Chapter

Mathematical Relationship Based on Experimental Data, for Corrosion Inhibition Mechanism of Phenolic Compounds Obtained from *Echium italicum* L.

Boudiba Sameh, Hanini Karima, Boudiba Louiza, Saouane Izzeddine and Benahmed Merzoug

Abstract

We highlight in this chapter the corrosion protection using phenolic extract. The building of mathematical models using experimental results obtained from the investigation of phenolic molecules or fractions extracted from *Echium italicum* L., used as corrosion inhibitors is one of the new trends in the study of steel protection. The evaluation of the corrosion inhibition of carbon steel (API 5 L-X60) in a solution 1 M of hydrochloric acid was performed using gravimetric method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS). The predicted mathematical relationships between the corrosion rate and the inhibitory efficiency in the presence of the butanolic extract of *Echium italicum* L. (BEEI), when increasing temperature proved a good agreement between experimental and mathematical studies.

Keywords: mathematical, relationship, *Echium italicum* L., phenolic compounds, corrosion inhibition

1. Introduction

Secondary metabolites, derived from natural plants, of which polyphenols constitute the grand part, have a wide range of activities [1]: biological (antibacterial, antioxidant [2, 3], anti-inflammatory [4], antidiabetic [5], anti-carcinogenic [6], etc.) and chemical (in connection with their chelating power with metals and their reducing properties generated by the hydroxyl functions of their aromatic rings). These molecules are used in several fields: as preservative food additives (constituting an alternative to the use of synthetic ones, such as buthylhydroxyanisol (BHA) and buthylhydroxytoluene (BHT), which have carcinogenic effects [7]; as flavoring in cosmetology [8]; as additives in electrolytic baths during the metals electrodeposition [9–11] and as corrosion inhibitors [12–14].

Even today, these molecules have not revealed all their secrets. Our research aims to understand the power of polyphenols in the field of metal protection against corrosion.

The *Echium italicum L.* is an annual herbaceous plant, available in most of Europe, Asia [15–18], and Africa [19]. This plant widespread in Tebessa area (Algeria) [20], is used traditionally for several infections [15, 17, 18]. Furthermore, the *Echium italicum L.* contains different polyphenolic compounds, known as effective additives in electroplating baths [16, 17, 21].

We continue in this investigation to focus on the *effect* of plant extract obtained from the aerial parts of *Echium italicum L.,* on the corrosion inhibition of carbon steel (CS, API 5 L-X60) against 1 M hydrochloric acid solution, using weight loss, potentiodynamic polarization and electrochemical impedance measurements.

On the other hand, and in order to better understand the underlying reaction mechanisms of the corrosion phenomena to choose which inhibitors to use to combat it, the prediction of the implementation behavior of effective corrosion control measures is paramount. For this purpose, mathematical simulation was used as a powerful method [12, 22] to evaluate the kinetic parameters of both corrosion rate and inhibition efficiency.

2. Corrosion

Corrosion, from the Latin "corrodere" (which means "to attack") is one of the harmful global problems affecting several industrial fields such as maritime installations, petroleum, chemical, civil engineering, electrical, nuclear, sanitary, and other industries, without forgetting the environmental impact [23–25].

The corrosion of metals and their transformation into various compounds cause an alteration in their appearance, either on the surface or in-depth, thus reducing their effectiveness (parts breakage, the toxicity of the resulting metal oxides, etc.).

Several factors come into play in this phenomenon. They can be chemical (water, oxygen, salinity, acidity, etc.), physical (temperature, pressure, etc.), or biological (marine biological deposit of plants or animals, bacteria, etc.).

This phenomenon has Several definitions:

- The ISO 8044 standard defines corrosion as a physicochemical process, which leads to the deterioration of a material (metal or alloy), or degrades its functional properties following its interaction with an aggressive environment, making it unsuitable for supposed application [26].

- The National Association of Corrosion Engineers (NACE) outlines this phenomenon as the deterioration of a material, usually a metal, generated by its interaction with its environment [27].

3. Corrosion protection

Corrosion control is the set of measures that can protect metallic materials from the harmful effects of the aggressive environment. Many of these methods were reported in the literature [28, 29]. The first protection is the choice of pure metal or alloys resistant to these attacks [30].

After designing the equipment using the appropriate material, it must be protected against corrosion should be considered to avoid many problems and ensure a certain service life. For this, the preferred outlet must comply with environmental protection requirements and allow the recycling or disposal of the various components at the end of their use by applying the following choices [31]:

- Prevention by an adapted shape of the parts;
- Protection by coatings;
- Electrochemical protection;
- Protection by corrosion inhibitors.

All these solutions have drawbacks of efficiency over time, cost and environmental pollution, which is why other alternatives are exploited in research for the benefit of sustainable development that respects the environment. To this end, there have recently been some new alternatives products both environmentally friendly and less expensive as the use of inhibitors from naturals origin [32].

4. Corrosion inhibitors

Inhibitors have been successfully applied to prevent corrosion and damage in many and varied technical fields for a long time. These products have been frequently studied because they provide simple solutions to protect metals from corrosion in the aquatic environment. With the originality of being the only means of interference of the corrosive environment with steel, these compounds reduce the rate of corrosion of metals when added in appropriate amounts, without apparent change [9, 14].

5. Materials and methods

5.1 Materials

The vegetable material was collected during May 2017 from the East-North of Tebessa (Algeria). The extraction and purification of the *n*-butanolic extract obtained from *Echium italicum* L. (BEEI) were performed as reported in litérature [10, 33, 34].

The tested aggressive medium was a chlorhydric acid solution (1 M), and the investigated inhibitors were freshly prepared solutions of BEEI with different concentrations (from 100 to 500 ppm).

Before each mesurements, the substrates were abraded using emery paper with different grades (from 200 to 2000), cleaned with distilled water and then acetone. The used substrates were carbon steels with the following composition: (by weight%): C (0.26%), Mn (1.35%), P (0.03%), S (0.03%) and Fe (98.33%). Weight loss measurements were performed with specimens with dimensions of 1 cm x 1 cm x 1 cm. For the electrochemical experiments, only an exposed surface of 1 cm^2 was used. All measurements were conducted in an aerated area.

5.2 Methods

5.2.1 Electrochemical measurements

All electrochemical measurements were accomplished through a Voltalab (PGZ 301) potentiostat and controlled by software model (Voltamaster 4) under given conditions. The electrochemical characteristics of CS sample in uninhibited and inhibited solutions were realized in conventional three-electrode cell: CS as working electrode, platinum electrode as counter electrode and saturated calomel electrode (SCE) as a reference.

5.2.1.1 Potentiodynamic polarization

Potentiodynamic polarization curves were recorded after total immersion of the working electrode (CS) in 1 M HCl solution containing different concentrations of the tested inhibitor by changing the electrode potential from +250 to −250 mV vs. open circuit potential (OCP) with a scan rate of 1 mV/s. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential (E_{corr}) to get corrosion current densities (i_{corr}). The $(\eta_w\%)$ at different concentrations of BEEI were calculated using the formula (1) [35]:

$$\eta_p(\%) = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100 \quad (1)$$

where i^0_{corr} and i_{corr} are the corrosion current density in the absence and presence of BEEI, respectively.

5.2.1.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) experiments were conducted in the frequency range of 100 kHz–10 mHz with a signal amplitude perturbation of 10 mV at open circuit potential (OCP) measured during 60 min of immersion in the tested solutions. The percentage of the inhibition efficiency $(\eta_w\%)$ was calculated using the polarization resistance by the following relationship [36]:

$$\eta_R = \frac{R_p - R^0_p}{R_p} \times 100 \quad (2)$$

where R^0_p and R_p are polarization resistances without and with inhibitor addition, respectively.

5.2.2 Gravimetric method

For these measurements, the prepared and pre-weighed CS substrates were totally immersed in beakers containing 1 M HCl without and with the addition of diverse concentrations of BEEI. The substrates were taken out after two hours, washed with 20% NaOH solution containing 200 g/l of zinc dust with a brush, rinsed severally with bidistilled water, dried with acetone, washed again with bidistilled water, dried and

reweighted [34]. From the weight loss data, the corrosion rate (CR) was calculated according to Eq. (3) [37]:

$$CR = \frac{w}{A.t} \tag{3}$$

where w is the average weight loss, A is the total area of one CS sample, and t is the immersion time. The inhibition efficiency η_w can be calculated by Eq. (4) [36]:

$$\eta_w\% = \frac{CR^0 - CR}{CR^0} \times 100 \tag{4}$$

where CR^0 and CR are the values of corrosion rate in absence and presence of BEEI respectively.

5.2.3 Mathematical regression

A mathematical model is used to correlate variables by fitting an equation to experimental data. When using two variables, one of them is considered as explanatory, whereas the other is considered as a dependent. The linear regression of $\boldsymbol{y}$ is given as a function of $\boldsymbol{x}$ in the equation $\boldsymbol{y} = \boldsymbol{ax} + \boldsymbol{b}$ which minimize the value $\Delta(a, b)$ [38]:

$$\Delta(a, b) = \sum_{i=1}^{i=N} \left[y_i - (ax_i + b)\right]^2 \tag{5}$$

where a and b can be calculated as follow:

$$a = \frac{\sum_{i=1}^{i=N} \left(x_i - \overline{X}\right)\left(y_i - \overline{Y}\right)}{\sum_{i=1}^{i=N} \left(x_i - \overline{\mathrm{X}}\right)^2} \tag{6}$$

and

$$b = \overline{Y} - a\,\overline{X}. \tag{7}$$

6. Results and discussion

6.1 Electrochemical impedance spectroscopy

EIS was performed to estimate CS corrosion behavior in the presence of 500 ppm of BEEI at 298 K.

The inspection of Nyquist plots presented in **Figure 1** shows only one depressed capacitive imperfect semicircle at the higher frequency range, indicating that the corrosion reaction is controlled by the charges transfer process on a heterogeneous and irregular steel surface electrode [39–41].

The electrical equivalent circuit model (EEC) adjusted by fitting from the resulting impedance diagrams for Nyquist plots is reported in literature [12].

From **Table 1**, a noticeable increase in R_{ct} values and a decrease in C_{dl} at 500 ppm of BEEI due to the formation of protective diapers on the CS surface are observed. This phenomenon can be explained by the higher adsorption of phytochemical

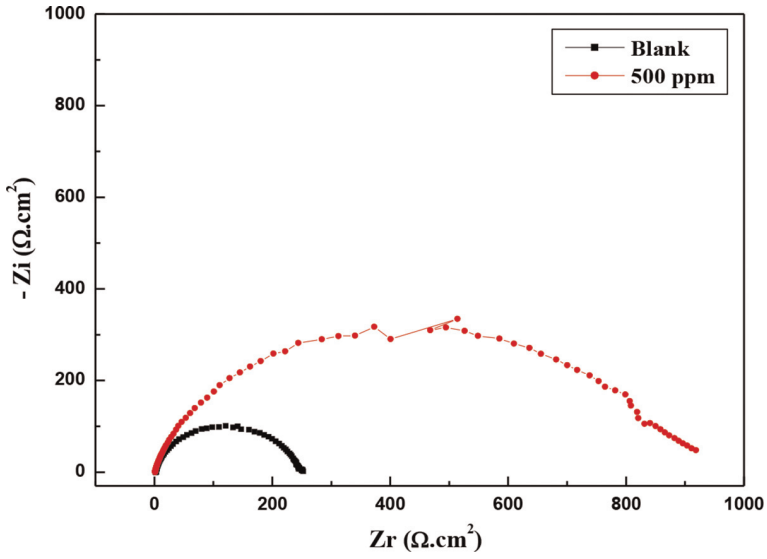


Figure 1.
Nyquist spectra for carbon steel in HCl solution in the absence and presence of 500 ppm of BEEI.

C (mg/l)	R_{ct} (Ωcm^2)	$Q \times 10^5$ ($\Omega^{-1}S^n cm^{-2}$)	n	C_{dl} ($\mu F cm^{-2}$)	η_R (%)
Blank	232.2	21.00	0.89	142.5	—
500	889.9	09.11	0.80	47.87	73.82

Table 1.
EIS parameters of CS in HCl solution in the absence and presence of 500 ppm of BEEI.

components above CS upon BEEI addition which ultimately reduces the charge transfer between the CS surface and the corrosion medium [42]. Consequently, we noticed that the η_R reached 74% at 500 mg.L^{-1}.

6.2 Potentiodynamic polarization measurement

To further evaluate the efficiency of the expected green inhibitor, the polarization technique was studied due to its excellent reliability. **Figure 2** shows the parameters given in **Table 2** and extracted from the CS electrode polarization curves for 500 ppm BEEI in the presence of 1 M HCl solution, at 293 K.

As can be seen in this figure, at 500 ppm of BEEI, the cathodic and anodic corrosion current densities will decrease. This comportment can be attributed to the adsorption of the inhibitor at the carbon steel interface [43] by reducing the dissolution of steel and delaying the hydrogen evolution reaction [44].

In our study, the maximum displacement in E_{corr} value for the optimum concentration of BEEI was −13.3 mV (< 85 mV), which exhibits that the inhibitor acts as a mixed type [43, 45]. The highest inhibition efficiency was 75% at a concentration of 500 ppm.

6.3 Weight loss measurements

To study the behavior of the steel protection in the presence of an aggressive solution, the weight loss method was used. Based on this approach, the *CR*, the η_w and

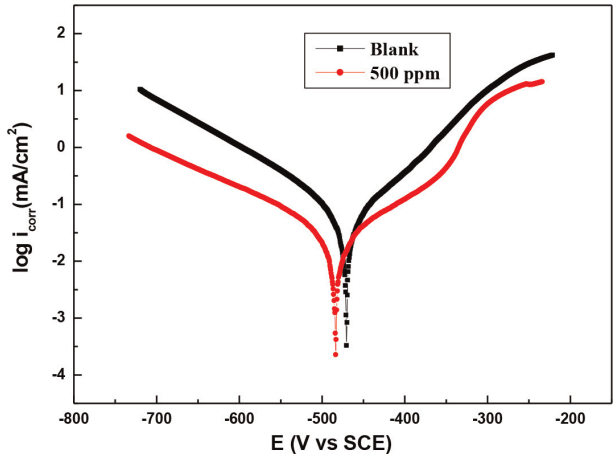


Figure 2.
Potentiodynamic polarization curves for carbon steel in HCl solution with and without inhibitor addition.

C (mg/l)	$-E_{corr}$ (mV)	i_{corr} (mA cm^{-2})	β_a (mV dec^{-1})	$-\beta_c$ (mV dec^{-1})	η_p (%)
Blank	470.6	0.0861	72.6	117.9	—
500	483.9	0.0216	75.8	134.2	74.91

Table 2.
Potentiodynamic polarizations parameters of CS in HCl solution in the absence and presence of 500 ppm of BEEI.

Temperature (K)	C (ppm)	CR (g cm^{-2} h^{-1})	θ	η_w%
293	Blank	0.1232	—	—
	500	0.0334	0.7288	72.88
303	Blank	0.1681	—	—
	500	0.0548	0.6740	67.40
313	Blank	0.1716	—	—
	500	0.0682	0.6025	60.25

Table 3.
Corrosion parameters obtained from weight loss measurements of CS in 1 M HCl with different concentrations of BEEI at different temperatures.

the degree of surface coverage θ were calculated and are very useful for discussing adsorption properties.

From **Table 3**, it can be observed that the *CR* values reduced progressively with increasing BEEI concentration, reaching 0.0334 g cm^{-2} h^{-1} for 500 ppm at 293 K. This result indicates that the addition of this inhibitor slows down the dissolution process of the CS. There was also a *CR* increase with increasing temperature.

This behavior can be attributed to the removal of some adsorbed molecules contained in the BEEI, through thermal energy-induced mechanical vibration [46]. As the inhibition efficiency is derived from the weight-loss method, the highest inhibition efficiency was 72.88% for 500 ppm of BEEI at 293 K.

6.3.1 Thermodynamic parameters

The good fitting for experimental data of gravimetric measurements at all measured temperatures supports the applicability of Freundlich adsorption model expressed by the subsequent Equation [47, 48]:

$$log\theta = log\, K_{ads} + \alpha\, logC \tag{8}$$

where,

K_{ads} is the adsorption constant which could be taken as a measure of the strength of the adsorption forces between the inhibitor molecules and the metal surface [49].

α is the parameter taking into account the heterogeneity of the intermolecular interactions in the adsorbed layer and the steel surface.

K_{ads} represent the values calculated from the intercept lines of $log\theta$ versus Log C.

The standard adsorption free enthalpy ΔG°_{ads} can be calculated from the equation given below [50, 51]:

$$\Delta G^{\circ}_{ads} = -RTln(C_{H_2O} \times K_{ads}) \tag{9}$$

where

R is the gas constant,

T is the absolute temperature,

C_{H_2O} is the water concentration expressed in mg L^{-1} with an approximate value of 10^6. [52].

The standard adsorption enthalpy $\left(\Delta H^{\circ}_{ads}\right)$ can be calculated by the relationship (10) [53]:

$$ln\, K_{ads} = \frac{-\Delta H^{\circ}_{ads}}{RT} + I \tag{10}$$

where

I is the integration constant.

The ΔH°_{ads} values were calculated from the intercept lines of $ln\, K_{ads}$ versus $1/T$.

The standard adsorption entropy $\left(\Delta S^{\circ}_{ads}\right)$ was calculated using the equation below:

$$\Delta S^{\circ}_{ads} = \frac{\Delta H^{\circ}_{ads} - \Delta G^{\circ}_{ads}}{T} \tag{11}$$

The obtained results for K_{ads}, ΔG°_{ads}, ΔH°_{ads} and ΔS°_{ads} are presented in **Table 4**.

From **Table 4**, we noticed the following:

$T(K)$	K_{ads} (L mg^{-1})	ΔG°_{ads} ($KJmol^{-1}$)	ΔH°_{ads} ($KJmol^{-1}$)	ΔS°_{ads} ($Jmol^{-1}K^{-1}$)
293	0.9809	−25.44	−22.22	10.99
303	0.9968	−25.99		12.44
313	0.9968	−25.65		10.96

Table 4.
Thermodynamic parameters of the adsorption of BEEI on the CS in 1 M HCl at different temperatures.

1. A decrease in K_{ads} values with increasing temperatures, indicating that the adsorbent molecules contained in the BEEI adsorbed from the metal surface [54].

2. Negative ΔG°_{ads} values point out the spontaneity of the adsorption process. Moreover, the results obtained for ΔG°_{ads} adsorption values below -40 kJmol^{-1} confirm the physisorption mechanism [55].

3. The negative sign of ΔH°_{ads} indicates that the BEEI adsorption process on the steel surface is exothermic [56, 57].

4. The positive sign of ΔS°_{ads}, indicates that the adsorption process is accompanied by increased disorder due to the substitution of water molecules during BEEI adsorption [58–60].

6.3.2 Activation parameters of the corrosion process

The Arrhenius-type process was used to calculate the activation energies (E_a) between the corrosion rate of CS in acidic solution, from the equation given below [61]:

$$lnCR = -\frac{E_a}{RT} + lnD \tag{12}$$

Where
E_a is the apparent activation energy of the CS dissolution.
D is the Arrhenius pre-exponential factor.
The logarithm of the CR versus $1/T$ can be branded by straight lines. The activation energy values were calculated from Arrhenius plots $lnCR$ versus 1/T and registered in **Table 5**.

For the evaluation of the enthalpy ΔH_a as well as the standard adsorption entropy ΔS_a of the corrosion activation process, the alternative formulation of Arrhenius equation was employed [62, 63]:

$$ln\ \frac{CR}{T} = \left[ln\ \frac{R}{hN_a} + \frac{\Delta S_a}{R}\right] - \frac{\Delta H_a}{RT} \tag{13}$$

where
h is the Planck's constant,
N_a is the Avogadro's number.
The plot of lnCR/T vs. 1/T gave a straight line with a slope of $(-\Delta H_a/R)$ and an intercept of $\ln(R/hN_a + \Delta S_a/R)$, from which the values of ΔS_a and ΔH_a were calculated and registered in **Table 5**.

C (ppm)	E_a (kJ mol^{-1})	ΔH_a (kJ mol^{-1})	ΔS_a (J mol^{-1} K^{-1})
Blank	12.75	10.23	−3.2822
500	27.32	24.80	- 2.7202

Table 5.
Activation parameters for carbon steel in HCl with 500 ppm of BEEI.

The activation energy values were higher in the presence of 500 ppm of BEEI than in its absence, which proved the adsorption of BEEI molecules on the substrate by electrostatic bonds (physisorption) [62, 64]. The positive signs of ΔH_a indicate the endothermic nature of the dissolution process [65].

The BEEI adsorption process is accompanied by a decrease in its entropy. This can be explained that before the adsorption of the extract on the steel, the disorder degree of the inhibitor molecules is high, but when the molecules are adsorbed on the surface of the substrate, there is a decrease the in the disorder (i.e. a decrease in the entropy) [66].

6.4 Mathematical regression

This investigation focused on how could the used inhibitor (BEEI) decrease the corrosion rate (CR) and offer a good inhibition efficiency (η_w).

For that, a mathematical method was employed to predict the influence of a variable (x) which is the BEEI concentration as a function of different variables (y_i) which are CR and η_w for 293 K, 303 K, and 313 K [51, 67]. The building of a mathematical model that can correlate between three variables (CR, η_w, and C) was also highlighted.

Based on experimental data of the CS behavior in the presence of BEEI at various temperatures, a linear regression relation between CR and η_w, was performed.

As reported by Khadom et al. [67], when the correlation coefficient of the correlation is < 0.30, the correlation is weak and when this coefficient is between 0.50 and 0.70, the correlation is important, while if it is >0.90, the correlation will be strong.

According to the plots shown in **Figure 3**, a decrease in the CR with a raise in the η_w, when adding BEEI with various concentrations at different temperatures was distinguished, and based on correlation coefficients r^2_{CR} and $r^2_{\eta_w}$ given in **Table 6**, the concordance between the experimental and the simulated results is very strong.

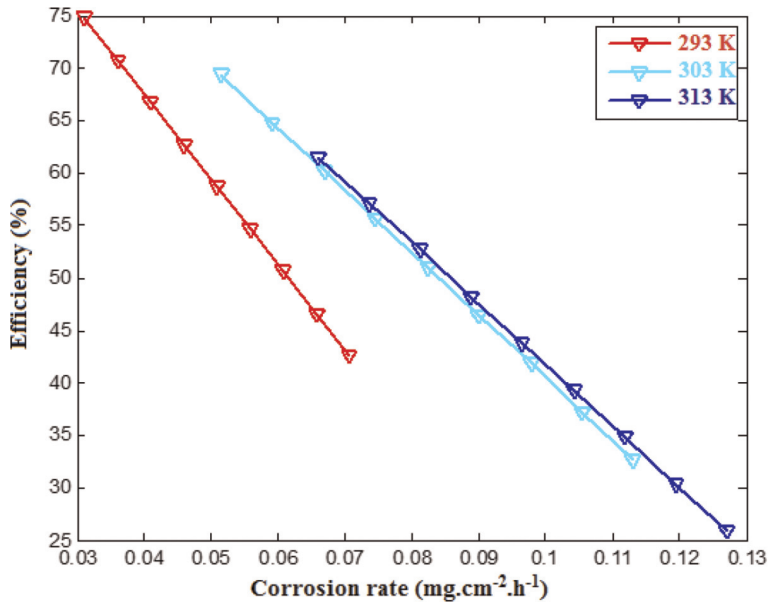


Figure 3.
Mathematical relationship between corrosion rate and inhibitory efficiency at different temperatures.

Temperature (K)	r^2_{CR}	$r^2_{\eta_w}$
293	0.9765	0.9625
303	0.9886	0.9775
313	0.9970	0.9890

Table 6.
Correlation coefficients evaluated from linear regression of CR and η_w for CS with and without BEEI solution.

As we can see from the obtained results, the correlation coefficients were almost >0.90 for considered temperatures. However, as the temperature rises the correlation coefficients go up. The Eqs. (12)–(14) construe the mathematical expression obtained for the relationship between the *CR* and the η_w at different temperatures.

This mathematical model exhibits a decrease in the corrosion rate when inhibition efficiency rises, with reducing in temperature. These results indicate the powerful concordance between experimental and predicted results.

T = 293 K

$$\eta_w = 99.9849 - 811.470.CR \tag{14}$$

T = 303 K

$$\eta_w = 99.9977 - 594.869.CR \tag{15}$$

T = 213 K

$$\eta_w = 99.9910 - 582.713.CR \tag{16}$$

7. Conclusion

In order to estimate the multiple benefits of phenolic compounds, a phenolic *Echium italicum* L. extract was evaluated as an efficient corrosion inhibitor. The subsequent conclusions can be pointed out:

- A concordance between the employed evaluating methods, suggesting that the phenolic extract could serve as an effective corrosion inhibitor for CS against corrosion.

- Depending on the gravimetric measurements, the investigated phenolic extract was spontaneously adsorbed on the CS surface following a physical model according to Freundlich isotherm.

- The prediction of the phenolic extract effect of as a corrosion inhibitor by the mathematical study was in good agreement with the experimental results, which confirms that the corrosion rate is affected by the temperature and the inhibitor concentration.

- The generated mathematical model shows a decrease in the corrosion rate with the increase of inhibition efficiency. These results indicate a strong agreement between experimental and mathematical results.

- The *Echium italicum* L. extract has prooved to be an effective corrosion inhibitor, and hence the phenolics can be useful on various existing industries to prevent losses caused by corrosion of steel without harming the environment.

For a more extensive valuation of phenolic products, many perspectives are envisaged, namely:

- Evaluate the synergy between phenolic extracts extracted from different plants looking for a better efficiency.
- The study can be extended to analyze the effect of these phenolic compounds in other corrosive media and on other types of steel.
- Perform a theoretical simulation to highlight the active compound (s) responsible for this inhibition.

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