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Green corrosion inhibition of mild steel to aqueous sulfuric acid by the extract of *Corchorus olitorius* stems

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Abstract

Extract of *Corchorus olitorius* stems (ECS) was used as a green inhibitor for the inhibition of mild steel corrosion in 0.5 M H₂SO₄ solution. GC/MS was used for both qualitative and quantitative analysis of the extract. The corrosion performance of the extract was evaluated using electrochemical impedance spectroscopy, potentiodynamic polarization and weight loss. The results showed that ECS is a mixed-type inhibitor which reduces both anodic and cathodic reactions and the inhibition efficiency was reached up to 93%. Adsorption isotherm data was recorded at different temperatures and analyzed by selected adsorption isotherm models to reveal characteristics of inhibition. Thermodynamic calculations showed that the inhibition efficiency increases with increasing inhibitor concentration, and decreases with increasing temperature. Adsorption of ECS on the mild steel surface was found to be spontaneous and exothermic. Adsorption is suggested to be physisorption according to El-Awady isotherm model. Also, the scanning electron microscopy (SEM) was used to investigate the surface morphology to confirm the corrosion results.

1. Introduction

Mild steel has been widely used in diverse applications because of its ease of fabrication and low cost. In some applications, acids come in contact with mild steel such as in cleaning of boilers, oil wells acidification and pickling [1]. Hence, mild steel is exposed to corrosion process. A versatile method to protect mild steel against corrosion is to apply inhibitors. Many synthetic inhibitors have been used to protect mild steel in acidic solutions; however, some of these inhibitors will be banned soon due to their adverse impact on the environment [2].

In the last few years, organic materials from natural sources have been studied for metallic corrosion inhibition as alternatives to synthetic inhibitors taking the advantage of being a green application. The primary source of such organic materials is plants [3–5]. Plants contain many antioxidants, fatty acids and other compounds. These materials can be extracted, by simple methods, from different parts of the plants and be applied as corrosion inhibitor in diverse corrosive media. Adsorption, forming protective layer is the most probable inhibition mechanism by these organic materials [6]. From the chemical structure point of view, these green inhibitors usually contain oxygen and/or nitrogen and/or sulphur atom(s) which play an important role for inhibition by adsorption. These atoms comprise non-bonded pairs of the electron that contribute in adsorption of the inhibitor (physically or chemically) onto the metal surface, consequently hindering the corrosive media from attacking the metal surface [7]. Some of these organic materials can be found and extracted from *Corchorus olitorius* plant [8].

C. olitorius is planted in Egypt, Algeria, Lebanon, Nepal, Thailand, and many other countries. In Egypt, its leaves are used to cook a traditional food dish while the rest of the plant roots and stem, are usually discarded as waste. In this study, stems of *C. Olitorius* were treated by warm water/ethanol solution for the extraction of organic content. The extract, collectively ECS, was used as a green corrosion inhibitor for mild steel corrosion in an aqueous solution of 0.5 M sulfuric acid.

2. Experimental work

2.1. Preparation of ECS inhibitor

Fresh *C. olitorius* plant was purchased from local market, Cairo, Egypt. Stems (50 g) were separated, washed with deionized water, trimmed and then treated by water/ethanol solution (200 ml, v/v = 80/20) in a closed vial at 60 °C for 8 h, followed by filtration. The filtrate was then kept under vacuum at 50 °C for 24 h. The formed dry extract powder, ECS inhibitor, was then collected and weighed. For each corrosion experiment, without any further purification or processing, a specified amount of ECS was directly added to the corrosive medium. The extract was completely soluble in 0.5 M sulfuric acid.

2.2. Coupons of mild steel and corrosive media

All electrochemical experiments were performed at ambient temperature for different ECS concentration (0, 80, 160, 240, 400 and 600 ppm) using freshly prepared coupons of mild steel (composition; C: 0.3%, Ni: 0.2%, Cu: 0.13%, Ti: 0.08%, W: 0.07%, Cr: 0.3%, Mn: 0.11% and Fe balance). Mild steel was purchased from EZZ Steel group, Cairo, Egypt. Coupons (dimensions: 50 × 30 × 1 mm) were well abraded with emery papers, 600 then 1200, of various grit and then washed with distilled water followed by washing with acetone. Finally, coupons were rinsed with deionized water, dried and stored in a desiccator. The corrosive stock solution, 0.5 M H₂SO₄, was prepared by dilution of analytical grade 98% H₂SO₄ from Sigma-Aldrich with deionised water.

2.3. Characterization and measurements

The Agilent 5975 T LTM GC/MSD with a stationary phase DB-5H30mx with 0.319 mm × 0.10 μm of phase thickness was used to analyse the ECS extract. ECS powder was dissolved in 1, 2 dichloroethane solvent forming the analyte solution. Helium carrier gas was used at a rate of 43.7 cm³ s⁻¹ and a sample of analyte solution (1 μl) was injected at a temperature of 50 °C in 1:50 split-mode. The initial column temperature was 50 °C. Heating was programmed to increase the temperature up to 150 °C at 10 °C min⁻¹ rate then to further increase the temperature up to 230 °C at 5 °C min⁻¹ rate. The temperature of the mass detector was 250 °C where the MS was operated in electron ionization mode with a potential of 70 eV. The mass spectra were obtained with a full scanning mode at a scan range of 40–1000 m/z. The mass spectrometer, the mass spectrum of the sample was compared with the internal standard mass spectrum (Mass Spectral Database NIST/EPA/NIH) to define the unknown components. Based on the total area values of the identified peaks, the percentage of each component was determined by the relative area of each peak.

Electrochemical corrosion experiments were carried out by GamryTM potentiostat equipped with three-electrode type cell. For each experiment, fresh mild steel coupon prepared specially for electrochemical experiments, of 30 cm² total surface area was used as working electrode, saturated calomel electrode as reference electrode and platinum as the auxiliary electrode.

The potentiodynamic polarization experiments were performed after immersion of the working electrode for at least 60 min, and applied the potential in the range of –250 to +250 mV with respect to open-circuit potential (OCP) at a scan rate of 1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) measurements were applied using GamryTM instrument model reference 600. The AC signal with ±10 mV peak to peak perturbation in the frequency range from 3 × 10⁴ to 10⁻² Hz was applied in these measurements.

Corrosion inhibition efficiency (IE%) was evaluated using weight loss technique. The coupons were polished with emery papers, degreased with acetone, washed with distilled water and finally dried at 110 °C for 30 min. The coupons were weighed using digital analytical balance with precision (±0.1 mg) before immersion in the corrosive solution for 72 h at different temperatures (10, 20, 30 and 40 °C). After immersion period, the coupons were then cleaned by wiping with a soft brush and then washed with deionized water and acetone. The coupons were then dried at 110 °C for 30 min. The weight loss was calculated as a difference between mild steel coupons before and after immersion in 250 ml of 0.5 M H₂SO₄ solutions in the absence and presence of inhibitor with the following concentrations; 80, 160, 240, 320, 400 and 600 ppm.

The surface morphologies of the mild steel coupons (fresh, immersed in the corrosive solution with and without inhibitor) were investigated using scanning electron microscopy (SEM, Zeiss EVO-10 microscopy).

3. Results and discussion

3.1. Inhibitor characterization

The ECS composition was investigated using GC-MS technique and the retention time chromatogram is shown in figure 1. The noticed intense peaks are recorded at retention times 17.3, 17.8, 20.3 and 24.1 min which correspond to stearic acid (4.91%), cetylic acid (28.84%), Linolenic acid (3.35%) and oleic acid amide (58.91%) respectively. The mass spectra of the compounds (not shown) reveal their chemical structures of these four components are considered as a fatty acid.

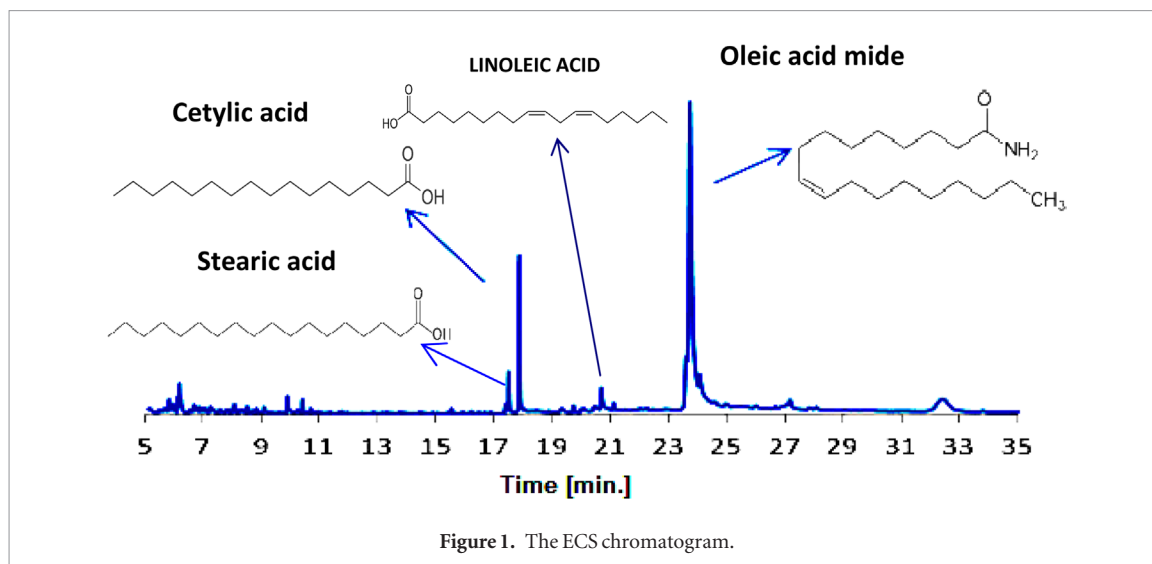
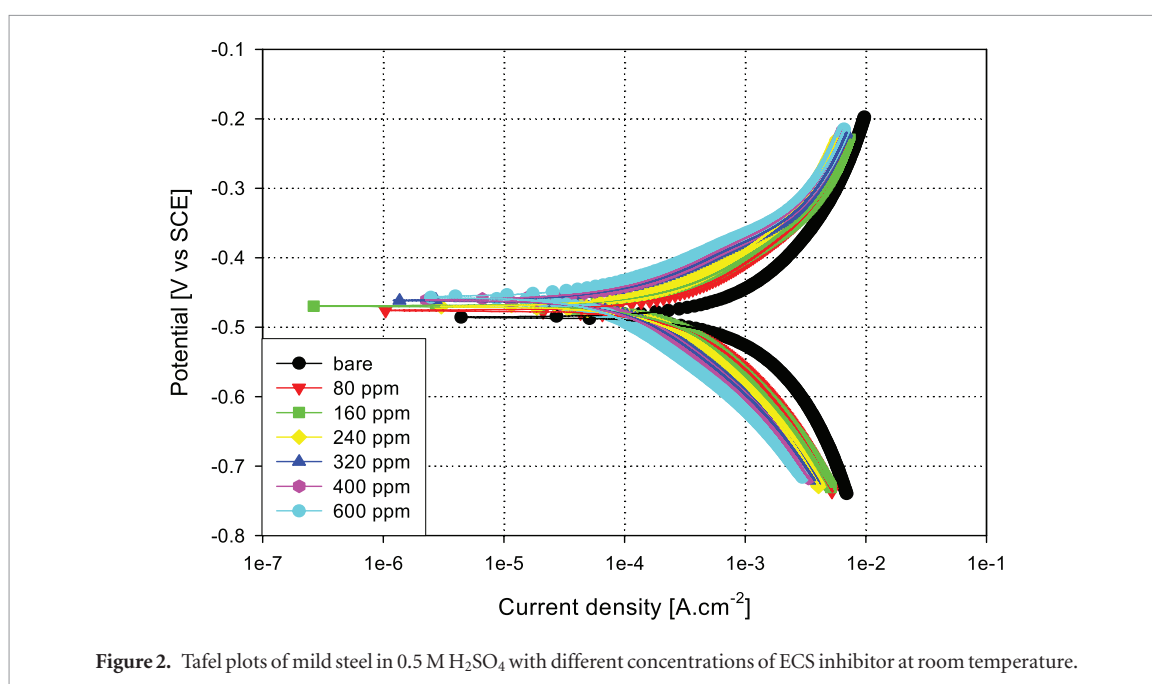


Figure 1. The ECS chromatogram.

Figure 2. Tafel plots of mild steel in 0.5 M H₂SO₄ with different concentrations of ECS inhibitor at room temperature.

3.2. Corrosion measurements

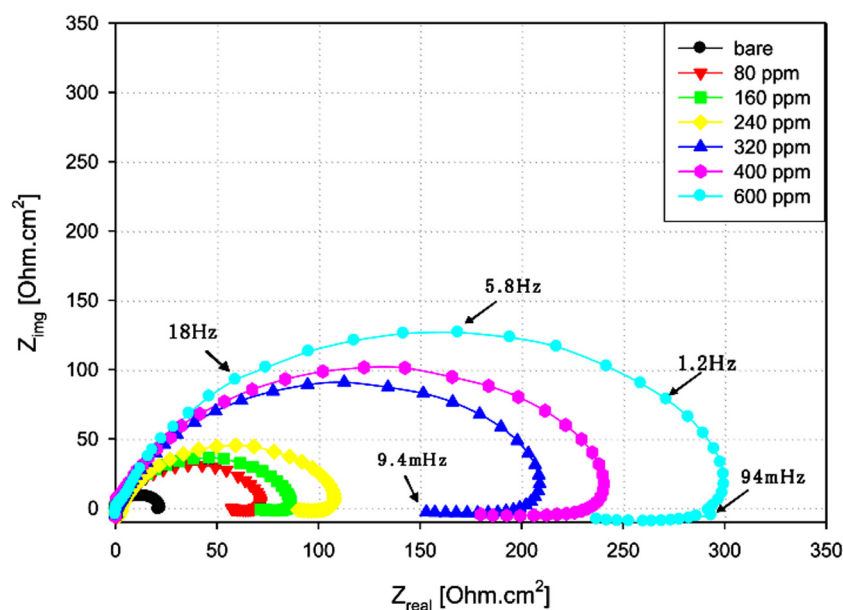
3.2.1. Potentiodynamic polarization.

The electrochemical parameters of both cathodic and anodic reactions are of great importance for studying corrosion process. When applying inhibitors, the most versatile technique for studying corrosion process is the potentiodynamic polarization. Figure 2 shows the anodic and cathodic polarization curves of the mild steel in 0.5 M sulfuric acid solutions in the presence and absence of different concentrations of ECS at room temperature. Not only current density of the blank sample is higher than that of samples with inhibitor but also, the slopes of both cathodic and anodic branches (β_c and β_a respectively) of the blank sample are higher than that of samples with inhibitor. Moreover, the anodic polarization branches did not show any evidence of passive film formation on the mild steel surface either with or without ECS inhibitor.

Table 1 gives the electrochemical kinetic parameters of Tafel extrapolations (E_{corr} , β_c , β_a , I_{corr} and IE%). From the table, the increase of inhibitor concentration causes a considerable regular decrease in corrosion current density (I_{corr}) which indicates the increase of inhibition efficiency (IE%). This result suggests that ECS acts as adsorption inhibitor [9]. In addition, β_c and β_a gradually decrease with increasing the inhibitor concentration suggesting that the reaction mechanism of mild steel in the acidic corrosive solution is influenced by the presence of ECS. The decrease of β_a values with increasing the inhibitor concentration may be related to that the adsorbed inhibitor molecules block the anodic reaction sites on the metal surface which hindering the passage of cations from the metal surface into the solution. Also, the formation of complex, via O and N atoms, with the metal surface is another postulate.

Table 1. Corrosion kinetic parameters with different concentrations of ECS inhibitor.

ECS conc. (ppm)	β_a (mV/decade)	β_c (mV/decade)	E_{corr} (mV)	I_{corr} ($\text{mA} \cdot \text{cm}^{-2}$)	IE%
0	538.9	-661.7	-485.0	3.310	—
80	235.7	-313.5	-477.0	0.785	76.3
160	210.1	-291.6	-472.0	0.641	80.2
240	213.9	-286.8	-470.0	0.510	84.6
320	175.2	-257.1	-464.0	0.356	89.3
400	175.0	-256.0	-464.0	0.320	90.3
600	156.5	-237.8	-462.0	0.231	93.0

**Figure 3.** Nyquist plots of mild steel in 0.5 M H_2SO_4 solution with different concentrations of ECS inhibitor at room temperature.

β_c also decreases by adding inhibitor, indicating modification in the kinetics of the cathodic reaction. The main cathodic reaction under activation polarization within acidic electrolyte is the hydrogen evolution. This change in the β_c may be due to the increase in the number of inhibitor molecules on the metal surface which impedes the hydrogen ions from the electrolyte to the electrode surface. The decrease in both β_c and β_a was reflecting in the decrease of the current densities (i.e decrease in the corrosion rate) and consequently, increases the degree of surface coverage with inhibitor concentration as shown in table 1. Besides, the corrosion potential (E_{corr}) seems to be stable where it changes within 23 mV (between -485 to -462 mV) as given in Table 1. The above results indicate that ECS is mixed-type inhibitor where inhibition occurs for both anodic and cathodic reactions by adsorption [10–13]. Consequently, both anodic metal dissolution and cathodic hydrogen ion reduction are inhibited by ECS inhibitor.

3.2.2. Electrochemical impedance spectroscopy (EIS).

EIS technique was used to study the interaction between the metal substrate and the acidic solution in the presence and absence of ECS inhibitor [14]. Nyquist plots, figure 3, shows irregular shape of the semicircle which may be due to surface inhomogeneity and/or the dispersion of frequency [15]. It shows a single capacitive semicircle for the blank sample, however; another inductive one appeared by adding the ECS inhibitor. This behaviour clarifies that adding inhibitor modifies both the anodic and cathodic electrochemical reactions. The continuous addition of ECS to the acidic electrolyte results in a continuous increase in the radius of the capacitive semicircle. This behaviour is a clear response to the inhibition of the corrosion process. Moreover, the single capacitive semicircle indicates that the charge transfer process controls the corrosion process. The inductive loop, in the low-frequency range, may be attributed to relaxation during adsorption process [16, 17].

The impedance plot figure 4 shows that the impedance increases as the inhibitor concentration increases. Samples with inhibitor showed a decrease in impedance at low frequency range which represents an inductive element. Also, the phase angle plot figure 5 shows a capacitive time constant at mid-low frequency ranges which increases with the increase of inhibitor concentration.

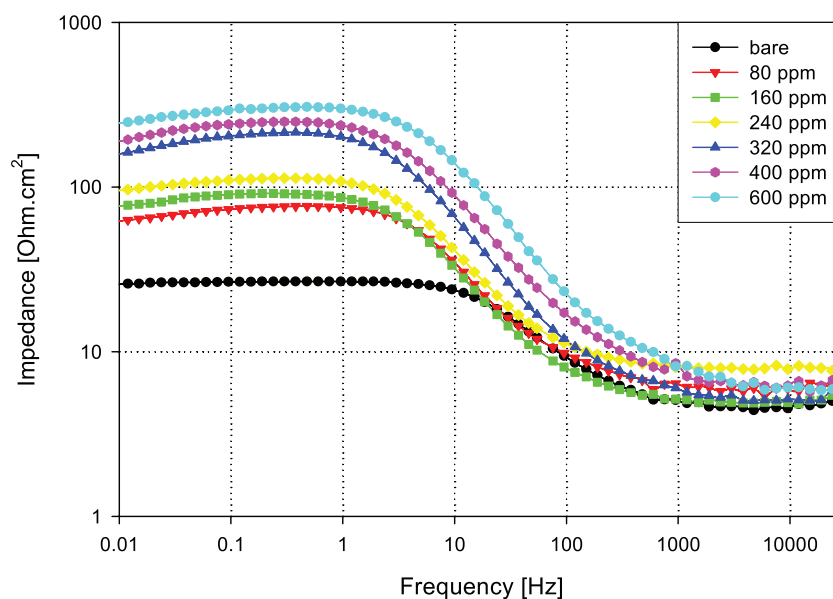


Figure 4. Impedance plots of mild steel in 0.5 M H₂SO₄ solution with different concentrations of ECS inhibitor at room temperature.

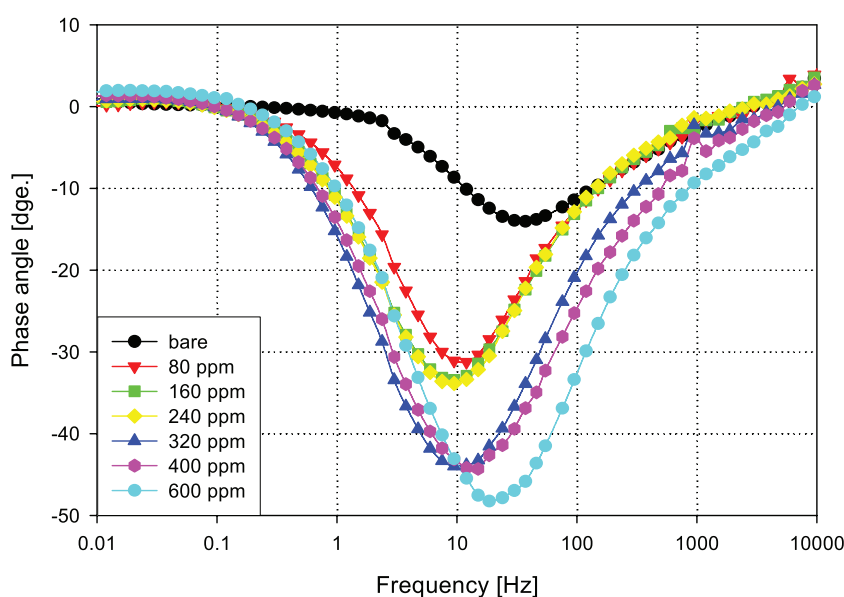


Figure 5. Phase angle plots of mild steel in 0.5 M H₂SO₄ solution with different concentrations of ECS inhibitor at room temperature.

One of the most significant results of EIS technique is to obtain qualitative information by fitting EIS data to an equivalent electrical circuit. The electrical equivalent circuits, shown in figure 6, were used to model the EIS experimental data where R_s represents the pseudo-ohmic solution resistance (between the working and reference electrode); R_{ct} is the charge transfer resistance associated with corrosion process at OCP; C_{dl} is the electric double-layer capacitance at metal/electrolyte interface, and L is an inductor. Such circuit has been widely used for model steel corrosion in sulfuric acid solution [18, 19]. Due to non-ideal frequency response during experimental work, a pure capacitor C is usually replaced by constant phase element, CPE. The capacitance values, C_{dl} , can be calculated from the constant phase element (CPE_{dl}), figure 6, according to the following equation [15]:

$$C_{dl} = \frac{Y_0 \omega^{n-1}}{\sin(n\pi/2)} \quad (1)$$

where Y_0 is the CPE constant, ω is the angular frequency (rad s^{-1}), and n is the CPE exponent. The CPE becomes pure capacitor when $n = 1$.

Figure 7 shows the change of both charge transfer resistance and double layer capacitance of mild steel in 0.5 M H₂SO₄ corrosive solution at different concentrations of ECS inhibitor. It is clear from the figure that the charge

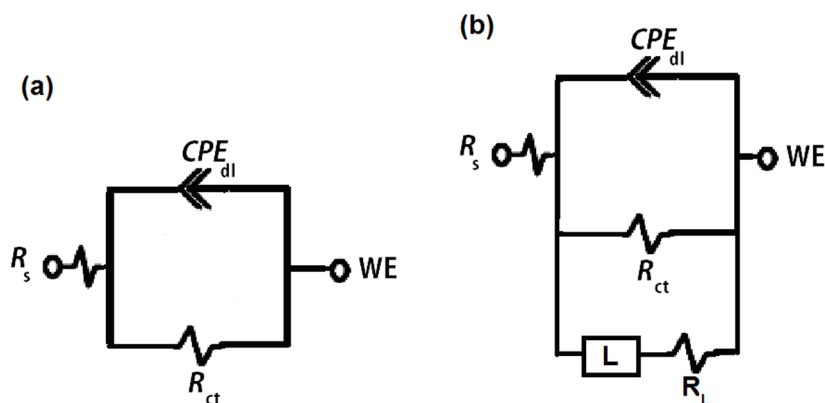


Figure 6. Equivalent circuits used for numerical fitting of the EIS data (a) in absent (b) presence of ECS inhibitor.

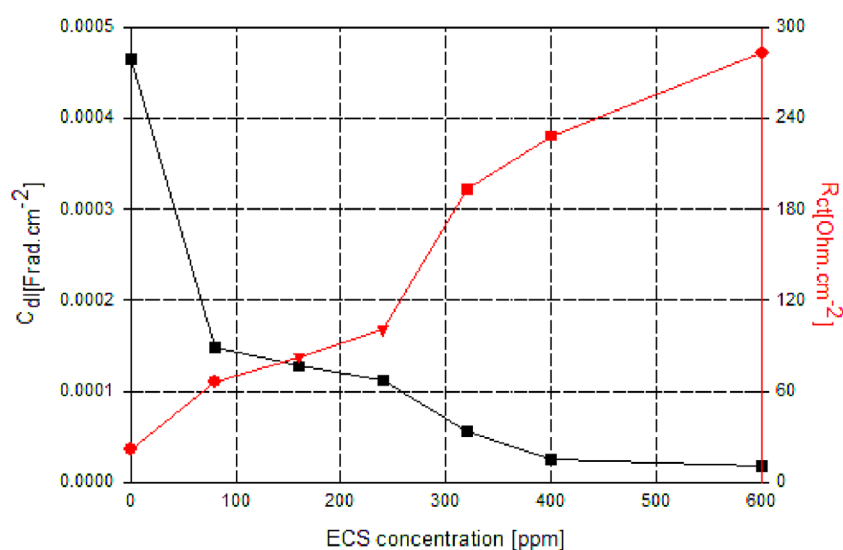


Figure 7. Changes of charge transfer resistance and double layer capacitance of carbon steel in 0.5 M H_2SO_4 solution with different concentration of ECS at room temperature.

Table 2. EIS fitting parameters with ECS concentrations.

ECS conc. (ppm)	R_s ($\Omega \cdot \text{cm}^2$)	R_{ct} ($\Omega \cdot \text{cm}^2$)	Y_0 ($10^4 \times \text{Frad} \cdot \text{cm}^{-2}$)	n	C_{dl} ($10^5 \times \text{Frad} \cdot \text{cm}^{-2}$)	IE%
0	2.9	22.2	6.44	0.86	46.4	—
80	1.8	66.5	1.87	0.90	14.8	66.9
160	1.9	82.8	1.69	0.88	12.7	73.4
240	2.01	101.2	1.45	0.89	11.2	78.2
320	1.6	192.7	0.72	0.89	5.51	88.5
400	1.25	228.3	0.35	0.86	2.52	90.3
600	1.3	283.4	0.23	0.87	1.72	92.2

transfer resistance, R_{ct} , values gradually increases with the increase of ECS concentration indicating a decrease in corrosion rates. This increase in R_{ct} values indicates that the charge transfer governs the corrosion process under the stated conditions. In the same time the double layer capacitance, C_{dl} , gradually decreases with the increase of ECS concentration. The replacement of H_2O molecules by organic inhibitor (lower dielectric constant with respect to H_2O) at the metal/electrolyte interface through adsorption process may decrease the C_{dl} values [20]. This gradual decrease in C_{dl} may be due to thickening the double layer and/or a decrease in local dielectric constant which reflects the adsorption of ECS inhibitor on the metal surface/electrolyte interface. Such mechanism can be supported by the following mathematical expression [9, 21];

$$\delta = \frac{\epsilon \epsilon_0 A}{C_{dl}} \quad (2)$$

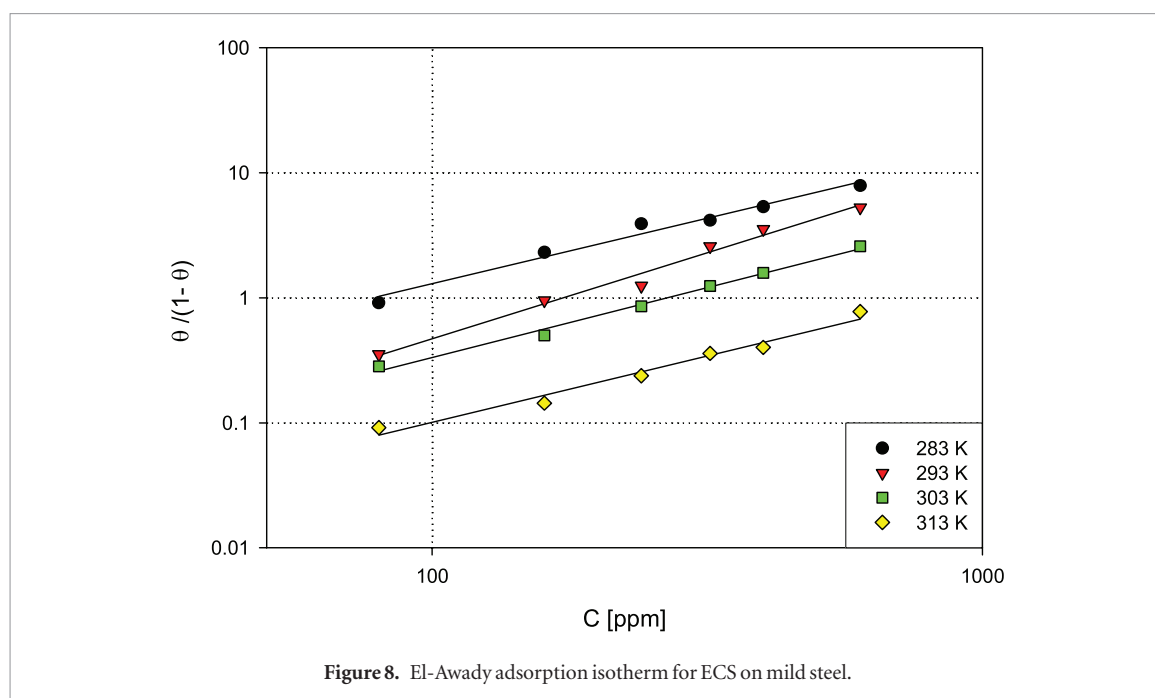


Figure 8. El-Awady adsorption isotherm for ECS on mild steel.

where δ is the thickness of the protective layer, ε is the dielectric constant of the medium, ε_0 is the vacuum permeability, and A is the electrode surface area. This above results suggests that ECS inhibitor acts by adsorption mechanism at the metal/electrolyte interface. All the EIS fitting parameters with ECS concentrations are also summarized in table 2. These results collectively suggest that there was a significant positive correlation between potentiodynamic polarization and EIS results.

3.3. Adsorption isotherms and thermodynamic parameters

From the above corrosion results, it is suggested that adsorption of ECS inhibitor onto mild steel surface plays the main role to inhibit corrosion. Study of adsorption isotherms is usually performed to investigate the adsorption process in diverse of corrosive solutions. Adsorption isotherm gives an important sight concerning the nature of the metal-inhibitor interaction. The most applied adsorption isotherm models are Langmuir [22], El-Awady [23], Temkin [18], Freundlich [19], Frumkin [20] and Flory-Huggins [21, 24]. Adsorption isotherm models correlate the degree of surface coverage (θ) with the concentration of the inhibitor at constant temperature. In this study, Langmuir and El-Awady isotherm models were investigated. The first model assumes a monolayer coverage of the inhibitor over the metal surface which usually attributed to chemisorption [22]. The second model assumes a multilayer coverage and is usually classified as physisorption [23]. The linear mathematical forms of Langmuir model is represented as follows:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (3)$$

The mathematical model of El-Awady isotherm is represented as follows:

$$\log\left(\frac{\theta}{1-\theta}\right) = \log K + y \log C_{\text{inh}} \quad (\text{where : } K_{\text{ads}} = K^{1/y}) \quad (4)$$

where C_{inh} is the inhibitor concentration, θ is surface coverage fraction, K_{ads} is the equilibrium constant of the adsorption process, and y represents the number of inhibitor molecules that occupies an active site on the surface of the metal substrate. The values of y should be greater than 1 to fit the data with El-Awady model (multilayer model) [23]. The surface coverage, θ , of ECS inhibitor on metal surface was calculated from the weight loss data using the following equation [25, 26]:

$$\theta = \frac{w_0 - w}{w_0} \quad (5)$$

where w_0 and w are the sample weight losses before and after immersion in corrosive solution respectively.

The fitting plots of El-Awady and Langmuir isotherms of steel in 0.5 M H_2SO_4 at different temperatures are shown in figures 8 and 9 respectively. The extracted parameters of both models (regression coefficient, R^2) are tabulated in table 3. From the table, referring to R^2 values, El-Awady model shows better fit to experimental data than Langmuir model. Values of y for all temperatures are higher than 1. These values give a preponderance of El-Awady model and therefore multilayer physical coverage of ECS on mild steel surface can be suggested.

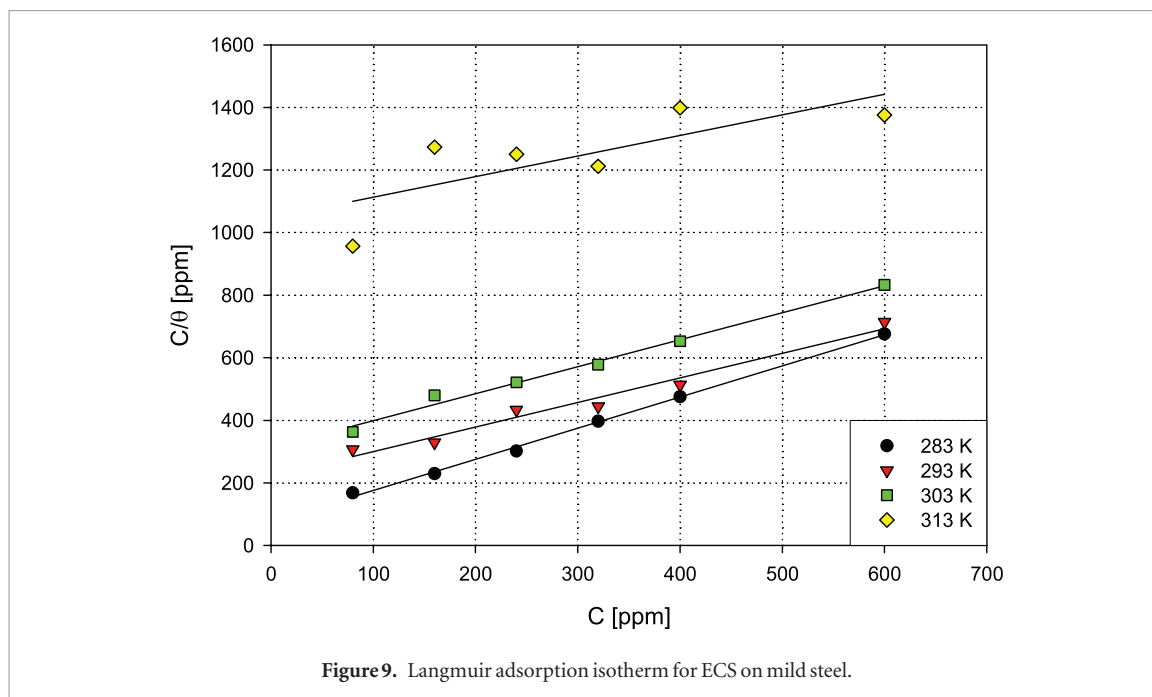


Figure 9. Langmuir adsorption isotherm for ECS on mild steel.

Table 3. Parameters of Langmuir and El-Awady adsorption isotherms.

T (K)	Langmuir		El-Awady		
	K_{ads}	R^2	K_{ads}	γ	R^2
283	0.0132	0.998	0.0128	1.046	0.978
293	0.0045	0.971	0.0058	1.373	0.983
303	0.0032	0.989	0.0038	1.119	0.992
313	0.0009	0.592	0.0011	1.059	0.975

The spontaneity of adsorption of organic inhibitors on metal surface reveals the effectiveness of inhibition. Spontaneity can be indicted through the calculation of the adsorption free energy ($\Delta G_{\text{ads}}^{\circ}$). Nature of adsorption; physical or chemical, is also important to indicate the stability of inhibitor on the metal surface. Adsorption process enthalpy ($\Delta H_{\text{ads}}^{\circ}$) can be used to indicate the nature of adsorption. Free energy change of adsorption, $\Delta G_{\text{ads}}^{\circ}$, can be calculated from the adsorption constant, K_{ads} , values of El-Awady model. The average molecular weight of the extract components was used in the calculation of $\Delta G_{\text{ads}}^{\circ}$ from the following equation [27–29]:

$$\Delta G_{\text{ads}}^{\circ} = -RT \ln(K_{\text{ads}}) \quad (6)$$

where T is the temperature in Kelvin and R is the universal gas constant. Enthalpy change of adsorption, $\Delta H_{\text{ads}}^{\circ}$, and also entropy change, $\Delta S_{\text{ads}}^{\circ}$, of adsorption can be determined by plotting the determined $\Delta G_{\text{ads}}^{\circ}$ versus temperature according to the following thermodynamic relation [30]:

$$\Delta G_{\text{ads}}^{\circ} = \Delta H_{\text{ads}}^{\circ} - T \Delta S_{\text{ads}}^{\circ} \quad (7)$$

Figure 10 shows the plot of $\Delta G_{\text{ads}}^{\circ}$ versus T from which $\Delta H_{\text{ads}}^{\circ}$ and $\Delta S_{\text{ads}}^{\circ}$ values (intercept and slope respectively) were determined. The thermodynamic parameters are summarized in table 4. From the table, for all applied temperatures, $\Delta G_{\text{ads}}^{\circ}$ are negative values. This indicates that adsorption is spontaneous for all applied temperatures [31–33]. Also, for the studied temperature range, the absolute values of $\Delta G_{\text{ads}}^{\circ} < 40 \text{ kJ mol}^{-1}$ suggesting physical adsorption process [34]. The value of $\Delta H_{\text{ads}}^{\circ}$ is negative indicating an exothermic process which is consistent with physical adsorption. The decrease of K_{ads} with temperature also indicates the exothermic nature of adsorption process of the inhibitor on the mild steel surface. Entropy change, $\Delta S_{\text{ads}}^{\circ}$, is negative indicating a decrease in randomness during adsorption process [35]. It can be concluded that ECS adsorption onto mild steel surface is an enthalpy-derived process. These results suggest that the adsorption of ECS inhibitor on mild steel surface in 0.5 M H_2SO_4 aqueous solution is spontaneous physisorption process, and the surface coverage is of multilayer type according to El-Awady model [36–38].

Activation energy is an important thermodynamic parameter that gives an indication of how difficult the corrosion process takes place. The apparent activation energy (E_a) can be determined from the following modified Arrhenius equation as [39–41]:

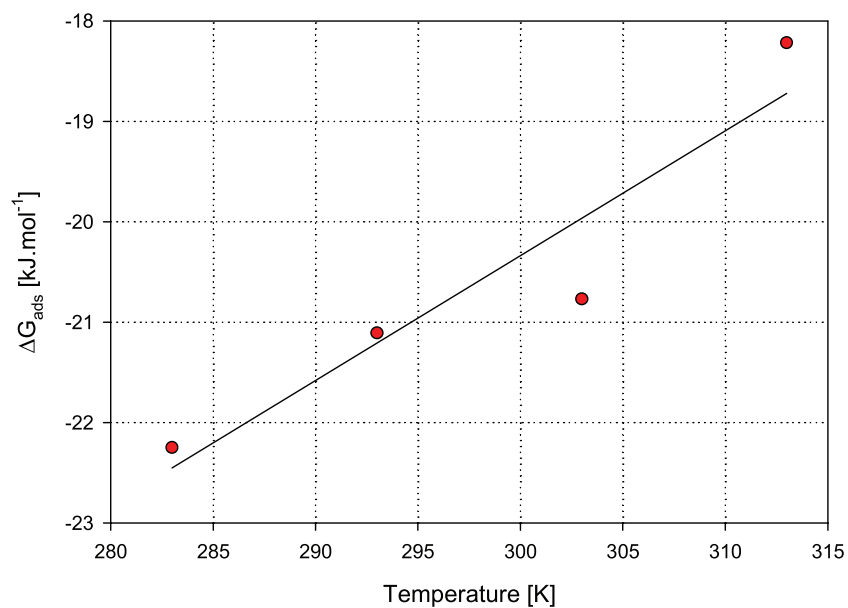


Figure 10. Change of adsorption free energy, $\Delta G_{\text{ads}}^{\circ}$, with the temperature.

Table 4. Thermodynamic parameters.

$T(\text{K})$	K_{ads}	$\Delta G^{\circ} (\text{kJ mol}^{-1})$	$\Delta H^{\circ} (\text{kJ mol}^{-1})$	$\Delta S^{\circ} (\text{J mol}^{-1} \cdot \text{K})$
283	0.0128	-22.25	-57.63	-124.3
293	0.0058	-21.11		
303	0.0038	-20.77		
313	0.0011	-18.22		

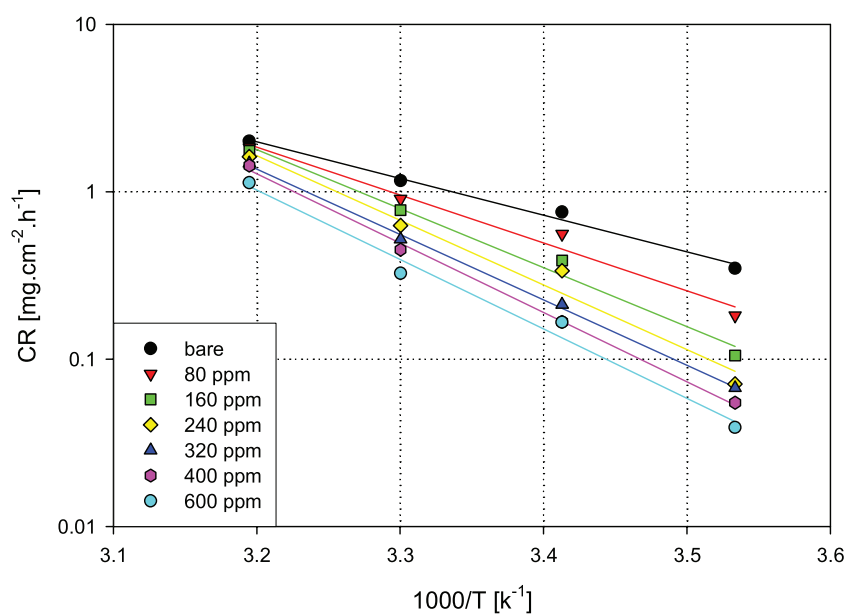


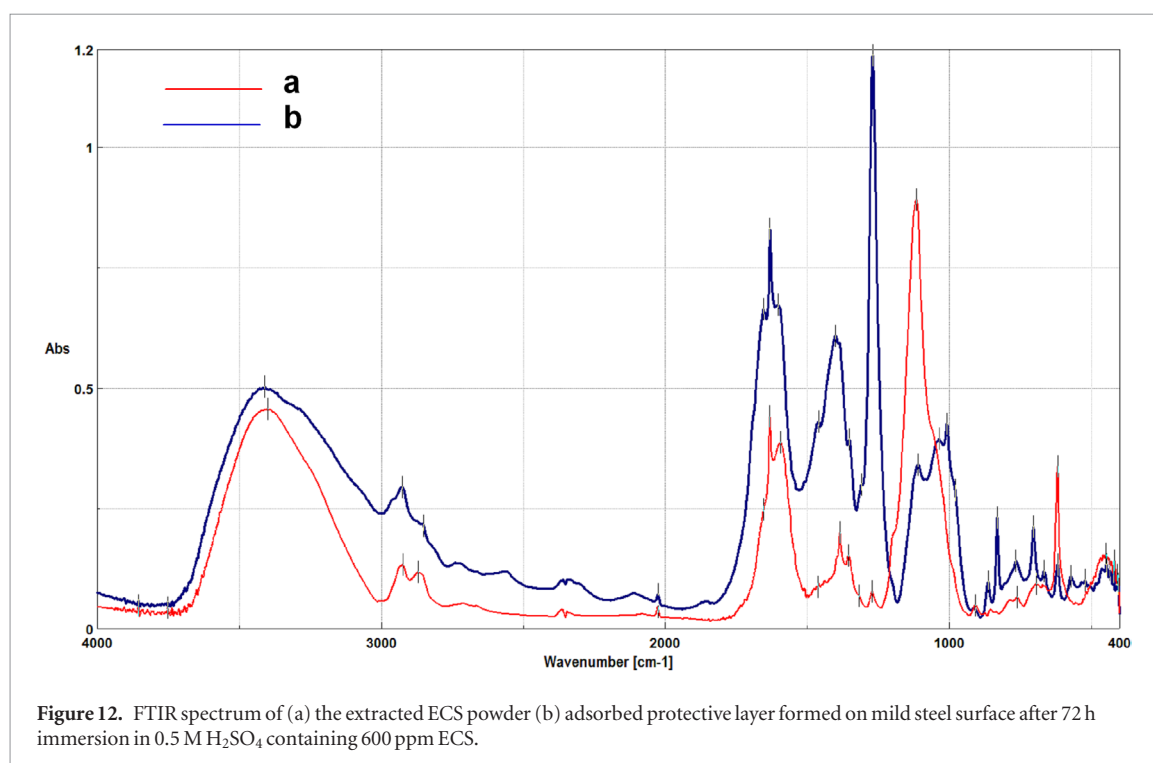
Figure 11. Change of corrosion rate of mild steel at different ECS concentration with the temperature.

$$\ln(\text{CR}) = \frac{-E_a}{RT} + \ln A \quad (8)$$

where CR is the corrosion rate ($\text{mg cm}^{-2} \text{h}^{-1}$), E_a is the apparent activation energy (kJ mol^{-1}), R is the universal gas constant, A is the Arrhenius pre-exponential factor, and T is the absolute temperature. The plot of the corrosion rate, CR, of mild steel versus $1/T$ for different concentrations of inhibitor in $0.5 \text{ M H}_2\text{SO}_4$ is shown in figure 11.

Table 5. Activation energies for different concentrations of ECS.

ECS concentration (ppm)	E_a (kJ mol ⁻¹)
Absent	41.97
80	54.83
160	67.39
240	73.91
320	74.87
400	79.27
600	79.46



From the figure, corrosion rate increases with temperature increase which is related to exothermic nature of adsorption process of the inhibitor on the mild steel surface.

The values of E_a can be determined from the slope of the obtained straight lines of the previous relation and presented in table 5. The table shows that the apparent activation energy increases with concentration which means stronger barrier against corrosion action.

FTIR has been used to confirm the adsorption of the organic inhibitor on different metal surfaces [34,42]. The FTIR spectra of ECS powder and the layer formed on the metal surface after 72 h immersion in a corrosive solution containing 600 ppm of ECS are shown in figures 12(a) and (b) respectively. The broad peak at 3409.4 cm⁻¹ can be assigned to the stretching of an O–H and/or N–H groups where CH₂ and CH₃ groups stretching at 2855 and 2925 cm⁻¹ [43]. The peak at 1631.8 cm⁻¹ may be attributed to the stretching mode of C=O group and peak at 1386 cm⁻¹ represents the deformation of CH₂ and/or CH₃ groups. By comparison of both spectra, it can be observed that the peaks of the inhibitor molecules are present in the adsorption layer on the mild steel surface. Some peaks intensity decreases (such as amide-I band C=O at 1656 cm⁻¹ [44]) due to protonation of organic acids in the presence of sulfuric acid [45]. Consequently, the extracted organic inhibitor seems to be protonated in 0.5 M H₂SO₄. Also, the peak position of some functional groups of the adsorbed inhibitor on the metal surface is slightly shifted than that of neat inhibitor powder; peak at 2925 shifted to 2928, 2855 shifted to 2864 and peak at 1386 shifted to 1383 cm⁻¹. These shifts in wavenumber can be explained by the physisorption process of the inhibitor on the mild steel surface [39,46,47] which confirms the thermodynamics calculations.

3.4. SEM analysis

Figure 13 shows the SEM images of the samples examined. Figures 13(a) showed the surface characteristics of the mild steel sample before exposure to the corrosive solution, while figures 13(b) and (c) present SEM images of samples after 72 h of immersion in 0.5 M H₂SO₄ without and with inhibitor respectively.

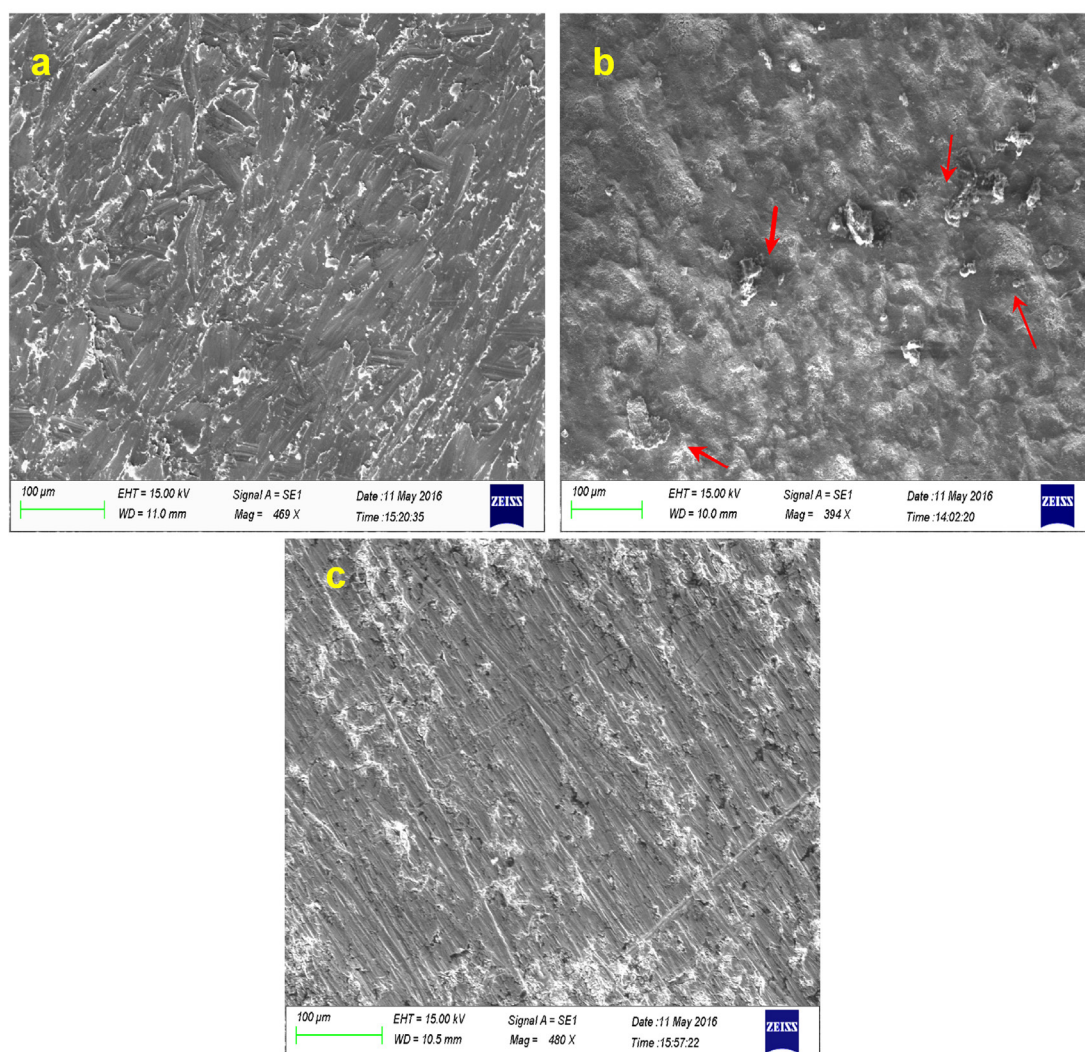


Figure 13. SEM images of mild steel samples (a) before immersion (b) without and (c) with 600 ppm ECS inhibitor after immersion in 0.5 M H₂SO₄ for 72 h.

It is clear from the SEM images that there was a significant difference between the two samples after immersion; hardly any corrosion products have been noticed on the surface of the mild steel after 72 h of immersion with ECS inhibitor and no pits were observed. On the other hand, the blank (without) sample shows severe corrosion and the corrosion products significantly cover the whole sample surface with some pits (arrows).

These results are in agreement with the electrochemical analysis. Thus, on the basis of achieved results, it could be stated that ECS inhibitor remarkably inhibited corrosion process of mild steel in 0.5 M H₂SO₄.

3.5. Proposed mechanism of inhibition

As a natural extract, ECS should contain several compounds; however the analysis of the extraction showed that oleic acid amide, cetylic acid and stearic acid represent the major constituent ($\approx 96\%$ of the extraction). Some of these compounds have a corrosion inhibition effect (oleic acid amide [48], stearic acid [49] and Linoleic acid [50]). Therefore, it can be suggested that the inhibitive performance of ECS is mainly attributed to these fatty acids [3]. The structures of these compounds (shown in figure 1) elucidate the presence of $-\text{OH}$, $\text{C}=\text{O}$, and $-\text{NH}_2$ groups [51, 52].

The mechanism of corrosion inhibition can be suggested as follows:

The metal type, the inhibitor chemical structure and the nature of corrosive solution; all control the adsorption process of the inhibitor on the metal surface. The adsorption process usually takes place because of (i) the electrostatic attraction between the inhibitor and charged metal and/or (ii) the interaction of inhibitor electrons with the metal [53]. Generally, during immersion of steel in sulfuric acid, the sulphate ions are adsorbed on the positively charged metal substrate [7, 54]. The positive charge on the metal substrate stimulates the adsorption of SO_4^{2-} ions and the metal surface become negatively charged (equation (9)) as follows;





Oleic acid amid is suggested to be protonated in sulfuric acid from FTIR result [45]. Consequently, the protonated fatty acids could attract to sulphate anion layer that physically adsorbed on the metal surface prohibiting further adsorption of sulphate anion i.e. no sulphate anions can reach metal surface. Also, the presence of non-bonded electron pairs of oxygen and nitrogen atoms, persuade the adsorption of the ECS inhibitor molecules on the metal surface and may react with Fe ions forming complexes which could be adsorbed on a metal surface hindering the interaction of iron ions with the acidic solution [52, 55]. Finally, the large size and molecular weight of the constituents of the extract of *C. Olitorius* play a major role in hindering the corrosion process by covering a wide area of the metal surface [25].

4. Conclusions

In this work, a green corrosion inhibitor was extracted from *C. Olitorius* plant's stems. The qualitative and quantitative analysis of the extracted powder revealed that it contains $\approx 92\%$ fatty acids. Based on weight loss studies, the inhibition effect is due to adsorption process and follows El-Awady adsorption model. The potentiodynamic polarization revealed that the extracted compounds are a mixed-type inhibitor and the efficiency of protection increases with inhibitor concentration. EIS investigation clarified that the increase of inhibitor concentration increases the charge transfer resistance. The thermodynamic study showed that the adsorption process is exothermic physisorption process. The inhibition results determined using weight loss, potentiodynamic polarization and EIS measurements are in a good agreement. SEM and FTIR analysis confirm the corrosion measurement results. The extraction of *C. Olitorius* is an efficient corrosion inhibitor for mild steel in 0.5 M H_2SO_4 .

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