Article

Green inhibitors for Carbon-steel corrosion in acidic environment

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Abstract

It is known that the extracts of most natural plants contain many chemicals that can be used in various fields, whether industrial or medical. In this study, the organic compounds present in the angelica plant were extracted using a solvent (hexane) and the extract was characterized using some spectroscopic methods (FT-IR, NMR) to determine the nature of the active groups in the extract. After that, the extract was used as an inhibitor to study the corrosion of carbon steel type (N80) in an acidic medium at different temperatures. The results proved that the inhibitor plays a role in preventing the corrosion process. It was also noted that the speed of corrosion decreases with increasing concentrations of the inhibitor, due to the formation of a protective adsorbent layer. The inhibitor on the surface of the alloy repels corrosive particles and forms a repellent wall, which reduces the current and therefore the rate of corrosion and increases the resistance to polarization. Corrosion increases with increasing temperatures, because increasing temperature leads to an increase in the number of molecules that have kinetic energy equal to or greater than the activation energy. Therefore, an increase in temperature will increase the speed of the corrosion reaction due to the increase in kinetic energy of corrosive environmental particles and a decrease in the activation energy necessary for the reaction to occur The reason for this can be attributed to the melting of the inhibitor present on the alloy as the temperature rises, which makes the alloy easy to be exposed to abrasion, which increases the rate of corrosion and the accumulation of this from the dynamic rate of hydration with the temperature rising over the studied range.

Keywords: Eco-friendly Inhibitors, Product, Soxhlet, Cathode, Anode, Plant extract.

1- Introduction

The extraction of plant involves the separation of active plant materials or secondary metabolites, including alkaloids, flavonoids, terpenes, saponins, steroids, and glycosides, from inert or inactive substances using a suitable solvent and a standardized extraction method. It has been observed that plant materials rich in phenolic compounds and flavonoids exhibit antioxidant properties.

Continuous hot extraction, also known as Soxhlet extraction, is a process that utilizes a glass apparatus called a Soxhlet extractor. This apparatus consists of a round bottom flask, extraction chamber, siphon tube, and condenser at the top. A porous bag made of clean cloth or strong filter paper, called a thimble, is filled with dried, ground, and finely powdered plant material and tightly closed[1-2]

A corrosion inhibitor is a compound that, when introduced into a liquid or gas (usually a metal or alloy), diminishes or hinders the corrosion of metal surfaces that are exposed to the surrounding environment. These inhibitors work by establishing a protective barrier between the metal surface and the corrosive surroundings, achieved through either adsorption or the formation of a protective film[3].

Green inhibitors are widely employed in the oil and gas industry to effectively manage the corrosion of various steel types in acidic environments. These inhibitors can be categorized into two groups, namely organic and inorganic, based on their chemical composition. Organic green inhibitors encompass a range of substances such as plant extracts, oils, ionic liquids, amino acids, drugs, and natural polymers. What sets these compounds apart is their heteroatoms, which consist of elements with a significant electron density[4].

2. Exprimental part

2.1 Chemicals

Plants were collected from Al-Ashar Market, Basra, Iraq, and were ground individually using an electric grinder, Then, a weight of 100 g was taken from the plant and extracted using a solvent[5-6] . The extraction solvent is poured into the bottom flask, followed by the thimble into the extraction chamber. The solvent is then heated from the bottom flask, evaporates, and passes through the condenser where it condenses and flows down to the extraction chamber, extracting the drug by coming in contact[7-8]. The process is repeated until the drug is completely extracted. This method is suitable for plant material that is partially soluble in the chosen solvent and for plant materials with insoluble impurities, but not for thermolabile plant materials. Advantages include the ability to extract large amounts of drug with a smaller amount of solvent, and it is applicable to heat-stable plant materials. Disadvantages include the inability to regularly shake the mixture and unsuitability for thermolabile materials[9].

After that, the extract was concentrated using a rotary distillation device, and the precipitate was dried at laboratory temperature. Then the inhibitor was prepared by taking a weight of 1 g of the extract and dissolving it with distilled water in a 1L volumetric flask[10].

- Composition of alloys:

Corrosion tests were conducted on coupon type N80 carbon steel rods contained 0.038% carbon, 0.50% manganese, 0.002% sulfur, and 0.03% phosphorus, with the remaining balance being iron. These rods were obtained from the AL-Ashar market in Basrah city.

- Smoothing:

The carbon steel rods were mechanically cut into circular disks with diameters ranging from 1.1 to 1.2 cm and thicknesses of 3-4 mm, to achieve different levels of smoothness. While the disks underwent a smoothing process using a grinder machine type ECOMET II with aluminum oxide sheets.

The process of smoothing was carried out by using a paper smoothing mesh size 1500, 2000 and 3000. The sample was then rotated in the opposite direction on a disk and water was used for cooling during the smoothing process to prevent overheating of the samples and to avoid the adhesion of paper granules to the surface, which could affect the smoothness. while alumina was added to achieve a shiny, mirror-like finish. Afterward, the model was washed with distilled water and the electrode was cleaned ultrasonically with ethanol. It was then washed again with distilled water and soaked in acetone for 15 minutes. Finally, the sample was air dried and stored in a small paper bag placed in a desiccator containing silica gel to prevent any effects from air humidity, following the specifications of ASTM standard GI-72(227). During the test, the specimen was placed on a metal base holder and inserted through an electrode mounting rod, which was secured with a Teflon cover to isolate the disc and prevent any leakage from the working environment.

2.2 Electrochemical Technique for Corrosion Measurement

The measurement of corrosion was conducted using an electrochemical technique that involved measuring the electrical current produced between the metal and electrolyte, this current was then converted into a corrosion rate and this technique is widely used due to its reproducibility and time efficiency compared to other methods such as weight loss and thickness reduction. The Tafel extrapolation method is a common approach used in electrochemical reactions under activation control, this method involves plotting polarization curves that exhibit linear behavior in E Vs. log (I) plots, known as Tafel behavior. The Tafel plot provides information on the typical polarization behavior of metals in acid solution with and without oxygen, as well as the extrapolation of cathodic and anodic Tafel slopes back to the corrosion potential (ECORR). The intersection point of these slopes corresponds to the corrosion current density (ICORR) or corrosion rate. To ensure accuracy, at least one decade of linearity in Tafel extrapolation is desirable, however, concentration polarization and ohmic resistance can affect accuracy, making steady state polarization curves necessary for more representative corrosion reactions. Potentiostatic and galvanostatic methods should be compared to determine the best technique for corrosion rate determination, while Tafel extrapolation has some limitations, such as non-reversible polarization curves and varying Tafel constants, it remains a widely used and effective method for corrosion measurement.

Electrochemical Measurements

The electrochemical measurements were conducted using the corrosion cell model (EG&G PARC model 350A). and the experimental setup consisted of a flat bottom glass vessel with a capacity of one liter, the vessel was equipped with a working electrode, which was attached to the specimen, two high density carbon graphite counter electrodes were also present, along with a saturated calomel electrode (SCE) used as the reference electrode.

Figure (1): commercially available electrochemical cell

To ensure accurate measurements, a lugging capillary arrangement filled with the same tested solution was employed to keep the reference electrode in close proximity to the working electrode. This arrangement helped minimize any potential IR drop. All measurements were carried out in solutions that were open to the atmosphere, under unstirred conditions.

The experimental procedure can be summarized as follows:

1. A cleaned specimen was mounted on the electrode holder, serving as the working electrode.

2. The auxiliary electrode (carbon graphite), reference electrode (SCE), lugging capillary, and other components were placed in the test cell.

3. 700 ml of the electrolyte was added to the test cell, and the lugging capillary was filled with the same test solution.

4. The temperature of the solution was adjusted to the desired value using a water bath.

5. The N80 carbon steel specimen was then polarized anodically and cathodically from the open circuit potential to obtain the corrosion potential, corrosion current, and Tafel slopes.and the polarization was done at approximately ±250 mV.

6. After the test, the contents of the corrosion cell were evacuated and cleaned with distilled water. The experiment was then repeated with another sample.

7. The experiment was repeated for various concentrations (10, 20, 30, 40, 50, and 60 ppm) at temperatures ranging from 298 K to 338 K for all samples.

To maintain the desired operating temperature, a water bath equipped with a temperature controller was used. and the temperature was monitored using a thermometer calibrated from 298 K to 338 K, with an accuracy of ±1°C.

These electrochemical measurements provided the necessary parameters for evaluating the inhibiting action.

3. Result and discussion

3.1 Studying the effect of inhibitor concentration on inhibition efficiency and corrosion rate in the presence of a corrosive HCl environment:

The following tables (1-1) to (1-5) show the results obtained using the Tafel method when evaluating the plant extract (angelica) as a corrosion inhibitor at different concentrations (10-60 ppm) and at constant temperature (25-65)℃ in the presence of (0.1M HCl)

Table (1) The electrochemical results obtained by the Tafel method in evaluating the angelica inhibitor at a temperature of 25℃.

Parameters	Angelica						blank
Temp.(k)	298	298	298	298	298	298	298
Conc.(mg/l)	10	20	30	40	50	60	0.1N
Area(cm^2)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ei(V)	-0.820	-0.820	-0.822	-0.808	-0.822	-0.848	-0.959
E_f(V)	-0.320	-0.320	-0.322	-0.308	-0.322	-0.348	-0.359
Scan(mv/s)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
(OC)E_{CORR}(V)	-0.570	-0.570	-0.572	-0.558	-0.572	-0.598	-0.609
Results							
I_{CORR} (nA cm^{-2})	0.00062644	0.0005701	0.00055546	0.00018419	0.00017449	0.00016139	0.00073148
CR(mmpy)	7.3683	6.7634	6.5334	2.1664	2.0524	1.5213	8.6038
E_{CORR}(V)	-0.6566	-0.60064	-0.58353	-0.5834	-0.59033	-0.40381	-0.61905
$_C$) (V/dec.)	125.14	122.78	160.38	112.63	102.76	112.74	154.11
) (V/dec.)	70.084	73.54	87.846	76.785	71.767	71.453	97.174
R_P(Ω)	33.096	37.839	47.488	116.38	105.71	50228	19.608
.	0.14359928	0.22062129	0.24063542	0.74819544	0.76145623	0.77690436	
I.E.%	14.359928	22.062129	24.063542	74.819544	76.145623	77.690463	

Table (2) The electrochemical results obtained by the Tafel method in evaluating the angelica inhibitor at a temperature of 35℃.

Parameters	Angelica						Blank
Temp.(k)	308	308	308	308	308	308	308
Conc.(mg/l)	10	20	30	40	50	60	0.1N
Area(cm^2)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ei(V)	-0.820	-0.820	-0.822	-0.808	-0.822	-0.848	-0.959
E_f(V)	-0.320	-0.320	-0.322	-0.308	-0.322	-0.348	-0.359
Scan(mv/s)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
(OC)E_{CORR}(V)	-0.570	-0.570	-0.572	-0.558	-0.572	-0.598	-0.609
Results							
I_{CORR} (nA cm^{-2})	8.7602E-05	6.5846E-06	4.9971E-06	4.2358E -06	4.1738E-07	8.735E-07	0.0013482
CR(mmpy)	1.0304	0.095738	0.058777	0.049822	0.044613	0.010274	15.858
E_{CORR}(V)	-0.21598	-0.25944	-0.38399	-0.33447	-0.30642	-0.4052	-0.58799
$_C$) (V/dec.)	256.46	234.52	389.47	294.9	243.7	203.7	72.638
) (V/dec.)	3494.3	253.49	1537.8	15364	12475	879.52	98.958
R_P(Ω)	1261.2	12113	25750	29136	2078.3	85112	13.656
.	0.9350229936	0.9951160065	0.9962929525	0.9965818128	0.9994678979	0.9993520991	
I.E.%	93.50229936	99.51160065	99.62929525	99.65818128	99.94678979	99.93520991	

Table (3) The electrochemical results obtained by the Tafel method in evaluating the angelica inhibitor at a temperature of 45℃.

Parameters	Angelica						Blank
Temp.(k)	318	318	318	318	318	318	318
Conc.(mg/l)	10	20	30	40	50	60	0.1N
Area(cm^2)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ei(V)	-0.820	-0.820	-0.822	-0.808	-0.822	-0.848	-0.959
E_f(V)	-0.320	-0.320	-0.322	-0.308	-0.322	-0.348	-0.359
Scan(mv/s)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
(OC)E_{CORR}(V)	-0.570	-0.570	-0.572	-0.558	-0.572	-0.598	-0.609
Results							
I_{CORR} (nA cm^{-2})	6.4339E-05	1.473E-06	9.9108E-07	6.6327E-07	4.718E-07	3.8276E-07	0.0014989
CR(mmpy)	0.75676	0.016467	0.011657	0.0078014	0.0075492	0.0071467	17.63
E_{CORR}(V)	-0.28749	-0.26368	-0.24758	-0.20207	-0.15452	-0.14927	-0.62577
$_C$) (V/dec.)	73.92	261.52	213.56	88.335	567.61	74.36	216.24
) (V/dec.)	73.671	2.9613E07	586.68	435.45	24.827	35.41	573.59
R_P(Ω)	236.94	69759	45861	82437	1806.9	1801.1	33.132
.	0.9570758556	0.9990172793	0.9993387951	0.9995574955	0.9996852358	0.9997446394	
I.E.%	95.70758556	99.90172793	99.93387951	99.95574955	99.96852358	99.97446394	

Table (4) The electrochemical results obtained by the Tafel method in evaluating the angelica inhibitor at a temperature of 55℃.

Parameters	Angelica						Blank
Temp.(k)	328	328	328	328	328	328	328
Conc.(mg/l)	10	20	30	40	50	60	0.1N
Area(cm^2)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ei(V)	-0.820	-0.820	-0.822	-0.808	-0.822	-0.848	-0.959
E_f(V)	-0.320	-0.320	-0.322	-0.308	-0.322	-0.348	-0.359
Scan(mv/s)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
(OC)E_{CORR}(V)	-0.570	-0.570	-0.572	-0.558	-0.572	-0.598	-0.609
Results							
I_{CORR} (nA cm^{-2})	5.8836E-05	1.0655E-05	1.2167E-06	4.6191E-07	1.5792E-07	8.2845E-07	0.042118
CR(mmpy)	0.69204	0.12533	0.014311	0.0054331	0.0024937	0.00097443	495.4
E_{CORR}(V)	-0.59251	-0.30338	-0.30414	-0.15757	-0.13579	-0.30504	-0.70117
$_C$) (V/dec.)	446.92	172.79	156.17	92.259	67.84	142.05	760.06
) (V/dec.)	498.32	1.2064E07	445.14	436.01	361.47	401.47	657.8
R_P(Ω)	5037.2	52654	75315	39620	1621	1700.1	3.2154
.	0.9986030676	0.9997470203	0.9999711121	0.999989033	0.9999962505	0.999980424	
I.E.%	99.86030676	99.97470203	99.99711121	99.9989033	99.99962505	99.9980424	

Table (5) The electrochemical results obtained by the Tafel method in evaluating the angelica inhibitor at a temperature of 65℃.

Parameters	Angelica						blank
Temp.(k)	338	338	338	338	338	338	338
Conc.(mg/l)	10	20	30	40	50	60	0.1N
Area(cm^2)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Ei(V)	-0.820	-0.820	-0.822	-0.808	-0.822	-0.848	-0.959
E_f(V)	-0.320	-0.320	-0.322	-0.308	-0.322	-0.348	-0.359
Scan(mv/s)	1.000	1.000	1.000	1.000	1.000	1.000	1.000
(OC)E_{CORR}(V)	-0.570	-0.570	-0.572	-0.558	-0.572	-0.598	-0.609
Results							
I_{CORR} (nA cm^{-2})	6.1191E-06	5.9042E-07	3.4809E-07	8.91355E-07	3.7767E-05	6.3731E-05	0.46658
CR(mmpy)	0.071974	0.069446	0.040943	0.010484	0.004442	0.0023962	5487.9
E_{CORR}(V)	-0.23796	-0.23878	-0.15021	-0.27979	-0.5886	-0.5786	-0.23803
$_C$) (V/dec.)	129.47	105.97	83.016	112.32	131.01	487.32	632.61
) (V/dec.)	175.46	367.45	299.63	301.57	873	517	382.32
R_P(Ω)	3797.3	58512	77519	35661	1254.9	1663.2	0.21308
.	0.9999868852	0.9999987346	0.999999254	0.9999980896	0.9999190557	0.9998634082	
I.E.%	99.99868852	99.99987346	99.9999254	99.99980896	99.99190557	99.98634082	

From the observation of the previous tables, the presence of an inhibitor against the corrosive environment (0.1M HCl) reduces the corrosion rate of the studied alloy due to a decrease in the corrosion current and an increase in the polarization resistance of the alloy, with the presence of (25℃) angelica as a corrosion inhibitor, the corrosion current (nA cm-20.00062644), the corrosion rate of N80 alloy decreased from (7.3683 mpy) to (0.00016139 nA cm-2) and (1.5213 mpy) at an optimum concentration of 60 ppm while the inhibition efficiency reached 77.690463%, and the polarization resistance increased from (33.096 Ω.cm2) to (50228 Ω.cm2) compared to the absence of the inhibitor, with an inhibition efficiency of (77.690463%).

The inhibition efficiency and the area of the covered layer were calculated from the following two equations[11]:

$E_{effeciency}\% = (CR_{Uninhib} – CR_{Inhib})/ CR_{Uninhib} \times 100$ ……………………………(1)

$\theta = (CR_{Uninhib} - CR_{Inhib})/ CR_{Uninhib}$ ……………………………………….……(2)

Whereas, CRUninhib and CRInhib represent the corrosion rate of the alloy in the absence and presence of the inhibitor, respectively.

It is also noted that the values of the anodic Tafel constant, β_a, and the cathodic, β_c, change in the presence of the inhibitor compared to its absence, and they also change with changing concentrations of the same inhibitor[12]. However, the behavior of the inhibitor tends to be anodic, as can be seen from the values of the corrosion voltage ECorr in the absence and presence of the inhibitor, as the difference between the values is more than 89mV. If the difference between them was within the range ∓89mV, the behavior of the inhibitor would be double[13], and the values of the anodic Tafel constants indicate And the cathodic one indicates that the inhibitor controls the mechanics of the anodic and cathodic reactions through simple blocking of the anodic and cathodic sites and it has a double inhibitory behavior because the difference in the values of the corrosion potential in the presence of overlays is different from the corrosion potential in the absence of the inhibitor within the range ∓89Mv[14]. The optimum concentration of the inhibitor is known as the concentration of the inhibitor at which the inhibitor gives the highest inhibition efficiency. This is not necessarily the optimum concentration that is the highest concentration of the inhibitor studied. The reason for the decrease in the corrosion current and rate and the increase in the polarization resistance of the alloy can be attributed to the absence of the inhibitor (in the presence of The alloy is used in a corrosive environment only) due to the presence of a protective adsorbent layer of the specific inhibitor on the surface of the alloy that repels corrosive particles and forms a repellent wall, which reduces the current and thus the corrosion rate and increases the resistance to polarization. When comparing the values of the corrosion potential Ecorr in the presence and absence of any inhibitor, Of the inhibitors studied at various concentrations, it is noted that these inhibitors tend to be more anodic than double, as the difference in the values of the corrosion potentials between the absence and presence of the inhibitor is more than (±89mV), and this is observed when comparing the values of the anodic and cathodic Tafel constants β_a. β_c in the presence and absence of an inhibitor and for any of the inhibitors studied is decreased in the case of the presence of an inhibitor for all inhibitors compared to the absence of a specific inhibitor and is oscillating, which indicates that these inhibitors are oscillating compared to the absence of a specific inhibitor and oscillating, which indicates that these inhibitors are undergoing a process of coupling through a block. The anodic and cathodic sites are adsorbed on the surface of the alloy with a simple inhibition called (simple blocking reaction) [15]. The anodic reaction was presented in equation (3)

$Fe \rightarrow Fe^{2+} + 2e^-$ (Anode) (Oxidation)……………………………………………. (3)

While the caodic reaction can occur depending on the following reaction:

$2H_2O + O_2 + 4e^- \rightarrow 4OH^-$ (Cathode) (Reduction)……………………………. (4)

In the second reaction in equation (1-4), which involves the reduction of dissolved oxygen in water, which is the origin of the rusting process that occurs for iron and its alloys[16].

$2H_2O + O_2 + 4e \rightarrow 4OH^-$ (Cathode) (Reduction)……………………………..(5)

$Fe^{2+} + 4OH^- \rightarrow Fe(OH)_2 \rightarrow Fe(OH)_3 \rightarrow Fe_2O_3.3H_2O$ (rust) ………………………(6)

In general, inhibitor on the corrosion of iron alloy in corrosive media is attributed to the fact that these organic compounds have inhibitory activity because they contain hetro atoms such as N, O, and their physicochemical properties and the presence of double bonds in the aromatic rings. The mechanism of inhibition is explained by the adsorption of these compounds on the surface of the metal through the double bond electrons of the aromatic rings and the unbonded free electron pairs of the oxygen and nitrogen atoms [17-19].

3.2 Study of the effect of temperature on the efficiency of corrosion inhibition using inhibitors at the optimum concentration and corrosion speed of the alloy:

Temperature is one of the most important factors affecting the speed of a chemical reaction. In general, the corrosion reaction, as one of the chemical reactions, is affected by the rise and fall of temperature. There is no doubt that increasing the temperature leads to an increase in the number of molecules that have a kinetic energy equal to or greater than the activation energy[20], and therefore it is expected that the increase in temperature will increase the rate of the corrosion reaction speed due to the increase in the kinetic energy of the corrosive environmental molecules and the decrease in the activation energy necessary for it to occur. The interaction, and it is noted from the previous tables, that in the presence of any of the studied inhibitors against the corrosive, acidic environment (0.1M HCl), the corrosion current increases, and consequently the corrosion rate, and the polarization resistance decreases. In the case of the presence of angelica as an inhibitor, an increase in temperature from 25℃ will increase the current and the rate of corrosion and the resistance to polarization decrease, this can be attributed to the dissolve of the inhibitor layer on the surface of the alloy with an increase in temperature, which makes the alloy easily exposed to the corrosive environment, which increases the rate of corrosion. This is observed from the decrease in the rate of inhibition efficiency with the increase in temperature in the range studied [21-22].

In the same way, the effect of temperature on the rate of corrosion speed of the studied alloy was studied in the presence of the studied inhibitor and within the range of temperatures mentioned above in the presence of 0.1M HCl acid. The corrosion process occurs in one of the following two possibilities, as in the following two equations:

$2H2^{+} + 2e^{-} \rightarrow H_2$ (Cathode)(Reduction) ……………………………….……. (7)

$4H2^{+} + O_2 + 4e^{-} \rightarrow H_2O$(Cathode)(Reduction)……………………………….. (8)

The process of reducing hydrogen ions occurs in the absence of oxygen according to Equation (7), while the reaction in Equation (8) occurs in the presence of oxygen, and the rate of the second reaction is the highest in atmospheric air. However, the efficiency of inhibiting this inhibitor with acidic media is high as it is a corrosive environment and Although the inhibition efficiency of the studied inhibitor and the polarization resistance of the alloy decrease due to the increase in corrosion current density and thus the increase in the corrosion rate when the temperature rises (25-65℃), the rate of decrease in inhibition efficiency is better, as can be seen in the tables above, which indicates that the strength The adsorption of the inhibitor layer in this acidic medium is better as a corrosive environment, and this can be attributed to the fact that the cathodic reaction in equation (3) in the case of acidic medium is more likely than the reaction. The liberated water molecules are less harmful than the hydrogen gas molecules, and the reaction is less harmful than the reaction, which creates more hydroxyl ions, which is also more harmful than the release of water molecules because the hydroxyl molecules cause rusting, which is more weight loss for the alloy [23-26].

3.3 Study of the kinetics of the corrosion reaction in the absence and presence of the inhibitor:

In order to clarify the effect of temperature on the corrosion rate of the alloy in the presence and absence of an inhibitor, the kinetics of the corrosion reaction must be studied based on the calculation of the thermodynamic functions of activation such as the activation energy Ea*, the enthalpy of activation ΔH*, the entropy of activation

ΔS*, and the free energy of activation ΔG*Activation energy is an important function to determine the rate of reaction speed, whether it is slow or fast. Since the reaction has a high activation energy, the slower it is, and vice versa. The activation energy of the reaction is calculated from the Arrhenius equation [27-29] and as follows [30]:

$$\ln CR = \ln A - Ea^{*}/ RT \quad \text{……} \quad (9)$$

Where CR is the average speed of the corrosion reaction, A represents the Arrhenius coefficient, Ea* represents the activation energy of the corrosion reaction in units of KJ.mol-1, and T represents the absolute temperature in units of K. The value of R represents the general constant for gases and its value is 8.314 J.K-1.mol- 1 By drawing the relationship between ln CR versus 1/T, we obtain a negative plot with a slope equal to -Ea*/R, and the plot equals ln A. Thus, it is possible to calculate the activation energy by having data on the rate of corrosion speed at each temperature within a certain range of temperatures. In this study, the temperature range was between 25-65℃, and the following figures illustrate the Arrhenius relationship to the presence of the acidic corrosive environment HCl at a concentration of 0.1M, and complete the following:

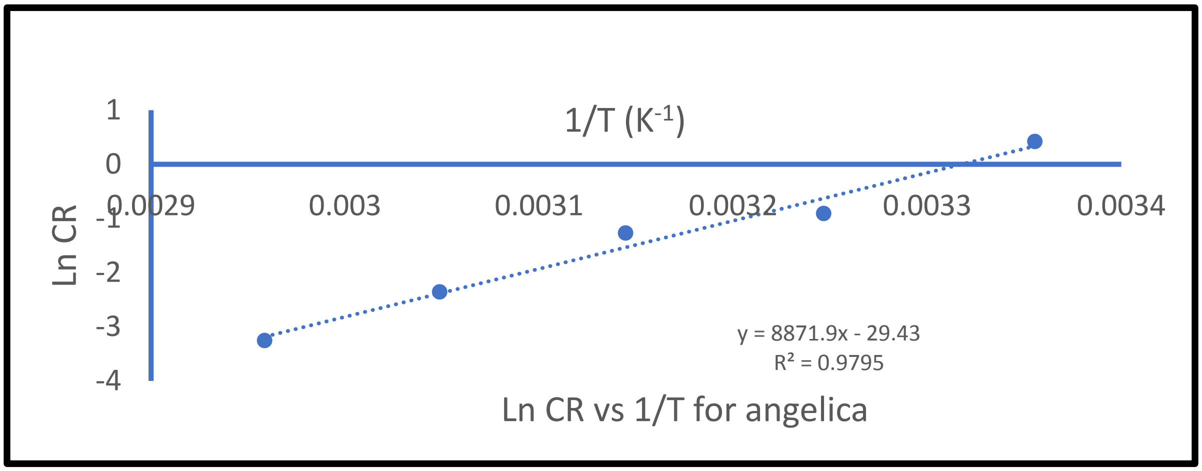

Figure (2) Calculation of the corrosion reaction activation energy for N80 alloy in the presence of angelica inhibitor against an HCl corrosive environment.

The values of enthalpy and entropy of activation are calculated from the following equation [31-32]:

Ln (CR/T) = (ln(R/Nh) + $\Delta S^*/R$) - $\Delta H^*/RT$ …………………………………… (10)

Where N is Avogadro's number and its value is 6.023× mol-1 1023, and h represents Planck's constant and is 6.625×10^{-34} J.s. By drawing the relationship between ln (CR/T) versus 1/T we get a straight line with a slope of -ΔH. */R and the y-cut represents the amount ln(R/Nh) +ΔS*/R from which the entropy of activation will be calculated. The following figure show the drawing of these relationships in the presence of the studied acidic corrosive environment and in the presence of any of the studied inhibitor at their optimal concentrations.

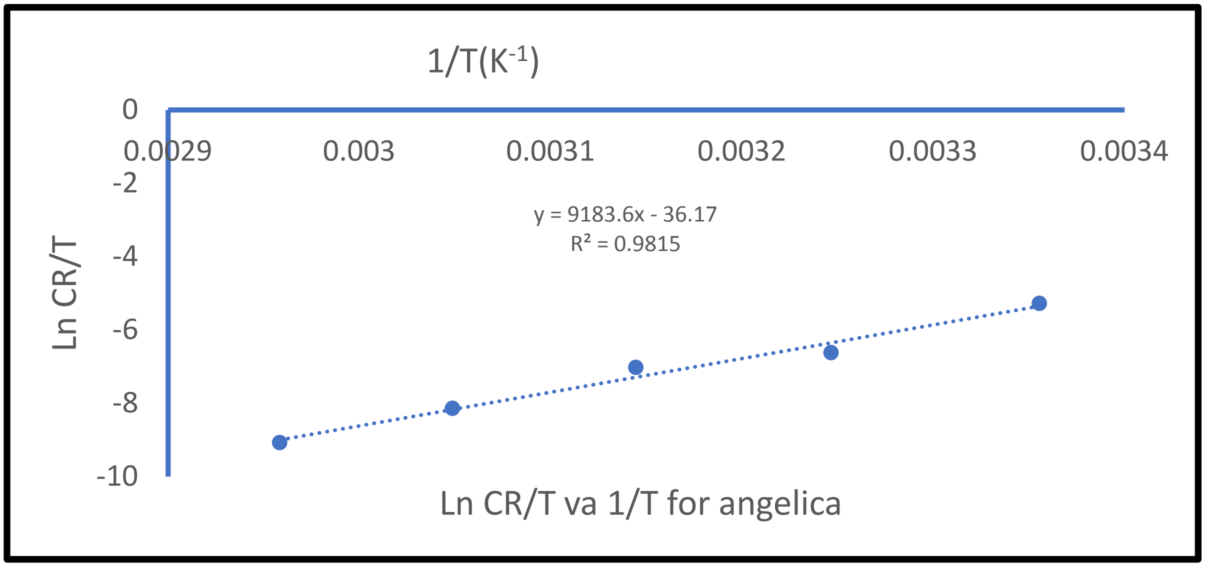

Figure (3) Calculation of the enthalpy and entropy of activation for the corrosion reaction of N80 alloy in the presence of angelica inhibitor against HCl as a corrosive environment at a concentration of 0.1M.

Table (6)

Comp.	E_a^* (KJ.mol^{-1})	ΔH^* (KJ.mol^{-1})	ΔS(J.K^{-1}mol^{-1})
Angelica	224.68102	-76352.4504	-498.2575296

The table shows the results of the kinetic functions for the corrosion reaction of the iron alloy in the presence of the optimal concentration against the corrosive medium.

In the case of the presence of HCl at a concentration of 0.1M as a corrosive medium, we notice that the activation energy in the presence of this inhibitor against the acidic corrosive medium is higher than in the presence of the acidic corrosive medium alone, and that the enthalpy of activation produces heat and is a higher value in the presence of the inhibitor than in its absence, which indicates that this inhibitor reduces The rate of corrosion speed of the alloy when there is an optimal concentration of the inhibitor studied, and the enthalpy of activation is a negative value, which indicates that the corrosion reaction increases with increasing temperatures in the absence and presence of the inhibitor, but the enthalpy values in the presence of inhibitors are higher, meaning that the presence of the inhibitor resists corrosion of the alloy even in the presence of Heat reduces its value compared to the absence of the inhibitor[27-31]. It is also noted from the table above that the value of the activation entropy is negative and the value increases in the presence of any of the inhibitors studied. This indicates that the presence of this inhibitor is a random cause due to the tendency of the inhibitor to expel corrosive environmental particles and the tendency of the inhibitor to combine with the corrosion products of the formed rust to form the active complex that forms a layer[32-34]. Inhibition is stable on the surface of the alloy, and the formation of the active complex is considered the step that determines the speed of the corrosion reaction. What indicates an increase in entropy is the increase in the values of the Arrhenius coefficient, which expresses the amount of vibration occurring to the interacting molecules[35]. The value of the Arrhenius coefficient increased in the presence of the inhibitor. In acidic environments, the release of hydrogen gas may be one of the main reasons for making the corrosion rate higher. On the other hand, it is noted that the entropy of activation in the presence of hydrochloric acid at the aforementioned concentration is a negative value, which indicates that the acid causes corrosion products that tend to be stable and the randomness of the interacting molecules decreases [36]. However, this high negative value decreases in the presence of any of the inhibitors studied [37-38].

4. Conclusions

Plant extracts and naturally modified polymers have been scientifically proven to be an exceptional resource for the development of environmentally friendly and highly effective corrosion inhibitors. The findings of this study demonstrate the efficacy of these inhibitors derived from readily available, renewable, and environmentally sustainable sources of phytochemical:

1. The results of this study confirm that plant extracts and modified polymers are excellent sources for environmentally friendly corrosion inhibitors. These inhibitors, derived from renewable and sustainable sources, have shown significant effectiveness in preventing corrosion of N80 steel in 0.1 N HCl solutions. The highest inhibition efficiency of 77% was achieved with the angelica inhibitor at a concentration of 60ppm.

2. The effectiveness of the modified natural products as corrosion inhibitors is influenced by various factors including temperature, concentration, and steric effects. A comparison with unmodified compounds highlights the superior performance of the modified inhibitors.

4. The corrosion potential (ECORR) shows minimal variation, indicating that all inhibitors function as mixed-type inhibitors. The decrease or increase in ECORR is less than 85mv.

5. The corrosion rate of all inhibitors increases with temperature, but at a slower rate compared to the blank solution at the same temperature.

6. The study thoroughly explains the impact of temperature on the inhibition efficiency of the inhibitors. It was observed that as temperature increases, the inhibition efficiency decreases.

7. The kinetic data obtained from the study reveals that the activation energies of the inhibitors are relatively lower than those observed without inhibitors. This suggests that the presence of the angelica inhibitor shifts the corrosion process to the surface site in the acid medium (0.1N HCl).

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خلاصة

ومن المعروف أن خلاصة معظم النباتات الطبيعية تحتوي على العديد من المواد الكيميائية التي يمكن استخدامها في مختلف المجالات سواء الصناعية أو الطبية. في هذه الدراسة تم استخلاص المركبات العضوية الموجودة في نبات حشيشة الملاك باستخدام المذيب (الهكسان) وتم تشخيص الاستخلاص باستخدام بعض الطرق الطيفية (FT-IR,NMR) لتحديد طبيعة المجموعات النشطة في المستخلص. بعد ذلك تم استخدام المستخلص كمثبط لدراسة تآكل الفولاذ الكربوني نوع (N80) في وسط حمضي عند درجات حرارة مختلفة. أثبتت النتائج أن للمثبط دور في منع عملية التآكل. كما لوحظ أن سرعة التآكل تتناقص مع زيادة تركيزات المثبط، وذلك بسبب تكوين طبقة ماصة واقية. يقوم المثبط الموجود على سطح السبيكة بصد الجزيئات المسببة للتآكل ويشكل جدارًا طاردًا، مما يقلل التيار وبالتالي معدل التآكل ويزيد من مقاومة الاستقطاب. ويزداد التآكل مع زيادة درجات الحرارة، لأن زيادة درجة الحرارة تؤدي إلى زيادة عدد الجزيئات التي لها طاقة حركية تساوي أو تزيد عن طاقة التنشيط. ولذلك فإن زيادة درجة الحرارة ستؤدي إلى زيادة سرعة تفاعل التآكل بسبب زيادة الطاقة الحركية لجزيئات البيئة المسببة للتآكل وانخفاض طاقة التنشيط اللازمة لحدوث التفاعل. ويمكن أن يعزى السبب في ذلك إلى ذوبان المانع الموجود على السبيكة مع ارتفاع درجة الحرارة مما يجعل السبيكة سهلة التعرض للتآكل مما يزيد من معدل التآكل وتراكم ذلك من معدل التميه الديناميكي مع ارتفاع درجة الحرارة عن النطاق المدروس.

الكلمات المفتاحية: مثبطات صديقة للبيئة، منتج، مستخلصات نباتية.