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## FULL LENGTH ARTICLE

# Thermodynamic, adsorption and electrochemical studies for corrosion inhibition of carbon steel by henna extract in acid medium

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Received 14 May 2012; accepted 19 June 2012

### KEYWORDS

Carbon steel;  
Corrosion inhibition;  
Henna extract;  
Thermodynamic parameters

**Abstract** Corrosion inhibition of carbon steel in the presence of different concentrations of aqueous extract from henna leaves in 1 M HCl solution has been studied using the weight loss and potentiodynamic polarization techniques. The effect of temperature on the corrosion behavior of carbon steel was studied in the temperature range 293–333 K. The inhibition efficiency increases with increasing inhibitor concentration but decreases with increasing temperature. The activation and free energies for the inhibition reactions support the mechanism of physical adsorption. The adsorption of henna extract on C-steel surface is endothermic, spontaneous and consistent with the Langmuir adsorption isotherm. The potentiodynamic polarization measurements indicate that henna extract acts as a mixed inhibitor. Surface and protective film analysis have been carried out using; energy dispersive X-ray (EDX), scanning electron microscopy (SEM), Fourier transforms infrared (FT-IR) spectroscopy and X-ray diffraction (XRD) analysis.

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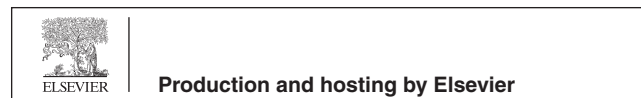
## 1. Introduction

The study of carbon steel corrosion phenomena has become important particularly in acidic media because of the increased

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Peer review under responsibility of Egyptian Petroleum Research Institute.



industrial applications of acid solutions. As an example, the refining of crude oil results in a variety of corrosive conditions. Refinery corrosion is generally caused by a strong acid attack the equipment surface. The other important fields of application are acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and the petrochemical processes [1]. Among the acid solutions, hydrochloric acid is one of the most widely used agents.

The effect of temperature on a chemical reaction is of practical and theoretical importance. Like most chemical reactions, the rate of corrosion of iron and steel increases with temperature especially in media in which evolution of hydrogen accompanies corrosion, e.g. during corrosion of steel in acids. Acid pickling of steel is usually carried out at elevated temperature

up to 60 °C in hydrochloric acid (HCl) solutions and up to 90 °C in sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) solutions [2].

Temperature effects on acidic corrosion and corrosion inhibition of iron and steel most often in acidic solutions had been the object of a large number of investigations [3–7]. Temperature dependence of the inhibitor efficiency and the comparison of the obtained thermodynamic data of the corrosion process both in absence and presence of inhibitors lead to some conclusions concerning the mechanism of inhibiting action.

Although many synthetic compounds show good anticorrosive action, most of them are highly toxic to both human beings and environment. These inhibitors may cause temporary or permanent damage to organs such as kidneys or liver, or to disturb a biochemical process or enzyme system at some sites in the body [8]. The toxicity may manifest either during the synthesis of the compound or during its applications. These lead investigations to focus on the use of naturally occurring substances in order to find low-cost and non-hazardous inhibitors.

Plant extracts have become important as an environmentally acceptable, readily available and renewable source of materials for wide range of corrosion prevention; therefore, in Egypt; finding naturally occurring substances as corrosion inhibitors is a subject of great practical significance [9–16].

Few studies have investigated corrosion inhibition of henna extract on some metals such as aluminum, iron, zinc and nickel in acidic and alkaline solutions [17–20]. Henna is a herb which has interesting dyeing properties used for centuries in Asia and North Africa for traditional decoration of the skin and hair.

In the present work, inhibitive action of henna extract as a cheap, eco-friendly and naturally occurring substance on corrosion behavior of carbon steel in 1 M HCl has been investigated through weight loss and potentiodynamic polarization measurements. Inhibited metallic surfaces are examined with energy dispersive X-ray (EDX) and scanning electron microscopy (SEM). Protective film was subjected to Fourier transforms infrared spectroscopy (FT-IR) and X-ray diffraction (XRD) analysis. This study aimed also to investigate the temperature effects on C-steel corrosion in 1 M HCl in the absence and presence of various additions of aqueous extract from henna leaves using a gravimetric method. Various thermodynamic parameters for inhibitor adsorption on carbon steel surface were estimated, discussed and the inhibition mechanism was suggested.

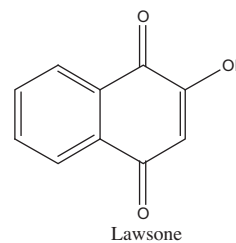
## 2. Experimental

### 2.1. Preparation of specimens

Carbon steel alloy specimens used in this investigation were cut from unused petroleum pipeline as regular edged cuboids, with dimensions 10 × 20 × 1 mm. The used mild C-steel coupons have percent composition (wt.%) of 98.38% Fe, 0.28% C, 1.25% Mn, 0.05% S and 0.04% P. These coupons were polished with emery papers with different grades, starting with the coarse one and proceeding in steps to the finest (600) grade, washed with deionized water, degreased with acetone, dried and weighed before experiments.

### 2.2. Preparation of plant extract

Hundred grams of crashed henna leaves were refluxed in 250 mL double distilled water for three hours. The refluxed



**Scheme 1** Lawsone structure.

solutions were filtered to remove any contamination and then dried under vacuum to a constant weight. This plant extract was found to be 40% (wt.%) of the used henna dry weight. The solid extract was used to prepare the required concentrations of henna to study the corrosion inhibition properties. It is reported that henna leaves extract contain lawsone (2-hydroxy-1, 4-naphthoquinone, C<sub>10</sub>H<sub>6</sub>O<sub>3</sub>), resin and tannin, coumarins, gallic acid and sterols [19], Scheme 1.

### 2.3. Solutions preparation

A stock solution of 1 M HCl was prepared from 35.4% HCl (Merck) using distilled water. The concentration range of henna extract employed was varied from 100 to 3000 mg/L.

### 2.4. Weight loss measurements

Experiments were performed at 20, 30, 40, 50 and 60 °C with different concentrations of henna extract. The immersion time for the weight loss measurements is 24 h. All experiments are in triplicates and illustrated data are mean values of obtained results.

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

$$IE\% = \left( \frac{W_1 - W_2}{W_1} \right) \times 100 \quad (1)$$

where  $W_1$  and  $W_2$  are the weight loss of C-steel in absence and presence of inhibitor, respectively.

### 2.5. Potentiodynamic polarization measurements

Electrochemical measurements were carried out in a conventional three electrode cylindrical glass cell. Platinum electrode was used as a counter electrode, saturated calomel electrode (SCE) as the reference electrode and cylindrical rod of C-steel alloy was used as working electrode. Potentiodynamic polarization curves were scanned at a rate of 1 mV/s using a potentiostat EG & G model 273 with computer driven (EG & G M352 software) manufactured by EG & G Instrument Inc. All the measurements were carried out at room temperature in air-saturated solutions under unstressed conditions. To test the reliability and reproducibility of the measurements, triplicate experiments were performed in each case of the same conditions. The inhibition efficiency IE% was calculated using the following equation:

$$IE\% = \left( \frac{I_1 - I_2}{I_1} \right) \times 100 \quad (2)$$

where  $I_1$  and  $I_2$ , are the corrosion current density of carbon steel in the absence and presence of inhibitor, respectively.

The polarization resistance ( $R_p$ ) was calculated using Eq. (3):

$$R_p = \frac{\beta_a \beta_c}{2.303 I_{\text{corr}} (\beta_a + \beta_c)} \quad (3)$$

where  $\beta_a$  and  $\beta_c$  are the slopes of the anodic and the cathodic Tafel lines, respectively.

## 2.6. Surface analysis

### 2.6.1. Energy dispersive X-ray analysis

The surface film formed on the metal specimen was examined by energy dispersive X-ray analysis (EDX). This was carried out with a Jeol 5400 scanning electron microscope (SEM) in conjugation with an energy dispersive spectrometer. The spectra were recorded on samples immersed for a period of 48 h in 1 M HCl in the absence and presence of optimum concentration of the inhibitor. The energy of the acceleration beam employed was 30 kV.

### 2.6.2. SEM analysis

Surface morphological examination of C-steel specimens after immersions for 48 h in acid solution containing optimum concentration of inhibitor and without inhibitor (blank) was performed using JEOL-model JSM-53000 scanning electron microscope (SEM). The working sample was analyzed at three different locations to ensure reproducibility.

## 2.7. Analysis of protective film

### 2.7.1. Fourier transforms infrared (FT-IR) spectroscopy

For FT-IR studies, analytical FT-IR Perkin Elmer, instrument was used. The surface of the dried specimens was scratched and the resultant powder was used. In case of FT-IR studies of plant extract, vacuum dried plant extract liquid was used. The samples were measured as KBr disks by mixing the sample with KBr (spectroscopic grade) where the solid samples were transferred into the cell after melting using an infrared lamp. The spectra of all studied samples were measured in the range of 400–4000  $\text{cm}^{-1}$  with suitable scan resolution 4  $\text{cm}^{-1}$  and scan rate 16  $\text{cm}/\text{min}$ .

### 2.7.2. X-ray diffraction analysis

C-steel coupons were immersed in 1 M HCl for 48 h in absence and presence of optimum concentration of the inhibitor. The corrosion products developed on the surface of the coupons were taken up, gently powdered and homogenized. The identification of the phases was carried out using PANalytical XPERT PRO MPD X-ray powder diffractometer.  $\text{Cu K}_\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) was used at a rating of 40 kV, 40 mA. The diffraction patterns were recorded at room temperature in the angular range of 4°–80° ( $2\theta$ ) with step size 0.02° ( $2\theta$ ) and scan step time 0.4 (s). The crystalline phases formed on the carbon steel surface, in both cases, were identified using the ICDD-PDF database.

## 3. Results and discussion

### 3.1. Weight loss measurements and effect of temperature

The corrosion rate and inhibition efficiency for C-steel in 1 M HCl solution at 20, 30, 40, 50 and 60 °C in the absence and presence of henna extract are given in Table 1. The presence of inhibitor leads to decrease the corrosion rate. It is indicated that inhibition efficiency of C-steel increases with the increase of henna extract concentration up to 88.42% at 20 °C. As the temperature increases, the corrosion rate (C.R.) increases and inhibition efficiency decreases. At 30, 40, 50 and 60 °C maximum inhibition efficiencies of 85.32%, 79.52%, 75.69% and 67.73% were obtained in 1 M HCl solution containing 3000 mg/L henna extract, respectively. The increase in C.R. is more pronounced with the rise of temperature for the uninhibited acid solution. The results show that the addition of henna extract decreases metal dissolution in 1 M HCl medium. This hindrance to dissolution may be due to the formation of the Fe–henna extract complex layer [1].

### 3.2. Activation energy calculations

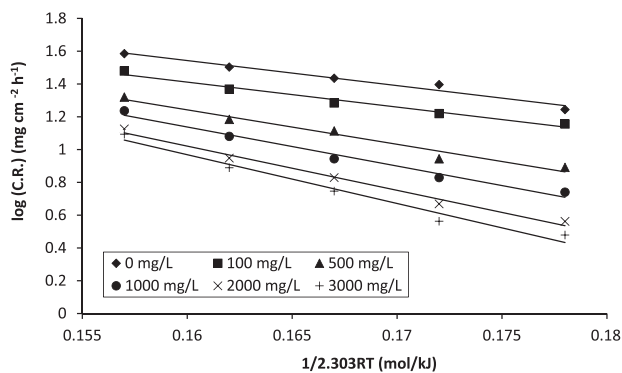
The activation energy ( $E_a$ ) can be determined from Arrhenius plots for C-steel corrosion rate (C.R.  $\text{mg}/\text{cm}^2 \text{ h}$ ) presented in Fig. 1 by the following relation:

$$\log(\text{C.R.}) = \log A - \frac{E_a}{2.303 RT} \quad (4)$$

where  $A$  is the Arrhenius pre-exponential constant,  $T$  is the absolute temperature (K) and  $R$  is the universal gas constant (8.314 J/mol K).

**Table 1** Corrosion parameters obtained from weight loss of C-steel in 1 M HCl containing various concentrations of henna extract at different temperatures.

Electrolyte (mg/L henna)	Temperature														
	293 K			303 K			313 K			323 K			333 K		
	C.R. $\text{mg}/\text{cm}^2 \text{ h}$	IE %	$\theta$	C.R. $\text{mg}/\text{cm}^2 \text{ h}$	IE %	$\theta$	C.R. $\text{mg}/\text{cm}^2 \text{ h}$	IE %	$\theta$	C.R. $\text{mg}/\text{cm}^2 \text{ h}$	IE %	$\theta$	C.R. $\text{mg}/\text{cm}^2 \text{ h}$	IE %	$\theta$
0	17.54	–	–	24.92	–	–	27.26	–	–	31.88	–	–	38.48	–	–
100	14.33	36.21	0.36	16.58	33.44	0.33	19.26	29.33	0.29	23.38	26.67	0.27	30.17	21.60	0.22
500	7.79	66.56	0.66	8.79	64.72	0.65	13	51.05	0.51	15.29	52.03	0.52	20.92	45.64	0.46
1000	5.5	74.85	0.74	6.75	72.91	0.73	8.79	67.75	0.68	12.04	62.22	0.62	17.25	55.17	0.55
2000	3.65	84.27	0.84	4.67	83.32	0.81	6.42	76.46	0.76	8.88	72.16	0.72	13.38	65.24	0.65
3000	3.01	88.42	0.88	3.66	85.32	0.85	5.58	79.52	0.79	7.75	75.69	0.76	12.42	67.73	0.68



**Figure 1** Arrhenius plot for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of henna extract.

It is obvious from data listed in Table 2 that,  $E_a$  of the inhibited solution in this study increases by increasing the inhibitor concentration indicating strong adsorption of the inhibitor molecules at the metal surface [21]. The range of  $E_a$  values (15.27–29.75 kJ/mol) are lower than the threshold value of 80 kJ/mol, required for chemical adsorption. This means that the adsorption is physical adsorption. It is clear from Eq. (4) that C.R. is influenced by both  $E_a$  and  $A$ . It is evident from Table 2 that the value of  $A$  and  $E_a$  increased on addition of henna extract in comparison to the uninhibited solution. Decrease in the C.R. by increasing inhibitor concentration in this study suggests that  $E_a$  is the deciding factor rather than  $A$  [21].

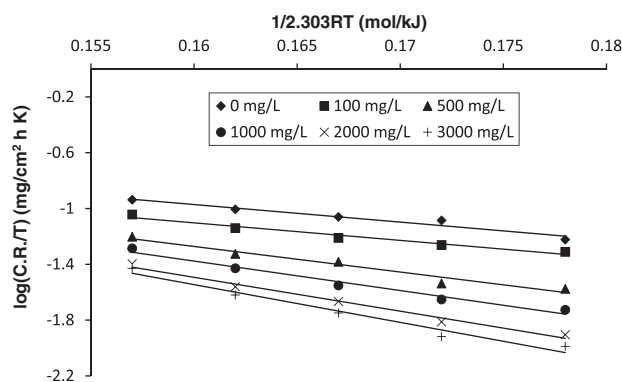
An alternative form of Arrhenius equation is the transition-state equation:

$$\log\left(\frac{\text{C.R.}}{T}\right) = \left[\log\left(\frac{R}{hN}\right) + \left(\frac{\Delta S^*}{2303R}\right)\right] - \frac{\Delta H^*}{2.303RT} \quad (5)$$

where  $h$  is the Planck's constant  $6.6261 \times 10^{-34}$  Js and  $N$  is the Avogadro's number  $6.0225 \times 10^{23}$  mol $^{-1}$ .

Fig. 2 shows a plot of  $\log(\text{C.R.}/T)$  versus  $1/2.303 RT$ . Straight lines are obtained with a slope, enthalpy of activation ( $\Delta H^*$  kJ/mol) and from the intercepts of  $\log(\text{C.R.}/T)$ -axis, the entropy of activation, ( $\Delta S^*$  kJ/mol) values were calculated and are given in Table 2. The positive values of  $\Delta H^*$  (12.56–27.08 kJ/mol) reflect the endothermic nature of metal dissolution process. The increase in  $\Delta H^*$  with increasing inhibitor concentration reveals that decrease in C-steel C.R. is mainly controlled by the kinetic parameters of activation [22].

It is well noticed that the values of  $E_a$  are larger than the analogous values of  $\Delta H^*$  indicating that the corrosion process involved a gaseous reaction, simply the hydrogen evolution



**Figure 2** Transition state plot for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of henna extract.

reaction, associated with a decrease in the total reaction volume [1]. Moreover, the average difference value of the  $E - \Delta H^*$  is 2.67 kJ/mol, which is approximately equal to the average value of  $RT$  (2.61 kJ/mol). Therefore, it is indicated that the corrosion process is a unimolecular reaction as it is characterized by the following equation:

$$E_a - \Delta H^* = RT \quad (6)$$

Large and negative values of entropy of activation  $\Delta S^*$ , show that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to the activated complex. It is clear from data listed in Table 2,  $\Delta S^*$  increased (lower negative values) in the presence of the studied inhibitor compared to free acid solution. In the free acid solution it can be explained as follows: the transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state, so a high value for the entropy of activation is obtained. In the presence of inhibitor, however, the rate determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms. Since the surface is covered with inhibitor molecules, this will retard the discharge of hydrogen ions at the metal surface causing the system to pass from a random arrangement, and hence entropy of activation is increased. The increase of  $\Delta S^*$  (–171.81 to –138.45 J/mol) with increasing inhibitor concentration, reveals that an increase in disordering takes place on going from reactant to the activated complex. This behavior can be explained as a result of the replacement process of water molecules during adsorption of henna extract on C-steel surface [23].

**Table 2** Activation parameters of the dissolution of carbon steel in 1 M HCl in the absence and presence of different concentrations of henna extract at different temperatures.

Electrolyte (mg/L henna)	A mg/cm $^2$	$E_a$ (kJ/mol)	$\Delta H^*$ (kJ/mol)	$\Delta S^*$ (J/mol K)
0.0	7037	15.23	12.56	–174.48
100	9685	15.27	12.60	–171.81
500	40169	21.01	18.34	–159.98
1000	88491	23.81	21.14	–153.42
2000	216023	26.96	24.29	–145.99
3000	535180	29.75	27.08	–138.45

### 3.3. Adsorption isotherm analysis and thermodynamic parameters

The effectiveness of organic compounds as corrosion inhibitors can be ascribed to the adsorption of molecules of the inhibitors through their polar functions on the metal surface. The metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, the adsorption of inhibitor molecules from aqueous solution is a quasi substitution process [24].

The observed inhibitive action of henna extract could be due to the adsorption of its molecules on the steel surface making a barrier for charge and mass transfer between the metal and the environment. It is well observed from data listed in Table 1., that at all the studied temperatures (293–333 K), as the concentration of inhibitor increased, the fraction of steel surface covered by the adsorbed molecules ( $\theta$ ) increases leading to higher inhibition efficiency ( $\theta = \text{IE}\%/100$ ).

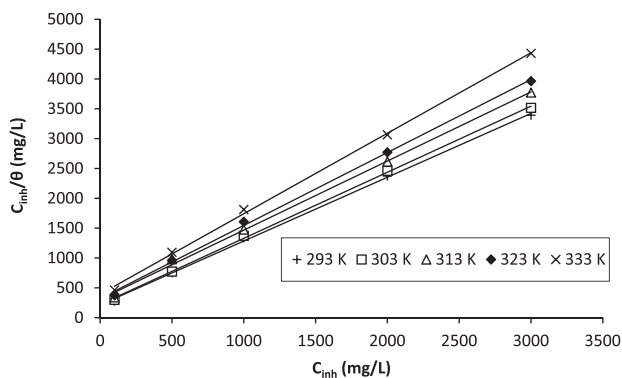
For testing the adsorption isotherm obeyed by this system, a graphic relation between the inhibitor concentration  $C_{\text{inh}}$  and  $C_{\text{inh}}/\theta$  at the studied different temperatures, is drawn and represented in Fig. 3. Straight line with almost unit slope and correlation coefficient ( $0.997 \leq R^2 \leq 0.999$ ) were obtained indicating that the system follows Langmuir adsorption isotherm (Eq. (7)) at all the studied temperatures. This indicates also, that mono-layer of the studied inhibitor must have been adsorbed to C-steel surface without interaction between the adsorbed molecules.

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (7)$$

where,  $K_{\text{ads}}$  is adsorption constant. The  $K_{\text{ads}}$  values can be calculated from the intercept lines on the  $C_{\text{inh}}/\theta$  axis. This is related to the standard free energy of adsorption ( $\Delta G^\circ$ ) by (Eq. (8)):

$$\Delta G^\circ = -RT \ln(55.5K_{\text{ads}}) \quad (8)$$

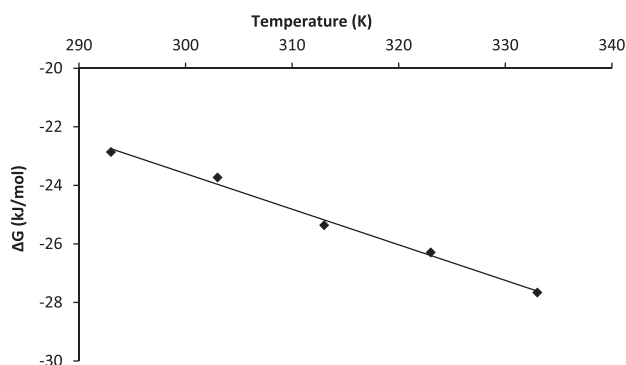
where 55.5 is the water concentration of the solution mL/L. The values of  $\Delta G^\circ$  for the inhibitor on the surface of C-steel are given in Table 3. The negative values of  $\Delta G^\circ$  indicate the stability of the adsorbed layer on the steel surface and spontaneity of the adsorption process.  $\Delta G^\circ$  decreased (become more negative) with increasing temperature, indicating the occurrence of endothermic process. In the present work, the calculated values  $-22.86 \leq \Delta G^\circ \leq -27.66$  kJ/mol, less than the



**Figure 3** Langmuir adsorption isotherm plots for carbon steel in 1 M HCl with different concentrations of henna extract.

**Table 3** Thermodynamic parameters for the carbon steel in 1 M HCl in the absence and the presence of different concentrations of henna extract.

Temperature (K)	$K_{\text{ads}}$ mol <sup>-1</sup>	$\Delta G^\circ$ kJ/mol	$\Delta H_{\text{ads}}^\circ$ kJ/mol	$\Delta S_{\text{ads}}^\circ$ J/mol K
293	214.2	-22.86	12.88	121.6
303	222.38	-23.73	12.88	121.6
313	308.16	-25.36	12.88	121.6
323	321.66	-26.29	12.88	121.6
333	392.85	-27.66	12.88	121.6



**Figure 4**  $\Delta G^\circ$  versus T plot for carbon steel in 1 M HCl solution with different concentrations of henna extract.

threshold value ( $-40$  kJ/mol) required for chemical adsorption and the IE% decreased with increasing temperature. These support the mechanism of physical adsorption.

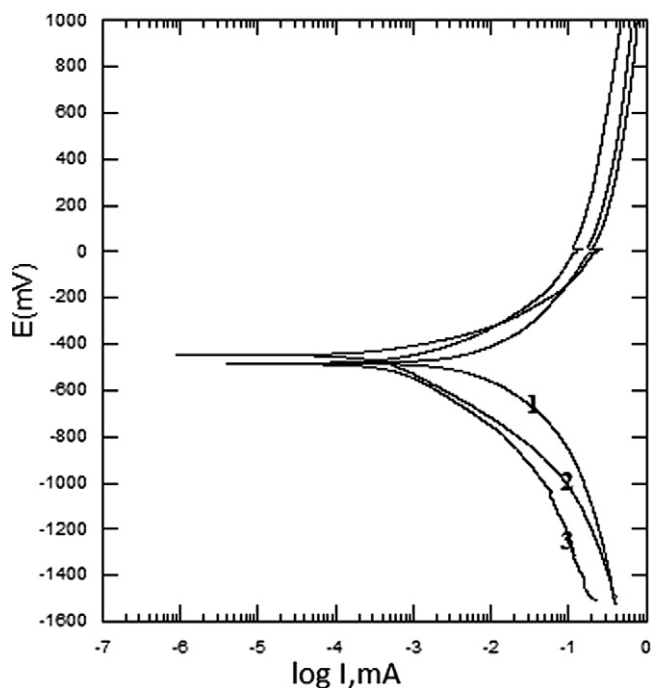
The thermodynamic parameters, enthalpy  $\Delta H_{\text{ads}}^\circ$  kJ/mol and entropy  $\Delta S_{\text{ads}}^\circ$  kJ/mol of adsorption can be calculated from the rearranged Gibbs–Helmholtz (Eq. (9)):

$$\Delta G^\circ = \Delta H_{\text{ads}}^\circ - T\Delta S_{\text{ads}}^\circ \quad (9)$$

Fig. 4 shows the dependence of  $\Delta G^\circ$  on  $T$  which indicates an appropriate relationship between thermodynamic parameters. The calculated values are listed in Table 3. The positive value of  $\Delta H_{\text{ads}}^\circ$  12.88 kJ/mol, reveals that the adsorption of inhibitor molecules is an endothermic process and suggesting the physical adsorption (physisorption). Generally, enthalpy values are less than or around the 40 kJ/mol, the adsorption process is physisorption while in case of the value more than 100 kJ/mol, the adsorption of inhibitor follows chemisorption process [21]. The positive value of  $\Delta S^\circ$  (121.6 J/mol K) shows the increased randomness at the metal/solution interface during the adsorption of inhibitor molecules onto the metal surface. This increase of disorder is due to more water molecules which can be desorbed from the metal surface by inhibitor molecules.

### 3.4. Potentiodynamic polarization measurements

The effect of henna extract concentration on the anodic and cathodic polarization behavior of C-steel in 1 M HCl solution has been studied by polarization measurements and the recorded Tafel plots for some studied concentrations are shown in Fig. 5. The respective electrochemical parameters derived from the plots including corrosion current density ( $I_{\text{corr}}$ ), cor-



**Figure 5** Potentiodynamic polarization curves for carbon steel in (1) 1 M HCl; (2) 1 M HCl + 100 mg/L henna extract; (3) 1 M HCl + 3000 mg/L henna extract at  $25\text{ }^{\circ}\text{C} \pm 1$ .

rosion potential ( $E_{\text{corr}}$ ), anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ , respectively), polarization resistance ( $R_p$ ) and inhibition efficiency (IE%) are given in Table 4. It is illustrated from the data listed in Table 4, that both anodic metal dissolution of

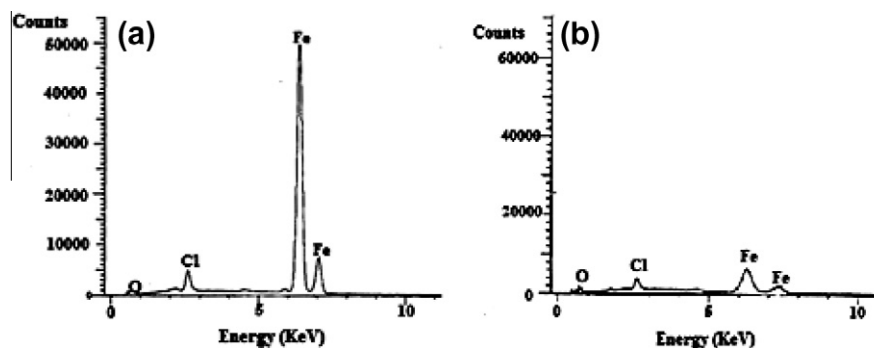
iron and cathodic hydrogen evolution reaction were inhibited after the addition of henna extract to 1 M HCl solution. The inhibition of these reactions was more pronounced on increasing henna concentration. The lower corrosion current density  $I_{\text{corr}}$  values in the presence of inhibitor without causing significant changes in corrosion potential ( $-498 \leq E_{\text{corr}} \text{ mV/SCE} \leq -474$ ) 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 presence of henna, the corrosion potential  $E_{\text{corr}}$  of C-steel shifted to the range (5–24) mV/SCE, compared to the blank. According to Yan et al. [25] an inhibitor can be classified as cathodic or anodic type if the displacement in corrosion potential is more than 85 mV/SCE, with respect to corrosion potential of the blank. This confirms that henna extract acts as mixed-type inhibitor. The observed decrease of the current densities  $I_{\text{corr}}$  with the increase in henna extracts 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. Surface analysis

Energy dispersive X-ray analysis (EDX) technique was employed in order to get information about the nature of the formed protective film. Fig. 6 presents an EDX panorama recorded for carbon steel samples immersed 48 h in 1 M HCl solution in the absence and presence of optimum concentration of henna extract, 3000 mg/L. In absence of the tested inhibitor, the EDX spectrum (Fig. 6a) shows the characteristics peak of iron which is the main element constituting the

**Table 4** Electrochemical parameters and corresponding inhibition efficiency for corrosion of the carbon steel in 1 M HCl in the absence and the presence of different concentrations of henna extract at  $25\text{ }^{\circ}\text{C} \pm 1$ .

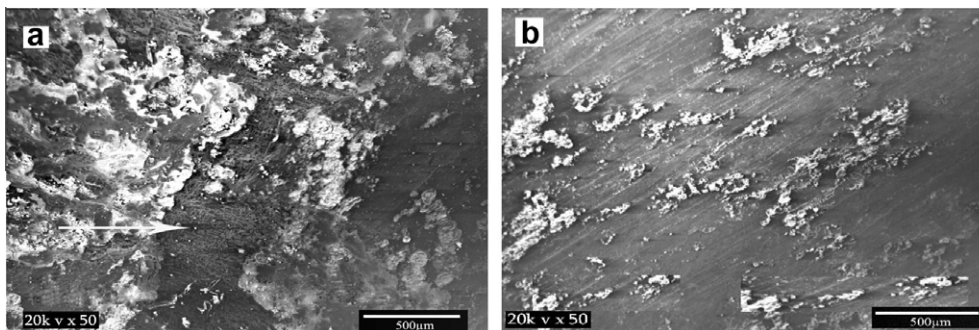
Electrolyte (mg/L henna)	$E_{\text{corr}}$ (mV/SCE)	$-\beta_c$ (mV/dec)	$\beta_a$ (mV/dec)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_p$ ( $\Omega \text{ cm}^2$ )	IE (%)
0	-498	141	124	0.227	126	–
100	-493	131	310	0.067	596	67.67
500	-488	112	280	0.041	847	80.34
1000	-483	114	193	0.026	1196	87.43
2000	-479	213	120	0.020	1666	90.53
3000	-474	138	107	0.015	1744	92.72



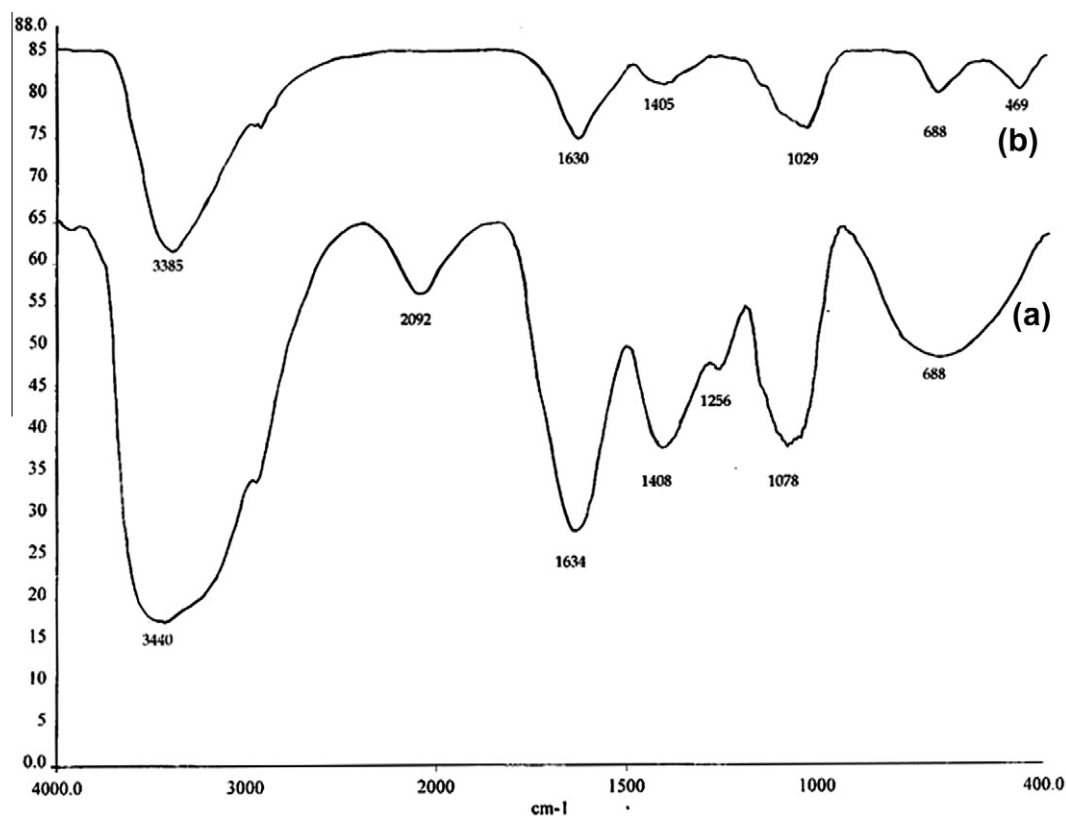
**Figure 6** EDX spectra of carbon steel specimens after 48 h of immersion in (a) 1 M HCl; (b) 1 M HCl + 3000 mg/L henna extract at  $25\text{ }^{\circ}\text{C} \pm 1$ .

C-steel sample. Also, small peaks characterizing chloride and oxygen are detected; these peaks represent the corrosion products formed on the surface (chloride and oxide). In presence of henna extract, the spectrum (Fig. 6b) shows that the Fe peaks are considerably suppressed relative to the samples immersed in 1 M HCl, free of inhibitor; the Cl and O peaks are also suppressed. The suppression of the Fe, Cl and O lines can be attributed to the overlying inhibitor film over the C-steel sample indicating that, the corrosion inhibition process was related to the development of an inhibition film over the metal surface.

Scanning electron microscope (SEM) images were taken in order to study the surface morphology of C-steel in absence and presence of green inhibitor. SEM image Fig. 7.a. reveals that in the absence of plant extract, the C-steel surface is highly damaged with pitted areas. This shape is typical to pitting corrosion [1]. Fig. 7.b. shows a smooth surface with deposited extract on it for the specimen after immersion in 1 M HCl solution containing 3000 mg/L henna extract; the best concentration of corrosion inhibitor. By comparison of SEM images at the same magnifications, it is indicated that the pits disap-



**Figure 7** SEM micrographs for surface of C-steel specimens after 48 h of immersion in 1 M HCl solution: (a) without henna extract; (b) with 3000 mg/L henna extract at  $25\text{ }^{\circ}\text{C} \pm 1$ .



**Figure 8** FTIR spectra: (a) vacuum dried henna extract; (b) Film formed on metal surface after 48 h of immersion in 1 M HCl + 3000 mg/L henna extract at  $25\text{ }^{\circ}\text{C} \pm 1$ .

pear and C-steel is almost free from corrosion in HCl with plant extract solution. This is because of the formation of an adsorbed film of plant extracts inhibit pitting corrosion of C-steel in 1 M HCl solution.

### 3.6. Analysis of the protective film

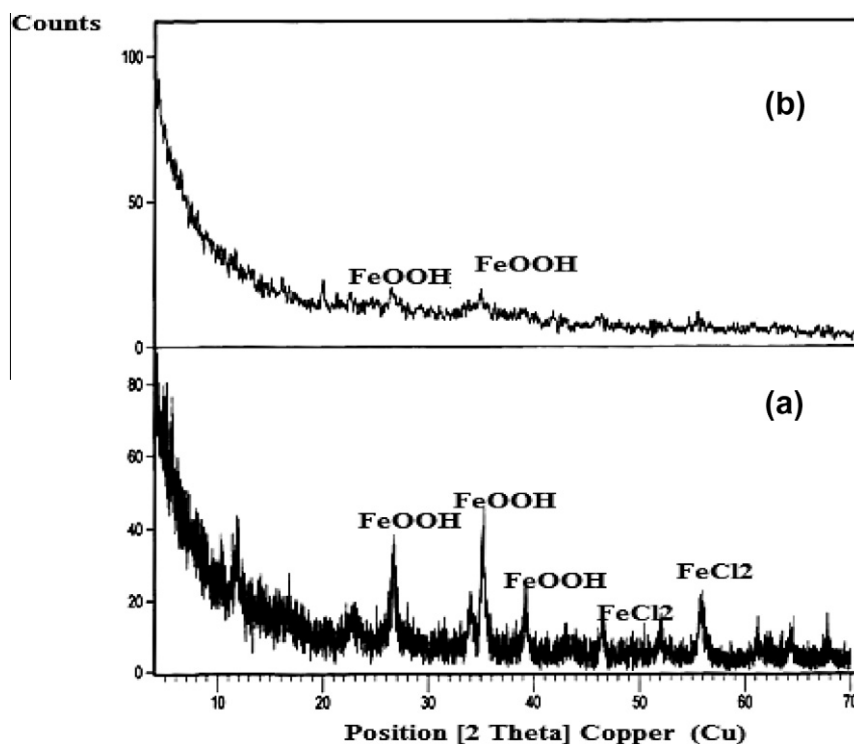
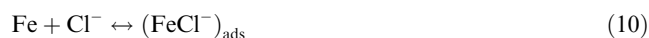
The above results were further confirmed by FT-IR spectra of plant extract and C-steel surface immersed in 1 M HCl with 3000 mg/L henna extract (Fig. 8). The main constituent of henna extract is lawsone (scheme 1); it contains benzene unit, *p*-benzoquinone unit and phenolic group. The FT-IR spectrum of henna extract is shown in Fig. 8.a. the phenolic –OH stretching appeared at  $3440\text{ cm}^{-1}$ . The peaks at  $2937$ , and  $2092\text{ cm}^{-1}$  can be assigned to aliphatic and aromatic C-H. The aromatic C=C stretching frequency appeared at  $1403\text{ cm}^{-1}$ . The C=O stretching frequency appeared at  $1634\text{ cm}^{-1}$ . The FT-IR spectrum of the protective film formed on the surface of the metal after immersion is shown in Fig. 8.b. It is found that, almost all the peaks observed for henna extract are also noticed for C-steel immersed in 1 M HCl containing 3000 mg/L of henna extract. Phenolic –OH stretching has shifted from  $3440$  to  $3385\text{ cm}^{-1}$ . The aromatic C=C stretching shifted from  $1403$  to  $1407\text{ cm}^{-1}$ . The C=O stretching frequency has been shifted from  $1634$  to  $1629\text{ cm}^{-1}$  indicates formation of Iron-plant extract complex or salt. The band at  $469\text{ cm}^{-1}$  probably originates mainly from  $\gamma\text{-Fe}_2\text{O}_3$  [24]. The phenol group of lawsone would donate electron to the metal to achieve its noble state of orbit, while the metal would receive the electron to become more stable. This indi-

rectly retard further redox reaction and could resist metal from corrosion attack.

The X-ray diffraction patterns of the corrosion products formed on the carbon steel surface immersed in 1 M HCl in the absence and presence of henna extract are shown in Fig. 9a and b, respectively. The identification of phase compositions (as opposed to elemental compositions) is crucial for the understanding of corrosion processes. Information about the chemical phases is not only helpful to explain the corrosion process, but can also, help to locate the origin of corrosion in a facility and, at the same time, provide solutions to the problem [26]. In the absence of inhibitor, the XRD pattern shows peaks at  $26.7$ ,  $35.2$ , and  $39.3$  ( $2\theta$ ), these peaks are characteristic of goethite ( $\alpha\text{-FeOOH}$ ) which is typical in the case of C-steel in environments that contain chloride [27],  $\text{FeCl}_2$  phase is also detected at  $46.5$  and  $55.8$  ( $2\theta$ ). The XRD pattern of inhibited surface (Fig. 9b) shows a smooth pattern with very small peaks of goethite and no characteristic peaks of  $\text{FeCl}_2$ . This indicates the amorphous nature of the surface film, which is expected to be the adsorbed film of Fe–henna extract complex layer as mentioned previously.

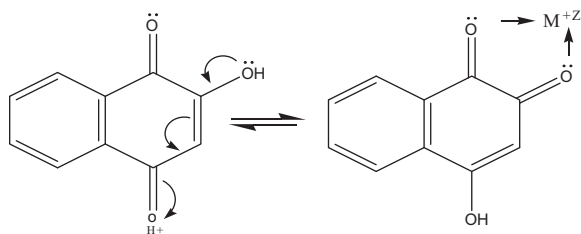
### 3.7. Suggested mechanism of corrosion inhibition

In hydrochloric acid medium, the metal surface is negatively charged due to the specifically adsorbed chloride ions on the metal surface.



**Figure 9** XRD patterns of corrosion products formed on the surface of carbon steel after 48 h of immersion in (a) 1 M HCl; (b) 1 M HCl + 3000 mg/L henna extract at  $25\text{ }^\circ\text{C} \pm 1$ .





**Scheme 2** Forms of lawsone due to electron delocalization.

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 (Scheme 2). 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  $e^-$  pairs of unprotonated oxygen atom of the inhibitor and vacant d-orbitals of metal surface atoms.

#### 4. Conclusions

- Henna extract acts as a good inhibitor for the corrosion of C-steel in 1 M HCl solution.
- Inhibition efficiency increases with increasing inhibitor concentration but decreases with increase in temperature.
- The values of apparent activation energy increases with the increase in the inhibitor concentration. Enthalpy of activation reflects the endothermic nature of C-steel dissolution process. Entropy of activation increases with increasing inhibitor concentration; hence increase in the disorder of the system.
- The adsorption of henna extract on C-steel follows the Langmuir adsorption isotherm.
- Gibb's free energy, enthalpy and entropy of adsorption indicate that the adsorption process is spontaneous and endothermic and the inhibitor molecules adsorbed on the metal surface through physical adsorption.
- The results obtained from polarization measurements revealed that henna extract behaves as a mixed type of inhibitor.
- EDX and SEM confirm the corrosion of C-steel in 1 M HCl and its inhibition by henna extract.

- FT-IR and XRD show that the compounds present in the plant extract form corrosion inhibitive layer by complexation with iron ions present on the C-steel surface.
- The inhibitor can be adsorbed on the metal surface through oxygen atom of lawsone; the main constituent presents in henna extract.

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