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## Inhibition of mild steel corrosion using the extract of *Foeniculum vulgare* in acid medium

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### ABSTRACT

*This paper describes the performance of essential oil of Foeniculum Vulgare Leaves FVL as corrosion inhibitors for steel mild in 1 M hydrochloric acid solutions in the concentration range of 0.4 g/l to 1g/l by weight loss measurements, polarization methods, impedance spectroscopy and scanning electron microscope as a surface treatment method. The effect of FVL extract on the corrosion rate was determined at different temperatures. The inhibition efficiency increased with inhibitor concentration but decrease with rise in temperature. All the data obtained indicate that FVL extract is capable of inhibiting the corrosion of steel mild in HCl solution with a very high efficiency. Polarization data show that FVL behaves as a mixed type inhibitor which is absorbed between the extract and the mild steel substrate by physical adsorption*

**Keywords:** Mild steel; Acid corrosion; EIS ; Corrosion inhibition ; DFT.

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### INTRODUCTION

The corrosion is of fundamental, academic and industrial concern that has been subject of study of many corrosion researchers [1] often difficult to eliminate completely, so the prevention would be more achievable than complete elimination. The use of inhibitors is a practical technique to secure metals and alloys from aggressive environment, the most organic compounds can be efficient inhibitors. However, most of these compounds are not only expensive, but also toxic. Now, it has become necessary to search for effective, safe, and environmentally friendly corrosion inhibitors especially with increasingly stringent environmental policies. In this context, Oil and plant extracts have become a source of inhibitors, ecological guarantee high efficiency at a cheaper price [2].

The Apiaceae or Umbelliferae are a family of mostly aromatic plants with hollow stems. The family contains more than 3,700 species; it is the 16th-largest family of flowering plants. [3] *Foeniculum vulgare* is an herb that belongs to this family, in this work; leaves oil is extracted from FV herb, collected in the Fés region of Morocco and used as corrosion inhibitor to prevent or retard corrosion of mild steel in hydrochloric acid medium. This oil proved his power inhibitor (~85%), Weight-loss measurements combined with linear potential scan voltammetry (I-E) and electrochemical impedance spectroscopy (EIS) were performed in order to complete and to compare the results obtained.

## MATERIALS AND METHODS

### 2.1. Substrates

Prior each experiment, the steel samples are polished with different emery papers up 1200 [4], rinsed with acetone, washed thoroughly with doubly distilled water, and finally dried in air, the sheets of steel used for Weight loss measures 2cm<sup>2</sup> have a square form (2.0 cm x 2.0 cm x 0.05 cm). Their chemical composition is given in Table 1. The aggressive solution 1 M HCl is prepared by dilution of Analytical Grade 37% HCl with doubly distilled water. The immersion time for the weight loss is 6 hours at 308 K and 2 hour at other temperatures

**Table 1. The chemical composition of mild steel**

%Fe	%C	%Si	%P	%Mn	%S	%AL
99.21	0.21	0.38	0.09	0.05	0.05	0.01

### 2.2. Weight loss measurements

Gravimetric measurements are carried out in a double walled glass cell equipped with a thermostated cooling condenser[5] by weighing the mild steel specimens before and after immersion in acid solutions in the presence and absence of various concentrations of FVL (0.4 g/l to 1 g/l). Weight loss allowed us to calculate the mean corrosion rate as expressed in mg cm<sup>-2</sup> h<sup>-1</sup> and the Inhibition efficiency (E<sub>w</sub>%) using the following equations (1) and (2)

$$W_{\text{corr}} = \frac{\Delta m}{S t} \quad (1)$$

$$E_w \% = \frac{(W_{\text{corr}} - W_{\text{corr}/\text{inh}})}{W_{\text{corr}}} \times 100 \quad (2)$$

Where  $\Delta m$  represented the weight loss, S the area of specimen and t experimental time.  $W_{\text{corr}/\text{inh}}$  and  $W_{\text{corr}}$  are respectively the corrosion rate with and without inhibitor.

### 2.3. Polarization measurements

Electrochemical experiments were carried out using a potentiostat PGZ100 A conventional three-electrode system consisting of saturated calomel as reference electrode, platinum foil as counter electrode and mild steel as working electrode was in the form of a disc cut from mild steel [6]. Before all experiments, the potential was stabilized at free potential during 30 min. The polarization measurements were performed by applying a controlled potential scan automatically from -800 to -200 mV with scanning rate of 1 mV s over a small range typically 10 mV with respect to E<sub>corr</sub>. The temperature was thermostatically controlled at 308 K. The resulting current is linearly plotted against potential, the slope of this plot at E<sub>corr</sub> being the polarization resistance (R<sub>p</sub>). The percentage inhibition efficiency was evaluated from the measured I<sub>corr</sub> values obtained using the relations hip(3), respectively, where I and I<sub>i</sub> are the corrosion current densities without and with the addition of the inhibitor.

$$E_i \% = \frac{I - I_i}{I} \times 100 \quad (3)$$

### 2.4. Electrochemical impedance studies (EIS)

Electrochemical impedance spectroscopy is carried out with a Voltalab PGZ 100 system at E<sub>corr</sub> after determination of the steady-state current at a given potential sine wave voltage 10mV peak to peak, at frequencies between 10 mHz and 100 kHz is superimposed on the rest potential [7]. EIS diagrams are given in the Nyquist representation. All electrochemical studies were carried out with an immersion time of 1 h, with different inhibitory concentrations of essential oil of FVL at 308 K. The inhibition efficiency has been calculated using the relationship(4):

$$E_{R_t} \% = 1 - \frac{R_t}{R_{t\text{inh}}} \times 100 \quad (4)$$

Where R<sub>t</sub> and R<sub>tinh</sub> are the charge transfer resistance in absence and in presence of inhibitor, respectively.

### 2.5. Scanning electron microscopic studies

After immersion of Samples of mild steel already prepared in 1M HCl without and with 1g/l of FVL for 6 h. the experiences were performed using an environmental scanning electron microscope [8] (FEI COMPANY QUANTA 200)

## 2.6. Energy dispersive analysis of X-rays (EDX)

EDX system attached with a scanning electron microscope was used for elemental analysis of the film formed on the mild steel surface before and after immersion in the inhibitor solution[9].

## RESULTS AND DISCUSSION

### 3.1. Components identification

The extraction of FVL oil is obtained by hydrodistillation in the laboratory of Physiology, Pharmacology and Environmental Health (EPSP) Fés, and analysed using Gas Chromatography (GC Ultra Trace), coupled with a type of mass spectrometer (PolarisQ) the Regional University Center Interface (C.U.R.I) University Sidi Mohamed Ben Abdellah. The results of the composition of the oil are summarized in Table 2. The figure 1 shows the chromatogram of the FVL. The analysis allowed the identification of several components which dominated by oxygenated monoterpenes accounted for 99.8% of the total weight. The major components were Trans anéthole (83 %), estragole (11.13 %), Fenchone (5.67 %). The molecular structures of these components are shown in Figure 2.

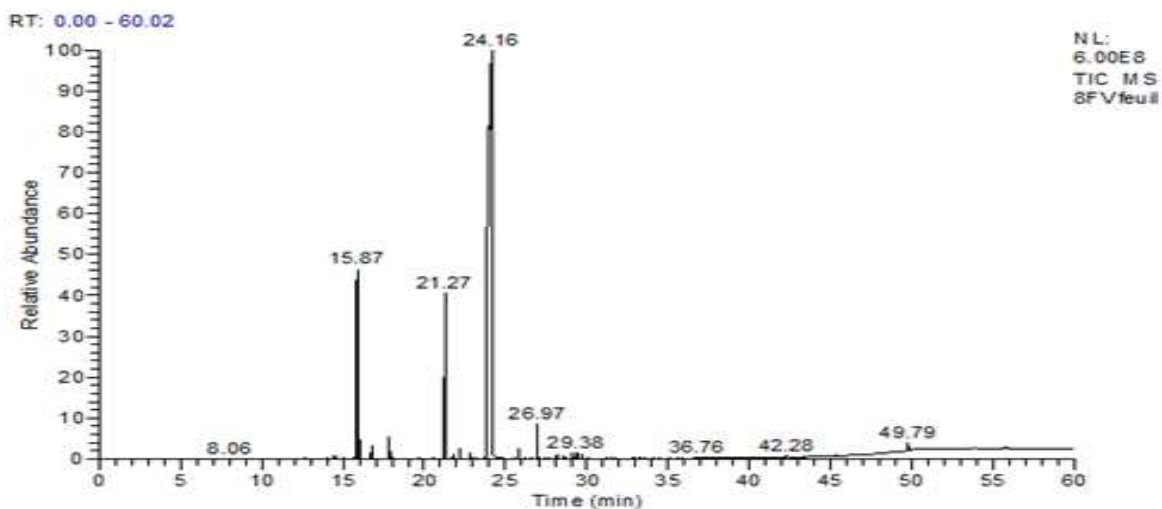


Figure 1: Chromatographic profile of HE of FVL

Table 2: Chemical composition of FVL

Noms chimiques des composés	TR (min)	Formules chimiques	Aire (%)
Estragole	15,87	C <sub>10</sub> H <sub>12</sub> O	11,13
Limonène	21,27	C <sub>10</sub> H <sub>16</sub>	5,67
Transanéthole	24,16	C <sub>10</sub> H <sub>12</sub> O	83

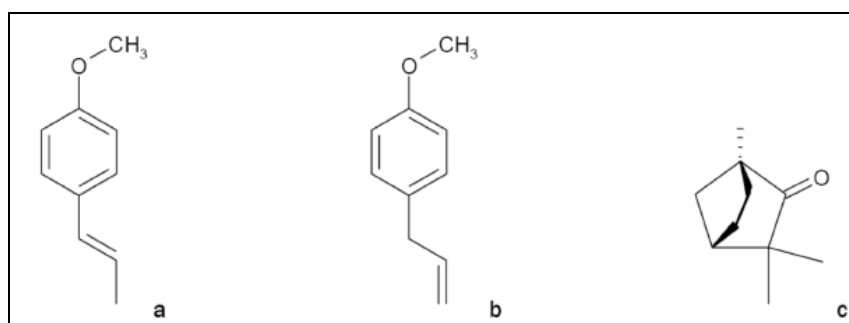


Figure 2: Chemical structure of trans-anethole (a) of estragole (b) and fenchone (c)

### 3.2. Polarization measurements

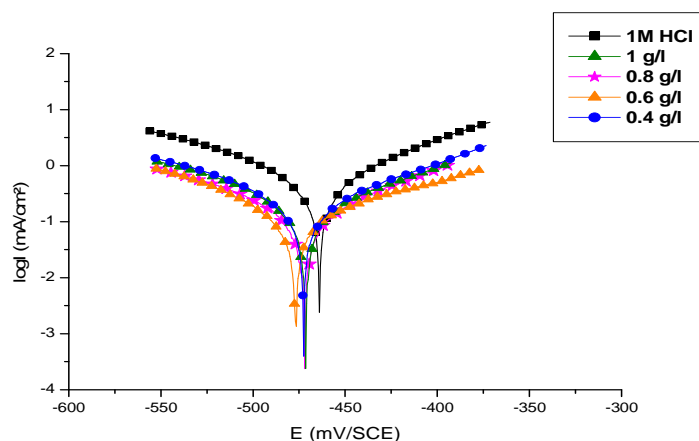


Figure 3: Polarization curves for mild steel in 1 M HCl in the absence and presence of different concentration of FVL at 308K

Figure 3 illustrate the cathodic and anodic polarization curves of mild steel in 1 M HCl recorded with the addition of various concentrations of FVL, These polarization curves demonstrate, as a first sight, that No significant changes were observed in  $E_{corr}$  values in presence of inhibitors, showing that it is a mixed-type inhibitors. As it can be seen, both cathodic and anodic reactions of mild steel electrode corrosion were inhibited by the increase in FVL concentration. Tafel lines of nearly equal slopes were obtained, indicating that the hydrogen evolution reaction was activation-controlled. The corrosion parameters such as corrosion potential ( $E_{corr}$ ), corrosion current density ( $I_{corr}$ ), and cathodic Tafel slope ( $bc$ ) deduced from the curves are presented in Table 3. The data show that the  $I_{corr}$  values decreased considerably and the inhibition efficiency of FVS increases with concentration, reaching a maximum value (92.2%) at 1g/l.

Table 3. Polarization parameters and corresponding inhibition efficiency for the mild steel corrosion in 1 M HCl without and with the addition of various concentrations of FVL

inhibitor	C (g/l)	$E_{corr}$ (mV/SCE)	$I_{cor}$ (mA/cm <sup>2</sup> )	$bc$ (mV)	$E_w$ (%)
Blank	1M HCl	-464	1,879	208,1	--
FVL	1	-471,3	0,1471	79,3	92,2
	0,8	-472,1	0,1486	100,2	92,1
	0,6	-472,6	0,1705	81	90,9
	0,4	-476,8	0,2212	126,4	88,2

### 3.3. Electrochemical impedance measurements

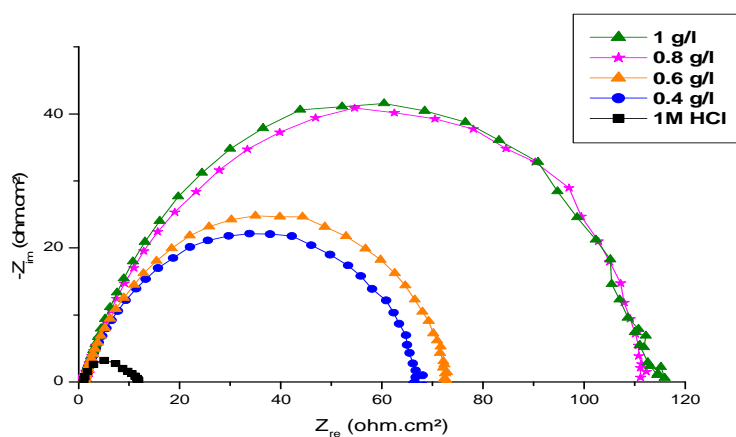


Figure 4. Impedance diagrams of mild steel in 1M HCl with and without different concentrations of FVL

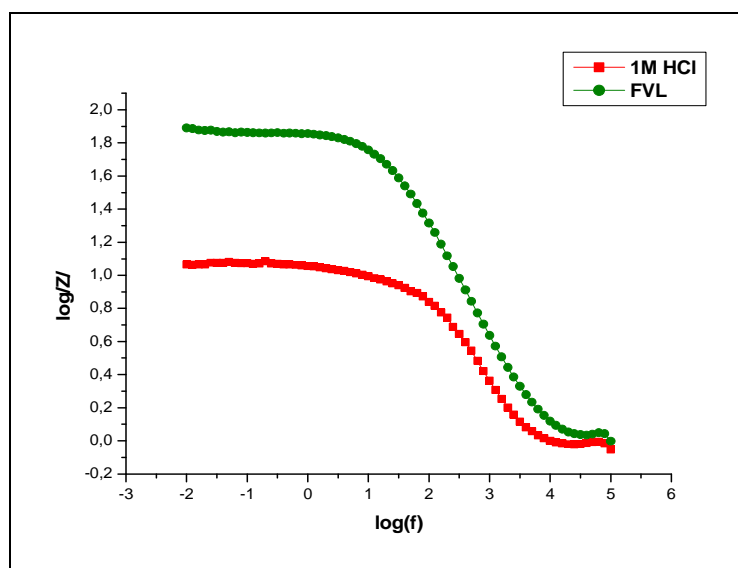
The corrosion behaviors of mild steel in 1 M HCl containing different concentrations of FVL were also investigated by the EIS method, the curves are presented in Figs.4, the Nyquist plots contain semi-circle whose size increases with the inhibitor concentration, showing a charge transfer process mainly controlling the corrosion of steel, The

existence of depressed nature of the semi-circle with its center is the characteristic of solid electrodes and is attributed to the increased micro-roughness of surface and other inhomogenetics of solid electrode during corrosion [10,11]. The characteristic parameters associated to the impedance diagrams (the charge transfer resistance  $R_t$  and the double layer capacitance  $C_{dl}$ ) and  $E$  (%) are given in Table 4.

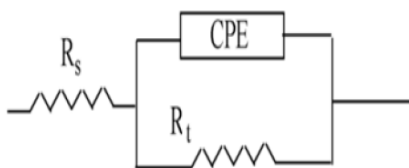
We note that the charge transfer resistance increases with increasing inhibitor concentration, On the other hand, the value of the double layer capacitance decreases from 145.4  $\mu\text{F}/\text{cm}^2$  in the acid to lower values in presence of inhibitors. The decrease in  $C_{dl}$  is due to the adsorption of inhibitor on the metal surface causing a change of the double layer structure [12] which led to an increase in the inhibition efficiency to achieve the maximum value of 90.2 % at a concentration of 1g/l

**Table 4: Impedance parameters for corrosion of steel in 1 M HCl in the absence and presence of different concentrations of FVL**

Inhibitor	C (g/l)	$R_{tc}$ ( $\Omega\cdot\text{cm}^2$ )	$R_s$ ( $\Omega\cdot\text{cm}^2$ )	$C_{dc}$ ( $\mu\text{F}/\text{cm}^2$ )	E (%)
Blank	1M HCl	11,76	0,820	145,4	
FVL	1	119,9	1,0	15	90,2
	0,8	112,0	1,5	16	89,5
	0,6	73,9	1,0	23	84,1
	0,4	69,5	1,4	25	83,1



**Figure 5: Bode diagrams for steel in 1 M HCl**



**Figure 6: Equivalent electrical circuit of the interface steel / FVL / HC**

We prefer sometimes represent the impedance of an electrode in a Bode diagram, indicating the  $\log Z$  versus the logarithm of frequency. Figure 5 shows the Bode diagram of the circuit shown in the Fig 6 for the same values of  $R_t$ ,  $R_s$  and CPE. The diagram show two levels, the electrolyte resistance  $R_s$  can be read from the high frequency and the low frequency portion of bode plots can be used to rate or compare the corrosion behavior of various organic coatings because the low frequency limit contains the values ( $R_t+R_s$ ).

The circuit model used is shown in Figure 6. Here,  $R_s$  is the solution resistance,  $R_t$  is the charge transfer resistance, CPE is a constant phase element that usually account for the electrode surface heterogeneity[13]. The good correlation between the SIE parameters and those obtained by the equivalent circuit shows that this circuit fits well our experimental results and could logically represent the metal/solution interface of mild steel in acidic medium containing FVL.

### 3.4. Weight loss measurements

#### 3.4.1. Effect of concentration

The inhibition efficiencies and weight loss for the immersion of the substrates for 6 h is given in Table 5. It is evident that the addition of FVL extract decrease the metal dissolution rate but the former is more effective at lower concentration than the latter. On the other hand, increase of concentration of inhibitor increases the inhibition efficiency to reach a value of 92.46% at a concentration of 1g/l. This behavior could be attributed due to strong interaction of compounds with the metal surface that results in the adsorption of inhibitor molecules [14]

**Table 5: Gravimetric results of steel in acid without and with addition of the FVL (t=6h, T= 298±1 K).**

C (g/l)	V <sub>corr</sub> (mg/cm.h)	E (%)
Blank	0,6134	--
1	0,0463	92,46
0,8	0,0570	90,71
0,6	0,0614	89,99
0,4	0,0643	89,52

When comparing the results obtained from testing methods used in this work (eight loss measurement and the electrochemical measurements) it can be concluded that there is a fair agreement between the obtained results. But also a little difference can be observed, A similar observation was also reported by several authors [15,16]. This difference can be attributed to the fact that the polarization method gives instantaneous corrosion rates whereas the gravimetric method gives average corrosion rates [17].

#### 3.4.2. Effect of Temperature

In order to get better understandings of the inhibiting process. The effect of temperature on the corrosion behaviour of steel in 1M HCl containing inhibitor at a concentration 2.00 g/l. The effect of temperature (318-348 K) with and without inhibitors is shown in Table 6. It is obvious that the weight loss has increased linearly with the increase in temperature in the presence and absence of inhibitors. The %IE depends upon the temperature and decreases with temperature.

**Table 6: Influence of temperature on the corrosion rate and inhibition efficiency of mild steel in 1 M HCl at 2g/l (t=2h)**

T	V <sub>cor</sub> (HCl)	V <sub>cor</sub> (FVL)	E%
318	1,85	0,332	82,07
328	2,73	0,477	82,53
338	3,99	0,955	76,03
348	5,42	2,596	52,15

The activation parameters for the studied system were determined from the Arrhenius equation and transition state equation. Eqs (5) and (6), Where  $E_a$  is the apparent activation corrosion energy, T is the absolute temperature, A is the Arrhenius preexponential constant, h is Planck's constant, N is Avagadro's number, R is the universal gas constant,  $\Delta S_a$  is the entropy of activation and  $\Delta H_a$  is the enthalpy of activation.

$$W = A \exp\left(-\frac{E_a}{RT}\right) \quad (5)$$

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (6)$$

Arrhenius plots for the corrosion rates of steel are shown in Figures 7 and 8 shows a plot of  $\ln(W_{corr}/T) \cdot 10^3/T$

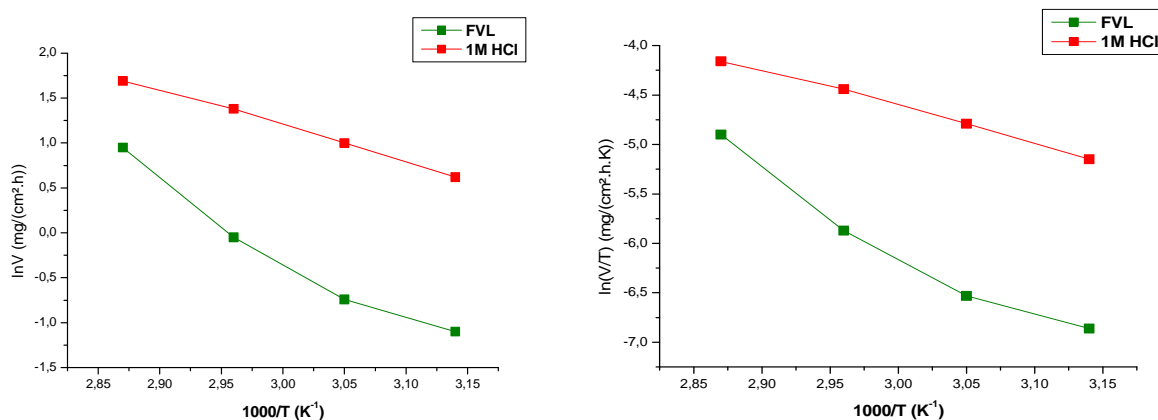


Figure7 & 8: Arrhenius plots of steel in Figure8: The relation between Log (W/T) and uninhibited and inhibited acid1/T for mild steel at different temperatures

Table 7: parameter thermodynamic for the dissolution of mild steel in 1M HCl with and without 1g/l of FVL

Thermodynamic data	Ea (kj/mol)	$\Delta H$ (kj/mol)	$\Delta S$ (j.K <sup>-1</sup> .mol <sup>-1</sup> )
1M HCl	33	31	-159
FVL	63,2	60,5	-81,6

The activation parameters calculated from these curves with and without addition of FVL are listed in Table 7. It's clear that the activation energy of the inhibited solution in this study increases by increasing the concentration of FVL.  $E_a = 33$  kJ/mol for free acid and  $E_a = 63.2$  KJ/mol with the addition 1.00 g/l of FVS. EA modified by the addition of an inhibitor, this modification shows the change in the mechanism of the corrosion process in the presence of adsorbed inhibitor molecules [18-19]Szauder and Brand and Szauder explained that the increase in activation energy may be attributed to an appreciable decrease in the adsorption of the inhibitor on the mild steel surface with the increase in temperature [20] and this is an indication that the physical adsorption occurs [21]

On the other hand, the positive values of  $\Delta H^*$  indicates that the corrosion process is an endothermic phenomenon. And The negative values of  $\Delta S^*$  show that the activated complex in the rate determining step represents an association rather than a dissociation step, indicating that a decrease in disordering takes place on moving from reactants to the activated complex [22]

### 3.5. Surface morphology

The surface morphology of the steel samples in the absence and presence of FVL extract was investigated using SEM technique (model: JEOL, JSM 6400). The SEM images with magnification 1000m of the metal surfaces were taken (Figure 9)

It can be seen that the surface before immersion shows some abrading scratches. due to polishing (Figure 9.A), From the photomicrographs after immersion in uninhibited 1M HCl shows an aggressive attack of the corroding medium on the steel surface (Figure 9.B ), in the presence of FVS Good results are obtained when compared with that in the absence of inhibitor. It also appears as small black holes which may be attributed to the defect of steel At Figure C, a film adsorbed on steel surface exposed to 1M HCl solutions containing FVL, which do not exist in Figure 9.B. This is attributed to the involvement of the compounds in the interaction with the active sites of metal surface; this reduces the contact between metal and the aggressive medium [23] it might be concluded so that the adsorption film can efficiently inhibit the corrosion.

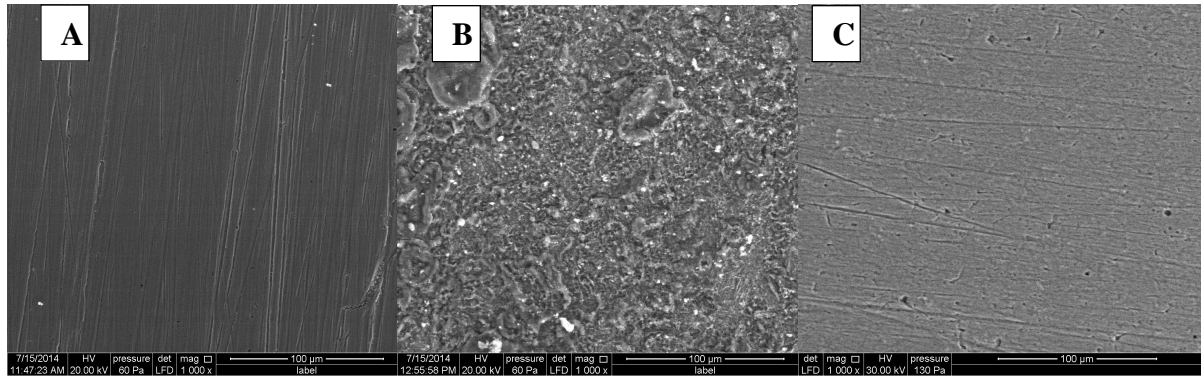


Figure 9: SEM images of mild steel (a) polished (×1000), (b) after immersion in acid solution 1 M HCl (×1000), (c) after immersion in acid solution 1 M HCl containing 1g/l of FVL (×1000)

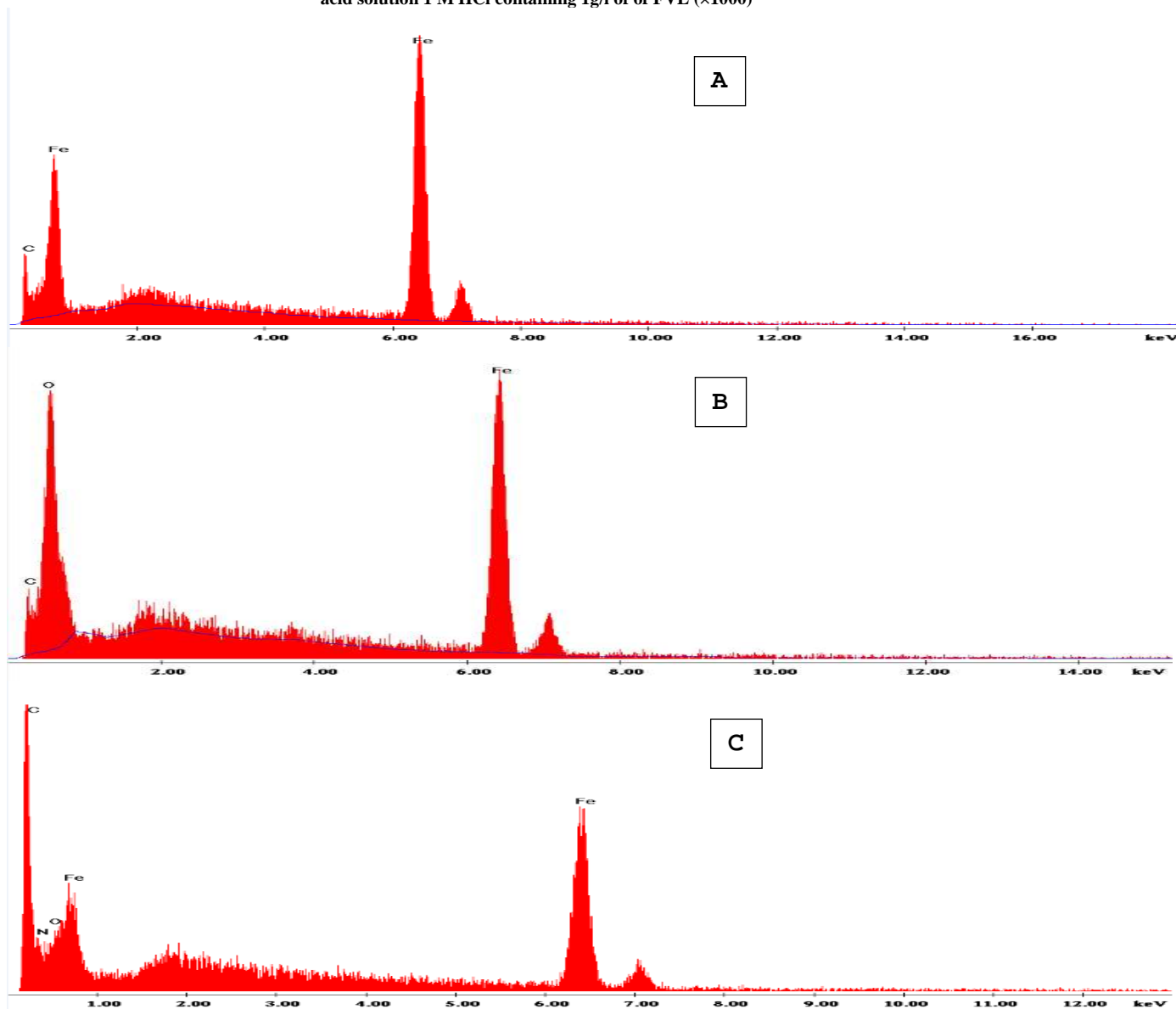


Figure 10. Percentage in mass obtained from EDX analyzes of the different elements composing the mild steel surface, (A) dry steel, (B) after immersion in 1 M HCl solution without inhibitor (C) after immersion in 1M HCl solution containing 1 g/lof FVL

Elements		Fe	C	O
W <sub>t</sub>	A	83.53	16.47	
	B	67.98	13.81	18.21
	C	31.88	57.73	10.39



EDX spectra is an analytical technique used for the elemental analysis or chemical characterization[20] of a mild steel before and after the exposure to the inhibitor solution containing 1g/l of FVL for 6h, the results are displayed in figure 10 and the Table 8. The spectrum in the case of the mild steel is shown in Fig 10A. Fig 10B shows the appearance of the oxygen peak on the EDX spectrum of steel in HCl 1 M with important percentages of Fe and low percentages of C which shows that corrosion of iron takes place through the formation of iron oxide. In inhibited solution (Fig 10C) the EDX spectra shows the appearance of low content of the oxygen and iron compared with the last spectrum confirms that inhibitor molecule precludes the formation of iron oxide and inhibits the corrosion through its strong adsorption on the mild steel surface

### CONCLUSION

FV Oil inhibits the corrosion of mild steel. Its inhibition efficiency increased with the concentration to attain a maximum value 92% at 1 g/L. a result that seems satisfactory in terms of protection of the steel especially in an acid medium. The chemical analysis showed Trans anethol as major component of FVL essential oil and Polarization studies showed that oil acts as a mixed inhibitor without modifying the hydrogen reduction mechanism. The thermodynamic values obtained from this study indicated that the inhibitor was physically adsorbed on the steel surface and SEM study confirmed the formation of protective layer over the steel surface by this green inhibitor. The results obtained from weight loss measurements, polarization curves and EIS study are in reasonable agreement.

### REFERENCES

- [1] M.E. Belghiti, Y. Karzazi, S. Tighadouini, A. Dafali, C. Jama, I. Warad, B. Hammouti, S. Radi, *J. Mater. Environ. Sci*, **2016**, 7 (3), 956-967.
- [2] Y. Filali Baba, H. Elmsellem, Y. Kandri Rodi, H. Steli, C. AD, Y. Ouzidan, F. Ouazzani Chahdi, N. K. Sebbar, E. M. Essassi, B. Hammouti, *Der Pharma Chemica*, **2016**, 8(4), 159-169.
- [3] M. Ellouz, H. Elmsellem, N. K. Sebbar, H. Steli, K. Al Mamari, A. Nadeem, Y. Ouzidan, E. M. Essassi, I. Abdel-Rahaman, P. Hristov, *J. Mater. Environ. Sci*, **2016**, 7(7), 2482-2497.
- [4] M. Sikine, Y. Kandri Rodi, H. Elmsellem, O. Krim, H. Steli, Y. Ouzidan, A. Kandri Rodi, F. Ouazzani Chahdi, N. K. Sebbar, E. M. Essassi, *J. Mater. Environ. Sci*, **2016**, 7(4), 1386-1395.
- [5] B. Zerga, M. Sfaira, Z. Rais, M. EbnTouhami, M. Taleb, B. Hammouti, B. Imelouane and A. Elbachiri, *Matériaux & Techniques*, **2009**, 97, 297-305.
- [6] O. Benali, H. Benmehdi, O. Hasnaoui, C. Selles, R. Salghi, *J. Mater. Environ. Sci*, **2013**, 4 (1), 127-138.
- [7] K. Ismaili Alaoui, F. El Hajjaji, M. A. Azaroual, M. Taleb, A. Chetouani, B. Hammouti, F. Abridgach, M. Khoutoul, Y. Abboud, A. Aouniti and R. Touzani, *Journal of Chemical and Pharmaceutical Research*, **2014**, 6(7), 63-81.
- [8] M. Y. Hjouji, M. Djedid, H. Elmsellem, Y. Kandri Rodi, Y. Ouzidan, F. Ouazzani Chahdi, N. K. Sebbar, E. M. Essassi, I. Abdel-Rahman, B. Hammouti, *J. Mater. Environ. Sci*, **2016**, 7(4), 1425-1435.
- [9] I. Chakib, H. Elmsellem, N. K. Sebbar, S. Lahmidi, A. Nadeem, E. M. Essassi, Y. Ouzidan, I. Abdel-Rahman, F. Bentiss, B. Hammouti., *J. Mater. Environ. Sci*, **2016**, 7(6), 1866-1881.
- [10] K. Juttner, *Electrochim. Acta*, **1990**, 35, 1501.
- [11] T. Rajkoss, *J. Electroanalchem*, **1994**, 364, 111.
- [12] Z. Szklarska-Smialowska, *Kluwer Academic, the Netherlands*, **1991**, 545.
- [13] A. Popova, E. Sokolova, S. Raicheva, M. Christov, *Corros. Sci.* **2003**, 45, 33-58.
- [14] R.S. Chaudhary, S. Sharma, *Indian J. Chem. Technol*, **1999**, 6, 202.
- [15] S. Muralidharan, M.A. Quraishi, S.V.K. Lyer, *Corros. Sci.* **1995**, 37, 1739.
- [16] E.E. Foad, Sherbini El, *Mater. Chem. Phys*, **1999**, 60, 286.
- [17] S. El Issami, L. Bazzi, A. Benlhachemi, R. Salghi, B. Hammouti, S. Kertit, *Pigment Resin Tech*, **2007**, 36, 161.
- [18] A. Chetouani, M. Daoudi, B. Hammouti, T. Ben Hadda, M. Benkaddour, *Corros. Sci.* **2006**, 48, 2987-2997.
- [19] K. Tebbji, B. Hammouti, H. Oudda, A. Ramdani, M. Benkaddour, *Appl. Surf. Sci.* **2005**, 252, 1378-1385.
- [20] S. El Arrouji, K. Ismaili Alaoui, A. Zerrouki, S. EL Kadiri, R. Touzani, Z. Rais, M. Filali Baba, M. Taleb, F. El-Hajjaji, A. Chetouani, A. Aouniti, *J. Mater. Environ. Sci.* **2016**, 7 (1), 299-309.
- [21] D. Ben Hmamou, R. Salghi, A. Zarrouk, M. Messali, H. Zarrok, M. Errami, B. Hammouti, Lh. Bazzi, A. Chakir, *Der Pharma Chemica*, **2012**, 4(4), 1496-1505.
- [22] D. Ben Hmamou, R. Salghi, Lh. Bazzi, B. Hammouti, S.S. Al-Deyab, L. Bammou, L. Bazzi, A. Bouyanzer, *Int. J. Electrochem. Sci.* **2012**, 7, 1303 - 1318.
- [23] S.S. Abd El-Rehim, S.A. Rwafeay, F. Taha, M.B. Saleh, R.A. Ahmed, *J. Appl. Electrochem*, **2001**, 31, 429-435.