Antifungal Activity and Anti-Corrosion Inhibition of *Origanum Compactum* Extracts

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The objective of this study was to evaluate antifungal activities of *Origanum compactum* extracts against the growth of the phytopathogenic fungus *Penicillium digitatum* and the corrosion inhibition behavior of carbon steel in 0.5 M sulfuric acid in the presence these extracts have been studied using the weight loss and electrochemical methods. The aerial parts of *Origanum compactum*, an endemic medicinal plant of the Moroccan North, were extracted with the soxhlet apparatus using the following solvents: petroleum ether, hexane, chloroform and methanol. The results showed that aqueous and methanol 80 % extracts were very effective to control the growth of the fungus with 100% of the inhibition percentage at the concentration of 25g/l. Moreover, the percentage of the inhibition of the mycelial growth was more than 97% at 1,125 g/l for the aqueous extract. From the soxhlet extracts, petroleum ether extract presented an important antifungal activity (83%) followed by methanol extract (45,9%). While hexane and chloroform extracts were less effective. For the corrosion application, the results showed variation in inhibition performance of the inhibitor with varying concentration. The results obtained with different methods are in good agreement. Langmuir model was tested to describe the adsorption behaviour of inhibitor on the carbon steel surface.

Keywords: Antifungal activity, *Origanum compactum,* corrosion inhibition, carbon steel.

1. INTRODUCTION

Research on natural products (including plant extracts) which can replace agrochemicals or lead to the development of new agents for pest control is extremely important [1-2]. Many natural substances play a role in the host plant/pathogen relationship. Fruits and vegetables are often susceptible to attack by phytopathogenic fungi, which affect their quality. Green mold caused by *Penicillium digitatum* is one of the most important post-harvest diseases of Citrus fruits [3].

To prevent the development of this pathogen and limit losses fruits, treatment with chemical fungicides is a widely used procedure. However, such treatment causes serious problems, with fungicide residues remaining on the fruit [4], the appearance of fungicide-resistant strains of *P. digitatum* [5], and the accumulation of fungicides in human adipose tissue, posing a health threat [6]. However, the plant extracts currently used for several applications at the same time, one of those applications we mention the field of corrosion inhibition. It should be noted that, iron and iron-based alloys were one of the major construction materials [7-8]. But its susceptibility to corrosion in humid air and its very high dissolution rate in acid medium are the major obstacles for its use on larger scale [9]. The inhibition of the corrosion of mild steel is of great importance and that can be done by many ways, among that the use of organic compounds as corrosion inhibitor is the most popular one [10-11]. Several inhibitors have been synthesized and used for the inhibition of the corrosion of mild steel in acidic [12-14]. Most effective inhibitors are organic compounds having hetero atom in their aromatic or long carbon chain systems. For these compounds, the presence of hetero atoms enhanced the electron donating ability of the inhibitor to the metal [15-18]. However, the short coming of these inhibitors is that they are not environmentally friendly. Therefore there is need to search for green corrosion inhibitors. According some works, green corrosion inhibitors are biodegradable and do not contain heavy metals or other toxic compound [19-23]. The successful uses of naturally occurring substances to inhibit the corrosion of metals in acidic and alkaline environment have been reported by some research groups. Increasing efforts is also been made in researching the possibility of using some extracts plants as green corrosion inhibitors. In our laboratories, many studies have been done on the corrosion inhibition by natural plant extract and their oils on steel in acidic solutions [24-31].

In the present work, we investigate to study the antifungal activity of *Origanum compactum* extract (**OCE**), family of Lamiaceae an endemic species in Morocco, to control *in vitro* the phytopathogenic fungus: *P. digitatu* and inhibitive action of this plant as a cheap, eco-friendly and naturally occurring substance on corrosion behaviour of C38 steel in 0.5 M H$_2$SO$_4$.

2. EXPERIMENTAL METHODS

2.1. Antifungal activity part

2.1.1. Collection and preparation of plant material

The aerial parts of *Origanum compactum* were collected in July 2011, Ouezzane region in the northwest of Morocco. Plant samples were air dried in the shade, at room temperature, and preserved from the humidity and from the light until use.

2.1.2. Extraction of the phenolic compounds

<u>Extraction by Soxhlet</u>

The aerial parts of *Origanum compactum* were crushed finely in 2000 towers/min in an electric crusher IKA-Universalmühle M20, then passed on a sieve of 250 µm. 100 g of this powder were extracted with four solvents: petroleum ether, hexane, chloroform and methanol using Soxhlet during 12 hours. The obtained extracts were concentrated by rotating evaporation.

<u>Cold extraction</u>

Two types of solvents were used: the methanol 80 % and the distilled water. The extraction by the methanol 80 % was realized by mixing 10 g of powder in 100 ml of solvent. The obtained solution was homogenized for 15 min, followed by sonication for 15 min and then filtered through a Wathman paper n°4 [32]. The filtrat was concentrated by evaporator rotator until complete elimination of the methanol.
The aqueous extraction was made by suspending 10 g of powder in 100 ml of distilled water then homogenized during 18 hours. The solution was then centrifuged for 30 min in 5000 rpm [33] and the obtained surnageant was tested for their antifungal activity.

2.1.3 Study of the antifungal activity

The antifungal activity of extracts was tested *in vitro* against mycelial growth of *Penicillium digitatum*. This later was isolated from infected fruits of clementine (*Citrus clementina hort*.) and identified in the laboratory of Mechanics, Processes of the Energy and the Environment, ENSA, Agadir. Extracts by Soxhlet were diluted in a solution of 2 % of Tween 80. The technique used was the method of incorporation in a solid medium. Potato dextrose agar (PDA) was autoclaved and cooled to 40°C in a water bath, and then the extracts by soxhlet were mixed with sterile molten PDA to obtain final concentrations of 500, 1000, 1500 and 2000 ppm. For the aqueous extracts and methanol 80 % a range of concentrations from 1 to 50 g/l of were used for the antifungal test [34]. Aliquots of 15 ml of solution were immediately dispensed to Petri dishes which were seeded with 6 mm diameter mycelium from the edge of 7-day old *P. digitatum.* The inoculated Petri dishes were incubated in the dark at 25± 1°C. The inhibition percentage of the *P. digitatum* mycelial growth was calculated using the following formula [35] :

$$IP = \frac{C - T}{C} \; x \, 100$$

where C is the average of 3 replicates of mycelial growth (cm) of control Petri dishes and T is the average of 3 replicates of mycelial growth (cm) of treated Petri dishes.

2.1.4.Statistical analysis

Statistical analysis was performed by applying test t for independent samples by group by the software Statistica version 6.

2.2. Corrosion inhibition part

2.2.1. Materials preparation and solutions

The material used throughout the experiments was a carbon steel with chemical compositions given in Table 1.

Table 1. Chemical composition of the carbon steel specimens

Element	C	Si	Mn	Cu	S	Fe
Weight%	0.179	0.165	0.439	0.203	0.034	balance

The corrosive solution used 0.5 M sulfuric acid was prepared by dilution of an Analytical Grade 98% H_2SO_4 with double distilled water.

The concentration range of **OCE** employed was 0.50 to 3.00 g/L in 0.5 M sulphuric acid.

The specimens were embedded in polyester, which had a surface area of 0.32 cm^2 that was in contact with the aggressive media. The working electrode was mechanically polished with emery paper up to 1200 grade, degreased in acetone and rinsed with double distilled water before immersed in the test solution.

2.2.2. Gravimetric analysis

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat cooling condenser. The carbon steel specimens used have a rectangular form (2 cm×1cm×0.3cm). The duration of tests was 6 h at 298K in 0.5 M H_2SO_4 solution contain different concentrations of **OCE**.

The specimens were abraded with a series of emery paper up to 1200 grade and then washed thoroughly with acetone and double distilled water. After weighing precisely, the specimens were immersed in beakers which contained 100 ml acid solutions with different concentrations of **OCE** at a certain temperature remained by a water thermostat. All the aggressive acid solutions were open to air. After 6 h the specimens were taken out, washed, dried, and weighed exactly.

2.2.3. Potentiodynamic polarization

Polarization measurements were carried out in a conventional three-electrode electrolytic cell. Saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary

electrodes respectively. The working electrode is in the form of a disc from carbon steel of the surface 0.32 cm^2. These electrodes are connected to Voltalab PGZ 100 piloted by ordinate associated to "Volta Master 4" software. The scan rate was 1 mV/s started from an initial potential of -700 to -100 mV/SCE. Before recording each curve, a stabilization time of 30 min was allowed, which was proved to be satisfactory to attain a stable value for E$_{cor}$. All experiments were repeated three times at temperature desired ±1°C. Corrosion current densities were obtained from the polarization curves by linear extrapolation of the Tafel curves.

2.2.4. Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) was carried out with a same equipment was used as for the polarization measurements, leaving the frequency response analyzer out of consideration. Quasi-potentiostatic polarization curves were obtained using a sweep rate of 1 mVs^{-1}. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz were superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potential after 30 min of exposure. All potentials were reported versus saturated calomel electrode (SCE). The impedance diagrams are given in the Nyquist representation. Experiments are repeated three times to ensure the reproducibility.

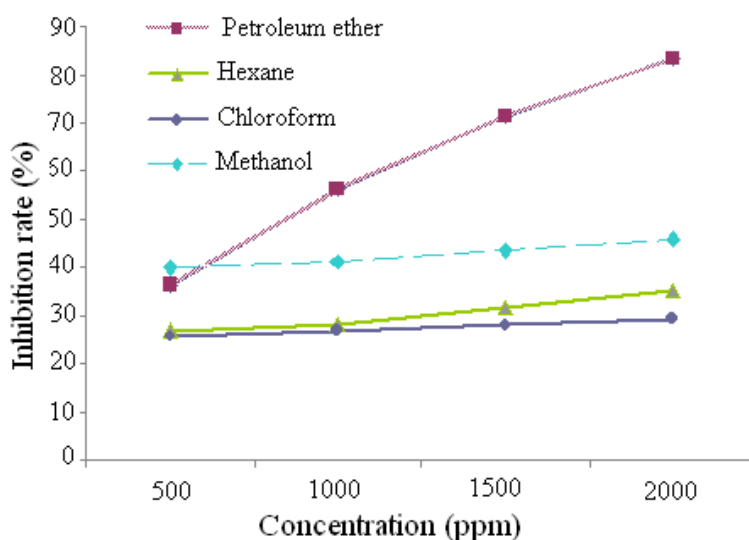## 3. RESULTS AND DISCUSSION

3.1. Antifungal activity part

Figure 1. Antifungal effect of the organic solvents extracts of *Origanum compactum* on the rate of growth inhibition of *penicillium digitatum*.
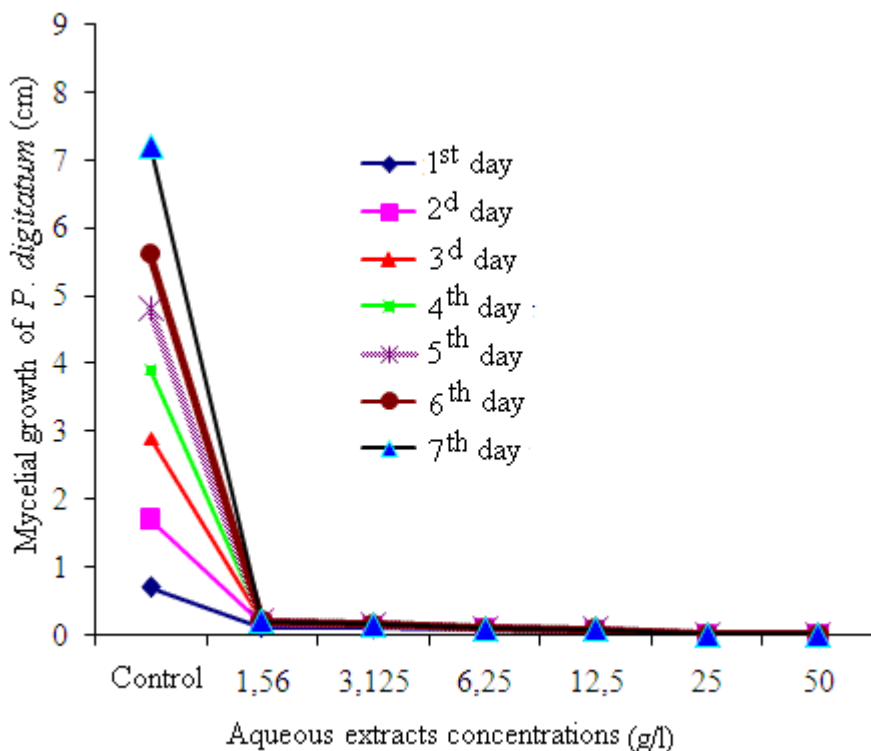
Figure 2. *Penicillium digitatum* mycelial growth treated with different concentrations of *Origanum compactum* aqueous extracts during seven days of incubation at 25± 1°C.
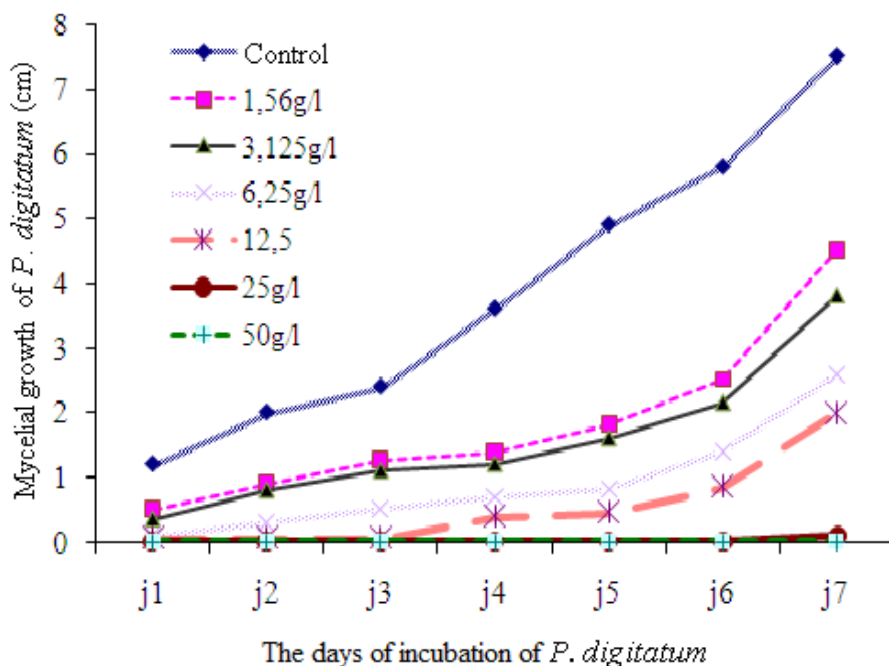

Figure 3. *Penicillium digitatum* mycelial growth treated with different concentrations of *Origanum compactum* of methanol 80% extracts during seven days of incubation at 25± 1°C.

The results of the antifungal effect of the organic solvents and aqueous extracts of *Origanum compactum* on the inhibition percentage of *Penicillium digitatum* mycelial growth are presented in the

figure1. These results showed that the inhibition percentage of the petroleum ether extracts was 83 % at the concentration of 2000 ppm (figure1). While for the other studied extracts, the inhibition was less important. Its represents respectively 29.4%, 35.3% and 45.9 % for chloroform, hexane and methanol extracts at the same concentration (Fig. 1).

The results obtained by the aqueous extract are presented in the Fig. 2. The aqueous extracts were highly effectif to control the mycelial growth of *Penicillium digitatum*. At 25 g/L the radial growth of the fungus was completely inhibited. Moreover, we found that the inhibition percentage exceeded 97 % for all the studied concentrations (Fig. 2).

The complete inhibition was obtained at the concentrations of 25 and 50 g/L for methanol 80% extracts (figs. 3 and 4). The concentration 6.25 g/L presented a very high antifungal activity with 70.66% inhibition percentage. While at the concentrations of 3.125 g/l and 1.65 g/l the antifungal activities were 49.33 % and 40 % respectively.
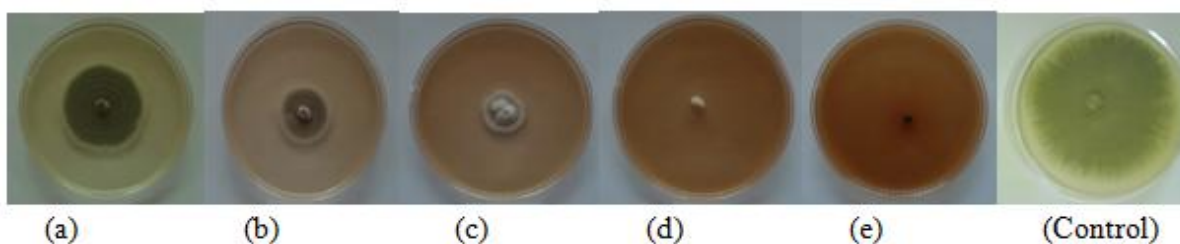

Figure 4. Inhibition of *Penicillium digitatum* mycelial growth treated with 3,125g/l (a), 6,25g/l (b), 12,5 g/l (c), 25 g/l (d) and 50 g/l (e) of *Origanum compactum* methanol 80% extracts after 7 days of incubation at 25± 1°C.

The petroleum ether extracts of *Origanum compactum* were highly actif against the mycelial growth of *P. digitatum*, The effectiveness of petroleum ether extract might be due to its high levels of carvacrol, p-cymène, thymol and terpinene [36], the antifungul activity of carvacrol, the main compound of *Lamiaceae* essential oil [37-39], has been the subject of several studies [40-41].

The methanol 80 % extracts of *Origanum compactum* aireal parts were also highly effectif against *P. digitatum* mycelial growth. It was demonstrated that the mechanism of toxicity of total phenols against the fungi is based on the inactivation of the fungal enzymes which contain the SH group in their actif sites [42-44] classified the pure compounds according to their antifungal activity towards seven fungi, this activity decreases according to the type of chemical functions : phenols > Alcohols > Aldehydes > Cetones > Ethers > Hydrocarbures.

3.2. Corrosion inhibition part

3.2.1. Polarization measurements

The characteristics of current–potential curves resulting from cathodic and anodic polarization of carbon steel in 0.5 M H_2SO_4 with various concentrations of **OCE** have been evaluated. Fig. 5 shows

the potentiodynamic polarization curves containing various concentrations of Origanum compactum extracts at 298 K. The corrosion parameters including corrosion current densities (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (bc) and inhibition efficiency ($E_I\%$) are listed in Table 2. In the case of polarization method the relation determines the inhibition efficiency ($E_I\%$):

$$EI \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \times 100 \qquad\qquad (1)$$

where I_{corr} and I'_{corr} are the corrosion current density values without and with the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.
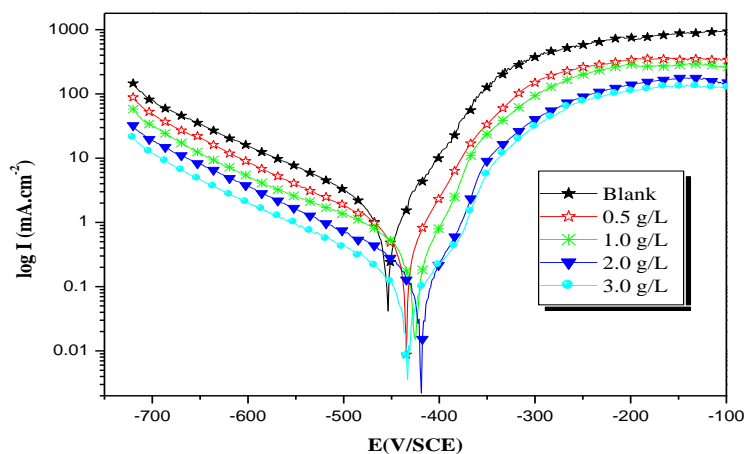

Figure 5. Potentiodynamic polarisation curves of carbon steel in 0.5 M H_2SO_4 in the presence of different concentrations of **OCE.**

From electrochemical polarization measurements, it is clear from the results that the addition of inhibitor causes a decrease of the current density. The values I_{corr} of carbon steel in the inhibited solution are smaller than those for the inhibitor free solution (Table 2). This decrease can be explained by the inhibitory action of this inhibitor. The parallel cathodic Tafel plots obtained in figure 5 indicate that the hydrogen evolution is activation-controlled and the slight change of bc indicates that the reduction mechanism is not affected by the presence of inhibitor. In the domain anodic, the polarization curves of carbon steel have shown that the addition of the **OCE** decreases the current density and moves the corrosion potential to positive values acting mainly on the dissolution reaction of metal. The inhibition efficiency ($E_I\%$) increases with inhibitor concentration reaching 93.25% at 3 g/L. However, a shift of corrosion potential (E_{corr}) towards cathodic side i.e -454 to -420 mV was established. The classification of a compound as an anodic or cathodic inhibitor is feasible when the corrosion potential displacement is at least 85 mV in relation to that one measured for the blank solution [45].

Table 2. Electrochemical parameters of carbon steel at various concentrations of **OCE** in 0.5 M H$_2$SO$_4$ and corresponding inhibition efficiency.

Conc. (g/L)	E_{corr} (mV/SCE)	I_{corr} (mA/cm^2)	$-b_c$ (mV/dec)	E_I (%)
Blank	-454	2.5477	186	——
3.00	-434	0.1718	145	93.25
2.00	-420	0.4113	171	83.85
1.00	-426	0.5409	151	78.76
0.50	-436	0.8297	144	67.43

In our case the displacement is lower than 24 mV, so we can classify our inhibitor as mixed. On the other hand, for anodic polarization, it can be seen from figure 5 that, in the presence of **OCE** at differents concentrations, two linear portions were observed. When the anodic potentials increases, the anodic current increases at a slope of b_{a1} in the low polarization potential region. After passing a certain potential E_u, the anodic current increases rapidly and dissolves at a slope of b_{a2} in the high polarization region. The rapid increase of anodic current after E_u may be due to desorption of **OCE** molecules adsorbed on the electrode. This means that the inhibition mode of **OCE** depends on electrode potential. In this case, the observed inhibition phenomenon is generally described as corrosion inhibition of the interface associated with the formation of a bidimensional layer of adsorbed inhibitor species at the electrode surface [46-49].

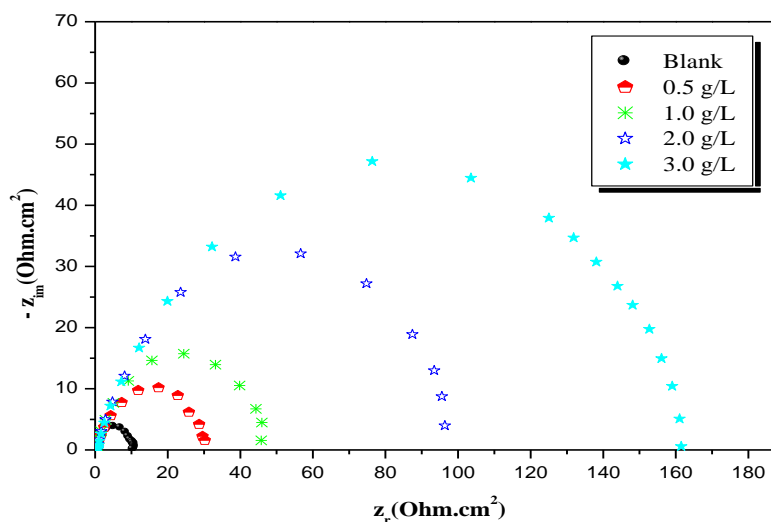*3.2.2. Electrochemical impedance spectroscopy measurements:*

Figure 6. Nyquist diagrams of carbon steel with different concentrations of **OCE** at 298K.

The corrosion behaviour of carbon steel, in acidic solution in the presence of **OCE**, was investigated by the EIS methods at 298 K. Nyquist plots obtained for frequencies ranging from 100 kHz to 10 mHz at open circuit potential for carbon steel in 0.5 M H_2SO_4 in the presence of various concentrations of **OCE** are shown in Fig. 6. The impedance diagrams obtained are not perfect semicircles and the difference was attributed to frequency dispersion [18]. The fact that impedance diagrams have a semicircular appearance shows that the corrosion of carbon steel is controlled by a charge transfer process. The equivalent circuit model employed for this system is presented in figure 7. The resistance R_s is the resistance of the solution; R_t reflects the charge transfer resistance and C_{dl} is the double - layer capacitance.
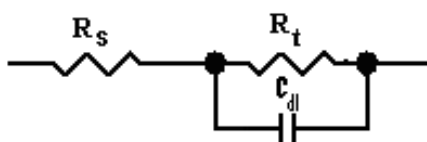

Figure 7. The electrochemical equivalent circuit used to fit the impedance spectra.

Values of the charge transfer resistance R_t were obtained from these plots by determining the difference in the values of impedance at low and high frequencies as suggested by Tsuru and Haruyama [50]. Values of the double–layer capacitance C_{dl} were calculated from the frequency at which the impedance imaginary component -Z_i is maximum using the equation:

$$f(-Zi_{max}) = \frac{1}{2\pi C_{dl} R_t} \qquad (4)$$

Table 3 gives the values of the charge transfer resistance R_t, double layer capacitance C_{dl}, and inhibition efficiency obtained from the above plots.

It can be seen that the presence of carob seed oil enhances the values of R_t and reduces the C_{dl} values. The decrease in C_{dl}, which can result from a decrease in local dielectric constant and / or an increase in the thickness of the electric double layer [52-53], suggested that **OCE** molecules function by adsorption at the metal / solution interface. Thus, the decrease in C_{dl} values and the increase in R_t values and consequently of inhibition efficiency may be due to the gradual replacement of water molecules by the adsorption of the extract molecules on the metal surface, decreasing the extent of dissolution reaction [28, 54].

Table 3. Electrochemical Impedance parameters for corrosion of carbon steel in acid medium at various contents of **OCE.**

Conc (g/L)	R_t ($\Omega.cm^2$)	C_{dl} ($\mu F/cm^2$)	E_{Rt} (%)
Blank	10.58	215.09	----
3	163.00	13.35	93.50
2	95.26	17.17	88.89
1	45.53	19.38	76.76
0.5	30.00	26.51	64.73

3.3.3. Weight loss, corrosion rates and inhibition efficiency

Values of the inhibition efficiency and corrosion rate obtained from the weight loss measurements of carbon steel for different concentrations of **OCE** in 0.5 M H_2SO_4 at 298 K after 6 h of immersion are given in table 4. The inhibition efficiency is defined as follows:

$$E_W \% = \frac{W_{corr}^0 - W_{corr}}{W_{corr}^0} \times 100 \qquad (1)$$

where W_{corr}^0 and W_{corr} are the corrosion rates of carbon steel due to the dissolution in 0.5 M H_2SO_4 in the absence and the presence of definite concentrations of inhibitor, respectively.

It is obvious from table 4 that the **OCE** inhibits the corrosion of carbon steel in 0.5 M H_2SO_4 solution at all concentrations used in this study, and that the corrosion rate (W) is seen to decrease continuously with increasing additive concentration at 298 K. Indeed, corrosion rate values of carbon steel decrease when the inhibitor concentration increases while E_W (%) values of **OCE** increase with the increase of the concentration; the maximum E_W (%) of 91.12 % is achieved at 3 g/L. The inhibition of corrosion of carbon steel by **OCE** can be explained in terms of adsorption on the metal surface.

Table 4: Effect of **OCE** concentration on corrosion data of carbon steel in 0.5 M **H_2SO_4**

Conc. (g/L)	W_{corr} (mg. cm^{-2})	E_w (%)
Blank	1.790	---
3.00	0.158	91.12
2.00	0.244	86.34
1.00	0.512	71.35
0.50	0.705	60.58

3.4. Adsorption isotherm and mechanism of inhibition

Adsorption isotherms are very important to understand the mechanism of inhibition corrosion reactions. The most frequently used isotherms are Langmuir [55], Frumkin [56] and Temkin [57]. The Langmuir isotherm (C/ θ vs C) assumes that there is no interaction between adsorbed molecules on the surface. The Frumkin adsorption isotherm (θ vs C) assumes that there is some interaction between the adsorbates, and the Temkin adsorption isotherm (θ vs lgC) represents the effect of multiple layer coverage [58]. Fig. 8 shows the dependence of C/ θ as function of the of **OCE** concentration from EIS measurements. The curve obtained clearly shows that the data fit well with Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the studied inhibitor, which obeys:

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

where C is the concentration of inhibitor, K is the equilibrium constant of the adsorption process, and θ is the surface coverage.

This suggests that the adsorption of **OCE** in present study obeyed the Langmuir isotherm and there is negligible interaction between the adsorbed molecules.
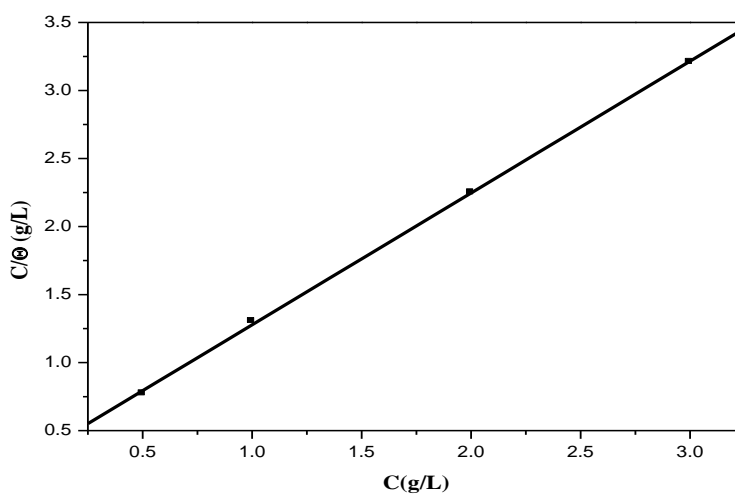

Figure 8. Langmuir adsorption isotherm of carob seed oil on the carbon steel surface by polarization measurements.

4. CONCLUSIONS

The main conclusions drawn from this study are:

- The aerial parts of *Origanum compactum* were extracted with the soxhlet apparatus using the following solvents: petroleum ether, hexane, chloroform and methanol.

- The aqueous and methanol 80 % extracts were very effective for antioxidant activity.

- The petroleum ether extract obtained by soxhlet extracts presented an important antifungal activity (83%) followed by methanol extract (45,9%). While hexane and chloroform extracts were less effective.

- This extract of plant inhibit the corrosion of carbon steel in 0.5 H_2SO_4 and the inhibiting effect of this latter increases with increase of inhibitor concentration.

- The inhibition is due to adsorption of the inhibitor molecules on the steel surface and blocking its active sites.

- Adsorption of the inhibitors fits a modified Langmuir isotherm model.

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