STM JOURNALS

Journal of
Thin Films, Coating Science Technology and Application

ISSN: 2455-3344
Volume 13, Issue 1, 2026
January–April
DOI (Journal): 10.37591/JoTCSTA

https://journals.stmjournals.com/jotcsta

Review JoTCSTA

Monitoring the Effectiveness of Water-Based Plants for the Inhibition of Metal

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Abstract

The temperature performance profile of the plant extracts showed that the inhibition efficiency increased with increasing system temperature up to approximately 323 K at an immersion time of 9.0 hours, after which it declined, indicating reduced inhibition efficiency at higher temperatures and longer immersion times. The corrosion rate parameters also changed with increasing temperature and immersion time. Plots of the corrosion rate against the volume of the test inhibitor in the corrosive medium showed that, at all tested volumes of the inhibitors—Pneumatopteris pennigera (gully fern, GF) and Selaginella myosurus (SM) water-based extracts—the corrosion rate decreased markedly. This decrease indicates that the acidic medium increasingly struggled to penetrate the protective film formed by the active phytochemical constituents of the extracts on the metal surface. The GC–MS and FTIR analyses confirmed that the SM and GF plant extracts contained compounds capable of inhibiting the corrosion of medium-carbon steel. Scanning electron microscopy (SEM) micrographs further showed that carbon steel samples exposed to SM or GF water-based extracts exhibited fewer pits and cracks than those exposed to 1.0 M HCl alone, particularly at higher extract concentrations. These observations indicate a substantial reduction in the corrosion rate, attributable to the adsorption of phytochemical constituents with a strong affinity for the medium-carbon steel (MCS) surface in the corrosive medium. The weight loss (g) of MCS samples was monitored as a function of immersion time (T, h) in the presence of varying volumes of SM extract, GF extract, and 1.0 M HCl at room temperature. In addition, the effect of temperature (T, K) on weight loss was evaluated for MCS samples immersed in varying volumes of SM extract, GF extract, and 1.0 M HCl at room temperature at constant immersion times of 3, 6, and 9 hours.

Keywords: Acidic medium, inhibition, metal, monitoring, plants, water-based, weight loss

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Received Date: February 25, 2026
Accepted Date: February 26, 2026
Published Date: March 25, 2026

Citation: Ukpaka Chukwuemeka Peter Chioma Onwubiko Hosanna, Okwu Kingsley. Monitoring the Effectiveness of Water-Based Plants for the Inhibition of Metal Weight Loss in Acidic Medium. Journal of Thin Films, Coating Science Technology and Application. 2026; 13(1): 37–46p.

INTRODUCTION

The effectiveness of *Acacia cyanophylla* leaf extract as an environmentally friendly inhibitor for mild steel in an aerated aqueous 1.0 M H_2SO_4 solution was analyzed using potentiodynamic polarization (PP) and electrochemical impedance spectroscopy (EIS and Tafel) measurements. The addition of the inhibitor reduced the corrosion current, while the corrosion potential values showed slight shifts in the positive direction. The inhibition efficiency was found to be approximately 93% (the maximum value was derived from the polarization curve), which was consistent with both electrochemical techniques (EIS and Tafel) [1–4]. Additionally, polarization curves were obtained at various temperatures to detect changes in the

corrosion rate. The adsorption of extract from *Acacia cyanophylla* leaves on mild steel surfaces in 1.0 M H_2SO_4 solution obeyed the Langmuir adsorption isotherm [5–7]. In H_2SO_4 solutions with and without *Acacia cyanophylla* extract, the corrosion current increased and the inhibition efficiency decreased as the temperature increased. The exposure duration also affects the corrosion characteristics [8].

There have been reports of investigations on the use of expired atorvastatin [9]. Atorvastatin belongs to the class of medications called statins, which are primarily used to decrease cholesterol levels and prevent cardiovascular diseases [10].

Using weight loss, electrochemical impedance spectroscopy, and potentiodynamic polarization (Tafel) techniques, atorvastatin, marketed under the brand name Lipitor, was used to suppress mild steel corrosion in 1.0 M HCl solution [11, 12]. To determine whether there is a substantial variation in the inhibitory efficiency of the two after the drug's expiration date, fresh atorvastatin was also employed for comparison in the aforementioned trials [13]. The adsorbed inhibitor molecules on the metal surface enhance the polarization resistance, according to an investigation using electrochemical impedance spectroscopy. [12]. Fresh and expired atorvastatin both function as mixed-type inhibitors; however, they mostly operate as cathodic inhibitors, according to potentiodynamic polarization [13].

The Langmuir adsorption isotherm governs the adsorption of both new and expired atorvastatin on mild steel surfaces at all temperatures. When mild steel is exposed to both fresh and expired atorvastatin in an acidic solution, scanning electron microscopy (SEM) reveals a smooth surface [14]. The viability of the expired atorvastatin medication as a unique and effective corrosion inhibitor for mild steel was confirmed by the nearly identical results that the fresh medication and its expired counterpart displayed in every study [15].

Using gravimetric and electrochemical analysis methods at 25 and 60°C, the adsorption and corrosion inhibition behavior of strawberry fruit extract on steel in 1.0 M HCl and 0.5 M H_2SO_4 was reported. The results showed that the extract inhibited the acid-induced corrosion of mild steel, which was more pronounced in HCl than in H_2SO_4. The effectiveness of the extract's inhibition increased with increasing extract concentration but decreased with increasing temperature [16]. The extract acted as a mixed-type inhibitor, as demonstrated by the potentiodynamic polarization curves. The Langmuir adsorption isotherm model was used to simulate the adsorption of the extract constituents on the mild steel surface, which was thought to represent the inhibition mechanism.

MATERIALS AND METHODS

Experimental Setup for the Determination of Corrosion Rate Inhibition

Chemical thermodynamics does not predict the rate of corrosion but rather offers an understanding of the associated energy forms and changes in corrosion and corrosion inhibition reactions. The kinetics of the reaction determine the rate at which corrosion reactions proceed. The carbon steel samples were tied using a rubber thread (conventionally used by hairstylists) through a hole drilled in them to help suspend the metal specimen completely and wholly as it is incubated in each 1.0 molar concentration hydrochloric acid-containing medium (the corrodent solution) for a regulated time of 5 days at 24.00 h daily interval withdrawal to determine weight loss of the metal samples. This was done for each carbon steel sample in the 1.0 molar concentration hydrochloric acid-containing medium, 250 ml corrodent solution of varying complementary volumes.

A known varying volume of the 1.0 M HCl acid was added into each glass container to which a known varying complementary volume of the *Selaginella myosurus* (SM) or *Pneumatopteris pennigera* (gully fern, GF) plant extract was added to make up 250 ml in each case differently to examine the inhibitive effect that could be established using plants extracts on 1.0 M HCl acid concentrations in a corrosive environment.

Figure 1. Weight losses and corrosion rate experimental setup at room temperature.

This was also repeated when the volume of the plant extract was varied to determine the effect of a change in volume of *Selaginella myosurus* or *Pneumatopteris pennigera* (gully fern) extract on corrosion inhibition on mild carbon steel (MCS) metal samples, with different volume-mass compositions of 1.0 M HCl. The experimental corrosive medium (corrodent mixture) containing a dilute concentration of hydrochloric acid and varying volumes of the test inhibitor were labelled A–O, as shown in Figure 1.

Ten carbon steel samples were completely steeped in 250 ml of each of the experimental media (corrodent medium), with the aid of a black rubber thread suspending the carbon steel samples upright. At the end of 24 hours, two carbon steel samples from each experimental medium were withdrawn, washed, and cleaned with a soft bristle brush in running water, cleaned with a dried rag, washed in ethanol for degreasing, cleaned with a dried rag, dipped into acetone, removed, and allowed to dry. In a short while, the acetone dried up, leaving a thin film on the metal sample surface, preventing the samples from interacting with the surroundings during weighing and reweighing. The carbon steel specimens were reweighed to estimate the changes in the weight of the metal specimen due to its incubation in the corrosive mixture, and the average weight loss was recorded. This was done every 24.00 hours for 5 days, and the average weight loss was noted in each case. This was carried out for the entire experimental medium labelled A–O, including the control experiment.

A control experiment (blank) was also set up as a reference standard to measure, estimate, and compare the inhibitive effect of the *Selaginella myosurus* (SM) and *Pneumatopteris pennigera* (gully fern) plant extracts on the corrosion of carbon steel samples in 1.0 molar hydrochloric acid concentrations.

Finally, the 9.00 hours used carbon steel metal samples for 20%, 80%, and 100% (Blank C) 1.0 M HCl were subjected to SEM, which enabled us to visibly perceive patterns established on the carbon steel metal samples as a result of varying the volume of the test inhibitor used in investigative experimentations using 1.0 molar dilute hydrochloric acid corrosive medium. The experiments were also performed at varying volumes/mass concentrations of the test inhibitors relative to the complementary volumes of 1.0 molar concentration HCl and at varying temperatures. This enabled us

to establish the corrosion rate and relevant thermodynamic parameters. Hence, the adsorption isotherm model was used to establish the contribution of the volume of the test inhibitor in the medium.

Formulated Inhibitor Performance Evaluation

In experimenting on the effectiveness of water-based plants in the inhibition of MCS samples in hydrochloric acid corrodent medium, it was found and can also be seen very clearly that a chemical reaction, oxidation-reduction reaction, took place as well as a physical process of adsorption of the test inhibitors active phytochemical molecular component of great affinity for the metal samples adsorbed on the metal surfaces in the corrodent mixture as shown below through electrochemical weight loss experiment, SEM and FT-IR analyses results.

Weight Loss Measurement at Different Temperatures and Immersion Times

Corrosion reactions involve electron transfer and hence are regarded as electrochemical processes. Weight loss measurements were accomplished in the process of complete immersion and suspension of the carbon steel metal specimen in stationary oxygenated surroundings with the aid of transparent glass bottles that are capable of accommodating over 250 ml of the experimental corrosive mixture (corrodent medium), first at room temperature and later at 30°–60°C, sustained each time at constant temperature in a thermostatic water bath. The pre-weighed carbon steel metal samples were hung with the aid of a rubber thread in a glass vessel containing 1.0 M hydrochloric acid and varying volumes of *Selaginella myosurus* or *Pneumatopteris pennigera* (gully fern) plant extract for 3.00, 6.00, and 9.00 h in a thermostatic water bath. Other concentrations of the test inhibitors were also tested. After 3 hours, at a particular temperature, the suspended and incubated carbon steel samples contained in the aggregated corrosive medium were withdrawn, thoroughly washed in running tap water with a soft plastic bristle brush, dried with a hand towel, degreased in ethanol, and finally dipped into acetone, withdrawn, and allowed to dry in a stream of warm air. The samples were then reweighed using an analytical balance to determine the average weight loss of the metal specimens. This temperature-dependent experiment was carried out at 3.00, 6.00, and 9.00 h at 303, 313, 323, and 333 K. The investigation was performed using nine carbon steel metal samples suspended and incubated in each glass bottle of the experimental setup. This ensured triplicates to randomize possible errors, and only the mean value of the weight losses was recorded and presented in Tables A and B in the Appendices. Furthermore, the weight loss data were employed to determine the rate of corrosion, inhibition efficiency, and thermodynamic parameters, applying where necessary appropriate equations. Weight loss was evaluated using Equation (1).

$$W = W_0 - W_{De} \quad (1)$$

W_0 = Original weight of the MCS samples
W_{De} = Depleted weight of MCS metal samples

RESULTS AND DISCUSSION

Formulated Test Inhibitor Performance

Weight Loss

According to the corrosion rate equation, the corrosion rate of a corrodible material is directly proportional to the weight loss in a corrosive environment. From the graphs plotted, weight loss (mg) versus temperature (K) and weight loss (mg) versus time (h) for Carbon Steel Corrosion in 1.0 M HCl, it can be deduced that the above proposition for the control experiment was completely true; however, for the corrosive medium where GF and SM plant extracts occupied small to higher percentages, an effect which censored this "directly proportional" relationship into something less. This proves the inhibitory effects of the mere presence of GF and SM plant water-based extracts by the formation of a thin film that blocks the active sites where corrosion occurs on the surfaces of the carbon steel samples. This fact is presented in Figures 2 to 5. From the plots, it can be deduced that samples with some volumes of the test inhibitor followed a similar pattern as the control experiment (blank), an increment in the weight loss as the experiment proceeds in hours, although the values were not as large as those of the Blank C samples' weight loss values (Figures 2 and 3). In the temperature experiment (Figures

4–5), the corrodent mixture containing some volumes of the test inhibitor followed paths almost parallel to the temperature axis (little deviation from samples like corrodent Sample B9 in Figures 2 and 5), implying a more significant reduction in the weight loss of the MCS metal samples as the temperature of the corrodent medium was raised slightly above room temperature. This proves that although there was an effect undulating pattern or inflexion points created by the presence of the test inhibitor in the corrodent mixture but the corrosive acid in the medium could still overcome the thin film protection of the test inhibitor on the metal surfaces which in many cases interacts with the metals atoms to attack the metal samples but in a very minimal mannered way when compared with the effect posed by Blank C sample.

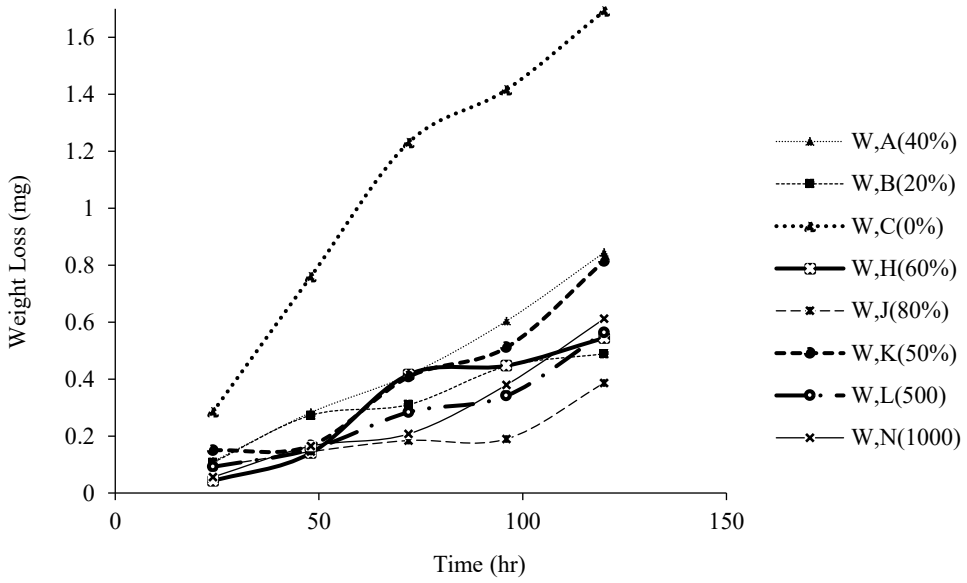

Figure 2. Weight loss (mg) versus time (hour) for MCS metal samples corrosion rate inhibition in complementary presence of varying volumes of GF plant extract and 1.0 molar concentration HCl corrosive solution at room temperature and different immersion times.

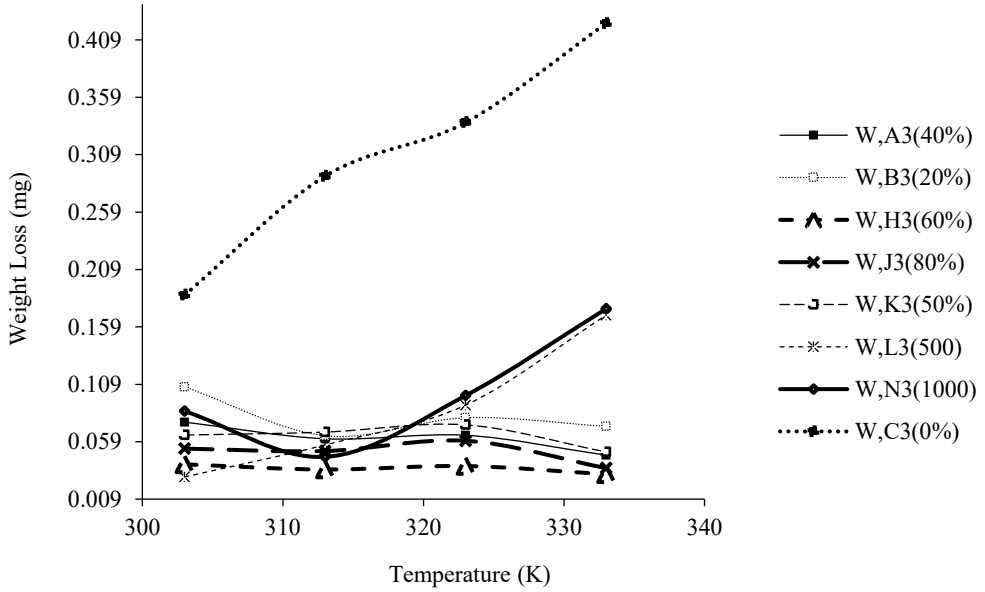

Figure 3. Weight loss (mg) against temperature (K) for MCS metal samples corrosion rate inhibition in the complementary presence of varying volumes of GF plant extract and 1.0 molar concentration HCl corrosive solution at constant retention/immersion time 3.00 hours.

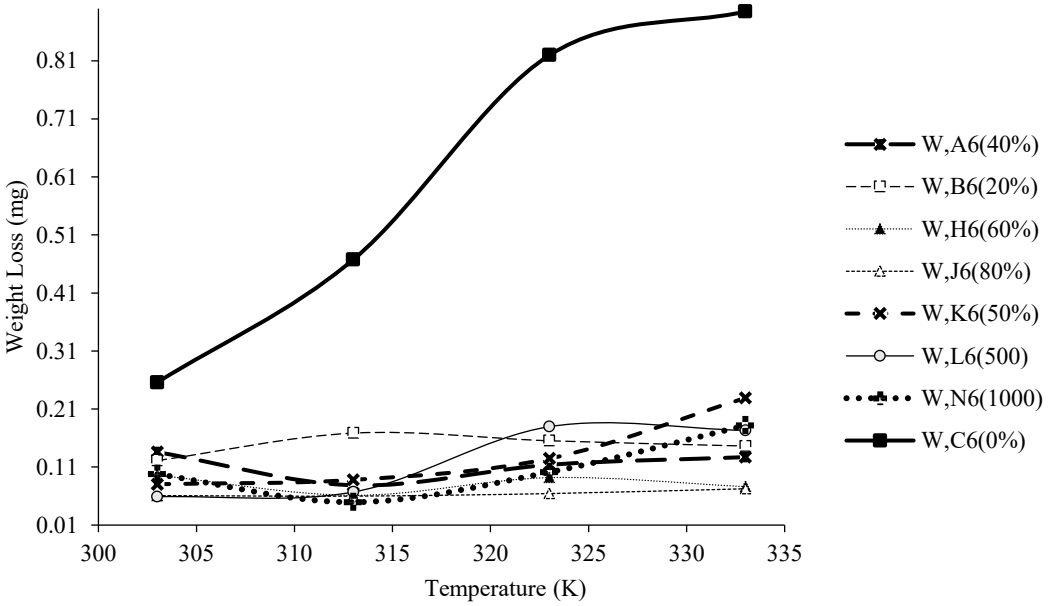

Figure 4. Weight loss (mg) against temperature (K) for MCS metal samples corrosion rate inhibition in the complementary presence of varying volumes of GF plant extract and 1.0 molar concentration HCl corrosive solution at a constant retention/immersion time of 6.00 hours.

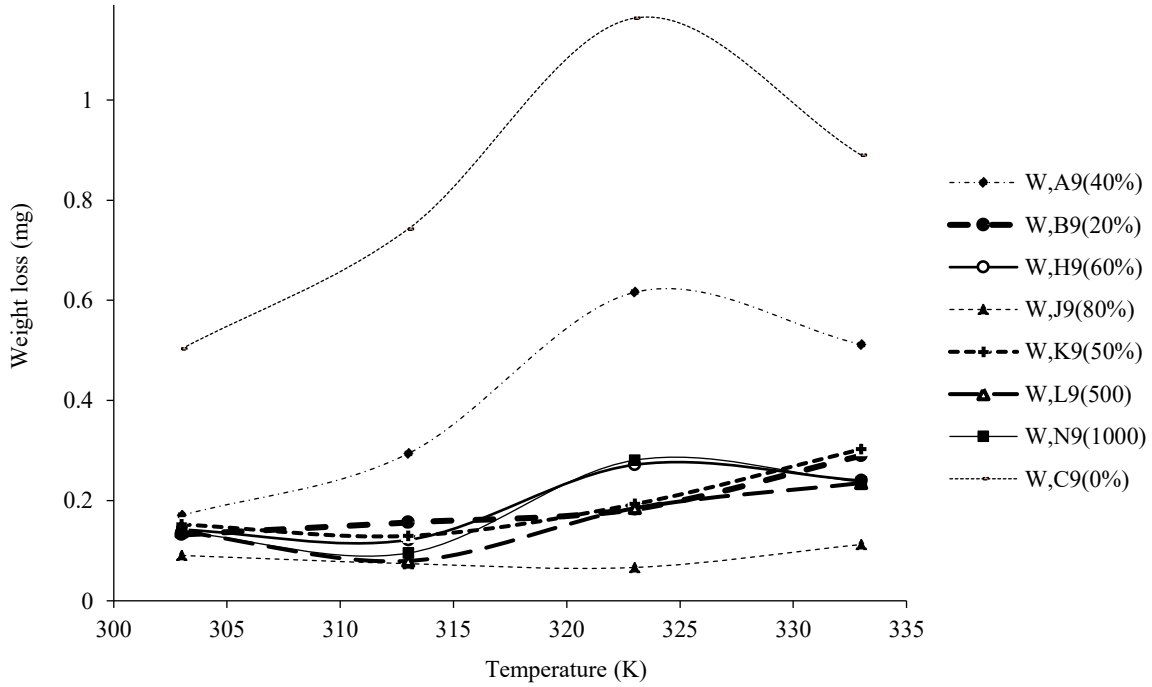

Figure 5. Weight loss (mg) versus temperature (K) for MCS metal samples corrosion rate inhibition in the complementary presence of varying volumes of GF plant extract and 1.0 molar concentration HCl corrosive solution at constant retention/immersion time 9.00 hours.

CONCLUSION

The literature shows that corrosion inhibition using plant extracts is not a new area of research. This implies that many plants have been used to establish their reliability in reducing metal corrosion during acid cleaning. On this note, no one or group of researchers has used *Selaginella myosurus,* SM, or *Pneumatopteris pennigera,* GF plant extracts to establish their metal corrosion inhibitory properties.

Therefore, this research contributes to the stock of knowledge in the following ways:

1. The prepared SM and GF extracts were established as effective corrosion rate inhibitors in HCl corrodent medium and can be applied effectively in medium carbon steel corrosion inhibition in acid cleaning where hydrochloric acid is employed as an oil well stimulation or cleaning agent.
2. The weight loss and corrosion rate, corrosion activation energy, enthalpy, entropy, and Gibbs free energy of activation at room and other temperatures for MCS metal samples in 250 ml combined volume of GF or SM extracts and HCl solution were established.

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APPENDICES

Appendix A

Tables A1 and A2 present the calculated weight loss, W (g), values for mild carbon steel (MCS) samples immersed in 1.0 M HCl solution at room temperature over exposure periods of 24–120 h. Table A1 summarizes the corrosion inhibition data in the presence of varying volumes of the SM plant extract, whereas Table A2 reports the corresponding results for the GF plant extract under identical experimental conditions.

These tabulated results provide an experimental basis for evaluating the influence of immersion time and extract concentration on corrosion behavior and comparative inhibition efficiency at room temperature.

Weight Loss Measurement at Room Temperature Tables

Table A1. Calculated values for the plot of weight loss, (g) versus time, T (hours) for MCS metal samples corrosion rate inhibition in the complementary presence of varying volumes of SM plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at different immersion times.

SM plant extract								
T/hr	***W, D***	***W, E***	***W, F***	***W, G***	***W, I***	***W, M***	***W, O***	***W, C***
24	0.1926	0.0948	0.0919	0.1256	0.1258	0.0432	0.0552	0.2855
48	0.344	0.1028	0.1871	0.2869	0.1814	0.1822	0.1927	0.7601
72	0.3644	0.1096	0.3609	0.3911	0.2686	0.3604	0.2309	1.2304
96	0.4824	0.258	0.3717	0.578	0.3873	0.5326	0.2973	1.4157
120	0.8088	0.266	0.5344	0.5815	0.7188	0.7155	0.4081	1.6926

Table A2. Calculated values for the plot of weight loss, W (g) versus time, T (hours) for MCS metal samples corrosion rate inhibition in the complementary presence of varying volume of GF plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at different immersion/retention time.

GF plant extract								
T/hr	***W, A***	***W, B***	***W, C***	***W, H***	***W, J***	***W, K***	***W, L***	***W, N***
24	0.1103	0.1072	0.2855	0.0425	0.0922	0.1496	0.092	0.0562
48	0.2825	0.2728	0.7601	0.1404	0.1452	0.1665	0.1529	0.1646
72	0.4139	0.3103	1.2304	0.4157	0.1843	0.4078	0.2836	0.2075
96	0.6038	0.4445	1.4157	0.4469	0.1898	0.511	0.3413	0.3796
120	0.8448	0.4888	1.6926	0.5443	0.3863	0.8143	0.5636	0.612

Appendix B

Appendix B: Weight Loss Measurements at Different Temperatures

Tables B1–B6 present the calculated weight loss, W (g) values for MCS samples immersed in 1.0 M HCl solution at temperatures ranging from 303–333 K and immersion times of 3, 6, and 9 hours.

Tables B1–B3 summarize results for corrosion inhibition in the presence of varying volumes of SM plant extract, while Tables B4–B6 report corresponding data for GF plant extract under identical experimental conditions.

The tabulated values provide the basis for evaluating the temperature dependence, immersion time effects, and comparative inhibition performance of both plant extracts on MCS corrosion behavior.

Weight Loss Measurement at Other Temperatures Tables

Table B1. Calculated values for the plot of weight loss, (g) versus temperature, T (K) for MCS metal samples corrosion rate inhibition in the complementary presence of varying volumes of SM plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at constant immersion time (3 hours).

SM plant extract								
T (K)	***W, C3***	***W, D3***	***W, E3***	***W, F3***	***W, G3***	***W, I3***	***W, M3***	***W, O3***
303	0.1867	0.1306	0.0293	0.0642	0.0748	0.0706	0.069	0.0608
313	0.2903	0.1305	0.0344	0.0503	0.0505	0.0452	0.0238	0.0578
323	0.3371	0.1029	0.0582	0.0622	0.0739	0.0569	0.1049	0.0181
333	0.4233	0.0503	0.0329	0.0289	0.0479	0.0334	0.0929	0.108

Table B2. Calculated values for the plot of weight loss, (g) versus temperature, T (K) for MCS metal samples corrosion rate inhibition in complementary presence of varying volumes of SM plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at constant immersion time (6 hours).

SM plant extract								
T (K)	***W, C6***	***W, D6***	***W, E6***	***W, F6***	***W, G6***	***W, I6***	***W, M6***	***W, 06***
303	0.2558	0.153	0.0561	0.1243	0.1113	0.1113	0.0772	0.0872
313	0.4676	0.1431	0.0504	0.0762	0.1221	0.0465	0.1112	0.0793
323	0.8197	0.1394	0.0657	0.0847	0.1344	0.0967	0.1124	0.1704
333	0.8949	0.1999	0.0442	0.0896	0.1041	0.0834	0.165	0.1204

Table B3. Calculated values for the plot of weight loss, W (g) versus temperature, T (K) for MCS metal samples corrosion rate inhibition in complementary presence of varying volumes of SM plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at constant immersion time (9.00 hours).

SM plant extract								
T (K)	***W, C9***	***W, D9***	***W, E9***	***W, C9***	***W, G9***	***W, I9***	***W, M9***	***W, O9***
303	0.5033	0.2107	0.0562	0.1348	0.1941	0.1941	0.0946	0.1085
313	0.7424	0.2282	0.0659	0.1579	0.1358	0.1806	0.1909	0.095
323	1.1637	0.2422	0.0774	0.2569	0.1666	0.1385	0.2845	0.1774
333	0.8899	0.2008	0.0695	0.2179	0.2213	0.2184	0.2208	0.1525

Table B4. Calculated values for the plot of weight loss, W (g) versus temperature, T (K) for MCS metal samples corrosion rate inhibition in complementary presence of varying volumes of GF plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at constant immersion/retention time (3.00 hours).

GF plant extract								
T (K)	***W, A3***	***W, B3***	***W, H3***	***W, J3***	***W, K3***	***W, L3***	***W, N3***	***W, C3***
303	0.0761	0.1068	0.0393	0.053	0.0648	0.0283	0.0856	0.1867
313	0.0616	0.0642	0.0348	0.0509	0.0674	0.0562	0.0458	0.2903
323	0.0646	0.0799	0.0378	0.0598	0.0737	0.0909	0.0992	0.3371
333	0.0473	0.0724	0.0307	0.036	0.0501	0.1692	0.1748	0.4233

Table B5. Calculated values for the plot of weight loss, W (g) versus temperature, T (K) for MCS metal samples corrosion rate inhibition in complementary presence of varying volumes of GF plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at constant immersion/retention time (6.00 hours).

GF plant extract								
T (K)	***W, A6***	***W, B6***	***W, H6***	***W, J6***	***W, K6***	***W, L6***	***W, N6***	***W, C6***
303	0.1357	0.1212	0.0958	0.0608	0.0804	0.0588	0.0976	0.2558
313	0.0786	0.1685	0.0613	0.0599	0.0879	0.067	0.0495	0.4676
323	0.1139	0.1553	0.0918	0.0643	0.1246	0.1796	0.1011	0.8197
333	0.1271	0.1462	0.0763	0.0726	0.229	0.1732	0.1816	0.8949

Table B6. Calculated values for the plot of weight loss, W (g) versus temperature, T (K) for MCS metal samples corrosion rate inhibition in complementary presence of varying volume of GF plant extract and 1.0 molar concentration HCl corrosive solution at room temperature at constant immersion/retention time (9.00 hours).

GF plant extract								
T (K)	***W, A9***	***W, B9***	***W, H9***	***W, J9***	***W, K9***	***W, L9***	***W, N9***	***W, C9***
303	0.1705	0.1324	0.1422	0.0905	0.1524	0.1381	0.1377	0.5033
313	0.294	0.1563	0.1216	0.0742	0.1297	0.0797	0.0953	0.7424
323	0.616	0.1833	0.2716	0.0666	0.1931	0.1848	0.2808	1.1637
333	0.5117	0.2896	0.2402	0.1124	0.3028	0.2352	0.2373	0.8899

