Comparative Study of S235 Steel Corrosion Inhibition by *Eucalyptus camaldulensis* and *Cyperus rotundus* Essential Oils in Hydrochloric Acid Solution

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Abstract: Synthetic compounds certainly exhibit good anticorrosive activity but also toxicity for humans and their environment. Because of these concerns, we turned to more environmentally friendly substances such as essential oils and of course other types of plant extracts. These products are considered green corrosion inhibitors. In this present study, we propose to make a comparative study of the inhibitory effect of extracts of two different essential oils, *Eucalyptus camaldulensis* (EC) and *Cyperus rotundus* (CR) on the corrosion of structural steel S235 in the medium 1 M hydrochloric acid. This inhibitory action was studied using potentiodynamic polarization measurements and electrochemical impedance spectroscopy. The GC-MS analysis of the essential oils extracts showed that EC contains 96.2% oxygenated terpenes (90.6% monoterpenes and 5.6% sesquiterpenes), whereas CR includes 78.1% oxygenated terpenes (70.6% sesquiterpenes and 7.5% monoterpenes). Polarization measurements indicate that EC and CR are mixed inhibitors. The experimental results gave an inhibition efficiency close to 78.9% for EC and 86.7% for CR for an inhibitor concentration of 4 gL⁻¹ at 293 K. The inhibition performances of these essential oils were correlated with their composition. The adsorption of the molecules of the oils responsible for the inhibition on the surface of the steel, in the hydrochloric acid solution, obeys the Langmuir adsorption isotherm. This present work has therefore shown that these two types of essential oils have a good inhibitory effectiveness on the corrosion of the metal S235 in 1M hydrochloric acid solution.

Keywords: Corrosion, Essential Oil, *Eucalyptus Camaldulensis*, *Cyperus Rotundus*, S235 Steel, Langmuir Isotherm

1. Introduction

Corrosion is a recurring phenomenon, difficult to eliminate completely and which is caused by aggressive environments. However, corrosion is perceived as an industrial problem which generates numerous environmental, economic and even human damages. Economically, for example, corrosion damages and repairs can be valued in billions of dollars each year [1]. The use of acids in crude oil refining, acid pickling, industrial cleaning and acid descaling exposes metals to these corrosive environments. Hydrochloric acid is extensively used in industry, but causes degradation of some metals. To deal with this unwanted and destructive phenomenon, several methods or techniques of protection have been developed. These methods of protection include the application of a protective barrier, electroplating, cathodic protection, etc., or the use of anti-rust solutions or corrosion inhibitors. The latter remains by far the most coveted method. Most synthetic compounds exhibit good corrosion inhibiting action, but the majority of them are highly toxic to humans and the environment [2]. New environmental demands encourage the development of new forms of inhibitors.
in the scientific world, which are less toxic and inherently safer. In view of these considerations, intensive research has been carried out on the substitution of toxic inhibitors for less toxic or non-toxic products. The use of clays as inhibitors for S235 steel corrosion has been investigated in our studies [3, 4]. Recently several extracts from various parts of plants (leaves, fruits, seeds and flowers) have been used as corrosion inhibitors [5-14]. In the same vein, in recent years a major importance was given to the use of essential oils as corrosion inhibitors. According to the literature, many studies have mentioned the good inhibitory effectiveness of essential oils on the corrosion of steel in acidic environment (hydrochloric and sulfuric) [15-29].

The objective of the present work is to make a comparative study of the inhibitory action of two types of essential oils on the corrosion behavior of S235 steel in a 1 M hydrochloric acid solution.

2. Experimental

S235 structural steel was provided by Pole de Développement Industriel, Dakar, Senegal. It is composed of (mass percentage): C = 0.17, Mn = 1.40, N = 0.012, P = 0.04, S = 0.04, Cu = 0.55, Fe = balance [30]. It was cut into rectangular sheets of 3.6 cm\(^2\) area. Before each test, it was sequentially polished using silicon carbide papers, rinsed with distilled water and dried in the open air.

The corrosion solution consisted of a molar (1 M) solution of hydrochloric acid prepared from a commercial (Sigma-Aldrich) solution of hydrochloric acid of 37% purity and 1.18 density. For each test, a quantity of the essential oils (Sigma-Aldrich) solution of hydrochloric acid of 37% purity was added to the 1 M HCl solution. This concentration range was determined after preliminary tests on the solubility of the essential oils in the corrosive medium. The corrosion of the steel and the inhibitory efficacy were studied in these media.

_Eucalyptus camaldulensis_ species were collected in February 2018 in Saint-Louis (northern Senegal), and _Cyperus rotundus_ was harvested in June 2018 in Mlomp (southern Senegal). The EC essential oils were extracted from the leaves of the plant whereas CR essential oils were isolated from the roots. These extractions were carried out by steam distillation during 90 min using a "Clevenger" type apparatus and the resulting essential oils were stored in amber bottles maintained at 4 °C until use.

The Gas Chromatography (GC) experimentations were carried out using a Thermo Electron TRACE GC Ultra chromatograph (Thermo Electron Corporation, Interscience Louvain-La-Neuve, Belgium), coupled to an Agilent Technologies 5973 Network Mass Spectrometry Detector (transmission quadrupole mass spectrometer) allowing the detection and quantification of compounds. The chromatograph was equipped with an Optima 5-accent type, 5% phenylmethylsilicone capillary column: 30 mL, 0.25 mm ID, 0.25 µm film thickness (Macherey-Nagel, Düren-Germany). The detailed procedure for the GC-MS analysis (operating conditions, temperature adjustment and identification procedure) is described elsewhere [29].

The electrochemical investigations were performed in a classical three-electrode cell containing a platinum grid as the counter electrode, Ag/AgCl reference electrode (+197 mV/NHE), and the working electrode consisting of the S235 steel sample. The measurements were carried out using a PalmSens 4 Potentiostat (PalmSens BV, NL) controlled by PSTrace 4.8 software. The corrosion behavior of S235 steel in 1 M HCl solutions with and without essential oils were studied by Tafel polarization method (0.5 mV/s scan rate and 30 minutes an equilibrium time) and Electrochemical Impedance Spectroscopy (EIS) at open-circuit-potential with a signal amplitude of 10 mV and a frequency domain ranging from 50 kHz to 100 mHz (10 points/decade). Before running the experiments, the working electrode was maintained at free corrosion potential for 1 hour in the proper solution with magnetic stirring, thus allowing an evenly solubilization of the essential oils in the aqueous electrolyte at the operating temperature.

The electrochemical parameters \(i_{corr}^{0}, E_{corr}, R_p, b_1, b_2\) were assessed from the Tafel polarization curves, according to the Stern-Geary equation after ohmic drop compensation. The inhibitory efficiency was evaluated using Eq. (1) [31]:

\[
IE = \frac{i_{corr}^{0} - i_{corr}}{i_{corr}} \times 100
\]

\(i_{corr}^{0}\) and \(i_{corr}\) being the corrosion current densities without and with inhibitor, respectively. The measured values of the impedance were then fitted to a Randles electrical-equivalent circuit and the results were used to calculate the inhibitory efficacy using equation (2) [31]:

\[
IE = \frac{R_{ct}}{R_{ct}^{0}} \times 100
\]

\(R_{ct}^{0}\) and \(R_{ct}\) represent the charge-transfer resistance in the absence and presence of inhibitor, respectively.

![Figure 1. Chromatograms of Eucalyptus camaldulensis (A) and Cyperus rotundus (B) essential oils.](image-url)
3. Results and Discussion

3.1. GC-MS Analysis of EC and CR Essential Oils

The composition of EC and CR essential oils extracts were first determined by GC-MS. The chromatograms are shown in Figures 1 and 2.

Table 1 gives the chemical composition of essential oils of *Eucalyptus camaldulensis* (EC). It shows that the main compounds present in the essential oil (EC) include: 1,8-Cineole (83.2%), α-Terpineol (3.7%), α-Pinene (2.2%). The total percentage of oxygenated terpenes represent almost 96.2% of the total (90.6% of monoterpenes and 5.6% of sesquiterpenes). In figure 2, we show the molecular structures of the major constituents.

**Table 1. Chemical composition of essential oils of Eucalyptus camaldulensis.**

| Compounds          | Retention Times (min) | Retention Indices | % of Compounds |
|--------------------|-----------------------|-------------------|----------------|
| α-Pinene           | 8.24                  | 940               | 2.2            |
| p-Cymene           | 10.91                 | 1026              | 1.6            |
| 1,8-Cineole        | 12.95                 | 1036              | 83.2           |
| Terpinen-4-ol      | 21.72                 | 1177              | 1.9            |
| Trans-p-Mentha-1(7) dien-2-ol | 22.42   | 1186              | 1.7            |
| α-Terpineol        | 42.76                 | 1190              | 3.7            |
| Caryophyllene-oxide| 46.62                 | 1157              | 0.7            |
| Globulol           | 49.35                 | 1587              | 0.7            |
| β-Eudesmol         | 50.22                 | 1655              | 1.9            |
| α-Eudesmol         | 50.39                 | 1659              | 2.2            |
| Hydrocarbon monoterpenes | 3.8       |                  |                |
| Oxygenated monoterpenes | 90.6    |                  |                |
| Oxygenated sesquiterpenes | 5.6      |                  |                |
| Total compounds identified | 100     |                  |                |

**Figure 2. Molecular structures of the main constituents of Eucalyptus camaldulensis essential oil.**

The chemical composition of CR essential oils is shown in Table 2. The extracts are mainly composed of *Caryophyllene oxide* (19.2%), *Humulene oxide II* (26.1%), *Isoaromadendrene epoxide* (3.7%) and *Longiverbenone* (11.3%). Like EC, CR mainly contains oxygenated terpenes (78.1% of the total). However, we counted in CR more sesquiterpenes (70.6%) than monoterpenes (7.5%). The molecular structures of the most important constituents are depicted in Figure 3.

**Table 2. Chemical composition of essential oils of Cyperus rotundus.**

| Compounds                                  | Retention Times (min) | Retention Indices | % of Compounds |
|--------------------------------------------|-----------------------|-------------------|----------------|
| trans-Pinoocarveol                         | 10.37                 | 1152              | 1.8            |
| Myrthenal                                  | 11.77                 | 1194              | 1.7            |
| Verbenone                                  | 12.11                 | 1203              | 1.2            |
| α-Copaene                                  | 16.35                 | 1340              | 3.5            |
| α-Cubebene                                 | 16.47                 | 1346              | 3.7            |
| δ-Selinene                                 | 17.15                 | 1374              | 2.0            |
| 9,10-Dihydro-isologifolene                 | 17.30                 | 1381              | 0.8            |
| non identifié                              | 18.78                 | 1501              | 0.7            |
| α-Guaiene                                  | 18.90                 | 1504              | 0.5            |
| γ-Cadinene                                 | 19.28                 | 1516              | 1.4            |
| β-Chamigrene                               | 19.50                 | 1523              | 0.6            |
| Valencene                                  | 19.74                 | 1530              | 1.0            |
| Not identified                             | 20.31                 | 1548              | 0.4            |
| Not identified                             | 20.57                 | 1556              | 0.9            |
| Calacorene                                 | 21.13                 | 1573              | 0.6            |
| cis-Caryophylleneoxide                     | 21.39                 | 1581              | 1.5            |
| Caryophylleneoxide                         | 22.25                 | 1608              | 19.2           |
| Humuleneoxide II                           | 22.97                 | 1632              | 26.1           |
| Viridiflorol                               | 23.50                 | 1649              | 1.2            |
| (-)(-)-Caryophylleneoxide                  | 23.61                 | 1653              | 1.6            |
| 4,4-Dimethyltetrayclo- [6,3,2,0(2,5)0(1,8)]tirdec-9-ol | 23.72   | 1656              | 0.5            |
| Nerolidol                                  | 23.97                 | 1664              | 0.5            |
| Isoaromadendreneepoxide                    | 24.36                 | 1677              | 3.7            |
| Not identified                             | 24.74                 | 1689              | 2.1            |
| Longiverbenone                             | 24.84                 | 1693              | 11.3           |
| (+)(-)-Caryophylleneoxide                  | 24.95                 | 1696              | 1.9            |
| Aristolone                                 | 25.29                 | 1707              | 1.4            |
| Not identified                             | 25.53                 | 1716              | 0.6            |
| Not identified                             | 26.09                 | 1735              | 3.4            |
| Limonenedioxide                            | 27.28                 | 1776              | 2.8            |
| Nootkatone                                 | 28.17                 | 1807              | 1.3            |
| Oxygenated monoterpenes                    | 7.5                   |                  |                |
| Hydrocarbon sesquiterpenes                 | 14.4                  |                  |                |
| Oxygenated Sesquiterpenes                  | 70.6                  |                  |                |
| Not identified                             | 7.5                   |                  |                |
| Total compounds identified                 | 92.5                  |                  |                |

**Figure 3. Molecular structures of some major Cyperus rotundus essential oil constituents.**
3.2. Tafel Polarization Curves

The stationary Tafel polarization curves, in the absence and in the presence of the inhibitors at various concentrations are shown in Figure 4.

We observed that the cathodic and anodic Tafel lines are quite parallel, which shows that the process follows a charge transfer mechanism [32]. The Tafel stationary polarization curves are characterized by a slight shift in the corrosion potential as a function of the concentration of the inhibitor. The intervention of the inhibitor in the transport process of electroactive species (oxygen, protons, reaction products) in the solution is unlikely, the effect of an inhibitor usually unfolds at the close vicinity of the surface. We can thus conceive the action of the inhibitor as giving rise to formation and interposition of a barrier between the metal and the corrosive environment. It is established that an inhibitor can be classified as of cathodic or anodic type if the displacement potential as a function of the concentration of the inhibitor.

In general, in hydrochloric acid solution, the anodic oxidation of iron by the Cl⁻ can be represented by the following reactions [36, 37]:

\[
Fe + Cl^- \rightarrow (FeCl^-)_{ads}
\]

\[
(FeCl^-)_{ads} \rightarrow (FeCl^+) + 2e^-
\]

\[
(FeCl^+) \rightarrow Fe^{2+} + Cl^-
\]

The cathodic reduction of hydrogen is given by the following reactions [36, 37]:

\[
Fe + H^+ \rightarrow (FeH^+)_{ads}
\]

\[
(FeH^+)_{ads} + e^- \rightarrow (FeH)_{ads}
\]

\[
(FeH)_{ads} + H^+ + e^- \rightarrow Fe + H_2
\]

![Tafel polarization curves of S235 steel in HCl (1M), at different concentrations of Eucalyptus camaldulensis (A) and Cyperus rotundus (B) at 293 K.](image)

The introduction of EC or CR in the hydrochloric acid solution does not modify the mechanism of evolution and reduction of hydrogen on the surface of the steel [38], but act simultaneously on the half-equations of oxidation and reduction by modifying the adsorption process.

The experimental results obtained in Table 3 indicate a fairly small variation of \(b_a\) and \(b_c\) in the HCl solution with or without inhibitor (EC or CR). In addition, they are roughly independent of the nature of the inhibitor. It can therefore be suggested that the mechanism of corrosion remains unchanged [39].

The strong decrease in current density observed with the introduction of essential oils of EC and CR shows the inhibitory action of these natural compounds on the corrosion of S235 steel in 1 M HCl medium. However, the current densities after inhibitor addition are much lower for EC compared with CR. This decrease in the corrosion rate is due to the adsorption of the majority of organic molecules contained in these essential oils on the interface of the steel. The presence of the inhibitors induces a reduction of the current on the metal surface. If this blockage is only partial, it can lead to an increase in the current density on these surfaces and therefore a localized corrosion process, more intense than in the absence of inhibitor and depending on the importance of its content. Inhibitors act by forming a passive layer and should be used with caution as lead to a modification of the corrosion nature [40, 41].

The slopes of the parallel cathode Tafel curves (Figure 4)
show that the reduction is not affected by the presence or absence of the essential oils and the release of hydrogen is controlled by an activation mechanism [42]. The inhibitor first adsorbs to the steel surface before acting by simply blocking its active sites. Cathodic inhibitors induce an increase in the cathodic overvoltage, and therefore reduce the corrosion current. While this inhibitor does not completely stop the corrosion reaction, it does not present the risk of causing a localized corrosion.

The inhibitory power increases with the concentration of substances and reaches for a content of 4 gL⁻¹ values of 77.52% for EC and 85.82% for CR. The differences of inhibition efficiencies may be related to the content of the essential oils. As noted in GC-MS study the CR essential oils contain 70.6% of sesquiterpenes and 7.5% of monoterpenes, whereas EC is made of 90.6% of monoterpenes and 5.6% of sesquiterpenes. It is worth to note that sesquiterpenes result from the combination of three and monoterpenes from two branched, unsaturated C5 units (isoprene) [43]. The higher efficiencies of CR compared with EC essential oils may be ascribed to the higher concentrations of the larger molecules of sesquiterpenes.

3.3. EIS Measurements

To better understand the inhibitory action of these two varieties of essential oils (EC or CR), we have also used EIS to study the corrosion of the S235 material in a 1 M HCl medium, in the presence and in the absence of essential oils of. Figures 5 and 6 show the electrochemical impedance Nyquist and Bode diagrams of steel in the 1 M hydrochloric acid solution at different concentrations of essential oils. They were recorded after 2 h of immersion at room temperature at the corrosion potential in frequencies ranging from 5000 Hz to 100 mHz.

Nyquist impedance diagrams (Figure 5) exhibit depressed semi-circles with the center under the real axis. This trend, typical for solid electrodes is often referred to as frequency of dispersion. It is generally related to different physical phenomena such as roughness and inhomogeneities of solid surfaces, impurities, grain boundaries and distribution of active sites on the surface [44]. The Nyquist curves recorded in the different solutions show a single capacitive loop. The shape of these graphs indicate that the metal dissolution process was mainly controlled by charge transfer. Rather imperfect semicircles are noticed. They could be result from dispersing phenomena which may be related to solid surfaces roughness and inhomogeneity and inhibitors adsorption [45].

The capacitance values for both inhibitors are comprised between 6.78 and 119.11 µF. They can especially be interpreted as a Nernstian process rather than as adsorptive film formation (capacitance values in the order of magnitude of few nF). We therefore used a constant-phase element (CPE) instead of a pure capacitance is used to fit of the experimental measurements. The impedance of a CPE is given by the following relationship [46, 47]:

$$Z_{\text{CPE}} = A^{-1} (j\omega)^{-n}$$  \hspace{1cm} (9)

where A refers to the CPE (in Ω⁻¹), ω = 2πf corresponds to the angular frequency of sinusoidal modulation (in rad/s), and n represents an empirical exponent (0 ≤ n ≤ 1) which allows to evaluate the deviation from a pure capacitance [48, 49] for which the n exponent is equal to 1. The double-layer capacitance (Z₀) can be obtained using Eq. (10):

$$Z_\text{dl} = \frac{j}{C_\text{CPE}}$$  \hspace{1cm} (10)

From Figure 5 A and B, it can be seen that the semi-circle diameters are higher and that the capacitances are lower for CR essential oil, which suggests lower corrosion process when this inhibitor is used, in comparison with EC.

The time constant (τ) and the double-layer capacitance (Cₐ) resulting from the CPE were calculated from Eqs. (11) and (12) [50]:

$$C_\text{dl} = (AR\text{ct}^{-n})^{-1/n}$$  \hspace{1cm} (11)

$$\tau = C_\text{dl}R_c$$  \hspace{1cm} (12)

Bode diagrams are shown on Figure 6 (module) and Figure 7 (phase angle) for both inhibitors. Bode phase angle diagrams exhibit a single peak which demonstrates prominence of the charge-transfer in the metal corrosion. [51]. It was noticed that the module and phase angle increased.
with inhibitor concentration. Also, the peak positions on phase angle diagrams slightly shifted to lower frequencies. These features confirm the previous observations made from the Nyquist diagrams, suggesting a lowering of the corrosion rate by the EC and CR essential oils [52]. The general aspects of the figures were not influenced by the nature of the inhibitor. However, both module and phase angle values were higher for CR inhibitor.

The EIS results (R_{ct}, CPE (A) related to the double-layer capacitance and the exponent) obtained after fitting of the measured values of the impedance to the equivalent electrical-circuit depicted in Figure 8 are shown in Table 4.

The analysis of the EIS results summarized in Table 4, shows that for both inhibitors, the charge-transfer resistance value (R_{ct}) increases with concentration and reaches 101.8 $\Omega$cm$^2$ (EC) and 162.1 $\Omega$cm$^2$ (CR) at a concentration of 4 gL$^{-1}$ for EC and CR. As glimpsed through the Nyquist and Bode diagrams, R_{ct} is higher and C_{dl} is lower for CR inhibited solutions. Moreover, the inhibition efficiencies are higher for CR essential oils. This is in accordance with the Tafel polarization results and confirms the key role played by the sesquiterpenes which are present at higher concentrations in EC essential oils.

High charge-transfer resistances are correlated with slower corrosion systems, owing to a decrease in the active surface required for the corrosion reaction [53, 54]. The empirical exponent (n) after addition EC and CR increases, which may support this conclusion. Indeed, the lower n value in the absence of inhibitors (n = 0.77) are homogeneity defects of the surface resulting from roughing and/or corrosion products deposition. Addition of the essential oils increases the value of the n coefficient indicating a reduction in surface inhomogeneity due to the adsorption of molecules on the S235 steel surface. In the inhibited solutions, the values of n are higher for EC (0.80-0.91) compared with CR (0.82-0.97). The adsorbed layer is therefore more uniform in the latter case which may be caused by a better protection of the metal.

In addition, adding these two varieties of essential oils to the corrosive solution decreases the double layer capacitance (C_{dl}) and increases the value of the time constant (\tau) (Table 4). Indeed, in the corrosive medium, the interface parameter (\tau) is comprised between 5.17 and 5.90 ms, while C_{dl} value decreases from 108.8 to 57.9 $\mu$Fcm$^{-2}$ for EC. An increase of \tau and a decrease of C_{dl} induced by the inhibitor mean that the charge and discharge rates at the metal-solution interface are drastically reduced. This shows an adequacy between the quantity of charge which can be stored, therefore the capacitance, and the discharge speed in the interface (\tau) [55]. The decrease in this capacity with increasing oil concentrations can be attributed to the formation of a protective layer on the electrode surface [56]. The time constants (4.80-5.20 ms) and double-layer capacitances (76.9-29.8 $\mu$Fcm$^{-2}$) are lower in CR than in EC containing media. If the result was predictable for C_{dl}, the reason why the \tau values are roughly lower with the CR inhibitor is actually not clear for us. Moreover, \tau varied randomly with the inhibitor content in each case.

The inhibition efficiency was calculated from R_{ct} values. It is observed that IE (%) increases with the concentration of inhibitor (Table 4) reaching a value of 77.52% for oil EC and 85.82% for oil CR for a concentration of 4 gL$^{-1}$. Furthermore, CR essential oils appear to be more efficient as inhibitor. The results obtained by EIS perfectly corroborate those obtained by the Tafel polarization method.

### 3.4. Adsorption Isotherm and Surface Analysis

In aqueous solution, the adsorption of an organic adsorbate at the metal / solution interface can be presented as a process of substitutive adsorption between organic molecules in the solution ($\text{Org}_{(sol)}$) and water molecules on a metallic surface ($\text{H}_2\text{O}_{(sol)(ads)}$) [57]:

$$\text{Org}_{(sol)} \rightleftharpoons \text{Org}_{(ads)} + \text{H}_2\text{O}_{(sol)}$$  \hspace{1cm} (13)

where $\text{Org}_{(sol)}$ and $\text{Org}_{(ads)}$ are the organic molecules in the solution and adsorbed on the metal surface, respectively. $\text{H}_2\text{O}_{(ads)}$ represents the water molecules on the metal.
surface, $X$ is the size ratio representing the number of water molecules exchanged with an organic adsorbate molecule. The use of isotherms to describe the adsorption behavior of corrosion inhibitors is important because they provide important clues about the nature of the metal-inhibitor interaction. The surface coverage ($\theta$) of the metal surface has been fitted to different isotherms, including Frumkin, Langmuir and Temkin. However, the best results were obtained with the Langmuir isotherm. In the present study, the values of $\theta$ were obtained using the EIS results according to Eq. (14) [58]:

$$\theta = \frac{IE}{100} = \frac{R_{ct}-R_{ct}^0}{R_{ct}} \quad (14)$$

where $R_{ct}^0$ and $R_{ct}$ are the charge-transfer resistance values without and with inhibitor, respectively.

The action of an inhibitor in aggressive acidic media is presumably due to its adsorption at the metal / solution interface, which hinders that of intermediate products of anodic and cathodic corrosion reactions on the same interface. The adsorption process is controlled by various parameters, including the electronic characteristics of the inhibitor, temperature, surface state of the metal, etc. [59]. The values of the degree of surface coverage ($\theta$) for different concentrations of EC and CR essential oils ($C_{\text{inh}}$) were used to study the adsorption processes according to the Langmuir isotherm.

$$C_{\text{inh}} / \theta = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad (15)$$

In Eq. (15), $K_{\text{ads}}$ refers to the adsorption equilibrium constant which is related to the standard adsorption Gibbs energy change ($\Delta G_{\text{ads}}^0$) according to Eq. (16) [60]:

$$\Delta G_{\text{ads}}^0 = -RT\ln (10^4 K_{\text{ads}}) \quad (16)$$

where $1.0 \times 10^4$ corresponds to the concentration of water (in g/L), $R$ represents the perfect gas constant ($\text{JK}^{-1}\text{mol}^{-1}$) and $T$ the temperature (K).

Figure 9 shows the linear plots of $C_{\text{inh}}/\theta$ vs. $C_{\text{ads}}$. $K_{\text{ads}}$ was obtained from the intercepts and were used in Eq. 9 to access $\Delta G_{\text{ads}}^0$.

The results are summarized in Table 5. A very good fit was observed in the studied range of concentrations (0.50 – 4 g L$^{-1}$), with good regression coefficients and slopes close to unity. Therefore, the Langmuir isotherm reasonably fits the experimental data. It is assumed in this type of isotherm, that there are no interactions among the species which are adsorbed on the electrode surface [61]. $K_{\text{ads}}$ illustrates the adsorption forces linking the molecules of the essential oils and the metal [62]. The negative sign of $\Delta G_{\text{ads}}^0$ values indicate that the adsorption process is spontaneous.

The type of adsorption is usually considered as a physisorption if the absolute value of $\Delta G_{\text{ads}}^0$ is of the order of 20 kJ mol$^{-1}$ or less, and as a chemisorption if from 40 kJ mol$^{-1}$. In this process, covalent bonds are formed by the sharing or charge transfer of inhibitory molecules at the metal surface [63, 64]. The values of $\Delta G_{\text{ads}}^0$ calculated in this work which are close to -21 kJ mol$^{-1}$ (Table 5) which suggests a physisorption process of organic molecules for both essential oils on structural steel S235 1 M HCl [65]. Similar results have frequently been reported for essential oils inhibitors for steel in HCl solution [18, 19, 23]. In a previous work, we showed that a physicochemical adsorption was more probable in the case of Cyperus articulatus essential oils in hydrochloric acid solution [29]. It was however revealed by Sathiyananrayan et al. [66] that adsorption of inhibitors to anodic sites follows chemical adsorption and adsorption to anodic sites is due to electrostatic attraction.

The average of adsorption free energy values obtained by Tafel polarization and EIS methods are almost identical for two inhibitors: -20.88 kJ mol$^{-1}$ for EC and -20.85 kJ mol$^{-1}$ for CR. Similar observation was made regarding the interaction of mild steel with the mercaptotiazole compound and 3, 4-dihydropyrimidin-2 (1H)-ones, respectively by Wang et al. [67] and Yadav et al. [68].

### 4. Conclusion

In this work, we studied the S235 structural steel corrosion inhibition effect of *Eucalyptus camaldulensis* (EC) and *Cyperus rotundus* (CR) essential oils in 1 M hydrochloric acid solution by Tafel polarization and EIS measurements. The studies showed that the corrosion inhibition efficiency could reach 78.9% for EC and 86.7% for CR essential oils at a concentration of 4 g L$^{-1}$. These inhibitors act as mixed inhibitors. The highest inhibitory efficacy of CR is ascribed to the greater presence of sesquiterpenes in these essential oils. The results confirm the preponderant role of larger organic molecules in the inhibition phenomena.

The adsorption of EC as well as CR on the steel surface in 1 M hydrochloric acid medium follows the Langmuir isotherm.
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References

[1] Hussin M. H., & Kassim M. J. (2011). The corrosion inhibition and adsorption behavior of Uncaria gambir extract on mild steel in 1 M HCl. Materials Chemistry and Physics, 125 (3), 461-468.

[2] Ostovari A., Hoseini S. M., Peikari M., Shadizadeh S. R., & Hashemi S. J. (2009). Corrosion inhibition of mild steel in 1 M HCl solution by henna extract: A comparative study of the inhibition by henna and its constituents (Lawson, Gallic acid, α-d-Glucose and Tannic acid). corrosion Science, 51 (9), 1935-1949.

[3] Gassama D., Seck S. M., Yade I., Fall, M., & Diop, M. B. (2014). Valorisation des tufs volcaniques argileux de Bafoudoung comme inhibiteurs de corrosion du fer à béton E400/Exploitation de clayeys volcanic tuffs of Bafoudoung as corrosion inhibitors for E400 concrete iron. Journal de la Société Ouest-Africaine de Chimie, 38, 64.

[4] Gassama D., Fall M., Yade I., Seck S. M., Diagne M., & Diop M. B. (2016). Clays valorisation as corrosion inhibitors for E400 reinforcing steel. Ovidius University Annals of Chemistry, 27 (1), 28-35.

[5] Olaschinde E. F., Olusegun S. J., Adesina A. S., Omogbehin S. A., & Momoh Y. H. (2012). Inhibitory action of Nicotiana tabacum extracts on the corrosion of mild steel in HCl: adsorption and thermodynamics study.

[6] Koffi A. A., Muralidharan S., Trokourey A., (2015). Corrosion inhibition of carbon steel using extract of Mussaenda erythrophylla leaves: interfacial action mode in sulfuric acid medium/Inhibition de la corrosion de l'acier à l'aide d'extrait de feuilles de Mussaenda erythrophylla: mode d'action interfaciale en milieu acide sulfurique, Journal de la Société Ouest-Africaine de Chimie, 040, 31-40.

[7] Shalabi, K., & Nazeer, A. A. (2015). Adsorption and inhibitive effect of Schinus terebinthifolius extract as a green corrosion inhibitor for carbon steel in acidic solution. Protection of Metals and Physical Chemistry of Surfaces, 51 (5), 908-917.

[8] Prabakaran, M., Kim, S. H., Kalaiselvi, K., Hemapiyri, V., & Chung, I. M. (2016). Highly efficient Ligularia fischeri green extract for the protection against corrosion of mild steel in acidic medium: electrochemical and spectroscopics investigations. Journal of the Taiwan Institute of Chemical Engineers, 59, 553-562.

[9] Fouda A. S., Abouaalem, A. S., & El-Ewady, G. Y. (2017). Mitigation of corrosion of carbon steel in acidic solutions using an aqueous extract of Tilia cordata as green corrosion inhibitor. International Journal of Industrial Chemistry, 8 (1), 61-73.

[10] Muthukrishnan, P., Jeyaprabha, B., & Prakash, P. (2017). Adsorption and corrosion inhibiting behavior of Lannea coromandelica leaf extract on mild steel corrosion. Arabian Journal of Chemistry, 10, 2343-2354.

[11] Bhuwaneswari T, Vasantha V, Jeyaprabha C (2018) Pongamia Pinnata as a green corrosion inhibitor for mild steel in 1 N sulfuric acid medium. Silicon 10 (5), 1793-1807.

[12] Prabakaran M, Kim S.-H, Saisireka A, KalaiSelvi K, Chung I-M (2018). Polygonatum odoratum extract as an eco-friendly inhibitor for aluminum corrosion in acidic medium. Journal of adhesion science and Technology, 32 (18), 2054-2069.

[13] Qiang Y, Zhang S, Tan B. Chen S (2018) Evaluation of Ginkgo leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution. Corrosion Science, 133, 6-16.

[14] Gawali IT, Usmani GA (2020) Novel Non-ionic Gemini Surfactants from Fatty Acid and Diethanolamine: Synthesis, Surface-Active Properties and Anticorrosion Study. Chemistry Africa, 3, 75-88.

[15] Bammou L, Mihit M, Salghi R, Bouyanzer A, Al-Salem S, Bazzi L, Hammouti B (2011). Inhibition Effect of Natural Artemisia Oils Towards Tinplate Corrosion in HCl solution: Chemical Characterization and Electrochemical Study. International Journal of Electrochemical Science, 6, 1454-1467.

[16] Znini, M., Paolini, J., Majidi L., Desjobert J.-M., Costa, J., Lahhit N, Bouyanzer A. (2011). Evaluation of the inhibitive effect of essential oil of Lavandula multifida L., on the corrosion behavior of C38 steel in 0.5 M H2SO4 medium. Research on Chemical Intermediates, 38 (2012) 669-683.

[17] Znini, M., Majidi, L., Bouyanzer, A., Paolini, J., Desjobert, J.-M., Costa, J., & Hammouti, B. (2012). Essential oil of Salvia acheri mesatlantica as a green inhibitor for the corrosion of steel in 0.5M H2SO4. Arabian Journal of Chemistry, 5 (4), 467-474.

[18] Guadalrón-Reyes, Andrés & Becerra, E. N. & Peña, D. Y. & Gutiérrez, J. C. & Becerra, H. Q.. (2013). Inhibitory effect of Eucalyptus and Lippia alba essential oils on the corrosion of mild steel in hydrochloric acid. Journal of Materials and Environmental Science, 4, 143-158.

[19] Manssouri, M. & Yassir, E. & Costa, J. & Bouyanzer, A. & Desjobert, J.-M. & Majidi, L. & Lhou. (2015). Adsorption proprieties and inhibition of mild steel corrosion in HCl solution by the essential oil from fruit of Moroccan Ammodaucus leucotrichus. Journal of Materials and Environmental Science, 6, 631-646.

[20] Toufik, F., Anejjar, A., Asdadi, A., Salghi, R., Chebli, B., Hadek, M. E. L., & Hassani, L. I. (2017). Synergic effect between Argania spinosa cosmetic oil and Thymus satureioides essential oil for the protection of the carbon steel against the corrosion in sulfuric acid medium. Journal of Materials and Environmental Science, 8, 582-593.

[21] Alami Y, Mouissa M, Raheem N, Elbekkali O, Gala M, Tazi S, Ebn Touhami M, Chaouche A, Ouhssine M (2018) Study of the Inhibitory Effect of Essential Oils of Indian Costus Against Corrosion of Steel of Iron C35 in a Medium Acid Der Pharma Chemica, 10 (7): 32-37.

[22] Hassain SMZ, Razzak SA, Hossain MM (2020) Application of Essential Oils as Green Corrosion Inhibitors. Arabian Journal Science Engineering, 45, 7137-7159.
study of new synthesized organic compounds on corrosion behaviour and the inhibition of carbon steel in hydrochloric acid solution. Der Pharma Chemica, 8, 114-133.

[36] Singh, A., Ahamad, I., Singh, V. K., & Quraishi, M. A. (2011). Inhibition effect of environmentally benign Karanj (Pongamia pinnata) seed extract on corrosion of mild steel in hydrochloric acid solution. Journal of Solid-State Electrochemistry, 15 (6), 1087-1097.

[37] Yurt, A., Balaban, A., Kandemir, S. U., Bereket, G., & Erk, B. (2004). Investigation on some Schiff bases as HCl corrosion inhibitors for carbon steel. Materials and Chemistry, 85 (2-3), 420-426.

[38] Saadouni, M., Galai, M., ElAoufir, Y., Skal, S., Boukhris, S., & Hassikou, A. (2018). Experimental, quantum chemical and Monte Carlo simulations studies on the corrosion inhibition of mild steel in 1 M HCl by two benzothiazine derivatives. Journal of Materials and Environmental Sciences, 9, 2493-2504.

[39] Umoren, S. A., & Solomon, M. M. (2015). Effect of halide ions on the corrosion inhibition efficiency of different organic species-A review. Journal of Industrial and Engineering Chemistry, 21, 81-100.

[40] Macdonald, J. R., & Barsoukov, E. (2005). Impedance spectroscopy: theory, experiment, and applications. History, 1 (8), 1-13.

[41] Jüttner, K., & Lorenz, W. J. (1989). Electrochemical impedance spectroscopy (EIS) of corrosion processes on inhomogeneous surfaces. Trans Tech Publications Ltd, In Materials Science Forum, 44, 191-204.

[42] Singh, A. K., & Quraishi, M. A. (2010). Effect of Cefazolin on the corrosion of mild steel in HCl solution. Corrosion Science, 52 (1), 152-160.

[43] Shukla, S. K., Quraishi, M. A., & Prakash, R. (2008). A self-doped conducting polymer “polyanthranilic acid”: An efficient corrosion inhibitor for mild steel in acidic solution. Corrosion Science, 50 (10), 2867-2872.

[44] Macdonald, J. (1987). WB Johnson in: JR Macdonald. Impedance Spectroscopy: Wiley, New York, 150-170.

[45] Lopez, D. A., Simison, S. N., & De Sanchez, S. R. (2003). The influence of steel microstructure on CO2 corrosion. EIS studies on the inhibition efficiency of benzimidazole. Electrochimica Acta, 48 (7), 845-854.

[46] Bousskr, A., Anegiar, A., Messali, M., Salghi, R., Benali, O., Karzazi, Y., & Hammouti, B. (2015). Corrosion inhibition of carbon steel in aggressive acidic media with 1-(2-(4-chlorophenyl)-2-oxoethyl) pyridazinium bromide. Journal of Molecular Liquids, 211, 1000-1008.

[47] Chizzola, R. (2013). Regular Monoterpenes and Sesquiterpenes (Essential Oils). Natural Products, 2973-3008.

[48] Popova, A., Christov, M., Vasiliev, A., Deligeorgiev, T., & Djambova, A. (2014). Impedance spectroscopy study of inhibitive properties of quaternary ammonium salts. Journal of chemical technology and metallurgy, 49 (3), 275-279.

[49] Brug, G. J., Van Den Eeden, A. L. G., Sluyters-Rehbach, M., & Sluyters, J. H. (1984). The analysis of electrode impedances complicated by the presence of a constant phase element. Journal of Electroanalytical Chemistry, 176 (1-2), 275-295.
[50] Growcock, F. B., & Jasinski, R. J. (1989). Time-resolved impedance spectroscopy of mild steel in concentrated hydrochloric acid. Journal of the Electrochemical Society, 136 (8), 2310-2314.

[51] Lebrini, M., Bentiss, F., Chihib, N. E., Jama, C., Hornez, J. P., & Lagrenée, M. (2008). Polyphosphate derivatives of guanidine and urea copolymer: Inhibiting corrosion effect of Armc iron in acid solution and antibacterial activity. Corrosion science, 50 (10), 2914-2918.

[52] Roque, J. M., Pandiyan, T., Cruz, J., & García-Ochoa, E. (2008). DFT and electrochemical studies of tris (benzimidazolate-2-ylmethyl) amine as an efficient corrosion inhibitor for carbon steel surface. Corrosion Science, 50 (3), 614-624.

[53] Lebrini, M., Lagrenée, M., Vezin, H., Traisnel, M., & Bentiss, F. (2007). Experimental and theoretical study for corrosion inhibition of mild steel in normal hydrochloric acid solution by some new macrocyclic polyether compounds. Corrosion Science, 49 (5), 2254-2269.

[54] Hsu, C. H., & Mansfeld, F. (2001). Concerning the conversion of the constant phase element parameter Y0 into a capacitance. Corrosion Science, 57 (9), 747-748.

[55] El-Awady, A. A., Abd-El-Nabey, B. A., & Aziz, S. G. (1992). Kinetic-thermodynamic and adsorption isotherms analyses for the inhibition of the acid corrosion of steel by cyclic and open-chain amines. Journal of the Electrochemical Society, 139 (8), 2149-2154.

[56] Bentiss, F., Bouanis, M., Mernari, B., Traisnel, M., Vezin, H., & Lagrenée, M. (2007). Understanding the adsorption of 4H-1, 2, 4-triazole derivatives on mild steel surface in molar hydrochloric acid. Applied Surface Science, 253 (7), 3696-3704.

[57] Bockris, J. M., & Yang, B. (1991). The mechanism of corrosion inhibition of iron in acid solution by acetyllic alcohols. Journal of the Electrochemical Society, 138 (8), 2237.

[58] Morad, M. S. (2008). Inhibition of iron corrosion in acid solutions by Cefateryl: Behaviour near and at the corrosion potential. Corrosion Science, 50 (2), 436-448.

[59] Kaesche, H. (2003). Stress Corrosion Cracking. In Corrosion of Metals, 420-524. Springer, Berlin, Heidelberg.

[60] Flis, J., & Zakroczymski, T. (1996). Impedance study of reinforcing steel in simulated pore solution with tannin. Journal of the Electrochemical Society, 143 (8), 2458-2464.

[61] Elayachy, M., El Idrissi, A., & Hammouti, B. (2006). New triazo-compounds as corrosion inhibitor for steel in 1 M HCl. Corrosion Science, 48 (9), 2470-2479.

[62] Amin, M. A., Abd El-Rehim, S. S., El-Sherbini, E. E. F., & Bayoumi, R. S. (2008). Chemical and electrochemical (AC and DC) studies on the corrosion inhibition of low carbon steel in 1.0 M HCl solution by succinic acid-temperature effect, activation energies and thermodynamics of adsorption. International Journal of Electrochemical Science, 3 (2), 199 - 215.

[63] Zhang, S., Tao, Z., Li, W., & Hou, B. (2009). The effect of some triazole derivatives as inhibitors for the corrosion of mild steel in 1 M hydrochloric acid. Applied Surface Science, 255 (15), 6757-6765.

[64] Mahdavian, M., & Ashhari, S. (2010). Corrosion inhibition performance of 2-mercaptobenzimidazole and 2-mercaptobenzoxazole compounds for protection of mild steel in hydrochloric acid solution. Electrochimica Acta, 55 (5), 1720-1724.

[65] Fouda, A., Elewady, G. Y., Shalabi, K., & Habouba, S. (2014). Tobacco plant extracts as save corrosion inhibitor for carbon steel in hydrochloric acid solutions. Int J Adv Res, 2, 817-832.

[66] Sathiyarayanan, S., Mariikkannu, C., & Palaniswamy, N. (2005). Corrosion inhibition effect of tetramines for mild steel in 1M HCl. Applied surface science, 241 (3-4), 477-484.

[67] Wang, H. L., Fan, H. B., & Zheng, J. S. (2003). Corrosion inhibition of mild steel in hydrochloric acid solution by a mercaptopyrazole compound. Materials Chemistry and Physics, 77 (3), 655-661.

[68] Yadav, D. K., Maiti, B., & Quraishi, M. A. (2010). Electrochemical and quantum chemical studies of 3, 4-dihydropyrimidin-2 (1H)-ones as corrosion inhibitors for mild steel in hydrochloric acid solution. Corrosion Science, 52 (11), 3586-3598.