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Corrosion inhibition of carbon steel using extract of *Mussaenda erythrophylla* leaves: interfacial action mode in sulfuric acid medium

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Abstract: The study of corrosion inhibition of carbon steel in sulphuric acid solution has shown that the extract from the leaves of *Mussaenda erythrophylla* (MELE) is an efficient green inhibitor. The inhibitory efficiency evaluated by gravimetric method was found to be 82% at 50°C with 400 mg L^{-1} as extract concentration and Tafel polarization curves indicated that MELE is mixed-type inhibitor. Furthermore, it was noticed that, in 1 M H_2SO_4, the constituents of MELE adsorb on the metal surface, while in 0.1 M H_2SO_4, they form a thin film which adheres strongly on the metal surface. The investigation with electrochemical impedance spectroscopy (EIS) has demonstrated that MELE does not change the corrosion mechanism. In addition, the thermodynamic parameters reveal chemical and physical adsorption according to the Langmuir model. The scanning electron microscopy (SEM) and the atomic force microscopy (AFM) confirm these results.

Keywords: Carbon Steel, Corrosion Inhibition, Polarization, AFM, Film formation, Adsorption.

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

Résumé: L'étude de l'inhibition de la corrosion de l'acier dans une solution d'acide sulfurique a montré que l'extrait de feuilles de *Mussaenda erythrophylla* (MELE) est un inhibiteur vert efficace. L'efficacité inhibitrice évaluée par la méthode gravimétrique a été de 82% à 50°C, avec une concentration en extrait de 400 mg L^{-1}. Les courbes de polarisation de Tafel ont montré que MELE est un inhibiteur de type mixte. En outre, il a été constaté que, dans la solution d'acide de concentration 1 M, les constituants de MELE s'adsorbent à la surface de l'acier, tandis que dans 0,1 M H_2SO_4, ils forment un film mince qui adhère fortement à la surface du métal. Les résultats de la spectroscopie d'impédance électrochimique (SIE) ont démontré que MELE ne change pas le mécanisme de corrosion. Par ailleurs, les paramètres thermodynamiques ont indiqué une adsorption chimique et physique selon le modèle de Langmuir. La microscopie électronique à balayage (MEB) et la microscopie à force atomique (AFM) ont confirmé ces résultats.

Mots clés : Acier, Inhibition de la corrosion, Polarisation, AFM, Formation de film, Adsorption.

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1. Introduction

Corrosion is a natural phenomenon of degradation affecting mainly metallic materials [1]. Unfortunately, it has heavy economic implications. It is a major problem which can be reduced by understanding the causes of the corrosion phenomenon and the better application of technical protection. The prevention of corrosion generates not only a significant economic gain, but also prevents the release of toxic metals in the environment [2]. Some ways of corrosion prevention are the use of more resistant alloys, protective coating and the addition of inhibitors to the corrosive environment [3].

Corrosion of metal infrastructures in industries is sometimes caused by the use of acidic solutions in some processes [4]. In these industrial applications, inhibitors are generally used to control the dissolution of the metal and the consumption of the acid [5]. Most of these synthetic substances are not only costly, but also very harmful to living beings [6]. Moreover, new worldwide standards for industrial waste are becoming more stringent in terms of ecology and safety. The exploration of plant extracts as corrosion inhibitors is a key area of interest for researchers. These plant products are rich in organic compounds that can be extracted by simple processes. In addition, they are biodegradable, non-toxic, readily available and renewable sources [4-12]. Their use as corrosion inhibitors can be regarded as an alternative to expensive and toxic synthetic compounds.

In this context, we have carried out studies on the extract from the leaves of *Mussaenda erythrophylla* as green inhibitor. The inhibitory action of the extract was evaluated by gravimetric method. Electrochemical measurements have been conducted to determine the type of inhibitor (anodic, cathodic or mixed-type). The surface analysis techniques have been used to describe the morphology of the studied metal. Thermodynamic parameters were investigated to understand the mechanism which underlied the action of extracted molecules.

2. Experimental

2.1. Materials and Reagents

The material used in this study was carbon steel with chemical composition in weight %: C = 0.18, Si = 0.03, P = 0.06, S = 0.05, Mn = 0.12 and Fe as remaining component.

The aggressive medium (sulphuric acid) was prepared by dilution of an analytical reagent (RANKEM) grade 35% with distilled water. Acetone (LR grade) was purchased from RANKEN and used as received.

The leaves of *Mussaenda erythrophylla* were picked in the CSIR-CECRI research center of Karaikudi. The inhibitors were extracted from these leaves. Ethanol, absolute (AR reagent) and petroleum ether (60-80 GR) were used for the extraction of MELE. 100-400 mg L^{-1} of MELE was used, made by dissolving in the acid solution.

2.2. Extraction procedure

The leaves of *Mussaenda erythrophylla* were cleaned with tap water to eliminate dust. They were then dried in shade at room temperature, to enrich the contained active constituent [7]. The dried leaves were crushed into fine particles, and extracted in ethanolic solution (80:20; v/v) using soxhlet apparatus. Appearance of colorless solvent in the siphon tube of soxhlet apparatus was taken as the end point of the extraction. The solution was concentrated to about 100 mL, and then was degreased with petroleum ether. The organic stage (alcoholic stage) was thereafter extracted with a separating funnel, and concentrated to about 50 mL using a distillation unit. Finally, the extract was dried in vacuum drying oven at 60°C for ~3 days. After completed drying, a dark brown solid residue (MELE) was obtained, and preserved in desiccator. The photographies of *Mussaenda erythrophylla* and the extract MELE are presented in **Figure 1**.

Figure 1: Photography of *Mussaenda erythrophylla* and the extract MELE

2.3. GC-MS analysis of MELE

2.3.1. Preparation of the sample

10 mg of MELE was dissolved in 10 mL of alcohol. The solution was filtered, centrifuged (20 min, 10000 rpm / min) and filtered again. 1µL of the obtained solution was employed for the analysis.

2.3.2. Instruments and chromatographic conditions

The volatile compounds of the extract were identified using a gas chromatography coupled to mass spectroscopy. The analysis was performed on a chromatograph Agilent Technologies, interfaced to a mass spectrometer model No. 5975C Inert MSD with Triple Axis detector. The column used was a capillary column DB5 fused silica (30 m × 0.25 mm ID × 0.25 micron). Helium was used as the carrier gas at a constant flow of 1 mL / min. An injection volume of 1 mL EI was employed (split ratio 10:1). The temperature of the ejector was 275ºC while the detector temperature was 280°C. The oven temperature was programmed as follows: 110°C for 2 min, with an increase of 10°C / min to 200°C, holding at 200°C for 9 min; then increase up to 280ºC at a rate of 5ºC / min and ending with a 2 min isothermal at 280ºC. A scan interval of 0.5 s and fragments of 20 to 600 Da has been applied.

2.3.3. Identification of MELE components

Interpretation of GC-MS results was done using the database of National Institute Standard and Technology (NIST), by comparing the mass spectrum of the compounds to be identified with the spectrum of the known compounds stored in the NIST library.

2.4. Weight loss measurements

The carbon steel samples size of 2 cm × 4 cm (and thickness 0.05-0.25 cm) were abraded with various grades of emery paper until a mirror finish, then washed with distilled water, degreased with acetone, and finally dried in air. The samples, in triplicate, were accurately weighed and immersed in H_2SO_4 solution without or with plant extract. After 1 hour, the three specimens were removed from the solution and thoroughly washed with distilled water. They were air dried, and reweighed. From the weight loss, corrosion rate (v) in mg cm^{-2} h^{-1} was calculated using the following equation:

$$v = \frac{W}{S \times t} \qquad (1)$$

where W is the average weight loss (mg), S the averagearea (cm^2), and t the exposure time (h).
The inhibition efficiency η_{W} (%) and surface coverage θ_{W} were calculated as follows:

$$\eta_W(\%) = \frac{v_o - v}{v_o} \times 100 \qquad (2)$$

$$\theta_{\mathrm{W}} = \frac{v_{\mathrm{o}} - v}{v_{\mathrm{o}}} \qquad (3)$$

where v_0 and v are the rate of corrosion in the absence and presence of MELE respectively.

2.5. Electrochemical measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were performed in a conventional three electrode cell assembly. This electrochemical cell was made with a platinum foil (1 cm^2) counter electrode (CE), a saturated calomel electrode (SCE) as reference electrode and carbon steel specimen as working electrode (WE). The specimens were cut from carbon steel sheets and embedded in epoxy resin leaving only a surface area of 1 cm^2. The exposed surface was prepared as described in the previous section.

All measurements were carried out on Gill AC Model 1566 electrochemical instrument. Before each measurement the WE was immersed in the test solution for 1 h 30 min to achieve a steady state. After the open circuit potential (OCP) was determined. EIS measurements were performed in a frequency range of 100 kHz to 0.01 Hz with 10 mV AC amplitude. Inhibition efficiency η_{EIS} (%) was calculated using the following relation:

$$\eta_{\mathrm{EIS}}(\%) = \frac{R_{\mathrm{ct(inh)}} - R_{\mathrm{ct(o)}}}{R_{\mathrm{ct(inh)}}} \times 100 \qquad (4)$$

where $R_{\mathrm{ct(0)}}$ and $R_{\mathrm{ct(inh)}}$ are charge transfer resistances for carbon steel in uninhibited and inhibited solution, respectively.

Thereafter, anodic and cathodic polarization curves are recorded from -200 mV to + 200 mV relative to the open circuit potential with a sweep rate of 1 mV s^{-1}. Inhibition efficiency η_{P} (%) is defined as follows:

$$\eta_{\mathrm{P}}(\%) = \frac{i_{\mathrm{corr}} - i_{\mathrm{corr(inh)}}}{i_{\mathrm{corr}}} \times 100 \qquad (5)$$

where i_{corr} and $i_{\mathrm{corr(inh)}}$ represent the corrosion current density value without and with MELE, respectively.

Each experiment was repeated at least three times to check the reproducibility in deaerated condition.

2.6. SEM and AFM characterizations

Scanning electron microscopy (SEM) was used to examine the morphology of carbon steel surface after immersion in acid solution without and with 400 mg L^{-1} of MELE. The analyses were performed on TESCAN scanning electron microscope with an accelerating voltage of 15kV. The micrographs were taken at a magnification of 200x and 1000x.

Further characterization of the uninhibited and inhibited carbon steel surfaces with respect to surface roughness was done using atomic force microscopy. The experiments were performed by contact mode AFM (Agilent Technologies, Picoview 1.12.2).

3. Results and discussion

3.1. GC-MS analysis

GC-MS chromatogram of the ethanolic extract of the leaves of *Mussaenda erythrophylla* and the chemical structure of the major compounds are represented in **Figure 2**. The results showed the presence of six volatile compounds in MELE (**Figure 2(a)**). These compounds were identified using the database of NIST. They are organic compounds having aromatic rings, and oxygen atoms involved in functional groups O–H, C=O and C–O. The main compounds are 1, 2-benzenedicarboxylic acid monobutyl ester (16.19 %), di-n-octyl phthalate (32.67 %), and 4, 8, 12-tetradecatrien-1-ol, 5, 9, 13-trimethyl (25.17 %) (**Figure 2(b)**).

3.2. Weight loss data

The corrosion rate of carbon steel in 0.5 M H_2SO_4 in the absence and the presence of different concentrations of MELE (100-400 mg L^{-1}) are depicted on **Figure 3(a)**. As shown, at a given temperature, the addition of MELE significantly reduces the dissolution of the metal. These results show that MELE has an inhibitory effect on the corrosion of carbon steel in H_2SO_4 medium. The inhibitory action of MELE is due to the adsorption of its constituents on the metal surface [15]. This inhibitory action of MELE is better as its concentration increases, due to the strengthening of the barrier formed by the inhibitor molecules. **Figure 3(a)** depicts also the effect of increasing temperature on the corrosion rate of the metal. There is an increase in the corrosion rate of the metal in both uninhibited and inhibited environments. However, the plant extract inhibits the carbon steel corrosion at all studied temperatures.

The inhibitory efficiency of the plant extract, calculated from the equation (3), was plotted against the concentration (**Figure 3(b)**). As can be noted, the inhibitory efficiency of MELE increases as its concentration increases. Thus, at 30°C, the inhibitory efficiency of the extract reached a value of 83.25% for a concentration of 400 mg L^{-1}. Besides, **Figure 3(b)** indicates that the increase in temperature leads to an increase in the inhibitory efficacy of the extract for temperatures between 30°C and 40°C. This could be attributed to an increase in the mobility of the inhibitory molecules. However, when the temperature further increases, the effectiveness decreases due to the desorption of some inhibitory species [22].

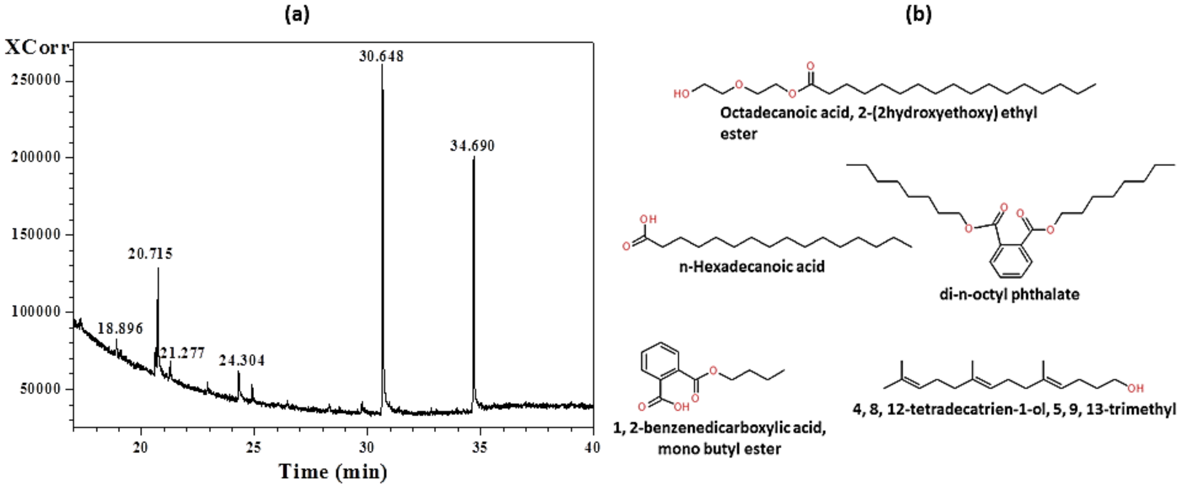

Figure 2: **(a)** GC-MS chromatogram and **(b)** chemical structure of the volatil constituents of MELE

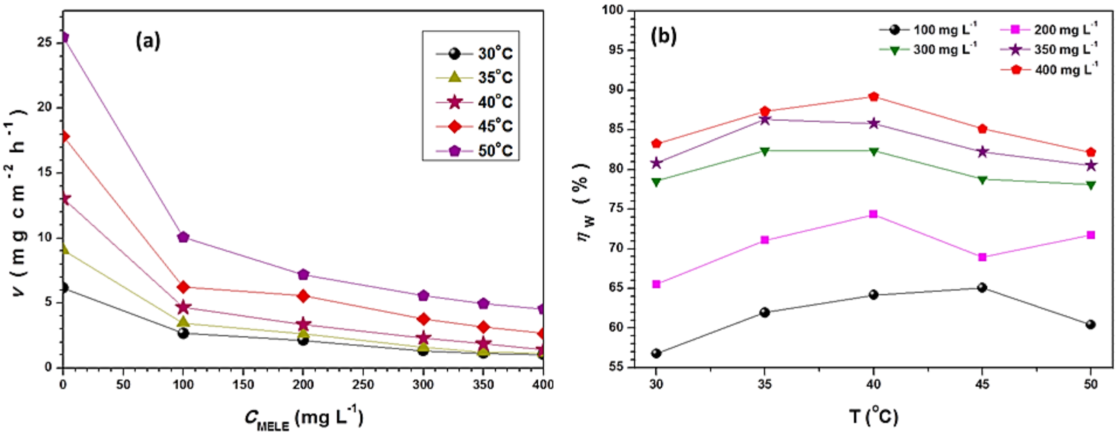

Figure 3: **(a)** Corrosion rate of carbon steel immersed in 0.5 M H_2SO_4 as a function of the concentration of MELE and **(b)** effect of temperature on MELE efficiency

3.3. Electrochemical results

3.3.1. Potentiodynamic polarization curves

From potentiodynamic polarization method, the type (anodic, cathodic or mixed) of the inhibitors extracted was determined. **Figure 4(A)** indicates that the addition of inhibitors shifted the corrosion current density i_{corr} towards lower values. The values of the corrosion current density (i_{corr}), and the corrosion potential (E_{corr}) obtained by extrapolating the polarization curves are shown in **Table I**.
The decrease in i_{corr} value reflects the inhibitory action of MELE on the corrosion of carbon steel in 0.5 M H_2SO_4. The shift in E_{corr} value (± 7 mV) of the inhibited solution, compared to that of the uninhibited solution, is smaller than ± 85 mV. The inhibitors extracted are thus mixed-type [23, 24]. The inhibitory efficacy η_P of inhibitors calculated from equation (5) is also mentioned in **Table I**. The results show an increasing inhibitory efficacy with increasing concentration of MELE.

In order to determine the effect of acid concentration on the inhibitory efficiency and the mechanism action of MELE, the Tafel curves (**Figure 4(B)**) were plotted for 0.1 M, 0.5 M and 1 M H_2SO_4. These curves were compared with those obtained in inhibited solutions (**Figure 4(B')**). We can see the difference in the shape of the anodic curve for various concentrations of acid in the case of inhibited systems. That is not the case without MELE. On the contrary, the cathodic curves of carbon steel immersed in acid solutions with inhibitors are identical. Therefore, the acidity of the medium affects the mode of interfacial action of the plant extract. Certainly there is adsorption of inhibitor molecules, but no film is formed for 1 M H_2SO_4 with 400 mg $L^{-1}$of MELE. For 0.1 M H_2SO_4 in the presence of MELE, the film is clearly observed while for an intermediate concentration of the acid solution, this film is very weak. The increase in concentration of acid would impede the formation of an inhibiting film to the metal surface.

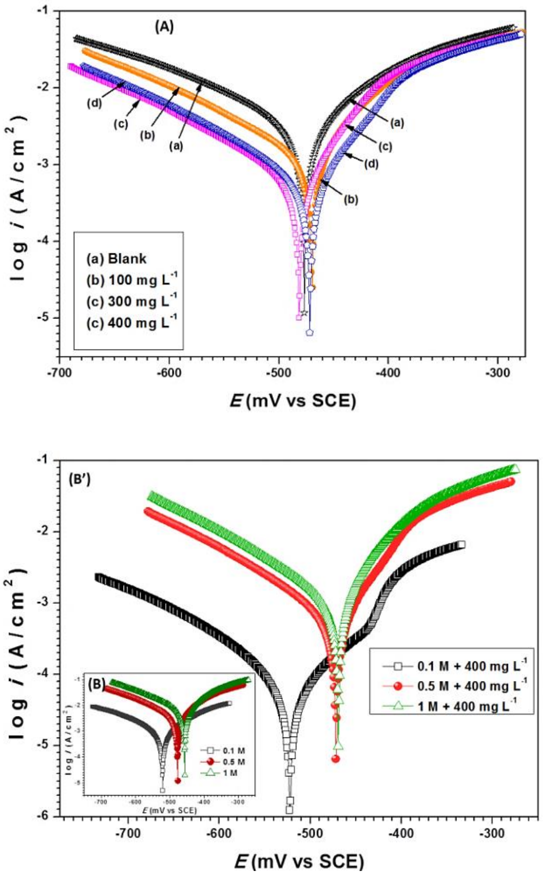

Figure 4: Tafel curves of carbon steel immersed in **(A)** 0.5 M H_2SO_4 without and with different concentration of MELE at 30°C and **(B, B')** influence of acid concentration

Table I: Electrochemical parameters of carbon steel immersed in 0.5 M H_2SO_4 without and with different concentrations of MELE.

C_{MELE} (mg L^{-1})	$-E_{\text{corr}}$ (mV vs. SCE)	i_{corr} (mA.cm^{-2})	η_{P} (%)	R_{ct} (Ω.cm^2)	C_{dl} (μF.cm^{-2})	η_{EIS} (%)
Blank	477	7.68	--	4.11	531	--
100	470	3.09	59.77	8.81	246	53.35
200	476	2.59	66.28	14.46	210	71.58
300	482	2.17	71.74	20.75	103	80.19
350	470	2.11	72.53	22.60	190	81.81
400	472	2.07	73.05	23.04	133	82.16

3.3.2.Electrochemical impedance spectroscopy (EIS)

The mechanisms involved in the corrosion process and the influence of the presence of MELE were detailed using electrochemical impedance spectroscopy. As can be seen in **Figure 5(a)**, the Nyquist curve has a capacitance loop. The shape of the curves is the same for all the medium and is maintained in the range of concentration of the extracted inhibitors. Therefore, the addition of inhibitors does not change the corrosion mechanism. This result is in good agreement with the literature [12]. It is clearly that the corrosion is controlled by electron transfer at the metal-acid interface [13]. In addition, it is found that the diameter of the capacitive loop increases after addition of inhibitors. Thus, the presence of MELE slows down the corrosion effect, by adsorption of its components on carbon steel surface.

Otherwise, one can detect that the capacitive loops are not perfect semi-circular. This reveals a heterogeneous metal surface; the result is the frequency dispersion effect [10, 14]. From the Bode impedance plots, it can be seen that the curves show a characteristic with one time constant (**Figure 5(b)**), corresponding to the large capacitance loop. The values of the electrochemical impedance of the metal with MELE acid medium are larger than those obtained for the medium without MELE. Hence, the molecules of MELE act as barrier between the metal surface and the acidic solution. The model chosen for the best parametric adjustment of the impedance spectra is shown in **Figure 5(c)**. The ohmic drop between the working and reference electrodes when a current flows is represented by the resistance of the solution (R_S). The charge transfer resistance R_{ct} and the constant phase element CPE are introduced in parallel to express that at the metal / solution interface, the transfer of electrons and the establishment of the double layer are effected simultaneously. The values of the double layer capacitance C_{dl} can be obtained from relation [10]:

$$C_{\text{dl}} = \frac{1}{2\pi f(-Z''_{max})R_{ct}} \qquad (6)$$

Table I lists the parameters obtained by extrapolation of the electrochemical impedance curves. Analysis of these data indicates that an increase in the inhibitor concentration causes an increase in charge transfer resistance and a decrease in the double layer capacitance simultaneously. The decrease in C_{dl} is the consequence of a decrease of the dielectric constant and / or the strengthening of the thickness of the electric double layer by inhibitory molecules adsorbed [8, 10, 14]. Indeed, inhibitors could gather at the metal / acid interface, forming the protective layer whose thickness increases with the increase of the concentration of plant extract. The formation of inhibitory barrier further generates an increase in the value of R_{ct}. However, after 300 mg L^{-1} of the plant extract there is no appreciable change in the value of R_{ct} due to potential saturation of the layer. Moreover, the values of the inhibitory efficiency of the plant extract calculated from equation (4) are given in **Table I**. The rise of η_{EIS} with the concentration of plant extract corroborates the conclusions previously made.

3.4. Study of carbon steel surface

3.4.1. Scanning electron microscopy (SEM)

Figure 6 reports the status of the carbon steel surface after one hour of immersionin 0.5 M H_2SO_4. A severe general corrosion of carbon steel is observed (**Figure 6(a)**), after immersionin the acid solution without inhibitor. Corrosion products cover substantially the entire surface of the metal. **Figure 6(a')** has disclosed further soluble corrosion products. These corrosion products form a porous layer which unfortunately can not protect the metal, hence the observed severe attack.

But, the addition of 400 mg L^{-1} plant extract in the aggressive environment has visibly reduced the corrosive attack of carbon steel (**Figure 6(b)**). MELE prevents the formation of corrosion products blisters (**Figure 6(b')**), leaving a relatively smooth and pleasing surface.

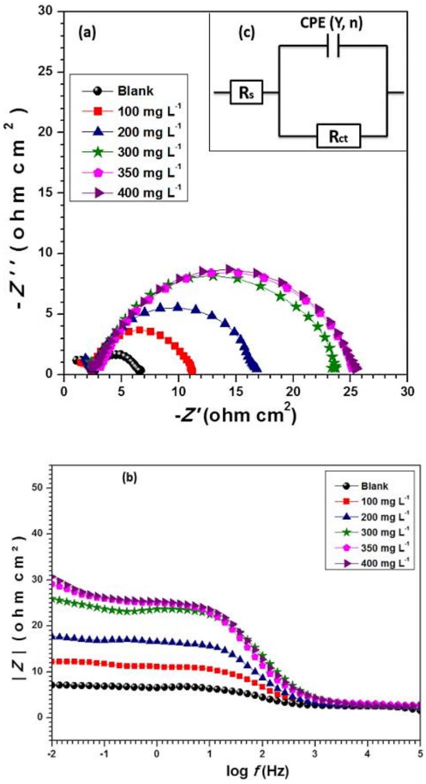

Figure 5: Electrochemical impedance spectra: **(a)** Nyquist and **(b)** Bode plots, and **(c)** equivalent circuit proposed for the metal / electrolyte interface

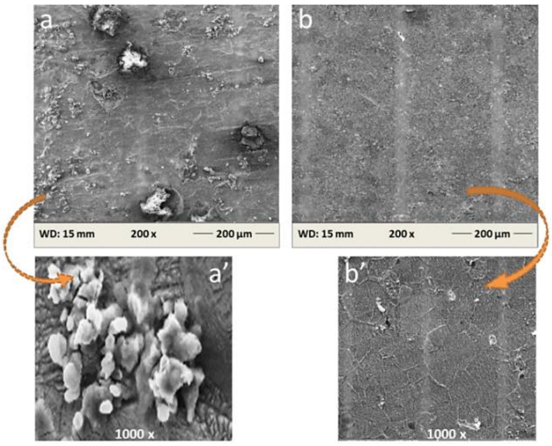

Figure 6: SEM image of the carbon steel after 1 hour of immersion in 0.5 M H_2SO_4 **(a)** without and **(b)** with 400 mg L^{-1} of MELE

3.4.2 Atomic force microscopy (AFM)

The morphology of the surface of carbon steel after immersion in 0.5 M H_2SO_4 solution without and with 400 mg L^{-1} of plant extract was examined in the light of an atomic force microscope. The three-dimensional images and roughness profile are shown in **Figure 7**. As observed, in the acid medium without MELE, the metal surface is very rough (**Figure 7(a)**). This surface has been greatly degraded by its environment. However, the addition of inhibitory molecules substantially reduced the degradation of the metal (**Figure 7(b)**). One can indeed observe a few bumps on a smooth enough surface.

In the solution without inhibitor the roughness profile shows a maximum peak height of 1.25 µm whereas the addition of the plant extract lowers the height of the peaks to a maximum of 0.40 µm (**Figure 7(a')** and **Figure 7(b')** respectively). The depth of the valleys of the metal is 1 µm and 0.5 µm after immersion in acid without and with inhibitors, respectively. These observations denote the roughness of the carbon steel surface after its immersion in the aggressive environment without inhibitor, beside a less corroded surface is obtained when inhibitors are added. Without the addition of plant extract, acid attacks the metal to a depth of 1 µm. But, in the presence of MELE the metal loss has been reduced.

3.5. Thermodynamic studies

3.5.1. Adsorption isotherm

The inhibitory action of organic molecules is generally done by their adsorption on the metal surface [12]. The information on the interactions between this inhibitor and the metal surface can be known using the adsorption isotherms [14]. Thus, the values of the surface coverage (θ) by the plant extract are used to determine the appropriate isotherm. In this study, the Langmuir model (**Figure 8**) is suitable to explain the interactions between the constituents of MELE and carbon steel surface. This isotherm is defined by the following expression:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \qquad (7)$$

However, there is a slight deviation in the value of the slopes from unity (**Figure 8**). Therefore, the corrected Langmuir model was applied to the adsorption of MELE compounds. The equation of the corrected model is as follows

$$\frac{C_{inh}}{\theta} = \frac{n}{K'} + nC_{inh} \qquad (8)$$

The correction of the Langmuir model takes into account the interactions between the species adsorbed. Thus, the deviation of the value of the slope from unity is due to the interactions between adsorbed species on the metal surface.

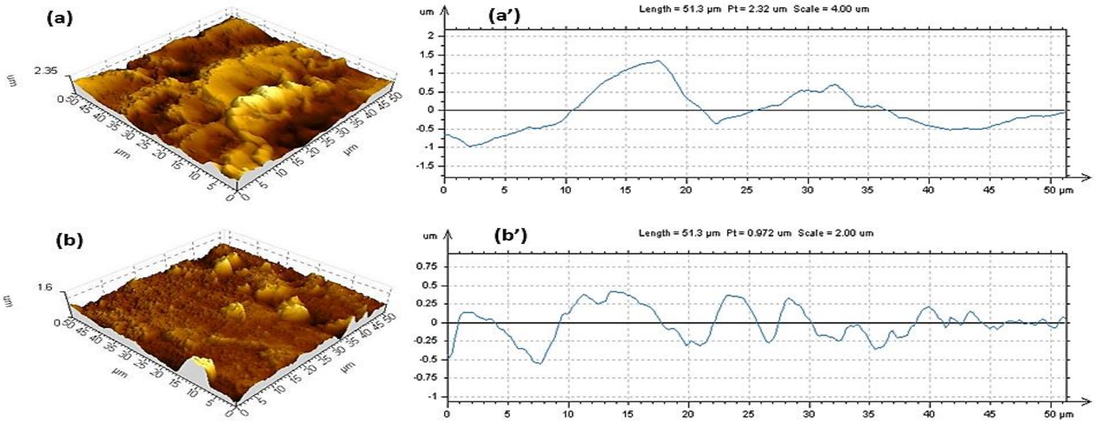

Figure 7: AFM image of the carbon steel after 1 hour of immersion in 0.5 M H_2SO_4 **(a)** without and **(b)** with 400 mg L^{-1} of MELE, and **(a', b')** roughness profile corresponding

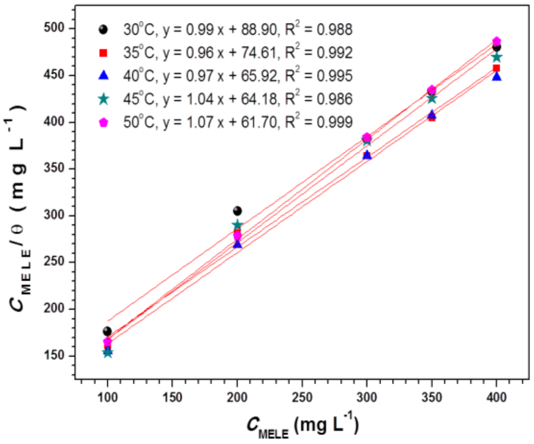

Figure 8: Langmuir isotherm applied to the adsorption of MELE compounds on the carbon steel surface

Indeed, inhibitors have polar atoms and aromatic rings, which are adsorbed on the anodic and cathodic sites of the metal [9, 15, 16]. These results indicate the possibility of formation of adsorbed multi-layer at temperatures between 30°C and 40°C, as the slopes are smaller than unity. For temperatures above 40°C, the slopes are larger than unity; this should mean the fixation of a species on several adsorption sites [17].

3.5.2. Activation parameters

The dependence of the corrosion rate with temperature can be expressed by the linear equation of Arrhenius [20]:

$$\log v = \log A - \frac{E_a^*}{2.303RT} \qquad (9)$$

where v represents the corrosion rate of the metal, A a pre-exponential factor and E_a^* the apparent activation energy.

The plot of the logarithm of the corrosion rate as a function of 1000/T gives a straight line as shown in **Figure 9(a)**, with a slope - $E_a^*/2.303R$.

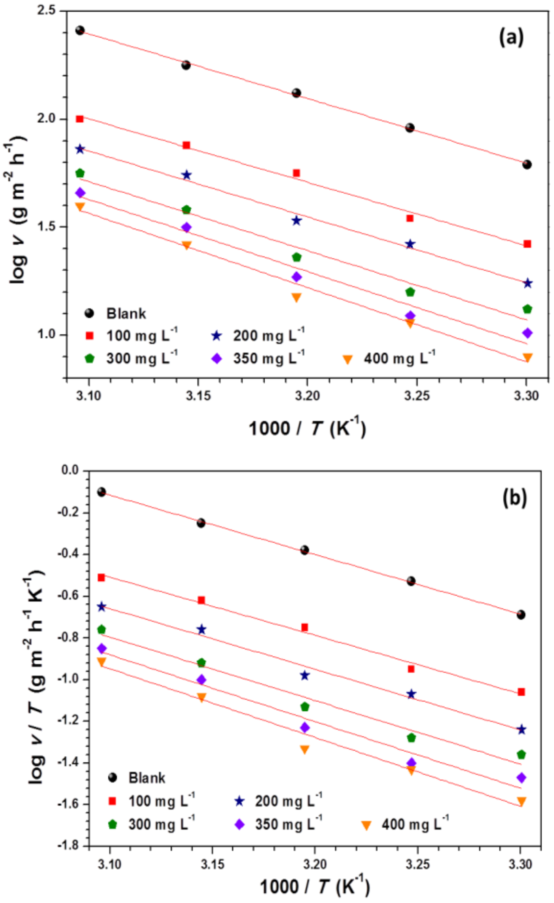

Figure 9: Plots of Arrhenius for carbon steel immersed in 0.5 M H_2SO_4 without and with MELE: **(a)**log$v$ as a function of 1000/T and **(b)**log v/T as a function of1000/T

The value of E_a^* is 57.4 kJ mol^{-1} (**Table II**) in the absence of MELE. This value increases in the presence of inhibitors (65.9 kJ mol^{-1}), suggesting a physical adsorption [7, 22].

Table II: Activation parameters

C_{MELE} (mg L^{-1})	E_a^* (kJ mol^{-1})	-ΔH_a (kJ mol^{-1})	-ΔS_a (kJ mol^{-1} K^{-1})
Blank	57.44	54.76	30.03
100	56.29	53.61	41.14
200	58.40	55.91	37.17
300	61.27	58.40	31.95
350	63.95	61.27	24.29
400	65.87	63.1	19.70

Furthermore, the value of variations of enthalpy of activation ΔH_a and entropy of activation ΔS_a can be determined from another linear formulation of the Arrhenius equation [18]:

$$\log\frac{v}{T} = \left(log\,\frac{R}{\aleph h} + \frac{\Delta S_a}{2.303R}\right) - \frac{\Delta H_a}{2.303RT} \qquad (10)$$

with N Avogadro's number and h is Planck's constant). Other factors were already defined.

Figure 9(b) displays the graphs log v/T as a function of 1000/T, which are straight lines with slope -ΔH_a/2.303R and intercept (log (R/Nh + ΔS_a/2.303R)). Values of ΔH_a deduced from the slope are positive (**Table II**). This embodies the endothermic nature of the dissolution process of carbon steel. The increase in the value of the enthalpy after adding MELE indicates that in the presence of inhibitory molecules the dissolution of the metal is more difficult [20]. The values of ΔH_a are negative in the presence and absence of MELE, indicating an associative mechanism to which the reagents form a single activated complex. The activated complex in the inhibitor-free solution is described as Fe-H_2O which decomposes to Fe^{2+}, H_2 and OH^-, during the corrosion process. In the presence of plant extract, the Fe-complex inhibitor is formed to replace Fe-H_2O. There is decline in the entropy value when inhibitors are added, suggesting that the Fe-complex-inhibitor is ordered than Fe-H_2O [9, 21].

3.6. Mechanism of the inhibition

The results showed that MELE inhibits corrosion of carbon steel in sulphuric acid. The plant extract reduces both reaction types of the corrosion process. The corrosion inhibition is possible by adsorption of the molecules in the extract, on the anodic and cathodic sites of the metal surface. Adsorption is done through the aromatic rings and functional groups involving the oxygen atom (**Figure 2(b)**). The mechanism of inhibition depends not only on the chemical structure of organic compounds, but also the charge of the metal surface [11]. Thus, when the surface of the electrode is negatively charged (by the sulfate ions SO_4^{2-}) organic molecules in cationic form (protonated form) are adsorbed directly to the metal surface. If the surface charge is positive, the sulphate ions are the first to be adsorbed, which facilitates the adsorption of protonated inhibitors. MELE molecules can also interact with the ions Fe^{2+} to form complexes that physically can be adsorbed to the surface of the steel. However, in 0.1 M H_2SO_4 the molecules extracted form an adhering film, probably by physical adsorption and chemical bonding with the metal surface.

4. Conclusions

Through this work, we have shown that MELE reduces carbon steel corrosion rate in sulphuric acid. It was found that the inhibition efficiency could reach around 89.19% at 45°C for inhibitors concentration of 400 mg L^{-1}. The minimum value of η, obtained at 50°C for the same concentration was 82.18%.

This inhibitory effect of MELE is mainly due to the adsorption of its components on the cathodic and anodic sites of carbon steel. However, it should be noted that for lesser acid concentration, an adsorbed thin film is formed to prevent efficiently the corrosion of carbon steel. In addition, it was shown that the inhibitor does not affect the reactions of the corrosion process, but rather block anodic and cathodic reaction sites.

This work presents clearly that MELE can be used as green corrosion inhibitor for carbon steel in processes involving the use of sulphuric acid.

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