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Bio-coating corrosion inhibition of X52 pipeline steel in 0.5M H_2SO_4 by *Rosmarinus officinalis* essential oil

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Abstract

The aim of this study is to examine the use of *Rosemary officinalis* essential oil as bio-coating of X52 mild steel and evaluate its corrosion behavior in 0.5M H_2SO_4 solution. To better understand the inhibition mechanism and to determine the best concentration of the studied inhibitor, both stationary electrochemical analysis (polarization curves, polarization resistance) and non-stationary electrochemical impedance spectroscopy (EIS) analysis were carried out. Fourier-transform infrared spectroscopy (FTIR) analysis reveals the presence of different functional groups and heteroatoms which contribute in the adsorption of *Rosemary essential* oil molecules onto metallic surface. This has been also confirmed by scanning electron microscopy (SEM) observations coupled with energy-dispersive X-ray spectroscopy (EDS). The electrochemical measurements indicate that the *Rosmarinus officinalis* essential oil's layer demonstrates interesting corrosion inhibition characteristics by forming a protective barrier against the hydrogen ions to reach the steel surface. The studied inhibitor presents an anodic behavior, as identified by the decrease of the anodic current density and displacement of corrosion potential to more electropositive values. The best inhibition efficiency of 64.18 % is achieved at the maximum studied inhibitor concentration of 0.4%.

Introduction

Corrosion is a natural and spontaneous phenomenon that results into conversion of pure metals and their alloys into several stable forms such as sulfides, oxides, and hydroxides by the chemical and/or electrochemical reactions with the surrounding environments [1].

Since it contains a wide variety of aggressive environments, corrosion phenomena affect several industrial sectors, specifically petroleum industry. Although some of these environments are unique to this particular industry, it is more convenient to consider all these environments together. It has been reported that in the petroleum industry, corrosion problems occur in at least three main areas; namely (i) production, (ii) transportation, storage, and (iii) refinery operations **[2, 3]**.

Acid solutions are very important environment in the oil industry for their use in different processes namely acid pickling, acid cleaning, acid descaling and oil well acidizing **[4]**. During these applications, metals are exposed to acidic fluids and are prone to corrosion and therefore corrosion inhibitors are needed to be added to these cleaning solutions.

Several types of corrosion inhibitors in acidic medium were the subject of different studies, due to their ease of synthesis and high effectiveness at relatively low concentrations. The unique characteristic of such inhibitors is to be adsorbed over the metal and alloys surface through their heteroatoms and π-electrons, thereby forming a protective surface barrier by protecting metals from corrosive degradation. Generally, heteroatoms of organic inhibitors exist in polar functional groups such as -CN, $-NO_2$, $-NH_2$, -OH, -COOH, $-COOC_2H_5$ and $-OCH_3$, and act as adsorption centers during adsorption of these compounds on the metallic surfaces. Also, it has been reported that the presence of polar functional groups enhances the solubility of the compounds in the polar electrolytic media like H_2O, HCl, H_2SO_4, H_3PO_4, and HNO_3 **[5-8]**.

The actual industry environmental guidelines require the use of biodegradable corrosion inhibitors named green inhibitors, which have the advantage to be ecofriendly, available, efficient and inexpensive **[9-12]**. Several compounds are used as green inhibitors such as drugs **[13, 14]**, ionic liquids **[15, 16]**, biopolymers **[17, 18]**, plant extracts **[19-21]** and more recently essential oils. An essential oil is an odoriferous fluid, with either fluid aspect to thick and of varied color according to the plants from which it is extracted. It is secreted by specialized cells lying in leaves (peppermint, large green basil), flowers (lavender, ylangylang), wood (Atlas cedar, white sandalwood), roots (ginger, valerian, vetivers), and seeds (coriander, green anise, carrot). The size of these droplets is in the range of micron. Essential oils can be obtained from a vegetable raw material, either by steam distillation or by hydro-distillation, or from citrus fruits by mechanical methods. They are then separated from the aqueous phase by physical methods.

Essential oils compose the bulk of natural aromatic compounds, which are nowadays used in different fields such as in therapeutic, medical, cosmetic, psychological, olfactory, massage aromatherapy, antioxidants, antibacterial and as well as corrosion inhibitors. These extracts are obtained by distillation as well asby solvent extraction and have a wide range of biological activities (antioxidant, antimicrobial, anti-carcinogenic, anti-inflammatory, etc.).

Similarly, green chemistry adopts in its principles all the necessary precautions for the protection of mankind and environment based on green extraction technologies, the use of natural extracts and natural solvents. That is why the application of essential oils in various areas especially in the field of the corrosion inhibition has become an important research topic **[22]**.

Several authors have studied the anti-corrosive properties of different types of essential oils. Znini et al. studied the corrosion inhibition effect of *Salvia Aucherimesatlantica* essential oil of mild steel in 0.5 M H_2SO_4. The results showed that the tested oil exhibits good anti-corrosive properties and acts as mixed inhibitor with predominance of anodic character and decreases the corrosion rate for the concentration 2g/l with an inhibition efficiency reaching 86.1%. The authors found that the adsorption mechanism of essential oil on the steel surface obey Langmuir adsorption isotherm **[23]**.

The effect of essential oils as corrosion inhibitors for mild steel in 1M HCl was also studied by Lahhit et al. by using Fennel (*Foeniculum Vulgare*) essential oil [24], while Boumhara et al. used *Artemisia Mesatlantica* essential oil [25]. The authors found that the tested essential oils provide good anti-corrosive properties with an inhibition efficiency of 76% at 3 ml/L and 91% at 2.76 g/l, respectively.

The corrosion inhibition performance of *Laurusnobilis* essential oil against corrosion of aluminum (Al) and AA5754 Al-based alloy in 3% NaCl solution was reported by Halambek et al. [26]. The results showed that the tested oil has better inhibition effect on corrosion of pure Al (91.3%) than AA5754 alloy (82.4%) for the same concentration 50ppm; this was attributed to the presence of small fraction of iron in Al (0.08%).

Salinas-Solanoa et al. tested the corrosion inhibition performance of rice-bran oil on 1018 steel in a brine-CO_2 saturated solution. The results showed that the tested inhibitor has good corrosion protection ability by forming a protective film adsorbed onto steel surface according to Langmuir adsorption isotherm. It was found that rice-bran oil provides the best inhibition efficiency up to 99.7 and 99.6% for 10 and 25 ppm concentrations, respectively [27].

As a contribution to the current interest on environmentally friendly corrosion inhibitors, the present study investigates the inhibition effect of *Rosmarinus officinalis* essential oil on X52 mild steel corrosion in acidic solutions using electrochemical and surface characterization techniques. The choice of this inhibitor is manifested by its ecofriendly and rich sources of natural chemical compounds, sustainable, abandoned, biodegradable and inexpensive, as well as it could be easily extracted by very simple methods.

2. Methodology

2.1 Material

The material used in this study is a mild steel X52 having the following chemical composition (wt%): C (0.1400), Mn (0.9710), Si (0.2400), P (1.1800), S (0.0018),Cr (0.0055), Mo (0.0580), Ni (0.0140), Nb (0.0130), Co (0.0130), Cu (0.0460), Al (0.0320), and Fe (balance). The mild steel rods were cut in a length of about 3 cm having surface area of 1 cm^2, where one side was inserted to a copper wire for electrical conductivity and covered with polyester block except the bottom surface having 1 cm^2 total exposed surface area. The sample surfaces were ground by means of abrasive papers up to No. 4000 followed by degreasing with absolute acetone and distilled water.

2.2 Experiments

The study medium is an aqueous solution of 0.5M H_2SO_4 prepared by dilution of a concentrated acid solution H_2SO_4 (98%) manufactured by BIOCHEM chemopharma. The prepared solution is used without and with the addition of various concentrations of *Rosmarinus officinalis* essential oil (0.1, 0.2, 0.3 and 0.4%) and the best concentration which correspond to the best inhibition efficiency was determined by taking into account the economic factors. *Rosmarinus officinalis* essential oil was isolated by hydro-distillation at the EXTRALBIO laboratory, Blida, Algeria.

2.3 Product characterisation

The FTIR spectrum of *Rosmarinus officinalis* essential oil was recorded using *Perkin Elmer* FTIR Spectrometer. Surface morphological observations were carried out by scanning electron microscopy

(SEM) using *Quanta 250* coupled with electron dispersive spectroscopy (EDS) for elemental chemical analysis. Before each analysis, the cleaned electrodes were exposed to 0.5M H_2SO_4 solution without and with the addition of 0.4% of *Rosmarinus officinalis* essential oil for 30 min at room temperature. After that, the specimens were taken out from the test solutions, cleaned with ethanol and distilled water then dried carefully.

2.4 Electrochemical measurements

Electrochemical experiments were performed in a three-electrode system: X52 mild steel as working electrode (WE), saturated calomel electrode (SCE) as reference electrode, and platinum as auxiliary electrode.

AutoLab PGSTAT30 Potentiostat/Galvanostat was used for electrochemical polarization and impedance spectroscopy measurements which were controlled by *Nova 2.0* software. Before each electrochemical test, the working electrode was immersed in the test solution for 30 min until the open circuit potential is established. The polarization curves were recorded by varying the electrode potential from -1000 mV to +200mV using a scan rate 1 $mV.s^{-1}$.

The electrochemical impedance diagrams were plotted in the frequency range from 100 kHz to 10 mHz using 20mV amplitude peak to peak.

3. Results and Discussion

3.1 FTIR analysis of Rosmarinus officinalis essential oil

In order to identify the mechanism of inhibition and characterize the chemical composition of *Rosmarinus officinalis* essential oil, infrared spectroscopy analysis was carried out for this oil. The FTIR spectrum of *Rosmarinus officinalis* oil is presented in Figure 1.

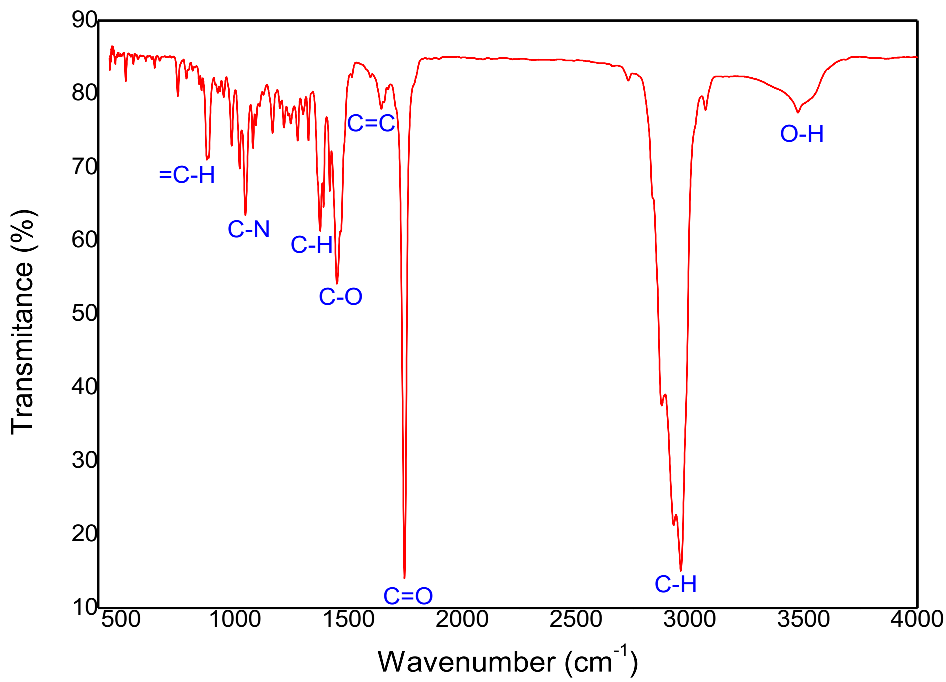


Figure 1. FTIR Spectrum of *Rosmarinus officinalis* essential oil.

The FTIR spectrum of *Rosmarinus officinalis* oil reveals several bands, indicating the existence of different functional groups and chemical compounds. The small band observed at 3500 cm^{-1} is attributed to the OH stretching vibration. The bands located at 2874, 2928 and 2960 cm^{-1} are characteristic of CH, CH_2 and CH_3 bending vibrations respectively in the aliphatic chains. Another more pronounced band located at the wavenumber 1744 $cm^{-1}$is ascribed to the bending vibration of C=O. The small band at 1642 cm^{-1} is assigned to C=C stretching vibration. The bands at 1374 and 1032 cm^{-1} are assigned to C-O and C-H stretching vibrations in phenol or alcohol. Another observed band at 880 cm^{-1} is attributed to the =CH bending vibration.

Different functional groups containing heteroatoms such as O–H, C–H, C=O, C=C, and C-N within *Rosmarinus officinalis* essential oil molecules responsible for the adsorption and the bio-coating of the mild steel surface were identified by FTIR spectroscopy, by comparison with the theoretical FTIR [28, 29] ; the results are presented in Table 1.

Table 1. FTIR spectroscopic data of frequencies and adsorption peaks of *Rosmarinus officinalis* essential oil [28]

Theoretical wavenumber (cm^{-1})	**Calculated wavenumber (cm^{-1})**	**Bond**	**Functional groups**
3400–3250 3500–3200	**3474.30**	O-H stretch, H-bonded, N-Hstretch	alcohols, phenols, 1°, 2° amines, amides
3300–2500 3000-2850	**2960.24**	O-H stretch, C-H stretch	carboxylic acids, alkanes
3300–2500 3000–2850	**2928.70** **2874.32**	O-H stretch, C-H stretch	carboxylic acids, alkanes
1760–1665 1760–1690 1750–1735	**1744.43** **1642.28**	C=O stretch C=C stretch	carbonyls (general), esters, saturated aliphatic
1550–1475		C-C stretch (in-ring), C-H bend	aromatics, alkanes
1320–1000 1300–1150 1250–1020	**1453.84** **1375.47** **1032.37**	C-O stretch, C-H wag (-CH_2X), C-N stretch	alcohols, carboxylic acids, esters, ethers, alkyl halides, aliphatic amines
1000–650 910–665 900–675 850–550	**880.54**	=C-H bend, N-H wag, C-H ‘‘oop”, C-Cl stretch	alkenes, 1°, 2° amines, aromatics, alkyl halides

3.2 Polarization curves

The polarization curves of X52 steel in H_2SO_4 0.5M solution recorded at room temperature in the absence and presence of inhibitor at various concentrations (0.1, 0.2, 0.3 and 0.4%), are displayed in Figure 2. The polarization curves indicate that the inhibition effect of *Rosmarinus officinalis* oil is observed by the reduction of the anodic branches of the Tafel straight lines, with a notable displacement of the corrosion potential values towards more electropositive values. This suggests the anodic character of the studied inhibitor. Ouariachi et al. [30] studied the inhibition effect of *Rosmarinus officinalis* oil on the corrosion of C38 mild steel in 0.5 M H_2SO_4. The authors suggest that oxygenated monoterpenes, particularly 1,8-cineol act on the corrosion inhibition of mild steel in acid solution. Table 2 gives the different parameters determined from the electrochemical polarization curves and the values of the inhibition efficiency.

The inhibition efficiency (E, %) values derived from Tafel plots were calculated from the equation given below:

$$E(\%) = (i_{corr}-i'_{corr})/i_{corr} \qquad \textbf{Eq. 1}$$

where i_{corr} and i'_{corr} are corrosion currents density of the X52 steel in the absence and presence of inhibitor respectively.

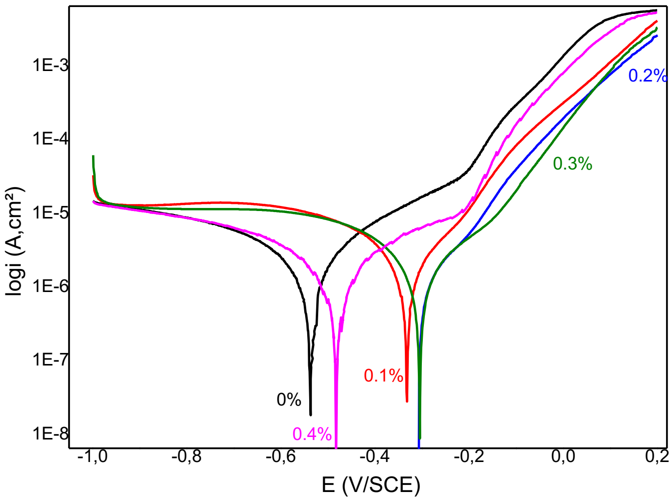


Figure 2. Polarization curves of X52 mild steel in 0.5M H_2SO_4 in absence and presence of *Rosmarinus officinalis* essential oil.

The analysis of Table 2 indicates that the cathodic slopes values b_c decreases upon the addition of *Rosmarinus officinalis* oil inhibitor. The corrosion current density i_{corr} value is found also to be reduced as well with a reduction in corrosion rate value *CR*. Meanwhile, the polarization resistance R_p value has increased with increasing the inhibitor concentration. The inhibition efficiency (64.18%) has been achieved for the maximum studied concentration of 0.4%.

Table 2. Electrochemical parameters and inhibition efficiency calculated from calculated from i_{corr} obtained from polarization curves.

C_{inhib} (%)	β_a (V/dec)	β_c (V/dec)	E_{corr} (V/SCE)	i_{corr} ($\mu A.cm^{-2}$)	CR (mm/year)	Rp (kΩ)	E (%)
0.0	0.104	0.130	-0.536	0.807	0.009	31.12	/
0.1	0.265	0.066	-0.333	0.474	0.006	35.01	41.26
0.2	0.276	0.071	-0.308	0.376	0.005	39.73	53.40
0.3	0.266	0.068	-0.304	0.374	0.005	39.84	53.65
0.4	0.056	0.062	-0.481	0.289	0.003	44.54	64.18

3.3. Electrochemical impedance spectroscopy

EIS technique is utilized in order to investigate the corrosion inhibition efficiency and explore the surface characteristics of mild steel since this technique does not disrupt metal/solution interface. Electrochemical impedance diagrams of mild steel plotted in corrosion potential E_{corr} after 30 minutes of immersion in 0.5M H_2SO_4 without and with the addition of various inhibitor concentrations are given in Figure 3.

The impedance diagrams (**Figure 3**) exhibit semi-circles shaped curves, indicating that charge transfer processes are mainly controlling the steel corrosion **[24].** The capacitive loops in these conditions are slightly depressed with a center under the real axis. This deformation can be attributed to the adsorption of inhibitor molecules at the metal surface, formation of porous layer and heterogeneity of the electrode surface **[31, 32]**.

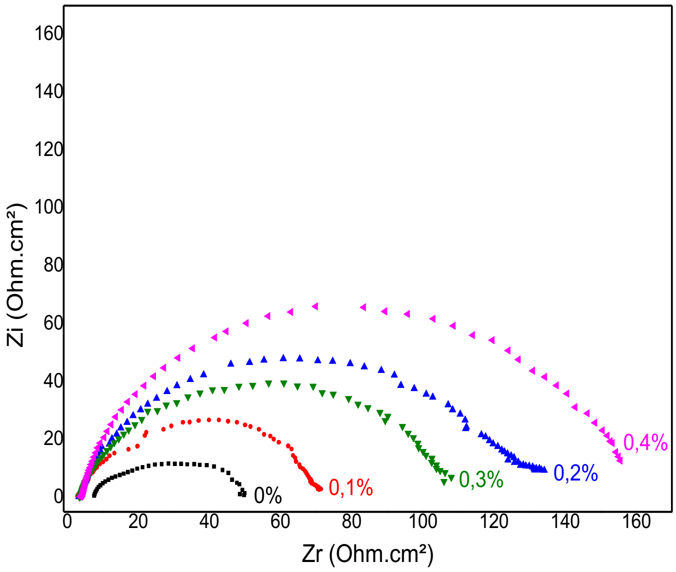


Figure 3. Impedance diagrams of X52 mild steel measured in 0.5M H_2SO_4 in the absence and presence of inhibitor.

The inhibition mechanism in acidic medium is generally explained by the adsorption of the inhibitor molecules at the metal/solution interface. Referring to FTIR spectrum of *Rosmarinus officinalis* essential oil (Figure 1), it has been found that this oil contains several functional groups such as alcohols, phenols, 1°, 2° amines, carboxylic acids, alkanes, carbonyls (general), esters, saturated aliphatic, aromatics alkanes, ethers, alkyl halides, aliphatic amines, alkenes, 1°, 2° amines, aromatics and alkyl halides, which significantly contribute in the process of adsorption and bio-coating of the mild steel surface.

Rosmarinus officinalis essential oil is generally composed from 1,8-cineole, α-pinene, and camphor **[33, 34].** This organic chemical compound contains functional groups and heteroatoms, which are responsible for the adsorption of the essential oil molecules onto metallic surface and therefore coating the mild steel. This bio-coating constitutes a barrier to avoid hydrogen ions to reach the mild steel surface and causes its corrosion.

Further studies have been carried out to evaluate the inhibition efficiency of *Rosmarinus officinalis* essential oil in acidic media and confirm that oxygenated monoterpenes ensure the corrosion inhibition of the studied metal. The authors found that *Rosmarinus officinalis* oil is more effective in a H_2SO_4 medium than in HCl and H_3PO_4 **[35, 36].**

The equivalent electrical circuit used to simulate the impedance diagrams is represented in Figure 4. This circuit is composed of the electrolyte resistance (R_e), a constant phase element (CPE), (C_{dl}) accounts for inhomogeneity of the metal surface positioned in parallel to the transfer charge resistance (R_{ct}), (CPE_c) the constant phase element of the inhibitor film, (R_c) the resistance of the inhibitor film and (α) the flattening coefficient. The electrochemical parameters deduced from the simulation of impedance diagrams are reported in Table 4. The inhibition efficiency ($E, \%$) reported in Table 3 has been calculated using the following equation:

$$E(\%) = (R'_{ct}-R_{ct})/R'_{ct} \qquad \textbf{Eq. 2}$$

where R_{ct} and R'_{ct} are the resistance of charge transfer of X52 mild steel in the absence and the presence of inhibitor respectively.

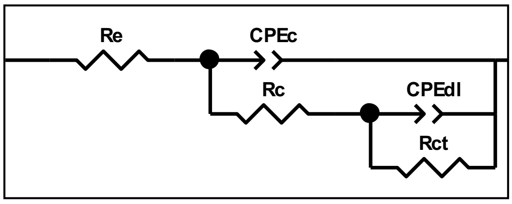


Figure 3. Equivalent electrical circuit used for simulation of the impedance diagrams.

Table 3. Inhibition efficiency and electrochemical parameters deduced from the impedance diagrams

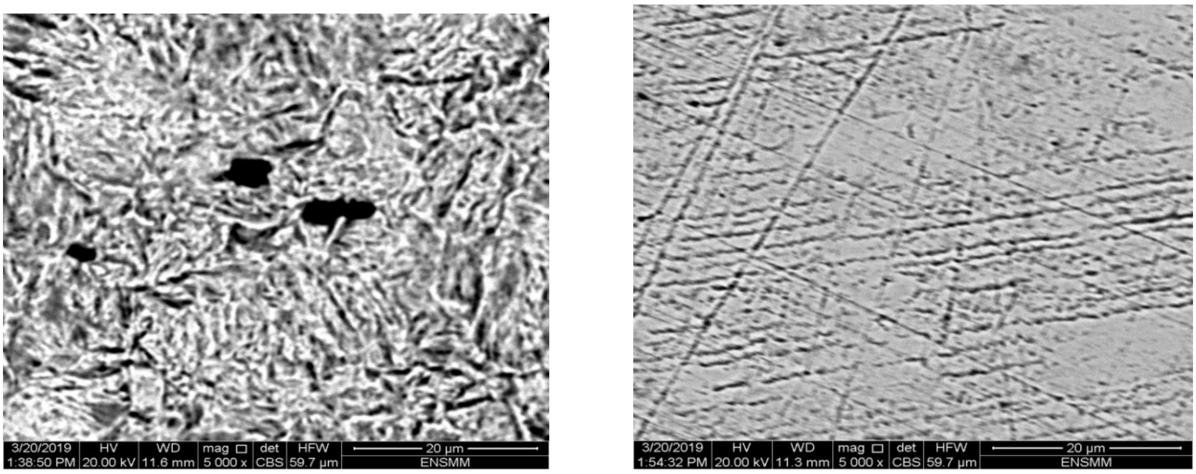
C_{inhib} (%)	R_e (Ω.cm²)	CPE_c (mF)	α_1	R_c (Ω.cm ²)	CPE_{dl} (mF)	α_2	R_{ct} (Ω.cm²)	E (%)
0.0	8.12	0.015	0.77	25.63	0.421	0.79	51.32	/
0.1	3.28	0.012	0.76	29.92	0.299	0.82	74.59	31.19
0.2	2.64	0.011	0.71	30.79	0.095	0.82	125.91	59.24
0.3	3.52	0.009	0.79	28.19	0.070	0.81	140.85	63.56
0.4	2.55	0.007	0.77	29.43	0,021	0.89	155.50	66.99

From the obtained results, it is noted that the addition of inhibitor induces an increase in the polarization resistance R_{ct} and a decrease in the value of the CPE_{dl}, which confirms the adsorption of oil molecules onto mild steel surface. The best inhibition efficiency is 66.99%, it was obtained for the maximum studied concentration 0.4%.

3.4. Surface characterization by SEM/EDS

The surface morphology of the X52 mild steel after 30 minutes immersion in H_2SO_4 solution in the absence and the presence of 0.4% of the *Rosmarinus officinalis* essential oil is represented in Figure 5. It can be observed that, in the absence of inhibitor, the mild steel surface has been strongly damaged with the presence of pits (few µm), whereas in the presence of inhibitor the metal surface has been less attacked and damage is less considerable which confirms the inhibitory effect of *Rosmarinus officinalis* essential oil.

The corresponding EDS spectra of X52 mild steel after 30 min immersion in the H_2SO_4 solution with the absence and the presence of 0.4% of *Rosmarinus officinalis* oil are shown in **Figure 6**. The EDS spectra indicate some characteristic peaks of the surface constituents. In the absence of inhibitor (**Figure 6a**), it is observed the appearance of peaks characteristic of Fe, Mn and O. The presence of oxygen is due to the oxidation of the steel surface when it is exposed to the acid solution. In the presence of inhibitor (**Figure 6b**), the oxygen peak disappeared, which confirms that essential oil molecules are adsorbed onto metallic surface and act as a barrier to prevent the oxidation of the mild steel **[37].**



(a) **(b)**

Figure 5. SEM images of X52 mild steel in 0.5M $H_2SO_4$with: (a) the absence of inhibitor, (b) the presence of 0.4% of inhibitor.

(a)

(b)

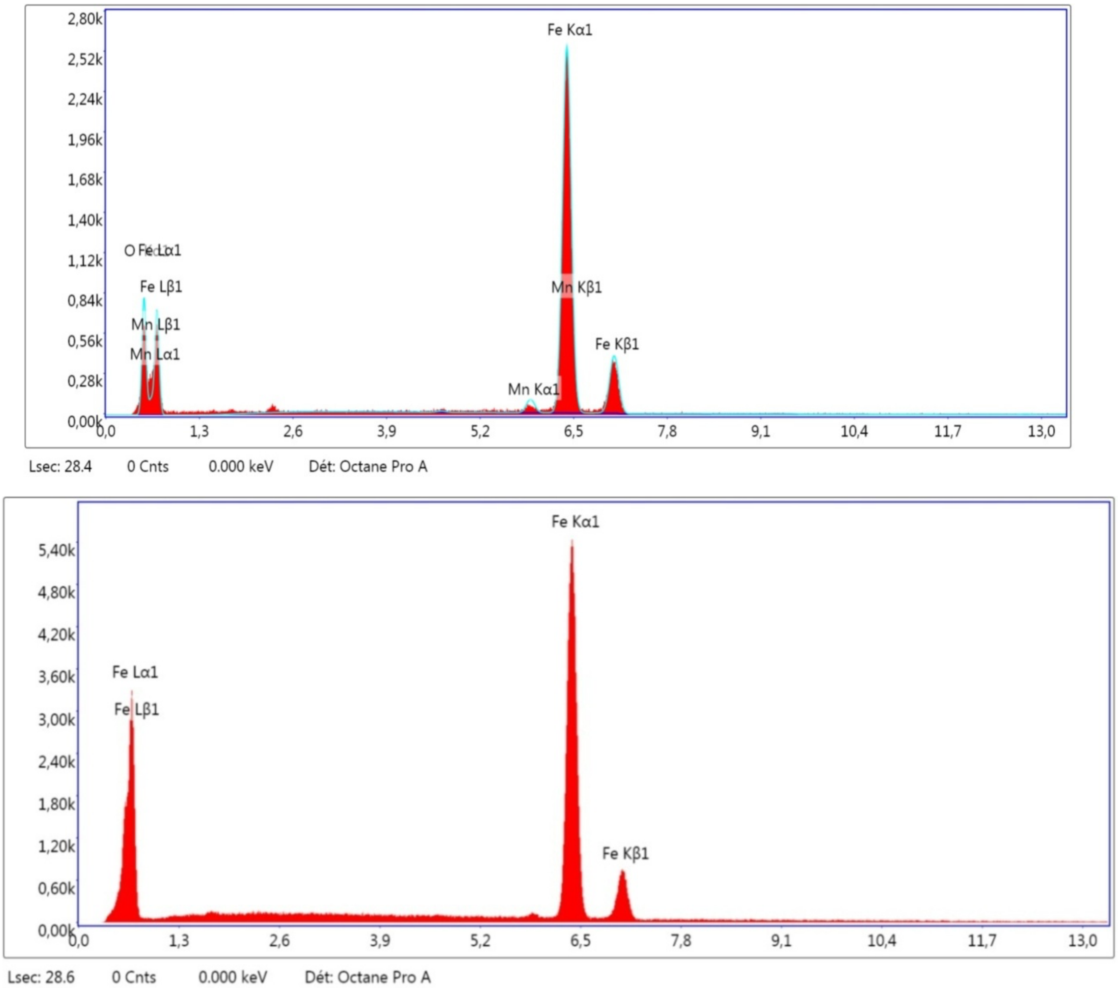


Figure 6.
EDS spectra of the X52 mild steel in 0.5M H_2SO_4 : (a) in the absence of inhibitor, (b) in the presence of 0.4% of inhibitor.

Conclusion

The present work focuses on the electrochemical behavior of X52 mild steel in 0.5M H_2SO_4 in the absence and presence of *Rosmarinus officinalis* essential oil. This study has been conducted using stationary and non-stationary electrochemical techniques such as plots of polarization curves and electrochemical impedance spectroscopy. The obtained results showed that the studied inhibitor demonstrates an anodic behavior by decreasing the anodic current density and displacing the corrosion potential towards electropositive values. The addition of inhibitor induces an increase in the polarization resistance of mild steel X52 in 0.5M H_2SO_4 especially for the maximum studied concentration 0.4%with an inhibition efficiency of 64%. *Rosmarinus officinalis* essential oil has been found to be adsorbed onto mild steel surface through the functional groups as identified by FTIR analysis. Surface analysis corroborates with the electrochemical results confirm the bio-coating of steel surface by a protective and homogeneously distributed film. Because of its biodegradable properties, human and environment benign as well as low cost and abundance, *Rosmarinus officinalis* essential oil can be suggested as potential corrosion inhibitor for mild steel protection in 0.5M H_2SO_4 solution.

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Conflicts of Interest: The authors declare no conflict of interest.

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