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Adsorption Isotherm, Thermodynamic and Electrochemical Studies of *Lawsonia Inermis* Leaf Extract as a Sustainable Corrosion Inhibitor of Mild Steel in Acid Medium

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Weight loss method, polarization techniques, and electrochemical impedance spectroscopy (EIS) experiments were used to evaluate natural corrosion prevention and adsorption capacities of Lawsonia inermis (Henna) leaf extract on mild steel in 1 M HCl medium. Effect of temperature on mild steel corrosion behavior was studied at a temperature range of 303K–33K. The efficiency of Henna leaf extract in inhibiting corrosion of mild steel increased with increasing concentration but decreased with increasing temperature. Activation and free energies for inhibition reactions support a mechanism of physical adsorption. The adsorption of henna extract on mild steel surface was endothermic and spontaneous, consistent with Langmuir adsorption isotherm. Polarization and EIS measurements indicated that henna extract could act as a mixed type inhibitor. Henna leaf extract as a protective coating was examined using Fourier transform infrared spectroscopy and scanning electron microscopy. Maximum inhibition efficiency at 1 M HCl was (66%) obtained when inhibitor concentration was 400 ppm.

Keywords: *Mild steel, Corrosion inhibition, Lawsonia Inermis Leaf extract, Thermodynamic parameters*

1. Introduction

Mild steel, sometimes referred to as plain-carbon steel, is one of the most significant alloys in engineering because, in addition to its affordability and strength, it possesses crucial mechanical properties that have made it widely used. Its poor corrosion resistance, particularly in acidic environments, is a problem, yet [1]. Because of their toxicity and disposal challenges, particularly in the marine industry where aquatic life is at risk, the use of synthetic and inorganic inhibitors is now restricted [2]. This has led scientists to look for alternative ways to create inexpensive, biodegradable, and environmentally benign green corrosion inhibitors that can replace inorganic and synthetic organic inhibitors. It has been observed that natural compounds such proteins, amino acids, plant extract, and biopolymers are effective corrosion inhibitors [3]. It has been shown that using plant extracts is the simplest and least expensive way to prevent and defend against corrosion in acidic environments [4]. The ability of plant extracts to suppress mild steel corrosion in a variety of media has been investigated. Examples of these extracts include Carica Papaya and Camellia Sinensis [5], Cola Acuminata and Camellia Sinensis [6], and Vernonia Amygdalina [7,8]. Using Lawsonia inermis leaf extracts, the inhibitive properties of mild steel in acetic acid medium [9] and in sea water [10] were studied.

The four main ingredients of henna, according to the earlier study, are lawsone, gallic acid, α-D-glucose, and tannic acid. These substances can be combined with metal cations and adsorbed on the metal's surface to form insoluble complex compounds that can protect the metal from corrosion attack because of their strong inhibitory qualities [11]. In order to give industrialists the essential comparative literature for considering the large-scale use of natural inhibitors in their operations, this study provides a summary of the inhibitory action of Lawsonia inermis leaf extract for mild steel in acidic medium. This will support environmentally friendly and sustainable production. The review of literature is summarized in the Table 1.

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Table 1. List of plant extracts as green inhibitors in acid medium for mild steel

S. NO	Plant Extract	Medium	Method	Inhibitor Efficiency	Adsorption Isotherm	Ref.
1	Terminalia Avicennioids	1M HCl	Weight loss, Electrochemical method	88.71%	Langmuir	[12]
2	Allium Ampeloprasum	1M HCl	Weight loss	98.3%	Langmuir	[13]
4	Bamboosa vulgaris	1M HCl	Weight loss	98.86%	Langmuir, Temkin, Freundlich	[14]
5	Ankado	1M HCl	Weight loss	96.10%	Langmuir, Temkin, Freundlich	[15]
6	Libyan	1M HCl	Weight loss	94.9%	-	[16]
7	Eriobotrya japonica thunb	1M HCl	Weight loss, EIS	90.0%	Langmuir	[17]
8	Curcuma longa	1MHCl	Weight loss	79.81%	-	[18]
9	Cnidoscolus aconitifolius	1MHCl	Weight loss	79.1%	-	[19]
10	Ginger	1MHCl	Weight loss	89%	-	[20]
11	Aloes	1MHCl	Weight loss, ESI	71.66%	Langmuir, Arrhenius	[21]
12	Tilia	1MHCl	Weight loss, EIS, Electro chemical method	60.8%	Temkin	[22]
13	Tiliacora accuminata	1MHCl	Weight loss, EIS	93.02%	Langmuir	[23]
15	Haloxylon scoparium	1MHCl	Electrochemical method, EIS	90.69%	-	[24]
17	Turmeric and ginger	1M HCl	Weight loss	92%	Langmuir	[25]
18	Traganum nudatum del	1M HCl	Weight loss, Electrochemical method, EIS	86.8%	Langmuir, Temkin	[26]
19	Acanthuus montanus	1M HCl	Gravimetric technique	72%	Langmuir	[27]
20	Canna indica	1M HCl	Weight loss, Electrochemical method, EIS	90.86%	-	[28]
21	Prosopis juliflora	1M HCl	Weight loss	95.12%	Langmuir	[29]
22	Tagetes erecta	1MHCl	Weight loss, EIS	97%	-	[30]
23	Pancratium foetidum pom	1MHCl	Weight loss, Electrochemical method, EIS	93%	Langmuir	[31]

A comparison was made between the effects of concentration and temperature on the efficiency of inhibition. Techniques for examining corrosion and the adsorption isotherms are also emphasized.

2. Materials and Methods

2.1 Test materials

The following weight percentages (compositions) were used in the pilot corrosion investigations on mild steel: C (0.12), Mn (0.85), S (0.06), P (0.05), Si (0.09), and Fe (98.83). Prior to the corrosion process, the mild steel was perforated into coupons measuring 5 cm by 2 cm by 0.2 cm. Afterwards, it was polished using different grades of silicon carbide sheets until it had a mirror-like sheen. After being thoroughly cleaned in 100% ethanol, the coupons were submerged in acetone and let to air dry. They were kept dry in a desiccator before being utilized in the corrosion trials.

2.2 Preparation of *Lawsonia inermis* (henna) leaf extract

Fresh *Lawsonia inermis* leaf material was ground into a powder after being dried at room temperature. Weighing 100 g of Lawsonia inermis leaves, 250 mL of ethanol was added, and the mixture was refluxed for 48 hours. To eliminate the ethanol from the extraction and evaporate their liquid contents, the filtrates were brought to a boil in a water bath at 48 ºC. Next, Whatmann filter paper was used to filter the ethanol extract.

2.3 Weight loss method

After being cleaned and weighed, mild steel coupons were suspended and immersed in 100 cm^3 of a 1M HCl solution (blank) and a 1M HCl solution containing 100 – 400 ppm of *Lawsonia Inermis* leaf extract (inhibitor) in open beakers using glass hooks and rods. For every experiment, one mild steel coupon was used per beaker. After that, the beakers were placed in a water bath with a thermostat that was set to 30, 40, 50, and 60 degrees, respectively. The mild steel coupons were taken out of the test solutions after a day and cleaned with a bristle brush under running water. They were drenched in acetone and then allowed to air dry before being reweighed [32]. Using the weight loss approach, the inhibitory efficiency was computed and reported as a percentage:

$$I.E.\% = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

where W1 and W2 stand for the corresponding weight loss with and without the bio-inhibitor. The mild steel corrosion rate (CR) in a 1M HCl solution was calculated using the following formula:

$$\text{Corrosion Rate (mmpy)} = \frac{87.6\ X\ w}{\text{DAT}} \quad (2)$$

where A is the specimen's size (cm^2), T is the time (in hours), D is the density (gm/cm^3), and w is the weight loss (g).

2.4 Electrochemical Technique

2.4.1 Polarization measurements

Electrochemical analysis was carried out using a potentiostat/galvanostat CH electrochemical workstation. The reference electrode was made of silver-silver chloride, whereas the counter electrode was made of platinum. The working electrode was a mild steel specimen about one centimeter square. The experiment was carried out in an aerated, undisturbed solution after a 24-hour immersion. The linear Tafel segments of the anodic and cathodic curves were extrapolated to corrosion potential in order to determine the corrosion current densities. The corrosion inhibition efficiency (I.E.%) was computed using I_{corr} data and the following relationship.

$$I.E.\% = (I^0_{corr} - I_{corr})/I^0_{corr} \times 100 \quad (3)$$

where the current density values in the presence and absence of the inhibitor are denoted by the numbers I^0_{corr} and I_{corr}, respectively.

2.4.2 EIS measurements

Electrochemical impedance spectroscopy (EIS) was carried out using a CH electrochemical system workstation. When measuring polarization, the same cell arrangement was used. Measurements of impedance were conducted between 100000 Hz and 0.010 Hz using an AC signal at the open circuit potential with a peak amplitude of 10 mV. The values of charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) were calculated. The inhibition efficiency was calculated using the following equation based on the observations of charge transfer resistance [33].

$$I.E.\% = (R_{ct} - R^o_{ct})100/R_{ct} \quad (4)$$

where R_{ct} and R^o_{ct} stand for the charge transfer resistance, respectively, in the presence and absence of an inhibitor.

2.5 Adsorption Isotherm

To ascertain the values of the thermodynamic properties, surface coverage and concentration data were fitted into the Langmuir and Temkin isotherms of Equations (5) and (6), respectively [34].

$$\frac{C}{\theta} = \frac{1}{K} + c \quad (5)$$

$$\theta = \frac{2.303 \log K}{2a} - \frac{2.303 \log C}{2a} \quad (6)$$

Where K is the adsorption equilibrium, an is the attractive parameter, and C is the inhibitor concentration. Afterwards, the free energy of adsorption ($\Delta G^{\circ}ads$) was determined using equation (7).

$$\Delta G^o_{ads} = 2.303\ \text{RT log (55.5 k)} \quad (7)$$

If the plot of C/θ *vs.* C produced a straight line, the experimental data followed the Langmuir adsorption isotherm. It is possible to calculate the K value from the intercept of Langmuir's adsorption isotherm. If the plot

of vs. log C yields a straight line, the experimental data follows the Tempkin's adsorption isotherm [35,36].

2.6 Surface Characterization Studies

The mild steel sample was treated with the acid solutions both with and without inhibitor. Several surface analysis techniques were used to analyze the type of coating that had developed on the specimen's surfaces.

2.6.1 FT-IR spectroscopy

Fourier Transform Infrared Spectra were obtained with a JASCO FT-IR 6300 type spectrophotometer. To identify the functional group contained in the henna extract, it was investigated.

2.6.2 Scanning Electron Microscope (SEM)

Test specimens of 1 cm^2 were subjected to a 1M HCl solution for 24 hours at room temperature, both in the presence and absence of an inhibitor. The surface of the corroded metal was identified using a high-resolution field emission electron microscope, which also prevented metal surfaces from being subjected to chemical examination. These studies offered more evidence that the electrochemical experiments had successfully created a protective layer on a metal surface.

3. Results and Discussion

The data was collected using a variety of methods, including as adsorption isotherms, weight loss measurements, electrochemical procedures, scanning electron microscopy (SEM), and Fourier Transform Infrared Spectroscopy (FT-IR). To display the gathered data, tables and graphs were employed.

3.1 Fourier Transform Infrared Spectroscopy (FT-IR)

The functional group included in the extract of henna leaves was identified through the analysis of FT-IR spectra, the results of which are shown in Fig. 1. There is a hydroxyl group present as evidenced by a broad absorption band at 3441 cm^{-1}. According to Musa *et al.* [37], this viewpoint is comparable. The C=O bond is attributed to the peak at 1636 cm^{-1}. Safie *et al.* [38] highlighted a related observation. 2931 cm^{-1} was the vibrational frequency of aromatic C-H stretching. It was

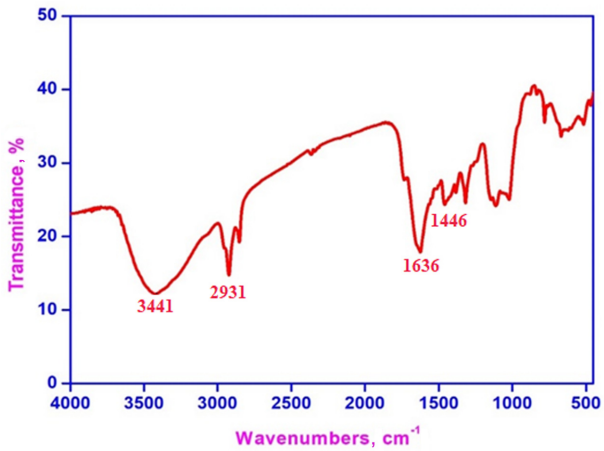
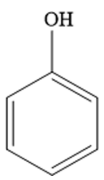
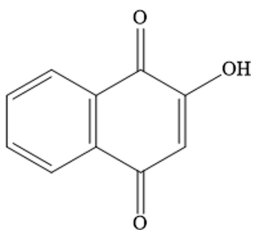
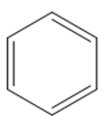


Fig. 1. FT-IR spectrum of henna leaves extract

Table 2. Main Components structure of Henna Leaves Extract

Main Functional group	Major Component
 Phenol O-H	 Structural: Lawsone Molecular Formula: $C_{10}H_6O_3$
 Aromatic ring C=C	
Carboxylic acid C=O	

believed that the aromatic C=C stretching in the benzene ring was responsible for the peak at 1446 cm^{-1}. As these peaks mirrored the pattern seen by Saadaoui *et al.* [39], they can be attributed to the vibration of the phenolic group's C-OH. Lawsone, which has the chemical formula $C_{10}H_6O_3$ and a molecular mass of 174, was found to be the primary constituent in henna. The main components are present in the henna leaves extract were listed in the Table 2. The metal would get an electron from the phenol group of lawsone, and the group would contribute an electron for the metal to reach its noble state of orbit. In addition to shielding metal from corrosion, this would stop additional redox reactions from occurring. The main components structure of henna leaves extract is mentioned in the Table 2.

3.2 Weight Loss Measurements

3.2.1 Effect of HCl concentration

Henna extract's anticorrosive properties were studied as an organic and natural inhibitor to stop mild steel from corroding in an acidic environment. The influence of the inhibitor on the corrosion behavior of mild steel in 1M HCl is shown in Fig.s 2 and 3. When the concentration of the inhibitor in HCl increases, the rate of mild steel corrosion is shown to decrease. The efficiency of the inhibition is observed to rise when the concentration of the inhibitor for leaf extract increases from 100 to 400 parts per million. Based on these results, it is possible that the inhibitor's organic molecules stuck to the mild steel surface during the inhibition activity might be the cause of the higher efficiency of inhibition [40]. The maximum inhibitory efficacy of 66% was obtained at 400 parts per milliliter of henna extract. The outcomes show that the henna extract successfully stops mild steel from corroding in a hydrochloric acid media for up to 24 hours. By utilizing inhibitor species to cover a metal surface's active areas, corrosion reactions are stopped. As a result, the inhibition efficiency and the inhibitor's surface coverage percentage are directly correlated [41].

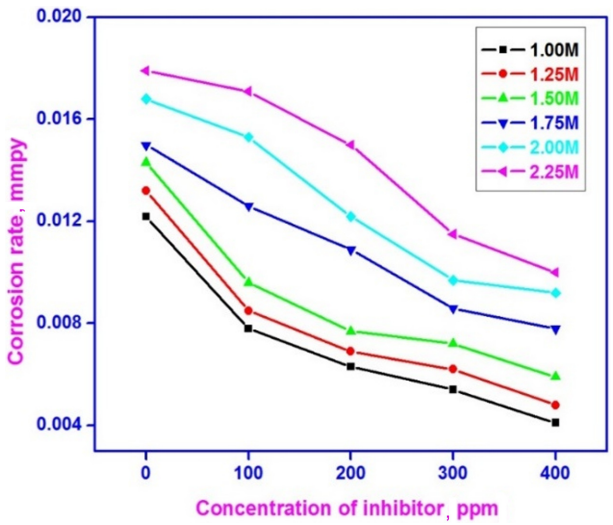


Fig. 2. Variation of corrosion rate with [henna extract] on mild steel in different [HCl] concentration

3.2.2 Effect of temperature

Effect of Temperature on the inhibitory action of the inhibitor was determined by weight loss method at various concentrations of henna extract at 303K to 333K and the results are shown in the Fig.s 4 and 5.

To again insight into the nature of inhibitor adsorption, the effect of temperature on the corrosion behaviour and the inhibition efficiency of mild steel in 1M HCl in the presence of different concentration of henna extract were studied by weight loss method for a fixed immersion time at 24 hours.

From the data revealed that the temperature increased from 303K to 333K, the corrosion rate increase while the I.E. (%) and surface coverage (θ) decrease. This

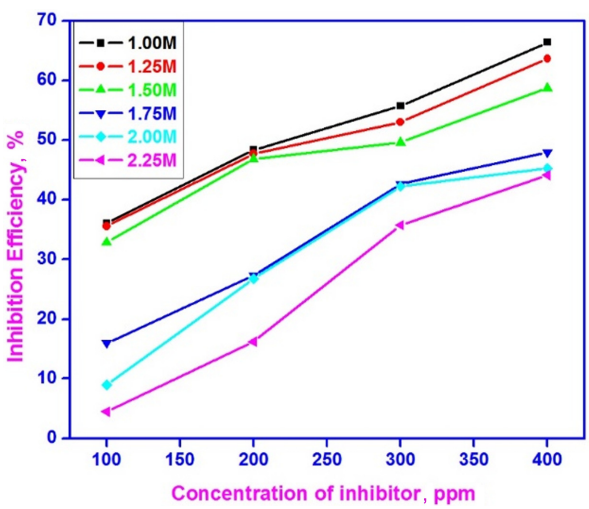


Fig. 3. Variation of Inhibition efficiency with [henna extract] on mild steel in different [HCl] concentration

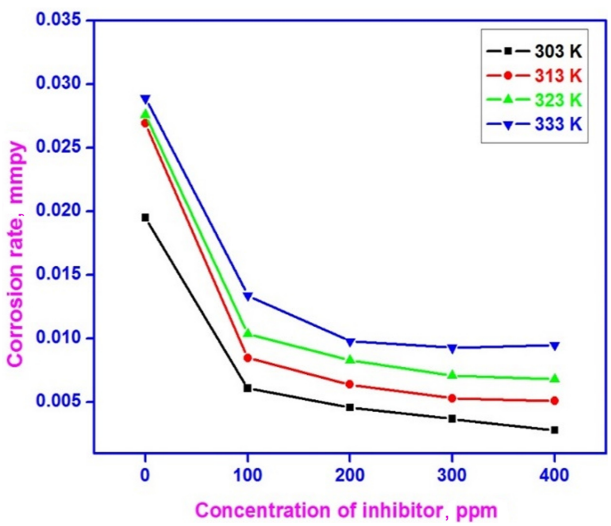


Fig. 4. Variation of corrosion rate with [henna extract] on mild steel at different temperature

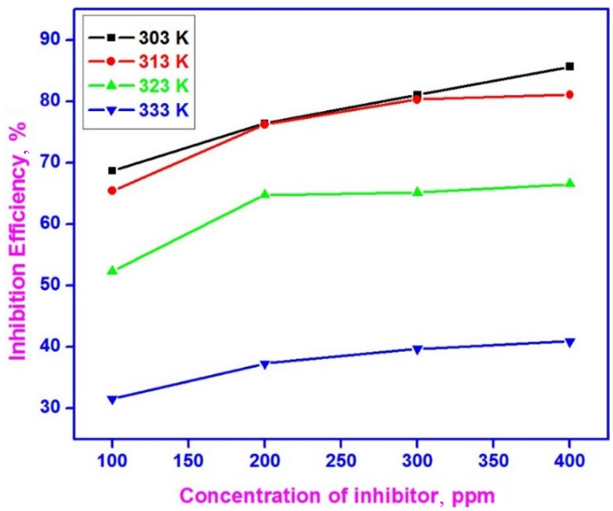


Fig. 5. Variation of inhibition efficiency with [henna extract] on mild steel at different temperature

suggests that some desorption of some of the adsorbed inhibitor from the metal surface at higher temperature. This gives a clue that the mechanism of adsorption of the inhibitor may be mainly due to physisorption, because the physisorption which is due to weak vander waal's force disappears at elevated temperature. Thus, as the temperature increases, the number of adsorbed molecules decreases, leading to a decrease in the inhibition efficiency.

3.3 Activation Energy and Heat of Adsorption Studies

The thermodynamic factors are necessary to understand the mechanism of inhibition. The activation energies (E_a), enthalpies (DH*), and entropies (S*) were measured in the presence and absence of henna extract and tabulated in Table 3. The mild steel corrosion in 1M HCl without and with varying amounts of henna extract were made into transition state plots (log (C_R/T) vs. 1/T) (Fig. 6) and Arrhenius plots (log C_R vs. 1/T) (Fig. 7) both showed sufficient linearity by providing correlation coefficient (R^2) values of up to 0.9 and above. The values of DH* and DS* were obtained from the slope (slope = DH*/2.303R) and intercept (intercept = log (R/Nh) + S*/2.303R) of the transition state plot, respectively. The slope of the Arrhenius plots (slope = E_a/2.303R) was used to compute the apparent activation energy (E_a).

The activation energy of a hydrochloric acid solution in the absence of a corrosion inhibitor is 13.4 kJ/mol, but it increases to 53.61 kJ/mol when henna extract is added as a corrosion inhibitor. The high activation energy suggests that the mild steel surface is shielded from the corrosive solution by a layer formed by the molecules in the henna extract. Physical adsorption explains the rise in activation energy [42,43].

The endothermic nature of the mild steel dissolution process is suggested by the positive values of ΔH* that

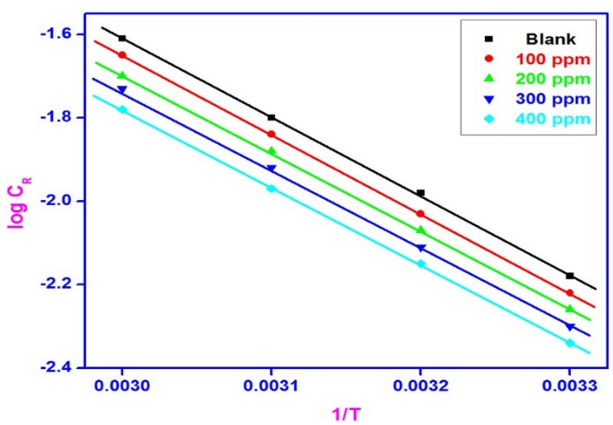


Fig. 6. Arrhenius plot for mild steel in 1M HCl solution in the absence and presence of different concentrations of henna extract

Table 3. Calculated values of Activation energy (E_a), Enthalpy (ΔH*) and Entropy (ΔS*) for henna extract on mild steel in 1M HCl

Concentration of Inhibitor (ppm)	Henna extract			
	E_a ($kJmol^{-1}$)	ΔH* ($kJmol^{-1}$)	ΔS* ($kJmol^{-1}$)	ΔG° ($kJmol^{-1}$)
Blank	13.40	17.41	-59.10	-20.20
100	36.38	19.74	-57.61	-22.24
200	41.36	22.26	-52.70	-23.04
300	47.10	33.93	-48.79	-25.13
400	53.61	47.87	-44.06	-28.70

were found both in the presence and absence of the inhibitor [44]. The fact that ΔS* is frequently negative suggests that disorderliness reduces as the reaction progresses from reactants to activated complex, and it also suggests that the formation of the activated complex during the rate-determining stage is an associative process rather than a dissociative one [45].

It was discovered from the following equation that the free energy of adsorption (ΔG^{o}_{ads}) is proportional to the henna extract adsorption equilibrium constant on the mild steel surface. [46,47].

$$\Delta G^{o}_{ads} = -2.303\ RT \log (55.5\ k)$$

3.4 Adsorption Parameters for the Corrosion Inhibition Study

It is well accepted that adhesion is the mechanism by which henna extract displays its inhibitory activity on steel surfaces. The inhibitor's adsorption, which creates a protective film layer that acts as a barrier to keep electrochemical reactions from reaching the metal surface, is assumed to be caused by the extract's heterocyclic constituents. Furthermore, a correct understanding of the kinetics process requires a detailed grasp of the adsorption characteristics of an inhibitor. The adsorption isotherms provide insight into the interaction between the mild steel surface and the molecules of henna extract. Plotting C/θ values against C values produced straight line graphs (Fig. 7) with an R^2 value of 0.996, demonstrating that the Langmuir adsorption isotherm is obeyed [48].

The relationship between the molecules in the extract and the quantity of metal surface coating is shown by the graph's linearity. Plots of θ against log C, as seen in Fig. 8, revealed a linear relationship that suggested the compounds adsorption on the mild steel surface followed the Temkin adsorption isotherm. This finding supports the theory that the compounds' adsorption on the metal surface causes their corrosion inhibition. The assumption of monolayer adsorption on a metal surface with an interaction in the adsorption layer is verified by the applicability of Temkin's adsorption isotherm [49].

3.5 Electrochemical Measurements

3.5.1 Polarization measurements

The effects of henna extract concentration on the anodic and cathodic polarization behaviour of mild steel in 1M HCl solution has been studied by polarization measurements and the recorded Tafel plots for some studied concentrations are shown in Fig. 9. The respective electrochemical parameters derived from the plots including corrosion current density (I_{corr}), corrosion potential (E_{corr}), anodic and cathodic Tafel slopes (β_a and β_c, respectively), polarization resistance (R_p) and inhibition efficiency (I.E. %) are given in Table 3. The

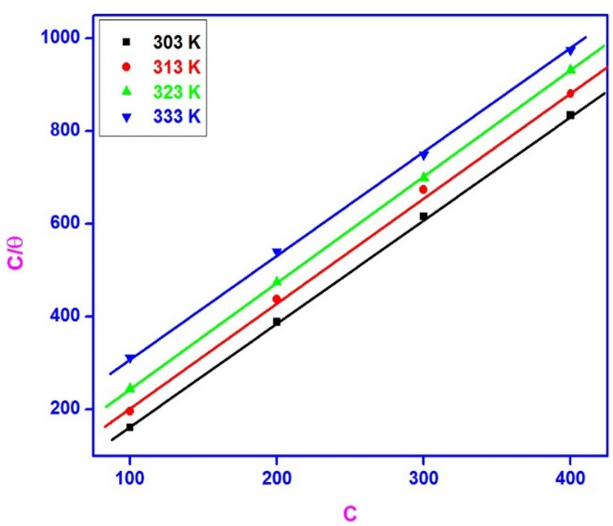


Fig. 7. Langmuir Adsorption Isotherm for henna extract adsorbed on mild steel in 1M HCl

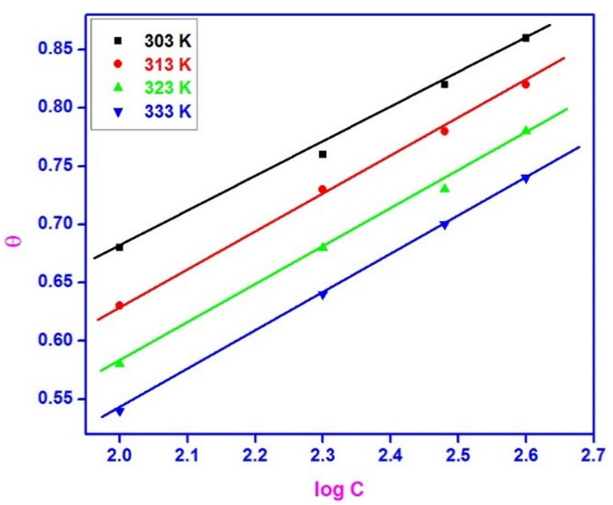


Fig. 8. Tempkin Adsorption Isotherm for henna extract adsorbed on mild steel in 1M HCl

Table 3. Polarization measurements for mild steel corrosion in 1M HCl in the absence and presence of different concentration of henna extract

Concentration of inhibitor (ppm)	E_{corr}	I_{corr}	I.E.%	β_a (mV/dec)	β_c (mV/dec)
Blank	-0.5200	0.0169	-	6.963	1.175
100	-0.5020	0.0092	45.56	8.0161	1.815
200	-0.4910	0.0070	58.58	9.765	2.740
300	-0.4660	0.0053	68.64	9.949	3.087
400	-0.4310	0.0040	76.33	9.841	3.865

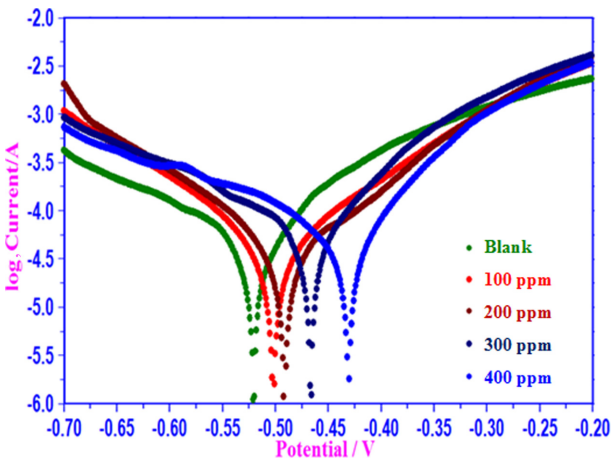


Fig. 9. Tafel curves for mild steel corrosion in 1M HCl without and with various concentration of henna extract

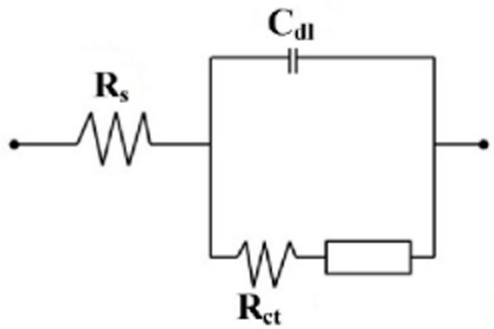


Fig. 10. Equivalent Electrical circuit used for modelling the impedance plots

inhibition of these reactions was more pronounced on increasing henna concentration. The lower corrosion current density I_{corr} values in the presence of inhibitor without causing significant changes in corrosion potential (0.0169 to 0.0040) suggests that, the compound is mixed type inhibitor (i.e., inhibits both anodic and cathodic reactions) and is adsorbed on the surface, thereby blocking the corrosion reaction. In the presence of henna extract, the corrosion potential E_{corr} of mild steel shifted to the range (-0.5200 to -0.4310) mV/SCE, compared to the blank. This confirms that henna extract acts as mixed-type inhibitor [50,51]. The observed decreases of the current densities I_{corr} with the increase in henna extract concentration, indicating the increased inhibition efficiency with the increase in the concentration of the inhibitor. This reflects also, the formation of anodic protective films containing oxides and henna.

3.5.2 EIS measurements

After being submerged for 24 hours, mild steel's corrosion behavior in an acidic solution with and without henna extract was examined using electrochemical impedance spectroscopy (EIS). As recommended by Tsuru *et al.* [52], the charge-transfer resistance (R_{ct}) values were computed using the difference in impedance at lower and higher frequencies. Following immersion, EIS was used to analyze the mild steel's corrosion behavior in 1M HCl with and without henna extract at open circuit potential. The values of solution resistance (R_s), charge transfer resistance (Rct), double layer capacitance (C_{dl}), inhibitory efficiency (%), and surface coverage (q) were obtained by curve fitting of impedance data using Z-view software. The simple equivalent Randle circuit for research is depicted in Fig. 10.

The Nyquist plot with and without henna extracts at different concentrations is shown in Fig. 11. Notably, the profile of the impedance diagrams stayed constant both with and without henna extract, and it was found to consist of a single semicircle, suggesting that the mild steel is where the rate-determining mechanism takes place. The charge-transfer resistance (R_{ct}) values are determined by comparing the impedances at lower and higher frequencies. The double layer capacitance (C_{dl})

Table 4. Electrochemical Impedance data for mild steel corrosion in 1M HCl in the absence and presence of different concentration of henna extract

Concentration of inhibitor (ppm)	R_{ct} (Ω cm^2)	C_{dl} (mF)	I.E.%	Surface Coverage (θ)
Blank	24.82	0.0066	-	-
100	33.43	0.0049	25.76	0.25
200	42.25	0.0032	41.25	0.51
300	66.23	0.0025	62.52	0.62
400	111.42	0.0015	77.72	0.77

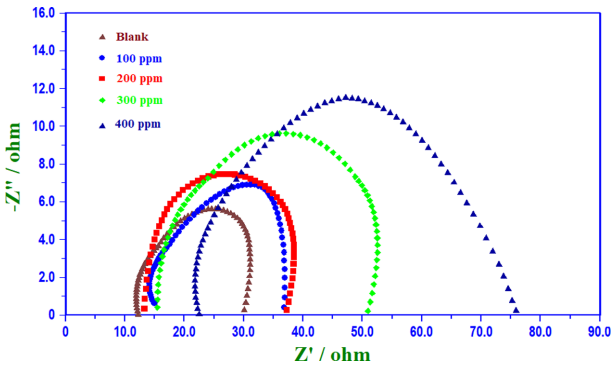


Fig. 11. Nyquist plot for mild steel corrosion in 1M HCl without and with various concentration of henna extract

was computed using the equation.

$$C_{dl} = \frac{1}{2\pi f_{\max} \cdot R_{ct}}$$

where f_{max} is the frequency at which the imaginary part of the impedance ($-Z_{max}$) reaches its highest value. The values of the double-layer capacitance, C_{dl}, and charge transfer resistance, R_{ct}, obtained from Nyquist plots, and the inhibitory efficiency, computed using equation 4, are shown in Table 4. It was determined from the impedance data that as the concentration of the inhibitor grows, so does the R_{ct} values and, in turn, the inhibition efficiency. In Nyquist plots, mild steel corrosion is primarily controlled by a charge transfer mechanism represented by depressed semi-circles with a center under the real axis, whose size increases with inhibitor concentration. Refs. [53] provided similar graphs for the iron and steel electrode with and without the inhibitor 1 M HCl. As the concentration of the inhibitor rises, the C_{dl} values fall. The reduction in C_{dl} values may be caused by the phytochemicals in henna extracts adhering to mild steel's surface [54]. At 400 ppm, it was discovered that the greatest inhibitory efficiency (I. E.%) of henna extract was 77.72%.

3.5.3 SEM Analysis

SEM analysis was performed on the surface morphology of mild steel surfaces that had been submerged in 1 M HCl solutions for 24 hours, both with and without 400 ppm of henna extract. The surface microphotographs of mild steel are provided in Fig. 12. The morphologies of polished mild steel are shown in Fig. 12a, where the entire surface is a plane. The rusted sample in Fig. 12b was exposed to a 1 M HCl solution for 24 hours, which is equivalent to the maximum rate of corrosion on a mild steel surface. The SEM picture of the mild steel specimen's surface, which was submerged in a 1 M HCl solution containing the inhibitor at its ideal concentration of 400 ppm for 24 hours, is shown in Fig. 12c. When henna extract was present, mild steel coupons' surface morphology significantly improved, as shown by surface analysis of Fig. 12c [55].

3.5.4 Suggested mechanism of corrosion inhibition

In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface. In acidic solution, the oxygen atom of the lawsone of the inhibitor can be protonated easily, due to high electron density on it, leading to positively charged inhibitor species (Fig. 13).

The adsorption can occur via electrostatic interaction between positively charged inhibitor molecules and negatively charged metal surface leading to physisorption of the inhibitor molecules. Further, co-ordinate bond may be formed between unshared electron pairs of unprotonated oxygen atom of the inhibitor and vacant d-orbitals of metal surface atoms.

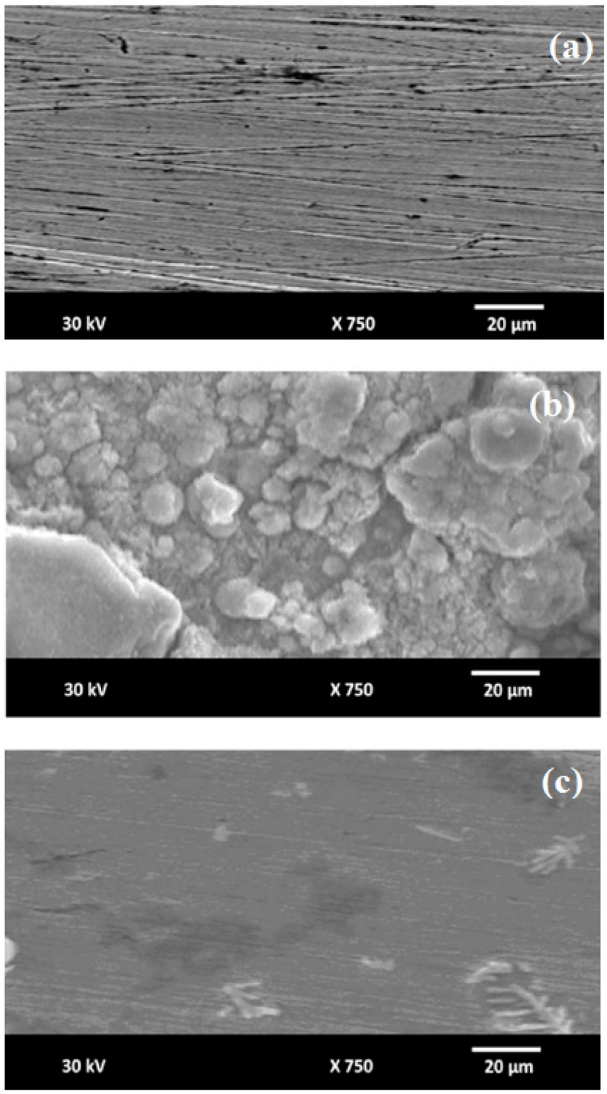


Fig. 12. SEM micrographs: (a) Polished mild steel; after 24 hours of immersion: (b) Untreated (Blank) mild steel in 1 M HCl, (c) Treated mild steel in the presence of 400 ppm Henna extract

4. Conclusion

The findings unequivocally show that mild steel in a 1M HCl solution is well protected against green corrosion by henna extract. Due to the *Lawsonia inermis* extract components adsorption on the metal surface, it was discovered that the inhibition efficiency rose with increasing inhibitor concentrations and decreased with increasing reaction temperature (303–333 K). The *Lawsonia inermis* extract's functional groups are what allow the extract's constituents to adsorb on the mild steel surface, preventing corrosion. The Langmuir

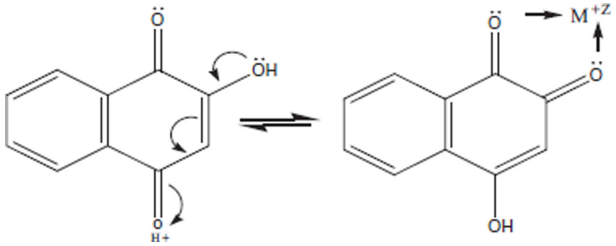


Fig. 13. Forms of lawsone due to electron delocalization

adsorption isotherm governs the *Lawsonia inermis* extract's adsorption on the mild steel surface. The temperature dependency of the inhibition efficiency suggests an inhibition mechanism, which is further corroborated by the activation energy and thermodynamic parameter values derived from the experimental data. When *Lawsonia inermis* extract is introduced, surface examination (FT-IR and SEM) demonstrates the improvements in the metal surface morphology. The extract from *Lawsonia inermis* leaves has the potential to provide a safer, more environmentally friendly substitute for the toxic, expensive, and non-biodegradable synthetic compounds now in use.

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