An insight on the corrosion inhibition of mild steel in aggressive medium by henna extract

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Abstract

Green chemistry becomes in the last decade a tool for the sustainable developments in various sectors, the reorientation of the use of environmentally ecofriendly alternatives is gaining attention in the field of corrosion protection. The use of natural plant extracts as corrosion inhibitors is counted by thousands of papers and industrial patents. Plant extracts contain complex phytochemicals that interact strongly with metallic surface through their electron rich sites. In this context, this review investigates the corrosion inhibitive action of henna (***Lawsonia Inermis***) leaves extracts on mild steel in various acid media by weight loss measurements (WL) as chemical measurements and by potentiodynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS) as electrochemical ones. The study indicates that as the acid concentration increases, the corrosion rate increases. The corrosion inhibition efficiency increases with an increase in the concentration of the extract. The results obtained reveal that the henna leaves extract acts as an efficient inhibitor. The adsorption of the henna leaves extracts obeys the Langmuir adsorption isotherm. The calculated thermodynamic parameters indicate that the adsorption is a spontaneous, exothermic process accompanied by an increase in entropy. Cathodic and anodic polarization curves show that the henna leaves extract is a mixed-type inhibitor. The inhibitory action is generally explained as an intermolecular synergistic effect of different components of the natural extract.

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1. Introduction

Corrosion is a constant and ongoing problem, often difficult to eliminate completely. Nowadays it has taken a considerable importance, due to the high budget problems caused to industrialized countries for renovating and protecting materials from deterioration and lost. Their consequences are important in various fields and particularly in industry: loss of production [1], replacement of corroded materials [2], serious accidents and pollution of the natural environment are frequent events with sometimes heavy economic impact [3]. For example, in the case of industrial processes, metals are exposed to the action of acids, which act as corrosive agents. These acids play an important role in industry, especially in crude oil refining [4], acid pickling [5], industrial cleaning, acidic descaling [6], and also in petrochemical processes [7], and consequently cause the degradation of metals, either by chemical or electrochemical reactions [8]. The use of mild steels in the industrial field is very important, and the big problem is that these steels are alloys more susceptible to be degraded by the phenomenon of corrosion in different corrosive environments, acid [9], basic and neutral [10], and therefore they suffer losses of their initial mechanical properties [11], which can have catastrophic consequences. Thus, it is necessary to protect them against the aggressions of these environments, in order to increase their lifespan [12]

There are several methods of protecting mild steels from corrosion, including the use of corrosion inhibitors [13], which are chemical substances that retard corrosion when added to a corrosive medium in low concentrations [14]. Inhibitors are divided into two types: inhibitors from synthetic compounds [15] and green inhibitors from essential oils and plant extracts [16]. Most synthetic compounds have good anticorrosive action, but most of them are highly toxic to humans and to their environment [5]. These inhibitors can cause temporary or permanent damage to the system of organs such as the kidneys or liver, or disrupt the enzyme system in the body [17], which is why they are being replaced by oils, and plant extracts which are increasingly considered a source of green and ecofriendly corrosion inhibitors [18].

In the world there are many scientific researches focused on corrosion prevention methods using green inhibitors for mild steel in acid solutions [19–23] or synthetic inhibitors based on heterocyclic compounds [24–27]. In the University Mohammed Premier, Oujda, Morocco, specially faculty of sciences there are several researchers who work in the field of corrosion for example: Bouyanzer, *et al*., they discovered that the natural oil extracted from pennyroyal mint (*Mentha pulegium*, PM) has an inhibition efficiency of 80% at 2.76 g/l for steel in HCl (1 M) [28], also Dahmani *et al*., they discovered that black pepper extract and the major product of this plant pipeline has an inhibition efficiency of 95% at 2 g/l for C38 steel [29]. The richness of black pepper, miraculously really the King of species due to very rich source of a wide variety of chemical constituents, most of which are biologically active, was documented in Ref. [30]. The application of extracts of an antibiotic and pyrimidine alkaloids bugbane and inline had shown that bugbane was a highly efficient corrosion inhibitor for iron corrosion in 1 M HCl [31], the excellent inhibitory action of bugbane was patented [32]. It was also found that the corrosion inhibition efficiency increased with the concentration of the jojoba oil to attain a 100% inhibition at 0.515 g/l of jojoba oil, indicating that jojoba oil was an excellent corrosion inhibitor [33]. These excellent and promoted findings incited our group to continue working on natural compounds [34–63]. The aim of this review is to expose the numerous researches on Henna extract as green inhibitor of metallic materials in various corrosive media.

2. Experimental details

2.1 Preparation of extract and corrosive media

a) Preparation of henna extract

In the study in HCl and acetic acid mediums henna leaves were crushed and extracted in boiled water for 2 h. The extracted solution was then filtered and concentrated until the water from the extract evaporated. This solid extract was used to study the corrosion inhibition properties and to prepare the required concentrations of henna [64].

b) Extraction of henna constituents

Textile demand increases with increasing appetite for color. Most of the coloring processes for the textile industries use synthetic dyes. The advantages of synthetic dyes include wider color variations, more practical, easier to use, as well as more economical. However, synthetic dyes also have disadvantages, one of which is the degradation of his waste generated after the staining process. The synthetic dye waste is harmful to aquatic ecosystems because it may contain chemicals or even heavy metals [65]. Henna leaves contain Lawsone dye that can be extracted as yellow and orange crystals. This dye can be used as a dye for skin, nail, hair, silk, and wool. Extracting the Lawsone from the Henna leaves can be carried out by the mass transfer of dyestuff from solid to liquid phase (solvent) [66]. This method of extraction is commonly called as solid-liquid extraction (leaching). Some conventional methods that are commonly used for extraction include maceration, by Soxhlet type extraction, and reflux method ones. These conventional methods have several weaknesses, such as abundant requirement of solvent, lower in yield and longer extraction time. It is necessary to use extraction technics which save chemical compounds, solvents and energy such as ultrasound extraction [67]. Ultrasound assisted extraction is simple method and eco-friendly than conventional methods [68]. Therefore, in this study the extraction method with ultrasonic waves or Ultrasound Assisted Extraction (UAE) were developed in order to optimize the extraction process.

c) Ultrasound assisted extraction

We mixed 100 ml of organic solvent with henna powder in the ultrasonic bath and were extracted by the ultrasound for 10 min. The extraction frequency of the ultrasonic bath was set up at 40 kHz. Then solvent was then separated from the extract using water jet pump and a filter paper on top of it. The solid was separated and sticked on the filter paper. The solvent became clear from solid and the color of the solvent was orange. The ethanoic acid or NaOH was then added into it to control the pH of this extract solution. The Lawsone contained in the solvent made the solvent turn orange and was separated with the solvent by heating. It was heated at 353 K using water bath until only the dye extract left [69].

d) Soxhlet extraction

We mixed 500 ml of aquadest and ethanol 60% were prepared and placed in a one neck flask round bed flat of 1000 ml 10 g of Henna powder was prepared and mixed in the filter paper which was placed in the Soxhlet accordingly. It was heated at 353 K for ethanol 60% and at 383 K for aqueduct. The extraction occurred until the solvent in the Soxhlet become clear or colorless. The Soxhlet extraction was counted to be one cycle when the solvent filled in Soxhlet and then turned back to the one neck flask round bed [69].

e) Gas chromatography–mass spectrometry (GC–MS)

About 10 μl of the henna extract sonicated with n-hexane were analyzed by GC–MS using Shimadzu Model GC-17A equipped with flame ionization detection (FID) and a CBP-5 capillary fused silica column (25 m, 0.25 mm *i.d.*, 0.22 mm film thickness). The oven temperature was held at 323 K for 2 min then programmed at 283 K/min to 523 K, held for 20 min. Other operating conditions were as follows: carrier gas, He (99.99%), inlet pressure 76 kPa, with a linear velocity of 20 cm/s; injector temperature, 523 K; detector temperature, 583 K; split ratios, 1:25 [17].

f) Specimen preparation

In a previous study, Ostovari *et al.* [17] used mild steel specimens having the nominal composition of C = 0.179%, Si = 0.165%, Mn = 0.439%, Cu = 0.203%, S = 0.034% and Fe balance were used. Coupons were cut into 2×2×0.2 cm dimensions used for weight loss measurements, whereas specimens with 2×2×0.7 cm dimensions, sealed by polyester resin, leaving a surface area of 4 cm^2, were used as working electrode for polarization and EIS measurements. The exposed area was mechanically abraded with 220, 400, 800 and 1000 grades of emery papers, degreased with acetone and rinsed by distilled water before each electrochemical experiment [17].

g) Solutions preparation

About (1 M) HCl solutions were prepared by dilution of 37% HCl (Merck) using distilled water. The concentration range of henna extract employed was varied from 0.2 to 1.2 g/l and the electrolyte used was 800 ml for each experiment [17].

2.2 Corrosive measurement

a) Weight loss measurements (WL)

Experiments were performed at 298, 313, 323 and 333 K with different concentrations of henna extract. The immersion time for the weight loss is 6 h. The results of the weight loss experiments are the mean of three runs, each with a fresh specimen and 800 ml of fresh acid solution [17].

The inhibition efficiency *IE*% was calculated using the following equation:

$$IE\% = \frac{W_2 - W_1}{W_2} \cdot 100\% \qquad (1)$$

Where W_1 and W_2 are the weight loss of the mild steel in the presence and absence of inhibitor, respectively.

b) Chemical measurements and potentiodynamic polarization (PDP)

In the first study electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell, containing 800 ml of electrolyte at the temperature of 298±1 K. Platinum electrode was used as a counter electrode and a saturated calomel electrode (SCE) as the reference electrode. Polarization studies were conducted using computer-controlled ZAHNER Elektrik model IM6eX potentiostat at a scan rate of 0.3 mV/s. THALES software was used for evaluating the experimental data. Before recording the polarization curves, the solution was de-aerated for 20 min and the working electrode was maintained at its corrosion potential for 10 min until a steady state was obtained [17]. In the second the potentiodynamic polarization was carried out using a C H instrument (CHI608C). A platinum and Ag/AgCl electrode were used as the auxiliary and reference electrodes, respectively. The test specimen of area 1 cm^2 was used as the working electrode. All the experiments were carried out at a constant temperature of 298 K [64].

The inhibition efficiency *IE*% was calculated using the following equation:

$$IE\% = \frac{I_2 - I_1}{I_2} \cdot 100\% \qquad (2)$$

Where I_1 and I_2 are the corrosion current densities of mild steel in the presence and absence of inhibitor, respectively.

c) Electrochemical impedance spectroscopy (EIS)

EIS experiments were conducted using computer-controlled ZAHNER Elektrik model IM6eX system with THALES software for calculation of polarization resistance (R_p) and double layer capacitance (C_{dl}) values. All experiments were performed with a frequency ranging from 100 mHz to 10 kHz and peak-to-peak A.C. amplitude of 10 mV. The impedance diagrams were plotted in the Nyquist representation [17].

The inhibition efficiency *IE*% was calculated using the following equation:

$$IE\% = \frac{R_2 - R_1}{R_2} \cdot 100\% \qquad (3)$$

Where R_1 and R_2 are polarization resistance of mild steel in the absence and presence of inhibitor, respectively.

3. Results

3.1 Weight loss measurements (WL) for (1 M) HCl

The corrosion rate and inhibition efficiency for mild steel in (1 M) HCl solution at 298, 313, 323 and 333 K in the absence and presence of henna extract are given in Table 1.

From the results obtained in Table 1 it can be concluded that the speed of corrosion decreases when the concentration of henna extract increases, however, when the temperature rises it also increases. Also, the evolution of the corrosion rate in the corrosive solution HCl (1 M) shows a regular and rapid growth, confirming an increasing metallic dissolution. The inhibitory efficiency of mild steel increases with increasing concentration of henna extracts up to 92.59% at 298 K at 6 h immersion. As the temperature increases, the inhibition efficiency decreases. At 313, 323 and 333 K the inhibition efficiencies decrease by 69.66, 54.38 and 37.95% in the HCl (1 M) solution containing 1.2 g/l henna extract, and at high temperatures, the corrosion rate is maximal for the uninhibited acid solution, however the presence of inhibitor leads to a decrease in the corrosion rate.

3.2 Chemical measurements and potentiodynamic polarization (PDP) for 1 M HCl

Potentiodynamic anodic and cathodic polarization plots for mild steel specimens in 1 M HCl solution in the absence and presence of different concentrations of henna extract are shown in Figure 1. The respective kinetic parameters including corrosion current density (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (β_c) and inhibition efficiency (*IE*%) are given in Table 2.

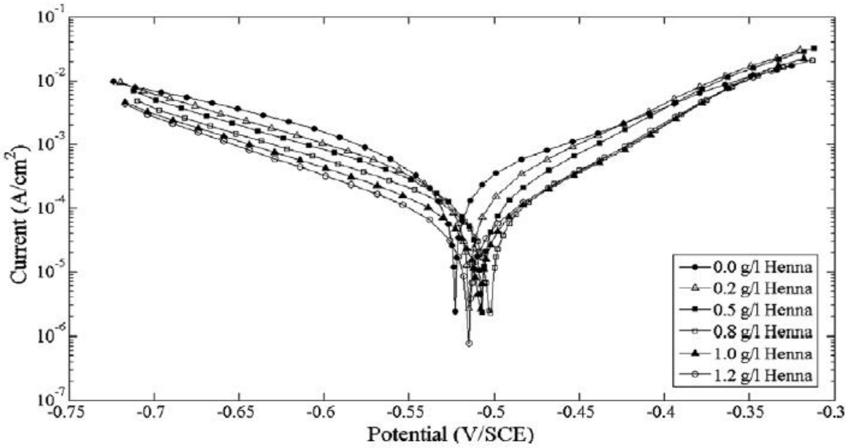


Figure 1. Polarization curves for mild steel in 1 M HCl at 298±1 K containing different concentrations of henna extract [17].

Table 1. Corrosion parameters obtained from weight loss of mild steel in (1 M) HCl containing various concentrations of henna extract at different temperatures [17].

Mediu mg/l henna	**298 K**			**313 K**			**323 K**			**333 K**		
	W **mg/cm^2·h**	***IE%***	**θ**	***W*** **mg/cm^2·h**	***IE%***	**θ**	***W*** **mg/cm^2·h**	***IE%***	**θ**	***W*** **mg/cm^2·h**	***IE%***	**θ**
0.0	0.54	–	–	0.66	–	–	1.14	–	–	1.66	–	–
0.2	0.22	59.26	0.5926	0.42	36.34	0.3634	0.91	20.17	0.2017	1.50	9.63	0.963
0.5	0.15	72.22	0.7222	0.34	48.49	0.4849	0.74	35.08	0.3508	1.33	19.87	0.1987
0.8	0.09	83.33	0.8333	0.72	59.09	0.5906	0.62	45.61	0.4561	1.16	30.12	0.3012
1.0	0.06	88.89	0.8889	0.24	63.61	0.6361	0.57	50.00	0.5000	1.09	34.33	0.3433
1.2	0.04	92.59	0.9259	0.20	69.66	0.6966	0.52	54.38	0.5438	1.03	37.95	0.3795

Table 2. Kinetic parameters of mild steel in 1 M HCl at 298±1 K containing different concentrations of henna extract [17].

Medium	–ß$_c$, mV/dec	E_{corr}, mV/SCE	I_{corr}, mA/cm^2	*IE*%
1 M HCl	149	–523.5	0.4825	–
0.2 g/l henna	125	–514.6	0.1911	60.39
0.5 g/l henna	130	–507.6	0.1290	73.26
0.8 g/l henna	124	–503.0	0.0813	83.15
1.0 g/l henna	119	–509.1	0.0669	86.13
1.2 g/l henna	111	–515.6	0.0383	92.06

From the results obtained in Table 2 and Figure 1, we can see the following observations. The presence of inhibitor causes a marked change in the cathode branches and to a lesser extent in the anode branches of the polarization curves. In addition, in the presence of henna extract the E_{corr} corrosion potential values are almost constant; therefore, henna extract could be classified as a mixed type inhibitor with predominantly cathodic efficiency. Also, the addition of henna extract decreases the density of the corrosion current. In addition, it can clearly be seen that the inhibition efficiency of henna extract increases with the inhibitor concentration. This behavior shows that henna extract acts as a good inhibitor of mild steel corrosion in HCl media.

3.3 Electrochemical impedance spectroscopy (EIS)

The corrosion of mild steel in 1 M HCl solution in the presence of henna extract was investigated by EIS at 298±1 K after 10 min of immersion.

a) Nyquist representation

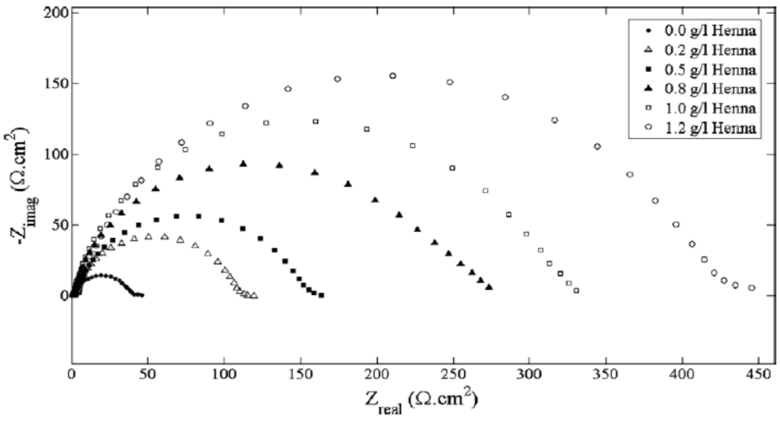


Figure 2. Nyquist plots for mild steel in 1 M HCl at 298±1 K containing different concentrations of henna extract [17].

Based on the analysis of the Nyquist diagram Figure 2, we can make the following interpretations: the curves represented in the Nyquist diagram are approximated by a single capacitive semicircle, showing that the corrosion process was mainly controlled by load transfer [70]. Also, the general shape of the curves is very similar for all samples; the shape is maintained in all concentrations, indicating that practically no change in the corrosion mechanism occurred due to the addition of the inhibitor [71]. And the diameter of the Nyquist diagram (R_p) increases with increasing concentration of henna extract.

b) Equivalent circuit

The Nyquist plots are analyzed in terms of the equivalent circuit composed with classic parallel capacitor and resistor (shown in Figure 3).

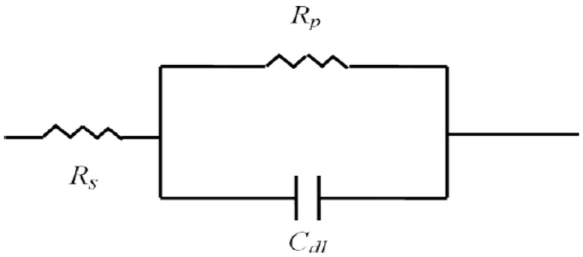


Figure 3. The equivalent circuit model [17].

c) Impedance parameters

The impedance parameters including polarization resistance R_p, double layer capacitance C_{dl} and inhibition efficiency *IE*% are given in Table 3.

Table 3. Impedance parameters of mild steel in 1 M HCl at 298±1 K containing different concentrations of henna extract [17].

Medium (g/l henna)	**R_p, Ω·cm^2**	**f_{max}, Hz**	**C_{dl}, μF/cm^2**	***IE*%**
0.0	42.28	41.89	89.85	–
0.2	114.13	24.74	61.32	62.95
0.5	158.35	18.62	56.67	73.29
0.8	273.82	13.79	55.77	84.55
1.0	331.06	18.62	33.94	87.22
1.2	437.99	24.74	20.18	90.34

From Table 3 we can see the following remarks: the polarization resistance R_p increases from 42.28 to 437.99 Ω·cm^2 and the double layer capacity C_{dl} decreases from 89.85 to

20.18 μF/cm^2 with increasing concentration of henna extract. The decrease in C_{dl} means that the adsorption of the inhibitor takes place on the mild steel surface in acid solution. In addition, the increase in polarization resistance leads to an increase in inhibition efficiency. The results obtained in EIS are in agreement with those of the polarization measurements in terms of corrosion efficiency values.

d) Thermodynamic parameters of adsorption

The inhibition of corrosion of metals by organic compounds is explained by their adsorption. The latter is described by two main types of adsorption, namely physical adsorption and chemical adsorption. The use of adsorption isotherms allowed us to determine the thermodynamic parameters. The curves of the adsorption isotherms of henna extract on mild steel in different temperatures can be represented by the Langmuir adsorption isotherm because their correlation coefficient (r^2) is the best for experimental data.

$$\frac{C_{\mathrm{inh}}}{\theta} = \frac{1}{K} + C_{\mathrm{inh}} \tag{4}$$

K is the adsorption constant.

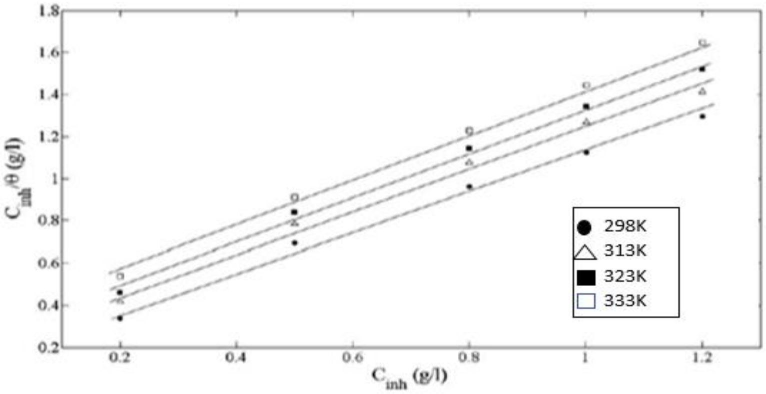


Figure 4. Langmuir adsorption plots for mild steel in 1 M HCl at different temperatures [17].

The adsorption constant, K, it is related to the free standard of adsorption energy, ΔG_{ads}, with the following equation [72].

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G_{\mathrm{ads}}}{RT}\right) \tag{5}$$

Where 55.5 is the water concentration of the solution in ml/l [73]. Therefore, the K–values allow calculating the most important thermodynamic adsorption parameter which is the free energy of adsorption (ΔG_{ads}). The values of the free energy of adsorption (ΔG_{ads}), the enthalpy of adsorption (ΔH_{ads}) and the adsorption entropy (ΔS_{ads}) are presented in Table 4.

Table 4. Thermodynamic parameters for the adsorption of henna extract in 1 M HCl on the mild steel at different temperatures [17].

Temperature, K	***K*, l/g**	**Slope**	r^2	ΔG_{ads}**, kJ/mol**	ΔH_{ads}**, kJ/mol**	ΔS_{ads}**, J/mol·K**
298	5.49	0.96	0.994	–14.170	–54.76	–135.1
313	2.63	0.99	0.985	–12.968	–54.76	–135.1
333	1.24	1.05	0.994	–11.363	–54.76	–135.1
353	1.02	1.10	0.994	–9.414	–54.76	–135.1

From the thermodynamic parameters given in the Table 4, we can make the following interpretations: the values in ΔG_{ads} increase with the increase in temperature, which indicates the presence of the exothermic process. In an exothermic process, the adsorption was unfavorable with the increase of the reaction temperature due to desorption of the inhibitor from the steel surface. Several researchers believe that for values of ΔG_{ads} close to –20 kJ/mol, this corresponds to electrostatic interactions between the charged molecules and the charges of the metal (physisorption), on the other hand, when ΔG^0_{ads} is close to –40 kJ/mol, it corresponds to a transfer of charges between the molecules of the inhibitor and the surface of the metal by forming covalent bonds (chemisorption) [74]. Indeed, in the case of henna extract it is a physisorption. Also, the negative sign of ΔH_{ads} reveals that the adsorption of inhibitor molecules is an exothermic process [75]. Since the absolute values of the enthalpy ΔH_{ads} are relatively high (more than 41.86 kJ/mol), indeed in the case of henna extract it is a physisorption.

3.4 Corrosion inhibition of henna constituents

It is now known that henna extract provides inhibition to mild steel corrosion in HCl media; however, the characteristic of the constituents that provide the inhibition is still unclear. To identify the probable constituents responsible for the inhibition, the chemical composition of the extract was studied by use of gas chromatography and mass spectrometry (GC–MS). Polarization measurements and EIS were conducted to compare the protection provided by the extract and its constituents alone in HCl. From GC–MS analysis (Table 5), the henna extract consists of lawsone (2-hydroxy-1,4-naphthoquinone, $C_{10}H_6O_3$), gallic acid (3,4,5-trihydroxybenzoic acid, $C_7H_6O_5$), dextrose (α-*D*-glucose, $C_6H_{12}O_6$) and tannic acid.

Table 5. GC–MS data of henna extract [17].

Retention time, min	**Compounds structure**	**Molecular formula**

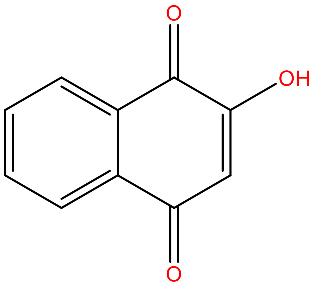
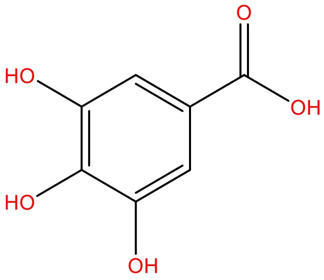
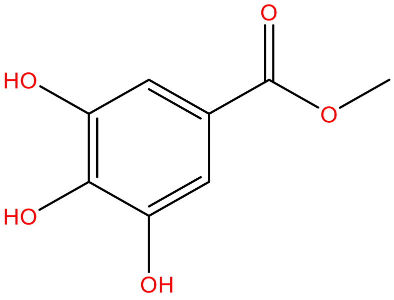
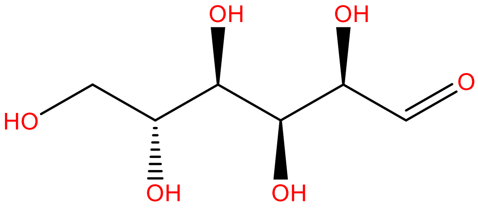
	Name	
3.72	 lawsone	$C_{10}H_6O_3$
4.17		$C_{10}H_6O_3$
4.37		$C_{10}H_6O_3$
4.54		$C_{10}H_6O_3$
4.63		$C_{10}H_6O_3$
5.23		$C_{10}H_6O_3$
7.45	 gallic acid	$C_7H_6O_5$
7.84		$C_7H_6O_5$
8.18		$C_7H_6O_5$
8.37		$C_7H_6O_5$
10.77	 Methyl gallate	$C_8H_8O_5$
11.22		$C_8H_8O_5$
14.74	 dextrose	$C_6H_{12}O_6$
15.18		$C_6H_{12}O_6$

Table 6 gives the evaluation of the inhibition characteristics of each component of the henna extract. The purpose of this section is to compare the inhibition provided by the henna constituents to find the main component of corrosion inhibition of the plant extract.

Table 6. Kinetic parameters of mild steel in 1 M HCl at 298±1 K containing different concentrations of henna constituents [17].

Medium	**$-ß_c$, mV/dec**	**E_{corr}, mV/SCE**	**I_{corr}, mA/cm^2**	***IE*%**
HCl	149	–523.5	0.4825	–
0.2 g/l Lawsone	137	–514.7	0.1789	62.92
0.5 g/l Lawsone	132	–507.5	0.1360	71.81
0.8 g/l Lawsone	129	–511.9	0.0802	83.37
1.0 g/l Lawsone	127	–508.5	0.0268	94.44
0.2 g/l Gallic acid	129	–512.9	0.3345	30.67
0.5 g/l Gallic acid	126	–502.7	0.2804	41.88
0.7 g/l Gallic acid	119	–515.8	0.1943	59.73
0.9 g/l Gallic acid	115	–509.6	0.1773	63.25
0.2 g/l α-D-Glucose	124	–506.4	0.3692	23.48
0.5 g/l α-D-Glucose	119	–510.1	0.3019	37.43
0.7 g/l α-D-Glucose	118	–513.6	0.2500	48.18
4.0 g/l Tannic acid	131	–508.1	0.3845	20.31
4.5 g/l Tannic acid	129	–513.7	0.3445	28.60
5.2 g/l Tannic acid	127	–504.6	0.3288	31.85
5.8 g/l Tannic acid	126	–509.0	0.3149	34.73

Figure 5 shows the potentiodynamic anodic and cathodic polarization plots for mild steel in (1 M) HCl solution in the absence and presence of different concentrations of henna constituents.

After analysis of the results obtained in Table 6 and Figure 5 we can make the following interpretations: The presence of different concentrations of henna constituents causes a marked change in both the cathodic and anodic branches of the polarization curves towards a lower current density compared to white. No change in the E_{corr} corrosion potential is observed. This behavior reveals that all henna constituents reduce mild steel corrosion in HCl solution and behave as a mixed type inhibitor. Also, the presence of different concentrations of henna constituents has no significant change in the cathodic slope of Tafel $ß_c$ compared to white. The inhibitory efficacy of Lawsone, tannic acid, Gallic acid and dextrose increases with inhibitor concentration up to a critical concentration for the respective constituent. The inhibitory action for these constituents increases in the following order: Lawsone > Gallic acid > α-*D*-Glucose > Tannic acid. Therefore, Lawsone can be attributed as the component responsible for the inhibitory action of henna extract. The Nyquist diagrams for mild steel in (1 M) HCl solution in the absence and presence of different concentrations of henna constituents are shown in Figure 6.

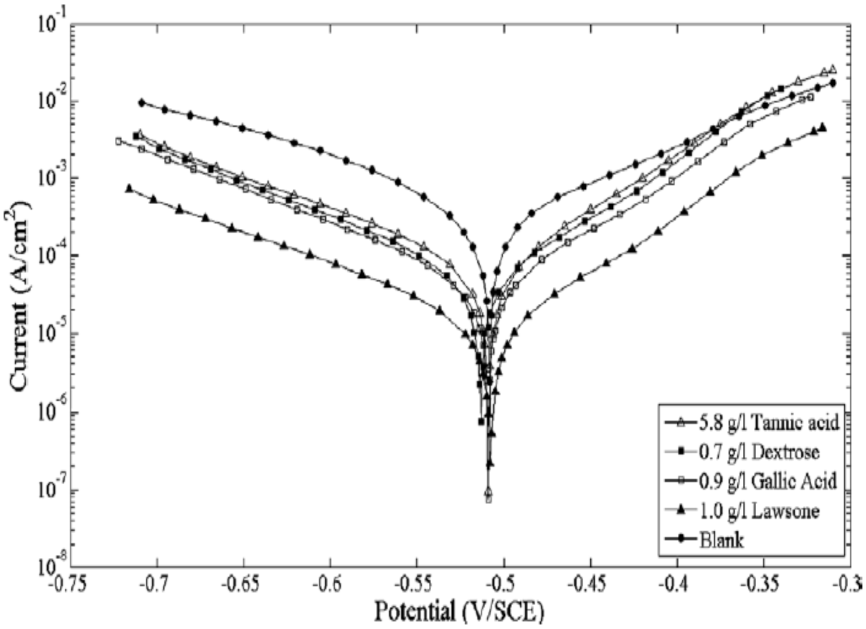


Figure 5. Polarization curves for mild steel in (1 M) HCl at 298±1 K containing different concentrations of henna constituents [17].

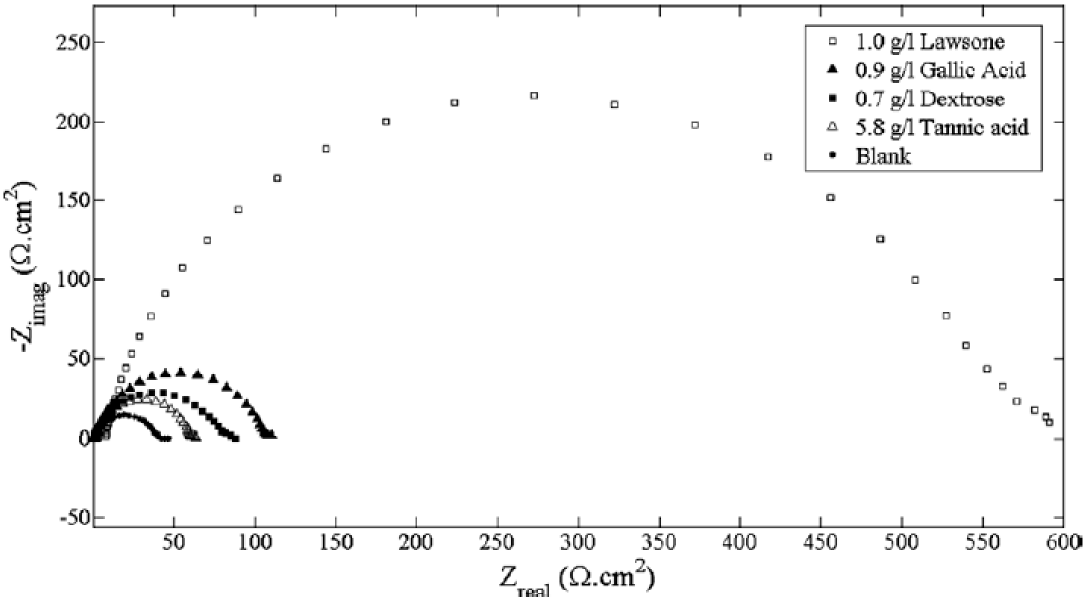


Figure 6. Nyquist plots for mild steel in (1 M) HCl at 298±1 K containing different concentrations of henna extract constituents [17].

The impedance parameters derived from these investigations (using an equivalent circuit from Figure 3) are given in Table 7.

Table 7. Impedance parameters of mild steel in (1 M) HCl at 298±1 K containing different concentrations of henna extract [17].

Concentration	R_p, $\Omega \cdot cm^2$	f_{max}, Hz	C_{dl}, $\mu F/cm^2$	*IE*%
HCl	42.28	41.89	89.85	–
0.2 g/l Lawsone	115.14	24.74	32.99	63.28
0.5 g/l Lawsone	158.58	18.62	23.95	73.34
0.8 g/l Lawsone	237.66	13.79	15.97	82.21
1.0 g/l Lawsone	588.85	18.62	6.44	92.82
0.2 g/l Gallic acid	59.45	13.79	63.90	28.88
0.5 g/l Gallic acid	74.92	18.62	50.70	43.57
0.7 g/l Gallic acid	98.39	18.62	38.60	57.03
0.9 g/l Gallic acid	109.50	24.74	34.69	61.39
0.2 g/l α-D-Glucose	56.47	24.74	67.27	25.13
0.5 g/l α-D-Glucose	66.90	18.62	56.78	36.80
0.7 g/l α-D-Glucose	85.03	18.62	44.67	50.28
4.0 g/l Tannic acid	52.04	18.62	73.00	18.75
4.5 g/l Tannic acid	57.76	24.74	65.77	26.80
5.2 g/l Tannic acid	60.09	13.76	63.21	29.64
5.8 g/l Tannic acid	62.30	18.62	60.98	32.13

Based on the analysis of the curves shown in Figure 6 and the results in Table 7, we can make the following interpretations: the impedance diagrams show capacitive semicircles indicating a load transfer process that mainly controls the corrosion of mild steels. The presences of different concentrations of henna constituents increase the R_p value in acidic solution. In addition, the values of the double layer capacitance are decreased in the presence of different concentrations of henna constituents. The decrease in C_{dl} is due to the adsorption of these compounds on the metal surface [76]. The inhibition efficiency of Lawsone, tannic acid, Gallic acid and dextrose increases with the inhibitor concentration up to a critical concentration for the respective component. The inhibitory action for these constituents increases in the following order: Lawsone>Gallic acid>α-D-Glucose>Tannic acid. This order reflects the important role played by lawsone molecules. It has the highest inhibitory efficacy among the other constituents. Therefore, Lawsone can be attributed to the constituent responsible for the inhibitory action of henna extract inhibitor.

3.5 Inhibition mechanism

As a result of weight loss, potentiodynamic polarization and SIE measurements, corrosion of mild steel in (1 M) HCl is retarded in the presence of different concentrations of henna extract. The results clearly showed that the inhibition mechanism involves blocking of the mild steel surface by adsorption of inhibitor molecules. In general, the adsorption phenomenon is influenced by the nature of the metal and the chemical structure of the inhibitor. The values of the thermodynamic parameters for the adsorption of inhibitors can provide valuable information on the corrosion inhibition mechanism [77]. As mentioned in Table 4 the values of ΔH_{ads} and the increase of the free energy of adsorption are typical for physisorption. The possible mechanism of physisorption can be attributed to the formation of the complex between the lawsone molecule and the metal cations. The lawsone molecule is a ligand that due to chelation with various metal cations can form complex compounds. The inhibitory action of Lawsone has been attributed to the formation of insoluble complex compounds combined with metal cations and lawsone molecules that are adsorbed on the mild steel surface

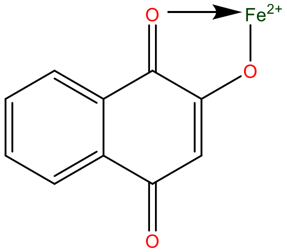


Figure 7. Structure formulas of the formed complex compounds [17].

3.6 Weight loss for acetic acid

In the second study the use Rectangular specimens of the size 4.5× 2.0× 0.2 cm having an area of 0.2097 sq.dm. of mild steel with small hole of 5 mm diameter near the upper edge, were used for the determination of corrosion rate. The specimens were polished by buffing, cleaned with distilled water several times, then degreased by acetone for 1–2 min, then dried in warm air by air drier and are preserve in desiccator till use [64].

In acetic acid medium, one specimen only was suspended by a glass hook, in each beaker containing 230 ml of the test solution and was open to air at room temperature for 24 h. After the immersion period, the test specimens were clean with distilled water, dried and weighted. Triplicate experiments were performed in each case and the mean value of weight loss data were presented in mg/sq.dm. The concentration of acetic acid studied were taken as 0.5, 1.0, 1.5 and 2.0 M without and with inhibitors having concentration of 1, 0.5, 0.25 and 0.1 g/l for weight loss measurement at the room temperature of 303±1 K [64].

Effect of different concentration (1, 0.5, 0.25 and 0.1 g/l) of henna leaves extract was studied in 0.5, 1.0, 1.5 and 2.0 M acetic acid solution at room temperature of 303±1 K for exposure period of 24 h. The obtained results are presented in Table 8.

Table 8. Effect of acid concentration on corrosion loss (*CL*) and inhibition efficiency (*IE*%) of henna leaves extract on mild steel [64].

Inhibitor concentration, g/l	**Acid concentration**							
	0.5 M		**1.0 M**		**1.5 M**		**2.0 M**	
	***CL* mg/dm^2**	***IE*%**	***CL* mg/dm^2**	***IE*%**	***CL* mg/dm^2**	***IE*%**	***CL* mg/dm^2**	***IE*%**
Blank	486.41	–	629.47	–	767.76	–	891.75	–
0.1	119.22	75.49	157.37	75.00	195.52	74.53	224.13	74.56
0.25	95.37	80.39	123.99	80.30	152.60	80.12	181.21	79.68
0.5	81.07	83.33	109.68	82.26	133.52	82.60	157.37	82.35
1.0	66.76	86.27	85.84	86.36	104.92	86.33	123.99	86.0 9

From the results shown in Table 8 it can be concluded that the corrosion loss has been increased from 486.41 to 891.75 mg/dm^2 in 1.0 to 2.0 M acetic acid solution. It has been observed that the corrosion rate increases with increase in the acid concentration. It can be concluded that corrosion rate is directly proportional to the acid concentration.

3.7 Chemical measurements and potentiodynamic polarization for acetic acid

The PDP plots for mild steel specimens in 0.5 M acetic acid solution in the absence and presence of different concentrations of henna extract are shown in Figure 8.

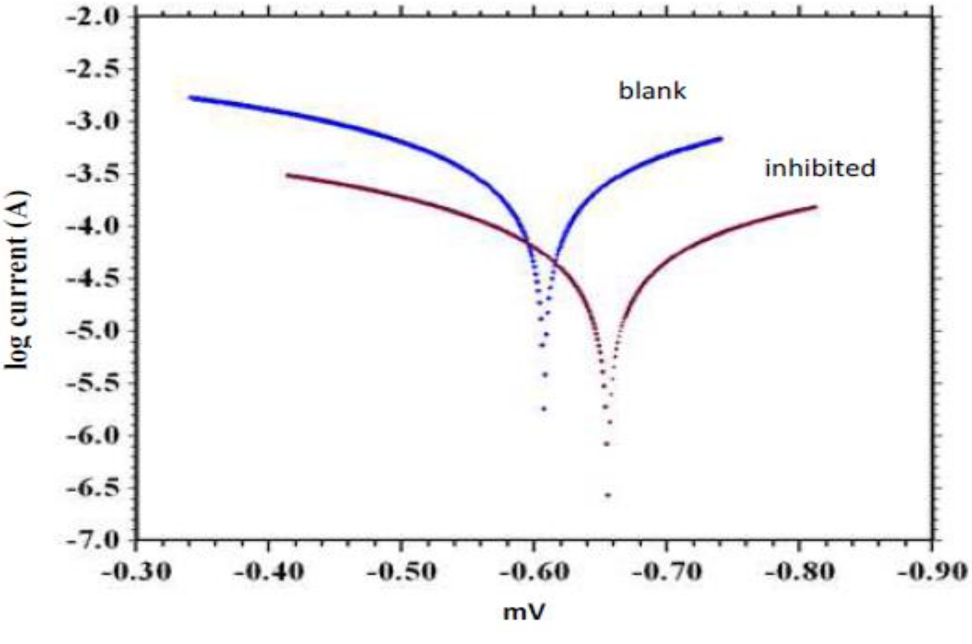


Figure 8. Polarization curves of mild steel in 0.5 M acetic acid blank and inhibited solutions [64].

Table 9. Polarization parameters of mild steel in absence and presence of henna leaves extract in 0.5 M acetic acid solution at 298 K [64].

Corrosion current density			**Tafel slope (mV/decade)**			**Inhibition efficiency (*IE*%) calculated from**	
System	**E_{corr}, mV**	**I_{corr}, mA/cm^2**	**Anodic, $+\beta_a$**	**Cathodic, $-\beta_c$**	**β, mV**	**Weight loss method**	**Polarization method**
Blank	–0.610	244	5.195	4.659	1.0679	–	–
Henna	–0.665	45.57	5.331	4.649	1.0797	86.27	80.91

The value of I_{corr} in Table 9 decreases significantly in presence of inhibitor, this observation indicates that henna leaves extract was effectively inhibit the corrosion of mild steel in acetic acid solution. The presence of henna leaves extract did not change cathodic Tafel slope (β_c) significantly, indicating that inhibitor molecule does not affect the hydrogen evolution reaction. The increase in anodic Tafel slope (β_a) with addition of inhibitor shows that the adsorbed inhibitor modifies the metal dissolution process [78]. The E_{corr} value of inhibited solution slightly shifted. The changes in E_{corr} less than ±85 mV indicate that the inhibitor is of mixed type inhibitor [79]. The change in E_{corr} is about 55 mV in presence of inhibitor according to uninhibited solution, reveals that the henna leaves extract act as mixed type inhibitor.

3.8 Electrochemical Impedance Spectroscopy (EIS) in 0.5 M acetic acid solution

In the second study electrochemical impedance spectroscopy (EIS) was carried out in frequency range 1 to 100 kHz and A.C. amplitude of 5.0 mV. The measurement was carried out after stabilization of the electrode at OCP for 30 min at room temperature [64].

The typical Nyquist plots of mild steel in the absence and presence of henna leaves extracts in acetic acid solution was presented in Figure 9.

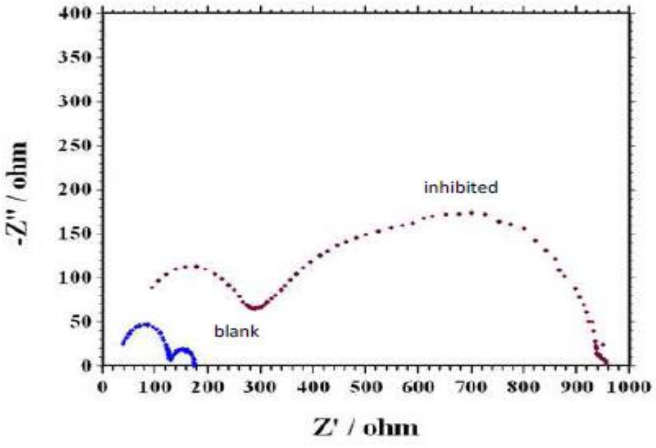


Figure 9. Impedance diagrams obtained for mild steel in 0.5 M acetic acid solution in the absence and presence of henna leaves extract at 1.0 g/l concentrations [64].

From the Figure 9 it was observed that the diameter of the semicircle increases in the case of inhibited acid solution indicated an increase in corrosion resistance of system.

Table 10. Impedance parameters for corrosion of mild steel in 0.5 M acetic acid in the absence and presence of henna leaves junipers extract [64].

System	R_{ct}, Ω·cm^2	C_{dl}, μF/cm^2	Inhibition efficiency (*IE*%) Calculated from	
			Impedance measurement	Weight loss method
Blank	56.22	145	–	–
Henna, 1.0 g/l	1399.97	0.6714	95.98	86.27

As the values stated in Table 10, the extract of henna leaves increases the value of R_{ct}. The value of C_{dl} decrease in presence of the inhibitor compare to uninhibited acid solution. This result may be attributed to the adsorption of the component present in the aqueous extract of henna leaves on metal surface [43].

3.9 Thermodynamic parameters of adsorption in 1 M acetic acid

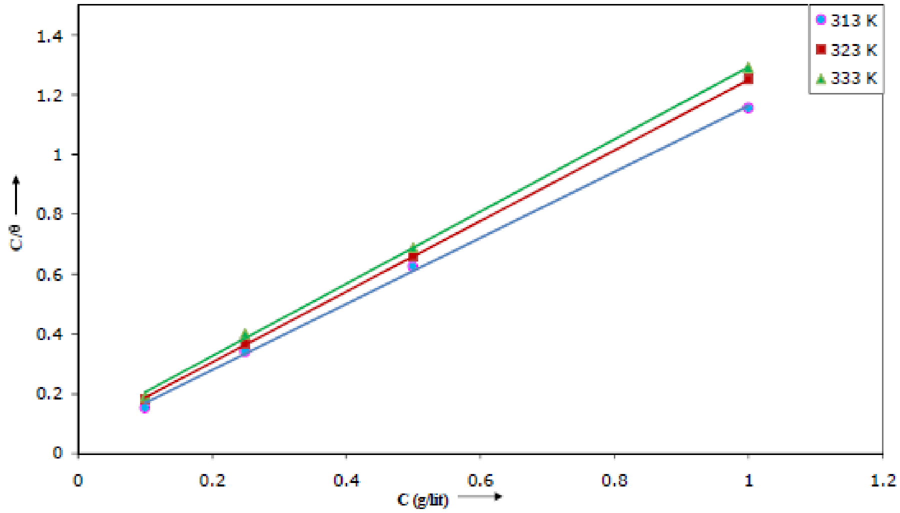


Figure 10. Langmuir adsorption isotherm plot for the adsorption of henna leaves extract in 1.0 M acetic acid solution at different temperature [64].

From Table 11 we can make the following interpretations: the negative value of ΔH^0_{ads} suggest that the process of adsorption of inhibitor on mild steel surface is exothermic. It can be assuming that the increases in temperature leads to the increase in desorption of the adsorbed inhibitor molecule from the mild steel surface [80]. The value of ΔS is positive. Generally, adsorption is an exothermic process and always accompanied by a decrease in entropy. The reason can be explained as; the process adsorption of inhibitor molecule is accompanied by desorption of water molecule from the mild steel surface.

Table 11. Thermodynamic parameters for the adsorption of henna leaves extract on mild steel surface [64].

Temperature, K	K_{ads}, kJ/mol	ΔH_{ads}, kJ/mol	ΔS_{ads}, J/mol·K	ΔG_{ads}, kJ/mol
313	18.18	–17.24	2.43	–17.99
323	15.38	–	2.74	–18.12
333	12.19	–	2.43	–18.04

The adsorption occurs as the result of substitution adsorption process between inhibitor molecule present in solution and the water molecule previously adsorbed on the metallic surface [81]. In addition, the thermodynamic values obtained are algebraic sum of the adsorption of inhibitor molecule and desorption of water molecule surface [81].

4. Conclusion

- The corrosion rate of mild steel increases with increasing acetic acid concentration and with increasing temperature in 1 M HCl medium.
- The henna leaves extract found to be effective inhibitor for mild steel in acetic acid and hydrochloric acid, their inhibition efficiency increase with increase in its concentration.
- Henna extract acts as a mixed inhibitor for the corrosion of mild steels in 1 M HCl and 0.5 M Acetic acid mediums; the inhibition efficiency increases with increasing inhibitor concentration up to a maximum value of 92.06% at 1.2 g/l henna extract in 1 M HCl and 95.98% at 1 g/l in 0.5 M acetic acid mediums.
- All henna constituents examined act as mixed type inhibitors for mild steel corrosion in 1 M HCl with good inhibition efficiencies in the following order: Lawsone > Gallic acid > α-*D*-Glucose (dextrose) > Tannic acid.
- The main inhibition mechanism is the physisorption of inhibitor molecules on the steel surface while the inhibitory action is slightly enhanced by oxygen scavenging.
- The main constituent responsible for the corrosion inhibition characteristic of henna extract is lawsone.
- The results obtained from weight-loss, potentiodynamic polarization and impedance measurement techniques were in good agreement.

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Competing interests

The authors declare that they have no competing interests.

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