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# 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<sup>-1</sup> 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

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## 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<sup>2</sup> 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 of *Eucalyptus camaldulensis* (EC) or *Cyperus rotundus* (CR) corresponding to concentrations ranging from 0 to 4 gL<sup>-1</sup> was added to the 1 M HCl solution. This concentration range was determined after preliminary tests on the solubility of the inhibitor 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-accnt type, 5% phenylmethylsiloxane 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 ( $i_{\text{corr}}$ ,  $E_{\text{corr}}$ ,  $R_p$ ,  $b_a$  and  $b_c$ ) 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]:

$$IE = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}^0} \times 100 \quad (1)$$

$i_{\text{corr}}^0$  and  $i_{\text{corr}}$  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].

$$IE = \frac{R_{\text{ct}} - R_{\text{ct}}^0}{R_{\text{ct}}} \times 100 \quad (2)$$

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

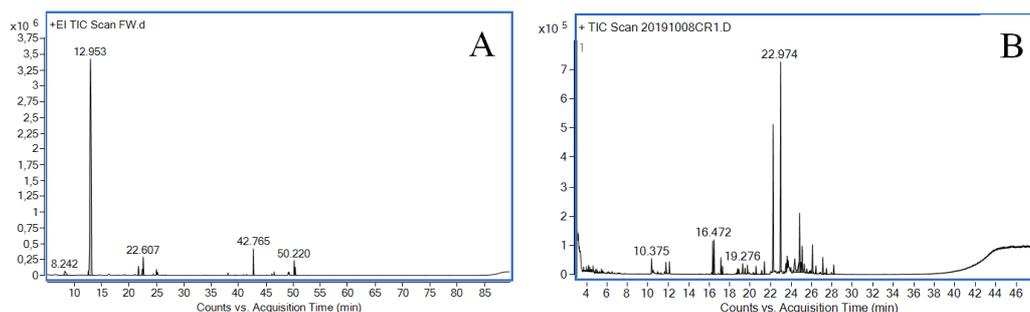


Figure 1. Chromatograms of *Eucalyptus camaldulensis* (A) and *Cyperus rotundus* (B) essential oils.

### 3. Results and Discussion

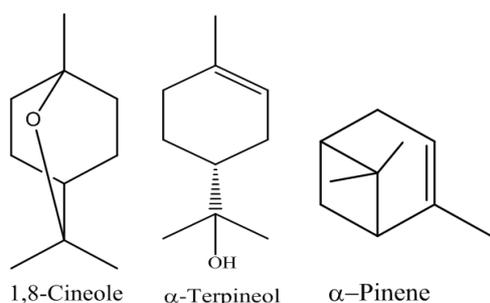
#### 3.1. GC-MS Analysis of EC and CR Essential Oils

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%),  $\alpha$ -Terpineol (3.7%),  $\alpha$ -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.

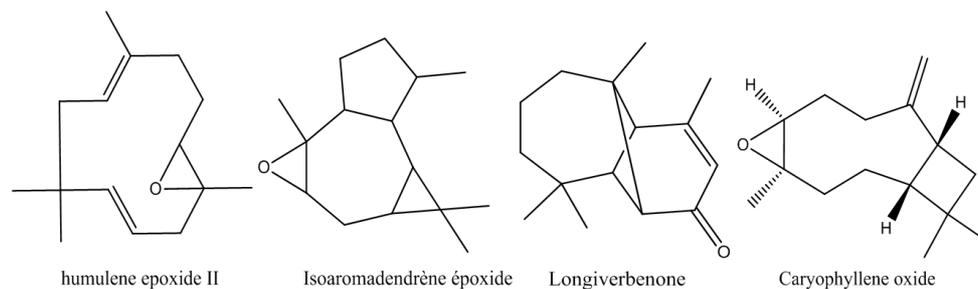
**Table 1.** Chemical composition of essential oils of *Eucalyptus camaldulensis*.

Compounds	Retention Times	Retention Indices	% of Compounds
$\alpha$ -Pinene	8.24	940	2.2
p-Cymène	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
$\alpha$ -Terpineol	42.76	1190	3.7
Caryophyllene-oxide	46.62	1578	0.7
Globulol	49.35	1587	0.7
$\beta$ -Eudesmol	50.22	1655	1.9
$\alpha$ -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%),



**Figure 3.** Molecular structures of some major *Cyperus rotundus* essential oil constituents.

*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*.

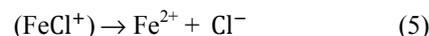
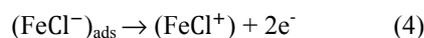
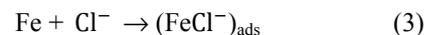
Compounds	Retention Times (min)	Retention Indices	% Compounds
trans-Pinocarveol	10.37	1152	1.8
Myrthenal	11.77	1194	1.7
Verbenone	12.11	1203	1.2
$\alpha$ -Copaene	16.35	1340	3.5
$\alpha$ -Cubebene	16.47	1346	3.7
$\delta$ -Selinene	17.15	1374	2.0
9,10-Dihydro-isologifolene	17.30	1381	0.8
non identifié	18.78	1501	0.7
$\alpha$ -Guaïene	18.90	1504	0.5
$\gamma$ -Cadinene	19.28	1516	1.4
$\beta$ -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-Dimethyltetracyclo-[6,3,2,0(2,5)0(1,8)]tridecan-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
(+)(-)-Caryophyllèneoxide	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

### 3.2. Tafel Polarization Curves

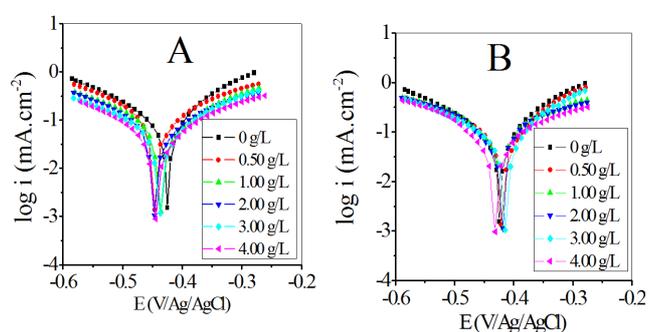
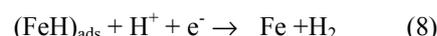
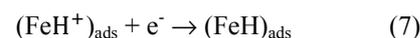
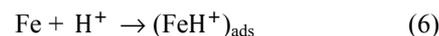
The stationary Tafel polarization curves, in the absence and in the presence of the inhibitors at various concentrations are shown in Figure 4.

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 in  $E_{\text{corr}}$  during the addition of the inhibitor is higher than 85 mV compared to the corrosion potential of the steel in an uninhibited environment [33, 34]. The shift is slightly cathodic for EC and comprised between 9 and 19 mV (in absolute value), but slightly anodic for CR (8-11 mV except for the higher concentration). CR and EC can be therefore be classified as mixed inhibitors. In this case and essentially in acidic environments, the role of adsorption at the surface will be essential [35]. Mechanisms of dissolution of mild steel in hydrochloric acid medium have been proposed by many researchers. In general, in hydrochloric acid solution, the

anodic oxidation of iron by the  $\text{Cl}^-$  can be represented by the following reactions [36, 37]:



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



**Figure 4.** Tafel polarization curves of S235 steel in HCl (1M), at different concentrations of *Eucalyptus camaldulensis* (A) and *Cyperus rotundus* (B) at 293 K.

**Table 3.** Electrochemical parameters and steel corrosion inhibiting efficiency of EC and CR essential oils in 1 M HCl at different concentrations at 293 K obtained by Tafel polarization.

	C (g/L)	$E_{\text{corr}}$ (V/Ag/AgCl)	$\Delta E$ (mV)	$i_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	$R_p$ ( $\Omega.\text{cm}^2$ )	$b_a$ (mV/dec)	$-b_c$ (mV/dec)	$V_{\text{corr}}$ (mm/year)	IE (%)
EC	0	-0.426	0	687.4	27.4	70	114	4.72	-
	0.5	-0.445	-19	303.9	73.8	87	127	1.77	55.8
	1	-0.435	-9	224.9	92.4	81	117	1.44	67.3
	2	-0.446	-20	191.6	107.0	77	122	1.22	72.1
	3	-0.438	-12	164.2	118.8	68	133	1.05	76.1
CR	4	-0.444	-18	154.5	123.9	74	109	0.99	77.5
	0	-0.426	0	687.4	27.4	70	114	4.72	-
	0.5	-0.419	7	239.8	80.3	79	101	1.53	65.1
	1	-0.418	8	165.7	111.9	66	121	1.06	75.9
	2	-0.415	11	143.7	141.3	77	119	0.92	79.1
	3	-0.416	10	130.8	152.7	76	116	0.83	81.0
	4	-0.432	-6	97.5	176.6	57	130	0.62	85.8

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  $b_c$  and  $b_a$  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)

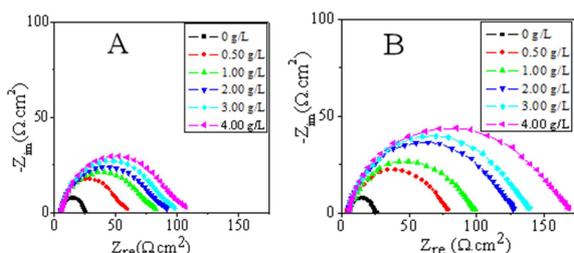
show that the reduction is not affected by the presence or absence of the essential oils and the release of hydrogen is controlled by an activation mechanism [42]. The inhibitor first adsorbs to the steel surface before acting by simply blocking its active sites. Cathodic inhibitors induce an increase 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<sup>-1</sup> 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.

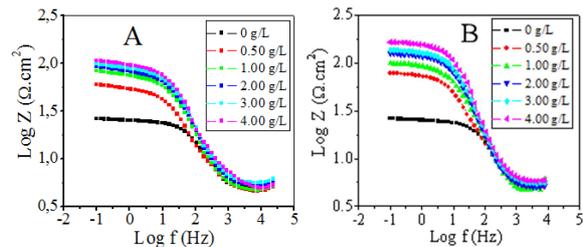
### 3.3. EIS Measurements

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. 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.

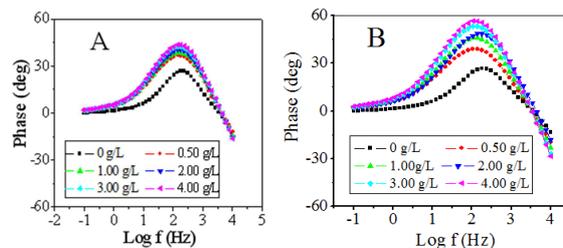
Nyquist impedance diagrams (Figure 5) exhibit depressed semi-circles with the center under the real axis. This trend, typical for solid electrodes is often referred to as frequency of dispersion. It is generally related to different physical phenomena such as roughness and inhomogeneities of solid surfaces, 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].



**Figure 5.** Nyquist diagrams of S235 steel in 1 M HCl acid at different concentrations of EC (A) and CR (B) essential oils at 293 K. Frequency-domain: 50 kHz - 100 mHz..



**Figure 6.** Bode diagrams for the corrosion of S235 steel in 1 M HCl at different EC (A) and CR (B) essential oils concentrations at 293 K.



**Figure 7.** Phase angle curves for the corrosion of S235 steel in 1 M HCl at different EC (A) and CR (B) essential oils concentrations at 293 K.

The capacitance values for both inhibitors are comprised between 6.78 and 119.11  $\mu\text{F}$ . 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]:

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

where A refers to the CPE (in  $\Omega^{-1}\text{s}^n\text{cm}^{-2}$ ),  $j$  is the imaginary number ( $j^2 = -1$ ),  $\omega = 2\pi f$  corresponds to the angular frequency of sinusoidal modulation (in rad/s), and  $n$  represents an empirical exponent ( $0 \leq n \leq 1$ ) 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 ( $Z_{\text{dl}}$ ) can be obtained using Eq. (10):

$$Z_{\text{dl}} = \frac{j}{C\omega} \quad (10)$$

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 ( $\tau$ ) and the double-layer capacitance ( $C_{\text{dl}}$ ) resulting from the CPE were calculated from Eqs. (11) and (12) [50]:

$$C_{\text{dl}} = (AR_{\text{ct}}^{1-n})^{1/n} \quad (11)$$

$$\tau = C_{\text{dl}}R_{\text{ct}} \quad (12)$$

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.

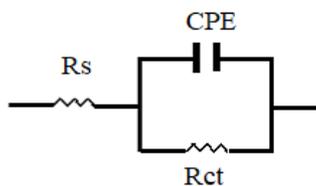


Figure 8. Equivalent electrical-circuit for the impedance spectra modeling.

Table 4. EIS results and inhibition efficiencies for S235 steel in 1 M HCl containing different concentrations of EC and CR essential oils

Inhibitor	C gL <sup>-1</sup>	R <sub>s</sub> (Ω.cm <sup>2</sup> )	R <sub>ct</sub> (Ω.cm <sup>2</sup> )	C <sub>dl</sub> (μFcm <sup>-2</sup> )	n	τ (ms)	IE (%)	
							(SIE)	(Tafel)
EC	0	5.8	21.5	119.1	0.77	2.56	-	-
	0.5	4.8	47.5	108.8	0.80	5.17	54.7	55.8
	1	4.7	78.2	75.4	0.83	5.90	72.5	67.3
	2	5.2	86.6	67.7	0.85	5.86	75.2	72.1
	3	5.5	92.5	63.8	0.87	5.80	76.7	76.1
CR	4	4.0	101.8	57.9	0.91	5.90	78.9	77.5
	0	5.8	21.5	119.1	0.77	2.56	-	-
	0.5	4.5	67.7	76.9	0.82	5.20	68.2	64.2
	1	5.1	93.6	54.9	0.87	5.13	76.9	73.1
	2	5.0	122.4	43.4	0.92	5.31	82.4	77.8
	3	5.5	133.1	36.3	0.93	4.80	83.8	79.9
	4	5.6	162.1	29.8	0.97	4.83	86.7	85.8

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<sub>dl</sub>) and increases the value of the time constant (τ) (Table 4). Indeed, in the corrosive medium, the interface parameter (τ) is comprised between 5.17 and 5.90 ms, while C<sub>dl</sub> value decreases from 108.8 to 57.9 μFcm<sup>-2</sup> for EC. An increase of τ and a decrease of C<sub>dl</sub> 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 (τ) [55]. The decrease in this capacity with increasing oil concentrations can be attributed to the formation of a

The EIS results (R<sub>ct</sub>, 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<sub>ct</sub>) increases with concentration and reaches 101,8 Ωcm<sup>2</sup> (EC) and 162,1 Ω cm<sup>2</sup> (CR) at a concentration of 4 gL<sup>-1</sup> for EC and CR. As glimpsed through the Nyquist and Bode diagrams, R<sub>ct</sub> is higher and C<sub>dl</sub> 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.

protective layer on the electrode surface [56]. The time constants (4.80-5.20 ms) and double-layer capacitances (76.9-29.8 μFcm<sup>-2</sup>) are lower in CR than in EC containing media. If the result was predictable for C<sub>dl</sub>, the reason why the τ values are roughly lower with the CR inhibitor is actually not clear for us. Moreover, τ varied randomly with the inhibitor content in each case.

The inhibition efficiency was calculated from R<sub>ct</sub> 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 g/L. 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 (Org<sub>(sol)</sub>) and water molecules on a metallic surface (H<sub>2</sub>O<sub>(ad)[(s)]</sub>) [57]:



where Org<sub>(sol)</sub> and Org<sub>(ads)</sub> are the organic molecules in the solution and adsorbed on the metal surface, respectively.

H<sub>2</sub>O<sub>(ads)</sub> 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 ( $IE / 100$ ) 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 ( $C_{inh}$ ) were used to study the adsorption processes according to the Langmuir isotherm.

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

In Eq. (15),  $K_{ads}$  refers to the adsorption equilibrium constant which is related to the standard adsorption Gibbs

energy change ( $\Delta G_{ads}^0$ ) according to Eq. (16) [60]:

$$\Delta G_{ads}^0 = -RT \ln(10^3 K_{ads}) \quad (16)$$

where  $1.10^3$  corresponds to the concentration of water (in g/L),  $R$  represents the perfect gas constant ( $JK^{-1}mol^{-1}$ ) and  $T$  the temperature (K).

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

The results are summarized in Table 5. A very good fit was observed in the studied range of concentrations ( $0.50 - 4 gL^{-1}$ ), 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].  $K_{ads}$  illustrates the adsorption forces linking the molecules of the essential oils and the metal [62]. The negative sign of  $\Delta G_{ads}^0$  values indicate that the adsorption process is spontaneous.

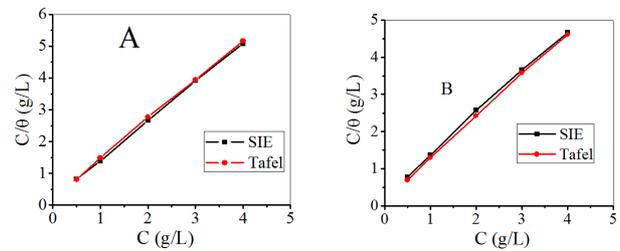


Figure 9. Langmuir adsorption plots for S235 steel in 1 M HCl containing EC (A) and CR (B) essential oils.

Table 5. Thermodynamic results of the Langmuir isotherm of EC and CR essential oils for S235 steel corrosion inhibition in the hydrochloric acid solution.

Inhibitor	R <sup>2</sup>		Slope		K <sub>ads</sub> (L/g <sup>-1</sup> )		ΔG <sub>ads</sub> <sup>0</sup> (kJmol <sup>-1</sup> )	
	EIS	Tafel	EIS	Tafel	EIS	Tafel	EIS	Tafel
EC	0.9997	0.9994	1.22	1.23	4.34	4.87	-20.74	-21.02
CR	0.9995	0.9983	1.12	1.11	4.71	4.37	-20.94	-20.76

The type of adsorption is usually considered as a physisorption if the absolute value of  $\Delta G_{ads}^0$  is of the order of  $20 kJmol^{-1}$  or less, and as a chemisorption if from  $40 kJmol^{-1}$ . 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  $\Delta G_{ads}^0$  calculated in this work which are close to  $-21 kJmol^{-1}$  (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 Sathiyarayanan *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:  $-20.88 kJmol^{-1}$  for EC and  $-20.85 kJmol^{-1}$  for

CR. Similar observation was made regarding the interaction of mild steel with the mercaptotriazole 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  $4 gL^{-1}$ . 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

and is of physical nature.

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