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Using of Extracted Tannin from the Bark of Gray Avicennia Marina (Avicennia Marina) and Cordia Myxa (Cordia Myxa) Trees as Corrosion Green Inhibitors for Carbon Steel Alloy in Acidic Media.

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Abstract

This study evaluated the corrosion inhibiting properties of natural tannins extracted from gray *Avicennia marina* bark and *Cordia myxa* bark for carbon steel alloys. Such alloys are widely used in shipbuilding construction where corrosion poses challenges. Tannin extracts were tested as green inhibitors across varying concentrations in 0.5 M hydrochloric acid solution, a corrosive medium. Trials were conducted at different temperature parameters to determine the inhibition efficiencies. The amount of hydrogen gas released over time was quantified to compare corrosion rates in the absence and presence of tannin inhibitors. The Langmuir and Freundlich isotherm models for adsorption were also studied, as well as the kinetic and thermodynamic functions, where the change in free energy and activation energy were calculated. The results of the study showed a promising possibility to use the compounds under study as corrosion inhibitors for carbon steel with high efficiency up to more than 83% at a temperature of 25 degrees Celsius. The results showed an increase in the free energy change (ΔG_{corro}) values for the corrosion reaction in the presence of the inhibitors under study compared to corrosion in the absence of inhibitors, The free energy change (ΔG_{corro}) values at 25 degrees Celsius were (184.4538, 184.9246, 111.9616) kJ.mol^{-1} in the presence of the *Avicennia marina* inhibitor, *Cordia myxa* inhibitor and blank) consecutively. As a result, the speed of the corrosion reaction will decrease in the presence of inhibitors.

Keywords: Corrosion, Tannins, Isotherm, Kinetic, Thermodynamic.

استخدام التانين المستخلص من لحاء أشجار المنجروف الرمادي وأشجار البمبر كمثبطات خضراء لتآكل سبائك الصلب الكربوني في الوسط الحمضي

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الخلاصة

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قامت هذه الدراسة بتقييم خصائص تثبيط التآكل للعفص الطبيعي المستخرج من لحاء المنغروف الرمادي (*Avicennia marina*)ولحاء البمبر (*Cordia myxa*) لسبائك الفولاذ الكربوني. وتستخدم هذه السبائك على نطاق واسع في بناء السفن حيث يشكل التآكل تحديات. تم اختبار مستخلصات التانين كمثبطات خضراء عبر تركيزات مختلفة في محلول حمض الهيدروكلوريك 0.5 م، وهو وسط مسبب للتآكل. أجريت التجارب عند بارامترات درجات حرارة مختلفة لتحديد كفاءة التثبيط. تم قياس كمية غاز الهيدروجين المنطلق مع مرور الوقت لمقارنة معدلات التآكل في غياب ووجود مثبطات التانين. كما تمت دراسة نموذجي لانجميور وفريندليتش للامتزاز، بالإضافة إلى الدوال الحركية والثرموديناميكية، حيث تم حساب التغير في الطاقة الحرة وطاقة التنشيط. وأظهرت نتائج الدراسة إمكانية واعدة لاستخدام المركبات قيد الدراسة كمثبطات تآكل للصلب الكربوني بكفاءة عالية تصل إلى أكثر من 83% عند درجة حرارة 25 درجة مئوية. أظهرت النتائج زيادة في قيم تغير الطاقة الحرة (ΔGcorro) لتفاعل التآكل في وجود المثبطات قيد الدراسة مقارنة بالتآكل في غياب المثبطات، إذ بلغت قيم تغير الطاقة الحرة (ΔGcorro) عند 25 درجة مئوية (184.4538، 184.9246، 111.9616 kJ.mol^{-1}) في وجود مثبط المانجروف ومثبط البمبر و بغياب المثبط على التوالي. ونتيجة لذلك، فإن سرعة تفاعل التآكل ستنخفض في وجود المثبطات.

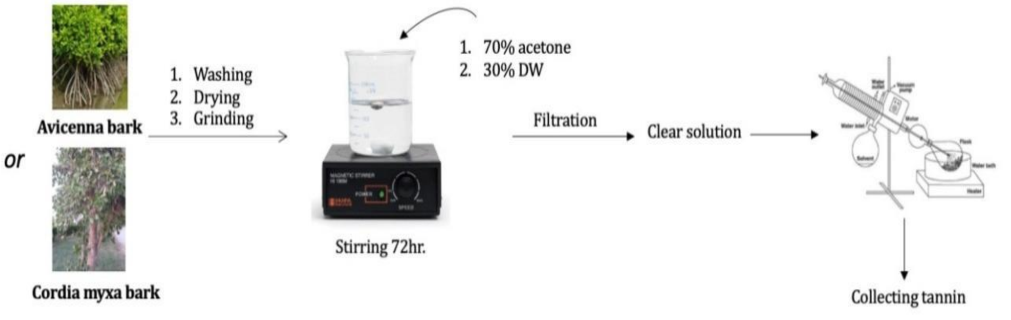
1. Introduction

Carbon steel is the most commonly contribute and highly applicable in engineering material [1,2]. Despite the unique properties of steel, it is susceptible to corrosion in hostile media. Carbon steel exposed to aqueous media and moist environments is susceptible to corrosion due to its poor thermodynamic stability. Therein the widespread steel corrosion problems have not prevented its widely use in the fields of shipbuilding and marine equipment, oil production, mining, construction [3]. Corrosion poses a considerable economic challenge across various industrial sectors that rely heavily on steel infrastructure, such as oil and gas production, offshore operations, and port facilities. On a global scale, corrosion mitigation accounts for a substantial portion of total maintenance costs within these domains. While fully preventing corrosion is realistically difficult to achieve, appropriate control strategies can meaningfully reduce associated safety, security and financial impacts to the lowest practicable levels. Left unchecked, corrosion undermines structural integrity and hastens replacement or repair needs. One of the most efficacious practical approaches for shielding steel assets from damaging corrosion in acidic and saline environments is the application of inhibitory compounds. By retarding corrosion kinetics, inhibitors provide a cost-effective means of extending metal service lifetimes [4-7]. Often the corrosion inhibitors are organic compounds which have hetero atoms such as nitrogen, oxygen, sulfur, and phosphorous Inhibitors can be chemically synthesized organic materials. or natural materials [7 and 8]. In recent years, there has been a growing interest from researchers in developing effective green erosion inhibitors of different minerals in different environments using natural products. Researches indicated the use of some natural environmentally friendly compounds that are extracted from some parts of the plants such as leaves, twigs and bark as effective anti-erosion in different minerals in different environments [9-14]. Where Tannins extracted from the bark of some plants (*Tamarix articulata*), *mimosa* and *quebracho* have been used as effective anticorrosives for copper and steel [14-16]. Tannins are polyphenols of plant origin that are usually extracted from tree bark such as caprachu, mimosa, chestnut and *Avicennia marina*. Tannins are non-toxic organic compounds in addition to being biodegradable substances that are divided into condensed and aqueous tannins [17]. The hydrolysis tannin is often extracted from fruits, while the condensed tannin is mostly found in wood bark. The main ingredients of tannins are sugars, gallic acid, allic acid, and flavonoids [16 and 18-20]. It has been reported that tannin extracted from the bark of *Rhizopora apiculata*, which is considered one of the varieties of *Avicennia marinas*, gave good results as an inhibitor of corrosion of steel [21]. The presence of hydroxyl groups in tannins is considered the ability to form chelating bonds with metal cations, which contributes effectively to preventing corrosion on metal surfaces [22]. *Avicennia marina* or grey mangrove is a species of *Avicennia marina* trees, classified in the plant family *Acanthaceae*. *Avicennia* is one of the approximately 100 types of *Avicennia marinas* found in the world [23]. *Avicennia marinas* are common in tidal flats close to river mouths. *Avicennia marinas* are found in most of the coasts of southeast, south and southwest Asia, the coasts of Emirates [24] Bahrain [25] Oman [26], southern Iran and also on both side of the Red Sea[27], Currently, there is an attempt to cultivate it in the Iraqi coast, south of Basrah Governorate, by the Marine Science Center - University of Basra [28]. Gray mangrove trees grow to a height of 3-10 meters and may reach 14 meters in the tropics. They are characterized by having aerial roots that reach a height of 20 cm, which has a major role in the plant's ability to withstand marine waters with high salt concentrations. Bemper or *Cordia myxa* is a species of flowering plant in the borage family, Boraginaceae. It is leaved deciduous tree. Common names include Assyrian plum, lasura, spistan and pember. It is growing in Asia, as well as, across the globe especially in tropical regions having the suitable environment. It is considered one of the local trees spread in southern Iraq. The bark of lasura is grayish brown in color with longitudinal and vertical prominent fissures. Assyrian plum lives 50 years, with a total height of 3-10 meters, Depending on the suitability of the environment. The tree begins to produce fruits at the age of about five years, and its fruits are edible, with a yellowish-brown color and a diameter of about a 2 centimeter [29]. This research aims to evaluate readily available, non-toxic and environmentally sustainable natural materials as potential green corrosion inhibitors for carbon steel. Specifically, extracts will be obtained from the abundant gray mangrove (*Avicennia marina*) and *Cordia myxa* (Barringtonia racemosa) plants that flourish along the coastlines of southern Iraq and the northern Arabian Gulf [30].

2. Experimental

2.1. Tannin extraction

Bark samples were collected separately from mature gray mangrove (*Avicennia marina*) and *Cordia myxa* (Barringtonia racemosa) trees growing along coastal regions. The bark tissues were thoroughly washed with distilled water to remove surface impurities and debris. Afterwards, the bark samples were allowed to air dry completely under ambient conditions. For tannin extraction, 100 grams of each dried bark powder was placed independently in pre-weighed conical flasks containing a polar extraction solvent. Based on reported efficacies, a 70:30 acetone-water mixture was used at room temperature for 72 hours with intermittent agitation. Then the mixture was filtered, the precipitate was removed, and the filtrate was transferred to the rotary evaporator to get rid of acetone and water and obtain solid tannin [15]. The percentage of tannin extraction was calculated by (dividing the weight of tannin extracted by the weight of the dry bark used) *100%. The percentage of extracted tannin was 20.3%, 16.7% for *Avicennia marina* and *Cordia myxa*, respectively.



Scheme of tannin extraction

2.2. Corrosive test media

Using analytical grade HCl acid (37%) and deionized water 0.5 M acidic solution was prepared and used as the corrosive medium for carbon steel alloy in the present of tannin (0,150,250,350) ppm at (25, 45 and 65°C) separately and respectively with 120 min. as corrosion time and 100 mL of acid media in 100 mL quick fit conical flask for all tests.

2.3. Preparation of high carbon steel specimens

The nominal composition (%) of high carbon steel (S355JOWP) for (C, Si, Mn, P, S, N, Cr, Cu) were (0.15, 0.8, 1.1, 0.05-0.16, 0.04. 0.01, 0.25-1.35, 0.2-0.6) respectively. Carbon steel plate with an average dimension of 4.7 cm length, 1 cm width and 0.8 cm thickness was prepared. The steel plate was polished by using silicon carbide abrasive papers of 120, 1000 and 2000 grits respectively to get a shiny and smooth surface. The steel plate washed with distilled water and acetone, dried and stored to be used later in weight loss experiments [31].

2.4. Weight-loss analysis- H_2 gas volume

Avicennia marina and *Cordia myxa* tannin extracts were evaluated as potential corrosion inhibitors by adding aliquots to produce concentrations of 0, 150, 250 and 350 ppm within the test solutions. Immersion periods were 120 minutes for each trial at controlled temperature. The hydrogen gas released from the corrosion process was collected using a glass device and hydrogen volume was calculated separately for each test as a function of the weight of the steel lost during the corrosion reaction [32 and 33].

3. Result and discussion

The lost weight of the steel alloy was calculated through the hydrogen gas released in each experiment [34], as well as the corrosion rate was determined by the presence or absence of inhibitors in varying concentrations and temperatures ,by following the following Faraday’s equations:

$$m = \frac{V_{H_2}}{V_{H_{2\,STc}}} \times E \qquad 1$$

$$m = V_{H_2} \times 0.0025 \qquad 2$$

$$CR(mpy) = \frac{KW}{Adt} = 3.5 \times 10^6 \times \frac{m}{Adt} \qquad 3$$

$$Effeciency\ of\ Inhibitor = \frac{CR_{(Uninhib)} - CR_{(Inhib)}}{CR_{(Uninhib)}} \times 100$$

$$CR(mpy) = \frac{0.13 \times I_{Corr} \times Eq.wt}{d} = 0.463 \times I_{Corr}$$

Where m is weight loss mass for iron, V_(H_(2 STc)) hydrogen’s volume at standard condition (1 atm, 25°C) =11200 mL, E is the equivalent weight of iron alloy =27.93 g.eq-^{1} [34]. The Corrosion data are shown in Tables (1-8). A=18.52Cm2, d=7.86 g.Cm^{3}

$$CR = 3.5 \times 10^6 \times \frac{m}{18.52 \times 7.86 \times 0.25hour} = 96175.52m$$

$$CR_{(Uninhib)} = \frac{(V_{H_2})_2 - (V_{H_2})_1}{t_2 - t_1} \qquad 4$$

$$CR_{(inhib)} = \frac{(V_{H_2})_2 - (V_{H_2})_1}{t_2 - t_1}$$

$$\theta = \frac{CR_{(Uninhib)} - CR_{(inhib)}}{CR_{(Uninhib)}} \qquad 5$$

$$effeciency = \frac{CR_{(Uninhib)} - CR_{(inhib)}}{CR_{(Uninhib)}} \times 100 \qquad 6$$

Table 1: Corrosion data for steel alloy (Blank) in the present of 0.5 M HCl at 25, 45, 65 °C

time min.	Vol. H_2 (mL) 25°C	w. loss (g) 25°C	Vol. H_2 (mL) 45°C	w. loss (g) 45°C	Vol. H_2 (mL) 65°C	w. loss (g) 65°C
15	0.06	0.00015	0.21	0.000525	0.66	0.00165
30	0.11	0.000275	0.37	0.000925	1.26	0.00315
45	0.17	0.000425	0.53	0.001325	1.88	0.0047
60	0.22	0.00055	0.69	0.001725	2.51	0.006275
75	0.27	0.000675	0.85	0.002125	3.14	0.00785
90	0.32	0.0008	1.01	0.002525	3.78	0.00945
105	0.37	0.000925	1.16	0.0029	4.42	0.01105
120	0.44	0.0011	1.29	0.003225	5.06	0.01265

Table 2: Corrosion data for steel alloy in the present of 0.5 M HCl and *Avicemmia marina* at 25°C

time min.	**Vol. H_2 mL (Avicennia marina 350ppm)**	**W.l (g) (Avicennia marina 350 ppm)**	**Θ**	**Vol. H_2 mL (Avicennia marina 250ppm)**	**W.l (g) (Avicennia marina 250 ppm)**	**Θ**	**Vol. H_2 mL (Avicennia marina 150ppm)**	**W.l (g) Avicennia marina 150 ppm)**	**Θ**
15	0.01	0.000025	0.8333	0.018	0.000045	0.7	0.03	0.000075	0.5
30	0.02	0.00005	0.8181	0.036	0.00009	0.6727	0.058	0.000145	0.4727
45	0.03	0.000075	0.8235	0.053	0.0001325	0.6882	0.086	0.000215	0.4941
60	0.04	0.0001	0.8181	0.07	0.000175	0.6818	0.115	0.0002875	0.4772
75	0.05	0.000125	0.8148	0.087	0.0002175	0.6777	0.142	0.000355	0.4740
90	0.06	0.00015	0.8125	0.103	0.0002575	0.6781	0.17	0.000425	0.4687
105	0.07	0.000175	0.8108	0.119	0.0002975	0.6783	0.198	0.000495	0.4648
120	0.078	0.000195	0.8227	0.135	0.0003375	0.6931	0.205	0.0005125	0.5341

Table 4: Corrosion data for steel alloy in the present of 0.5 M HCl and *Avicemmia marina* at 45°C

time min.	**Vol. H_2 mL (Avicennia marina 350ppm)**	**W.l (g) (Avicennia marina 350 ppm)**	**Θ**	**Vol. H_2 mL (Avicennia marina 250ppm)**	**W.l (g) (Avicennia marina 250 ppm)**	**Θ**	**Vol. H_2 mL (Avicennia marina 150ppm)**	**W.l (g) Avicennia marina 150 ppm)**	**Θ**
15	0.04	0.0001	0.8095	0.07	0.000175	0.6666	0.08	0.0002	0.6191
30	0.07	0.000175	0.8108	0.13	0.000325	0.6486	0.16	0.0004	0.5675
45	0.1	0.00025	0.8113	0.18	0.00045	0.6604	0.24	0.0006	0.5472
60	0.13	0.000325	0.8115	0.23	0.000575	0.6666	0.32	0.0008	0.5362
75	0.16	0.0004	0.8117	0.28	0.0007	0.6705	0.4	0.001	0.5294
90	0.19	0.000475	0.8118	0.33	0.000825	0.6732	0.47	0.001175	0.5346
105	0.21	0.000525	0.8189	0.38	0.00095	0.6724	0.53	0.001325	0.5431
120	0.245	0.000612	0.8101	0.43	0.001075	0.6666	0.63	0.001575	0.5116

Table 5: Corrosion data for steel alloy in the present of 0.5 M HCl and *Avicemmia marina* at 65°C

time min.	**Vol. H_2 mL (Avicennia marina 350ppm)**	**W.l (g) (Avicennia marina 350 ppm)**	**ϴ**	**Vol. H_2 mL (Avicennia marina 250ppm)**	**W.l (g) (Avicennia marina 250 ppm)**	**ϴ**	**Vol. H_2 mL (Avicennia marina 150ppm)**	**W.l (g) Avicennia marina 150 ppm)**	**ϴ**
15	0.37	0.000925	0.4394	0.48	0.0012	0.2727	0.6	0.0015	0.0909
30	0.7	0.00175	0.4444	0.93	0.002325	0.2619	1.15	0.002875	0.0873
45	1.02	0.00255	0.4574	1.39	0.003475	0.2606	1.68	0.0042	0.1063
60	1.33	0.003325	0.4701	1.86	0.00465	0.2589	2.19	0.005475	0.1274
75	1.64	0.0041	0.4777	2.32	0.0058	0.2611	2.7	0.00675	0.1401
90	1.95	0.004875	0.4841	2.78	0.00695	0.2645	3.2	0.008	0.1534
105	2.26	0.00565	0.4886	3.24	0.0081	0.2669	3.7	0.00925	0.1628
120	2.66	0.00665	0.4743	3.7	0.00925	0.2687	4.2	0.0105	0.1699

Table 6: Corrosion data for steel alloy in the present of 0.5 M HCl and *Cordia myxa* at 25°C

time min.	**Vol. H_2 mL (Cordia myxa 350ppm)**	**W.l (g) (Cordia myxa 350 ppm)**	**ϴ**	**Vol. H_2 mL (Cordia myxa 250ppm)**	**W.l (g) (Cordia myxa 250 ppm)**	**ϴ**	**Vol. H_2 mL (Cordia myxa 150ppm)**	**W.l (g) (Cordia myxa 150 ppm)**	**ϴ**
15	0.011	0.0000275	0.8166	0.019	0.0000475	0.6833	0.03	0.000075	0.5
30	0.022	0.000055	0.8	0.038	0.000095	0.6545	0.06	0.00015	0.4545
45	0.032	0.00008	0.8117	0.057	0.0001425	0.6647	0.09	0.000225	0.4705
60	0.043	0.0001075	0.8045	0.075	0.0001875	0.6590	0.12	0.0003	0.4545
75	0.054	0.000135	0.8	0.093	0.0002325	0.6555	0.15	0.000375	0.4444
90	0.064	0.00016	0.8	0.111	0.0002775	0.6531	0.18	0.00045	0.4375
105	0.074	0.000185	0.8	0.128	0.00032	0.6540	0.21	0.000525	0.4324
120	0.08	0.0002	0.8182	0.146	0.000365	0.6682	0.24	0.0006	0.4545

Table 7: Corrosion data for steel alloy in the present of 0.5 M HCl and *Cordia myxa* at 45°C

time min.	**Vol. H_2 mL (Cordia myxa 350ppm)**	**W.l (g) (Cordia myxa 350 ppm)**	**Ɵ**	**Vol. H_2 mL (Cordia myxa 250ppm)**	**W.l (g) (Cordia myxa 250 ppm)**	**Ɵ**	**Vol. H_2 mL (Cordia myxa 150ppm)**	**W.l (g) (Cordia myxa 150 ppm)**	**Ɵ**
15	0.05	0.000125	0.7619	0.08	0.0002	0.6190	0.18	0.00045	0.1428
30	0.08	0.0002	0.7837	0.16	0.0004	0.5675	0.31	0.000775	0.1621
45	0.11	0.000275	0.7924	0.23	0.000575	0.5660	0.42	0.00105	0.2075
60	0.14	0.00035	0.7971	0.29	0.000725	0.5797	0.54	0.00135	0.2173
75	0.17	0.000425	0.8	0.35	0.000875	0.5882	0.64	0.0016	0.2470
90	0.2	0.0005	0.8019	0.41	0.001025	0.5940	0.75	0.001875	0.2574
105	0.23	0.000575	0.8017	0.47	0.001175	0.5948	0.85	0.002125	0.2672
120	0.26	0.00065	0.7984	0.52	0.0013	0.5968	0.95	0.002375	0.2635

Table 8: Corrosion data for steel alloy in the present of 0.5 M HCl and *Cordia myxa* at 65°C

time min.	**Vol. H_2 mL (Cordia myxa 350ppm)**	**W.l (g) (Cordia myxa 350 ppm)**	**Ɵ**	**Vol. H_2 mL (Cordia myxa 250ppm)**	**W.l (g) (Cordia myxa 250 ppm)**	**Ɵ**	**Vol. H_2 mL (Cordia myxa 150ppm)**	**W.l (g) (Cordia myxa 150 ppm)**	**Ɵ**
15	0.38	0.00095	0.4242	0.51	0.001275	0.2272	0.65	0.001625	0.0151
30	0.73	0.001825	0.4206	1.01	0.002525	0.1984	1.25	0.003125	0.0079
45	1.08	0.0027	0.4255	1.51	0.003775	0.1968	1.81	0.004525	0.0372
60	1.41	0.003525	0.4382	2.02	0.00505	0.1952	2.36	0.0059	0.0597
75	1.75	0.004375	0.4426	2.51	0.006275	0.2006	2.91	0.007275	0.0732
90	2.09	0.005225	0.4471	3.02	0.00755	0.2010	3.44	0.0086	0.0899
105	2.43	0.006075	0.4502	3.52	0.0088	0.2036	3.97	0.009925	0.1018
120	2.76	0.0069	0.4545	4.01	0.010025	0.2075	4.5	0.01125	0.1106

3.1. Corrosion rate

Quantitative analysis of corrosion rates calculated from hydrogen gas volume measurements revealed a significant inhibitory effect for both tannins. At 25°C and 350 ppm concentration, rates decreased approximately fivefold compared to uninhibited steel. The natural extracts therefore markedly slowed the corrosion kinetics in a concentration-dependent manner (Figures 1 and 2).

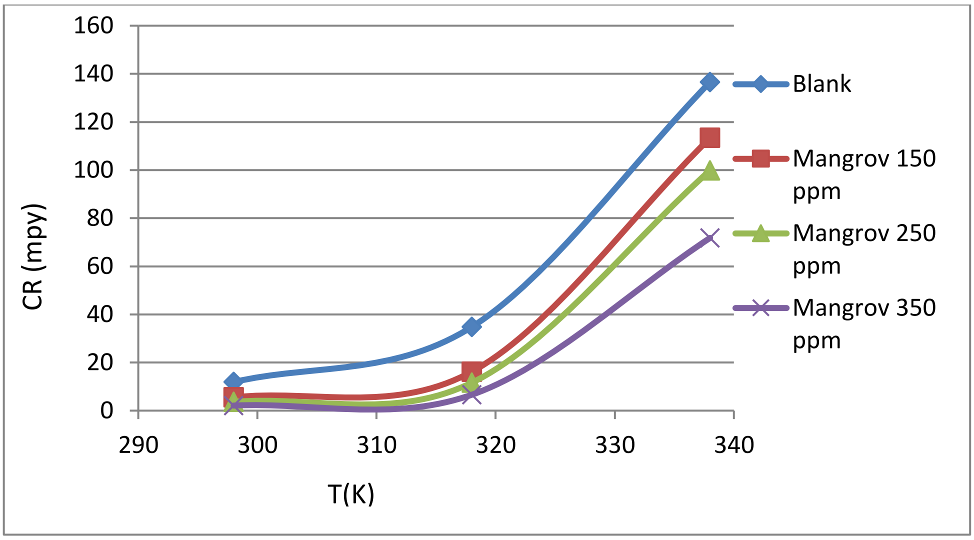


Figure 1: plot of corrosion rate (minch/Year) of alloy versus concentration of *Avicemmia marina*s tanine inhibiters in the present of 0.5 M HCl at 25 °C.

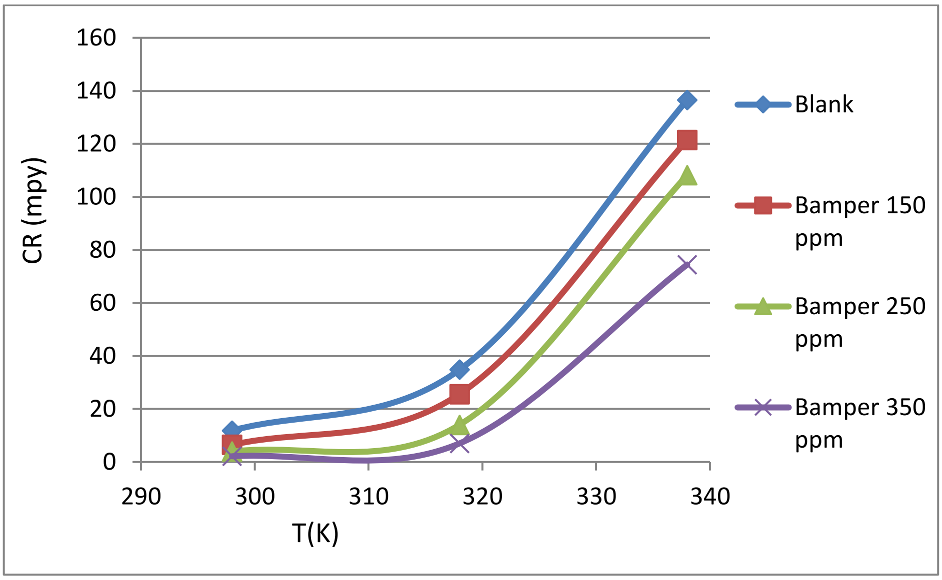


Figure 2: plot of corrosion rate (minch/Year) of alloy versus concentration of *Cordia myxa*s tannin inhibiters in the present of 0.5 M HCl at 25 °C.

3.2. Adsorption isotherm

The adsorption behavior of the *Avicennia marina* and *Cordia myxa* tannin inhibitors on the carbon steel surface was analyzed based on the Langmuir and Freundlich isotherm models at test temperatures of 25°C, 45°C, and 65°C. In all cases, the experimental data correlated preferentially with the Freundlich model, suggesting that multilayer inhibition occurred through physisorption. Freundlich isotherm is an ideal isotherm for physical adsorption where there is no interaction between the adsorbent and the adsorber. The general form of the Langmuir equation is shown below

$$\frac{\theta}{1-\theta} = KC \qquad 7$$

Where θ is the value of surface coverage on the carbon steel alloy, C is the inhibiter concentration in the HCl solution, k is the equilibrium constant of the adsorption process. The plots of $\frac{\theta}{1-\theta}$ versus the inhibiter concentration were linear and have a slope value equal to k. Where (K) is adsorption equilibrium constant, as shown in Figures (3-5).

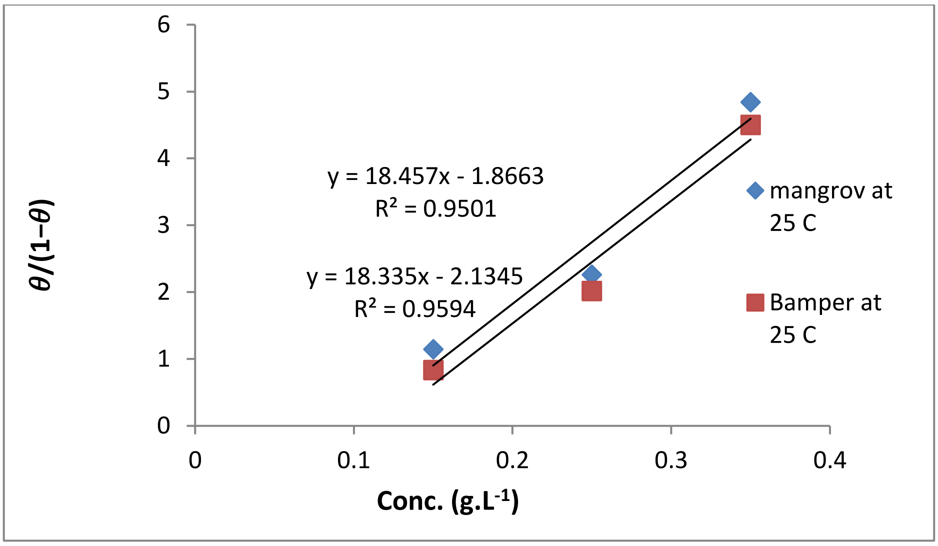


Figure 3: Langmuir adsorption isotherms for corrosion inhibiters at 25 °C onto steel alloy in the present of 0.5 M HCl.

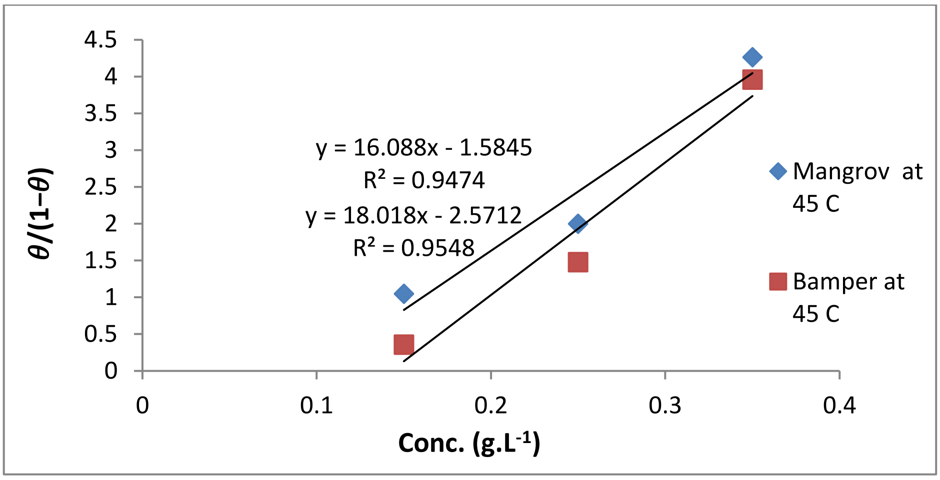


Figure 4: Langmuir adsorption isotherms for corrosion inhibiters at 45 °C onto steel alloy in the present of 0.5 M HCl.

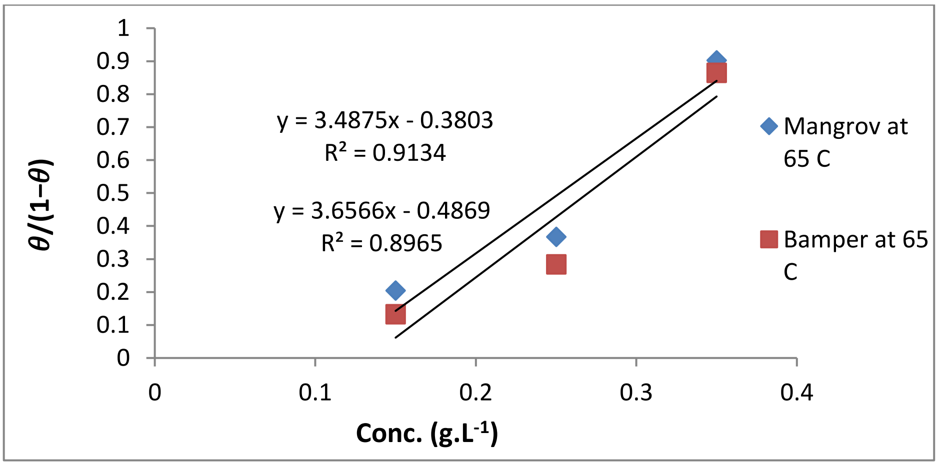


Figure 5: Langmuir adsorption isotherms for corrosion inhibiters at 65 °C onto steel alloy in the present of 0.5 M HCl.

Were as the general form of the Freundlich equation is shown below:

$$\log\theta = \log K + \frac{1}{n}\log C \qquad 8$$

The plots of log θ versus the log C (inhibiter concentration) were linear as shown in Figures (6- 8)

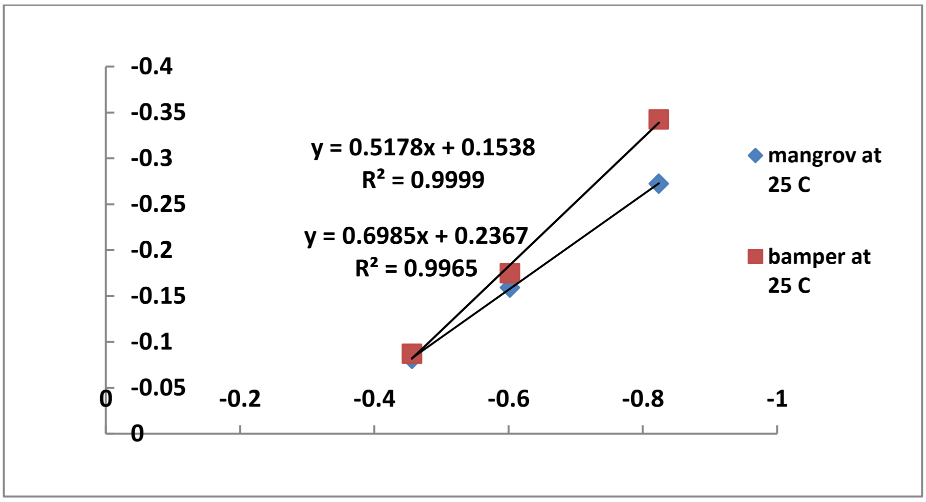


Figure 6: Freundlich adsorption isotherms for corrosion inhibiters onto steel alloy in the present of 0.5 M HCl at 25 °C.

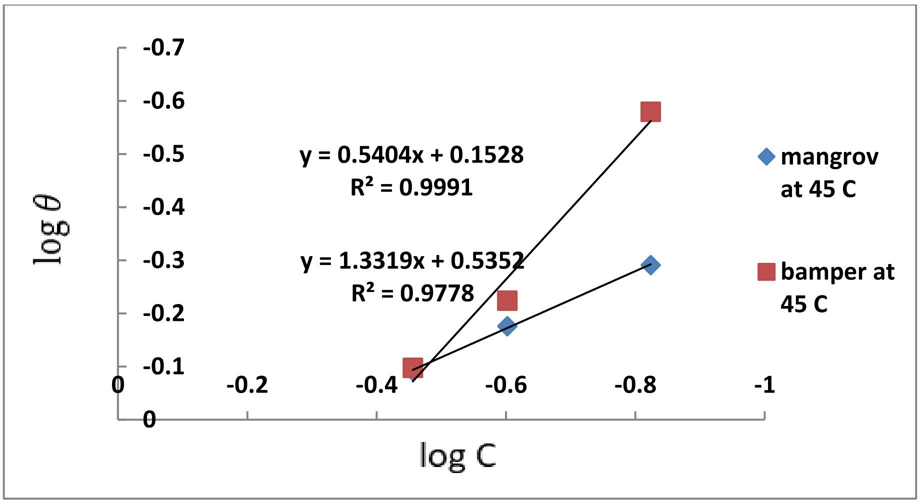


Figure 7: Freundlich adsorption isotherms for corrosion inhibiters onto steel alloy in the present of 0.5 M HCl at 45 °C.

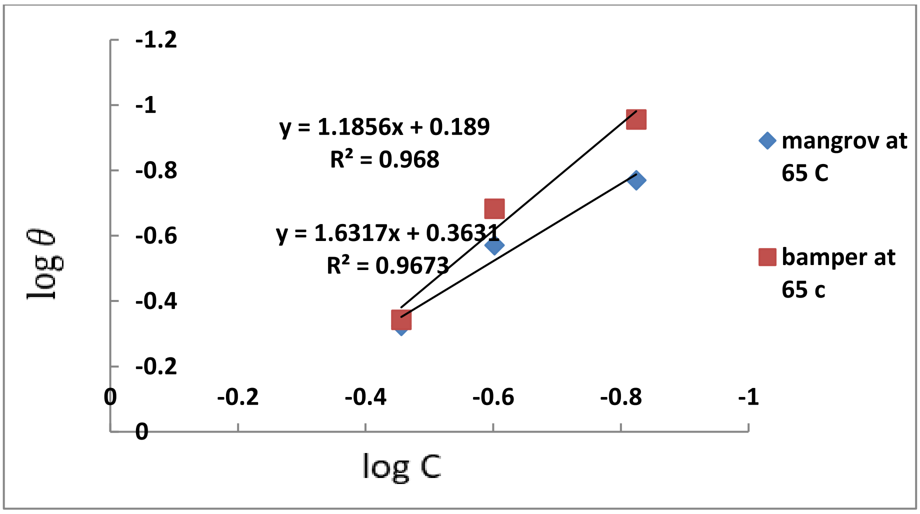


Figure 8: Freundlich adsorption isotherms for corrosion inhibiters onto steel alloy in the present of 0.5 M HCl at 65 °C.

The results of the isothermal study of the tannins under study as corrosion inhibitors showed that the Freundlige model is the most suitable for all the studied temperatures [14] and [16].

3.3. Thermodynamics of the corrosion process:

The standard free energy can be determined from the intercept of more suitable equation (Langmuir or Freundlich) by using the results for the adsorption process and using the following equation:

$$\Delta G^{\circ}_{ads} = -2.303RT\log 55.5K_{ads} \quad 9$$

ΔG°_{ads} were calculated from Freundlich equation at three different temperatures by using the calculated values of $K_{ads.}$ for each compound. These parameters are given in Tables (9 and 10)

Table 9: calculated parameters from Freundlich adsorption isotherms

		***Avicennia marina* at 25 °C**		***Cordia myxa* at 25°C**	
C (g.L^{-1})	**LOG C**	**Ɵ**	**LOG Ɵ**	**Ɵ**	**LOG Ɵ**
0.15	**-0.8239**	0.5341	-0.2723	0.4546	-0.3423
0.25	**-0.6020**	0.6932	-0.1591	0.6682	-0.1750
0.35	**-0.4559**	0.8287	-0.081	0.8182	-0.0871
		***Avicennia marina* at 45 °C**		***Cordia myxa* at 45 °C**	
C (g.L^{-1})	**LOG C**	**Ɵ**	**LOG Ɵ**	**Ɵ**	**LOG Ɵ**
0.15	**-0.8239**	0.511628	-0.2910	0.263566	-0.5791
0.25	**-0.6020**	0.666667	-0.1760	0.596899	-0.2241
0.35	**-0.4559**	0.810078	-0.0914	0.79845	-0.0977
		***Avicennia marina* at 65 °C**		***Cordia myxa* at 65 °C**	
C (g.L^{-1})	**LOG C**	**Ɵ**	**LOG Ɵ**	**Ɵ**	**LOG Ɵ**
0.15	**-0.8239**	0.16996	-0.7696	0.110672	-0.9559
0.25	**-0.6020**	0.268775	-0.5706	0.20751	-0.6829
0.35	**-0.4559**	0.474308	-0.3239	0.454545	-0.3424

Table 10: calculated parameters from Freundlich adsorption isotherms.

		298 K		**318 K**		**338 K**	
	C(g.L^{-1})	K_{ads}	ΔG°_{ads} (kJ.mol^{-1})	K_{ads}	ΔG°_{ads} (kJ.mol^{-1})	K_{ads}	ΔG°_{ads} (kJ.mol^{-1})
Avicennia marina	0.15	1.426403	-10812.56	1.426246	-11537.94	1.611291	-12605.83
	0.25	1.421036	-10803.24	1.410139	-11507.97	1.3905631	-12192.53
	0.35	1.427180	-10813.91	1.428605	-11542.31	1.6466968	-12666.81
Cordia myxa	0.15	1.710526	-11261.84	3.29801	-13750.49	2.4457350	-13776.55
	0.25	1.759727	-11331.98	3.782550	-14112.29	1.9925997	-13201.71
	0.35	1.703444	-11251.58	3.232237	-13697.31	2.5207019	-13861.25

The negative values of the change in free energy (ΔGads) indicate a spontaneous process of adsorption of tannins on the surface of carbon steel in the acidic media under study. The free energy change values indicate that the adsorption of tannins on the surface of carbon steel is physical adsorption whereas in chemical adsorption the values of the change in free energy (ΔG_{ads}) must be around–40 kJ.mol^{-1}[35]. Arrhenius- type relationship between the corrosion rate (CR) of carbon steel in acidic media and temperature (T) as often expressed by Arrhenius equation used to determine the activation energies (Ea).

$$\ln CR = \ln A - \frac{E_a}{RT} \tag{10}$$

Where A is Arrhenius constant, Ea is activation energy, R is the gas constant T is absolute temperature and CR is corrosion rate [36].

Figure (9) gives the plots of ln CR versus 1/T for the carbon steel corrosion in the present and absence of inhibiters at different temperatures. The values of *Ea* were calculated from the slopes. These parameters are given in Table (11).

Table 11: calculated parameter from Arrhenius Graphic.

1/T (K^{-1})	**CR-Blank**	**CR-*Avicennia marina***	**CR -*Cordia myxa***
0.003355705	11.87565954	2.105230554	2.159210825
0.003144654	34.81727455	6.612583151	7.017435181
0.00295858	136.5700847	71.79375992	74.49277345
1/T (K^{-1})	**lnCR-Blank**	**lnCR-*Avicennia marina***	**lnCR -*Cordia myxa***
0.003355705	2.474490888	0.744424988	0.769742796
0.003144654	3.550113659	1.888974372	1.948397792
0.00295858	4.916837924	4.273797563	4.31070212
Ea(kJ.mol^{-1})	738.1445783	1061.46988	1065.337349

The inhibitors have Ea values higher than blank. Therefore, the corrosion process is difficult for the steel alloy in the presence of inhibitors due to the high value of activation energy. The presence of inhibitors leads to an increase in the activation energy necessary for the corrosion reaction to occur on the steel surface, and leads to a decrease in the corrosion rate and an increase in the life of the alloy in acidic environments. While in the absence of inhibitors, the decrease in activation energy required for corrosion to occur leads to an increase in the corrosion rate.

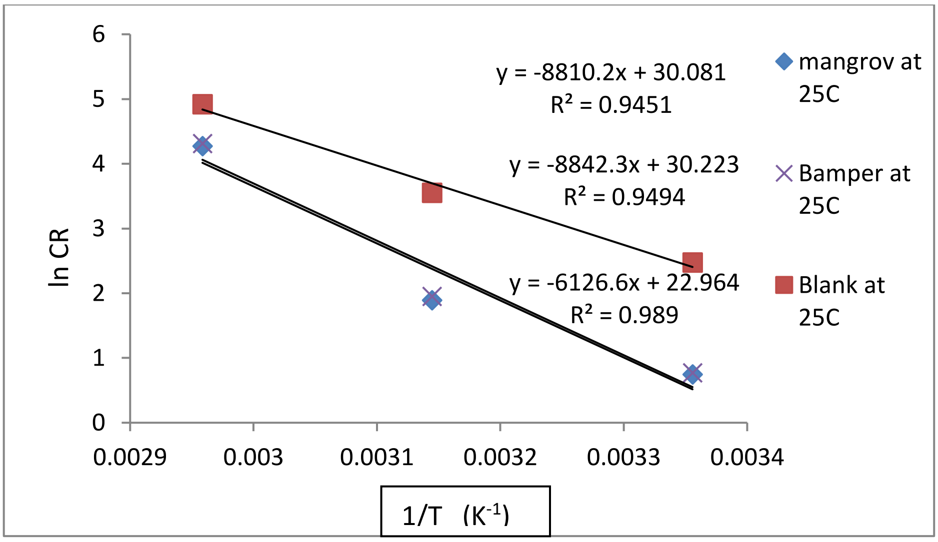


Figure 9: Arrhenius Graphic for corrosion inhibiters in the present of 0.5 M HCl onto alloy in different temperatures.

whereas $\Delta G_{corrosion}$ were calculated from the fallowing equation [35]:

$$\Delta G = \Delta H - T\Delta S \tag{11}$$

Enthalpy change ΔH_{ads} and entropy change ΔS were calculated from the Eyring transition state equation:

$$\ln CR / T = \Delta S/R - \Delta H/RT \tag{12}$$

Figure 10 gives the plots of $\ln \frac{CR}{T}$ versus $\frac{1}{T}$. The values of ΔH and ΔS were calculated from the slopes and intercept respectively. These parameters are given in Table 12.

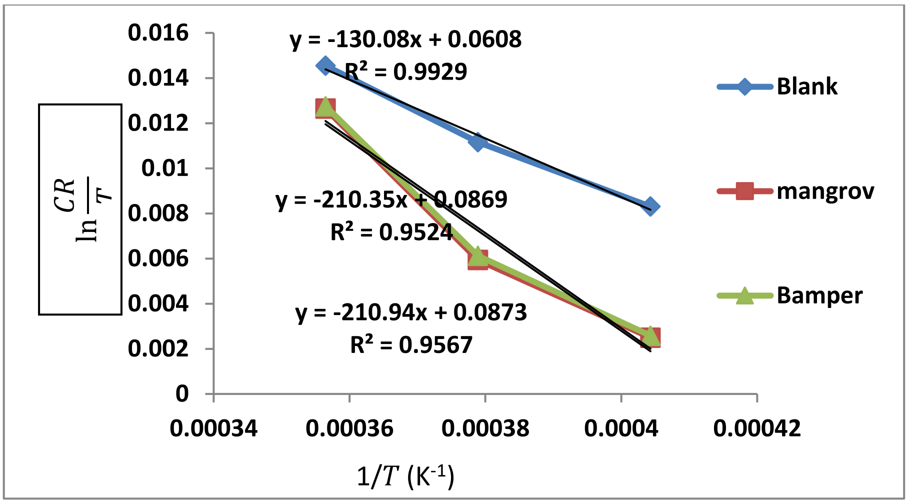


Figure 10: Eyring Graphic for alloy corrosion in the present of inhibiters and 0.5 M HCl in different temperatures.

Table 12: calculated parameter from Eyring Graphic

	ΔH(kJ. mol^{-1})	ΔS(J.K^{-1}. mol^{-1})	ΔG(kJ.mol^{-1}) at 298 K	ΔG(kJ.mol^{-1}) at 318 K	ΔG(kJ.mol^{-1}) at 338 K
Blank	130.08	0.0608	111.9616	110.7456	109.5296
Avicennia marina	210.35	0.0869	184.4538	182.7158	180.9778
Cordia myxa	210.94	0.0873	184.9246	183.1786	181.4326

The increase in the free energy change (ΔGcorro) values for the corrosion reaction of carbon steel alloys in acidic media in the presence of inhibitors indicates a decrease in the corrosion rate of carbon steel alloys. Thermodynamic parameters were also calculated from corrosion rates to gain insight into the inhibition mechanism. It was observed that decreasing ΔGcorr values in absence of inhibitors caused a corresponding increase in corrosion, implying greater spontaneity of the corrosion reaction. The results also indicate that (ΔG_{corro}) decrease with increasing temperature, even with the presence of inhibitors, thus increasing the corrosion rate, which attributed to increasing of kinetic energy and break the correlations between the inhibitors molecules and steel alloy. The positive values of ΔH indicated that the corrosion reactions of steel alloy in acidic media were endothermic reactions, therefore, the corrosion process increased with temperature increasing [14] and [16].

Conclusions

The findings of this study demonstrate the viability of *Avicennia marina* and *Cordia myxa* tannin extracts as green corrosion inhibitors for carbon steel in acidic media. Compared to trials lacking inhibitors, several thermodynamic trends were observed in the presence of the natural extracts. Specifically, addition of the tannin inhibitors led to an elevation in the activation energy (Ea) required to initiate the corrosion process. This suggests the extracts increase the energy barrier that must be surmounted for corrosion to proceed. Likewise, more positive ΔGcorr values were recorded in inhibited trials versus the uninhibited system. The larger ΔGcorr implies greater free energy is necessary for the corrosion reaction to occur spontaneously when tannins are adsorbed on the steel surface. Both the increased Ea and ΔGcorr are indicative of inhibitor chemisorption and impeded corrosion kinetics. By increasing the energy and Gibbs free energy hurdles, the naturally-derived *Avicennia marina* and *Cordia myxa* tannins successfully retard the acid-catalyzed corrosion of carbon steel under the test conditions evaluated. As a result, the tannins under study achieved an inhibition efficiency of the corrosion reaction of up to 83% at a temperature of 25°C, which indicates a good possibility of using the two substances extracted from natural plants as green corrosion inhibitors to reduce corrosion in carbon steel.

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