEM before and after immersion in 0.6 M sodium chloride. The outcomes can be observed in Figure 4. The refined carbon steel alloys are illustrated in Figure (a), the carbon steel immersed in Figure (b) in 0.6M sodium chloride, and the carbon steel dipped in Figure (c) in 0.6M sodium chloride with 800 ppm of MS leaves extract.



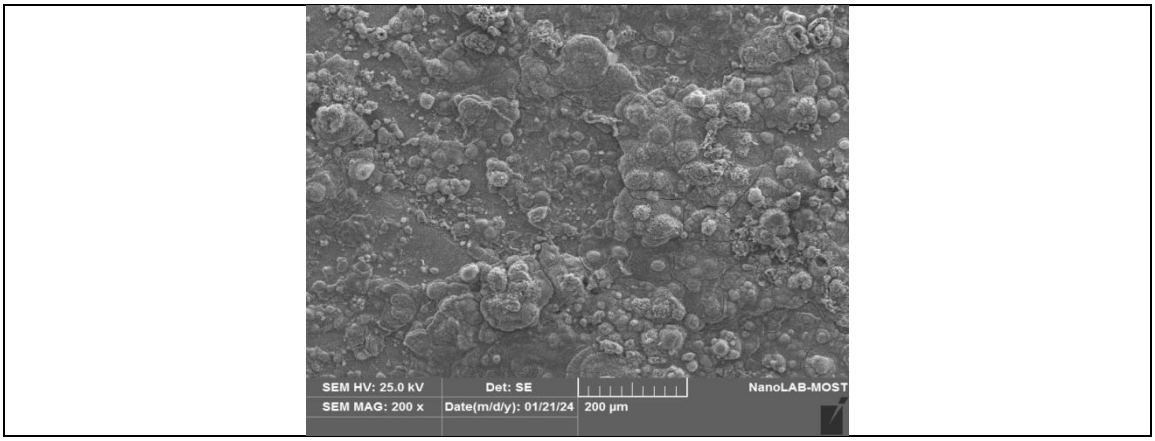


Figure (4) Scanned micrographs for electron (a) polished carbon steel alloys, (b) CS dipped in 0.6 M NaCl and (c) CS alloys in 0.6 M NaCl solutions with a 800 ppm of MS leaves extract , At 298 K.

Conclusions

Results showed that in 0.6 M NaCl solutions, MS leaves extract effectively inhibited carbon steel. A negative value of ΔG indicates that the inhibitors adsorb on the metal surface of their own will. The noticed Ea besides ΔH magnitudes for the corrosion process upkeep this discovery. Due to the activation complex representing an association rather than a dissociation for ΔS*ads in the rate-determining stage, all inhibited and blank solutions are negative. The Langmuir adsorption isotherm was employed to refer to the adsorption data of MS on a metal surface, and the results showed that the model was very accurate. It was shown that the effectiveness of the inhibitor's protection increased as its concentration raised. The maximal value reaches 86.5% at 800 ppm of MS leaves extract.

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