Application of a Formulation Based on Oil Extracted from the Seeds of Nigella Sativa L, Inhibition of Corrosion of Iron in 3% NaCl

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***Abstract*— this work focuses on the enhancement of black *Nigella Sativa L*, as natural substance. In this context, the study of fatty acid composition and physicochemical properties of the seed oil was performed and showed that it is an unsaturated oil, with carbonized long-chains (mainly oleic and linoleic acid).The use of black *Nigella,* which was limited in traditional medicine, is now highly sought because it could be used into the composition of various pharmaceuticals, cosmetics or other products [1]. In our study, to highlight another aspect of the use of black oil *Nigella,* we tested the effect of its formulation based on *Nigella Sativa L* (FBN) in the characteristics of iron samples in 3% NaCl medium [2]. The inhibiting effect of this formulation was studied by gravimetric measurements, stationary electrochemical and transitory methods complemented by surface analysis using Scanning Electron Microscopy (SEM) coupled with Energy Dispersive of X-ray (EDX). The inhibiting effect is more important when the concentration increases with the FBN formulation. For a concentration around 2000ppm, the inhibiting efficiency is in the order of 94% for the 3% NaCl/iron system. This result is very interesting because it highlights a corrosion inhibitor called "green", natural and biodegradable, unlike most of the corrosion inhibitors that are pollutants and often toxics.**

***Keywords*— *Nigella Sativa L, Formulation FBN, Inhibition of Corrosion, Iron, 3% NaCl Medium*.**

I. INTRODUCTION

The importance of our patrimonial heritage in the field of archaeological and historical metal objects is indisputable. Indeed, Morocco, a North African country, has one of the most leading and imposing collections of antique objects in the Mediterranean Basin. These vulnerable objects of historical and cultural interest require special protection both in storage conditions and in their exposition where the risk of corrosion is inevitable [3]. An extensive collection of metal objects is preserved in the archaeological museum of Rabat; unfortunately it faces corrosion problems caused essentially by humidity, pollution and the absence of vigilance to this scourge. Indeed, archaeological iron objects exhibited in museums have often undergone spontaneous degradation due to aggressive environment [4, 5]. The humidity, aggressive pollutants and the presence of chloride ions in the medium are damaging to the metal surface.

In the field of protection against corrosion, several pathways can be envisaged [6], because it is possible to act on the material itself and on its surface (use of surface coating as paint, varnishes and treatments using corrosion inhibitors). However, the restriction increasingly harsh of organic inhibitors linked to the toxicity incites the researchers to develop green environmentally and friendly inhibitors. Indeed, in the last years, research studies have been aimed at the development of effective products of plant molecules [7, 8]. It is in this context that appears our work as an aim to develop a formulation of corrosion inhibitor based on seed oil of *Nigella Sativa L.* to protect iron. At first, we are interested in the extraction of oil from seeds, the determination of physico-chemical characteristics and its fatty acid composition. Then we investigated the protective effect of the formulation based on oil. We tested the inhibitory effect of corrosion iron on FBN with a similar composition to the archaeological iron in a 3% NaCl solution.

This study was performed by gravimetric, stationary and transitory electrochemical measurements. In order to confirm our results, we used the surface SEM coupled with EDX elemental analysis.

II. MATERIALS AND METHODS

2.1. Methods for extracting the oil seed

The Soxhlet method is a conventional solid-liquid extraction [9-11]. The extraction of the glyceride fraction of the seeds was taken from the seeds dried at 50°C for 48 hours in the oven and the finely crushed. The extraction material is weighed and then put in the Soxhlet cartridge. The solvent is introduced into the flask and then heated to start the extraction. The extraction was stopped when the liquid surrounding the cartridge become clear and whose color indicates that the solvent extracts nothing more from the solid.

In this study, we have chosen cyclohexane as a solvent. After filtrating and evaporating the solvent using a rotary evaporator, the oil ready for the following steps is refrigerated at 4°C.

2.2. *Fatty acid content of the oil*

The dosage of methyl esters is carried out by gas chromatography after the trans-esterification of the oil [12]. The quantitative determination of fatty acids in the oil of *Nigella Sativa L* was accomplished using the chromatograph GC 3900 [13-15].

2.3. Determination of physico-chemical characteristics of the oil

Different physico-chemical indices of the oil were determined according to French Standards [16].

2.4. Electrochemical measurements

The corrosion inhibitor used in this work is a formulation based on the seed oil of *Nigella Sativa L*, noted in the following paper FBN. The choice of electrolyte in this study was based on the composition of the atmosphere of the museum of Rabat, which is an urban atmosphere polluted with chloride ions in view of its proximity to the sea, and the corrosive medium chosen is 3% NaCl solution (simulating the marine environment), which is highly aggressive.

The material used in this study is iron whose composition was determined by Energy Dispersive Spectroscopy (EDS) is reported in Table 1.

Table 1: Composition of iron (%)

Elements	Si	Mn	C	P	S	Fe
Weight (%)	0.201	0.514	0.157	0.007	0.009	≥99

2.4.1. Methods of direct measurements

2.4.1.1. Gravimetric measurements

This method consists of measuring the weight loss experienced by a sample of iron surface S when it is immersed for 24 hours in a 3% NaCl solution (Table 1).

For gravimetric study, we used a double cell wall equipped with a thermometer. The temperature is set at 25 ± 0.1°C with a thermostatically controlled circulating water bath mark Julabo. The samples were cut in a rectangular form with dimensions of (2x1x0.05) cm. The samples of iron were prepared by the polishing the decreasing particle size of up to 1200 with abrasive paper, before immersing them in the solutions. They are then rinsed with distilled water, degreased with acetone and dried in an oven. The coupons are weighed using electronic balance. After an immersion time of 24 hours, the samples are removed, rinsed with distilled water, washed with acetone, dried and then weighed.

2.4.1.2. ICP technique analysis

The Induction by Coupling Plasma (ICP) technique is based on the study of rays emitted by atoms where the ions in an excited state under the effect of a very high temperature. Transitions between energy states are subject to the rules of selection.

2.4.2. Methods of indirect measurements

All stationary electrochemical tests were performed using a Potentiostat- Galvanostat (PGZ VoltaLab 201) associated with the "Volta Master 4" software. The current-potential curves were obtained by potentiometric dynamic mode with a scan rate of 1 mV/s. This rate has allowed us to place in quasi-stationary conditions and to have a good reproducibility of the results [17].

The transitory electrochemical measurements (Nyquist diagrams) were performed using an apparatus EG&G Model 6310. These measurements were performed at 25°C after one hour of immersion in 3% NaCl solution. The amplitude of the sinusoidal voltage applied to the abandonment potential is 10mV peak to peak, with a frequency sweep from 100 KHz to 10 mHz.

The electrochemical measurements were obtained using a three-electrode montage: platinum grill as a counter-electrode, a reference electrode with saturated calomel (SCE) loaded with Luggin Capillary whose end is placed near the working electrode to minimize the influence of the ohmic fall, and working electrode of iron (Table1) in the form of a disc surface S =1cm^2. The latter is introduced into a sample holder of polytetrafluoroethylene (PTFE) disposed to face the auxiliary electrode.

The surface morphology of the electrode was performed by using SEM coupled with EDX elemental analysis.

III. RESULTS AND DISCUSSION

3.1. Extraction kinetic

Tracking results the average yield as a function of extraction time are summarized in Table 2.

Table 2: Average yield function of time extraction

Extraction time (hours)	4 h	6 h	8 h	10 h
% of average yield	30.5	37.5	40	41

According to the results of Table 2, the maximum percentage is 41%. It is obtained after 10 hours of extraction.

3.2. Chemical composition of seeds of *Nigella Sativa L.*

Because of their use in traditional medicine, the *Nigella Sativa L.* seeds have been subjects to many phytochemicals intensive studies in the aim of identifying its active principles. Since 1880, Greenish [18] published the first report about the presence of 37% oil and 4.1% ashes in seeds. These studies revealed that these seeds are rich in several constituents as primary or secondary metabolites, the content of which varies according to geographical, climatic conditions and research methods used [13-19].

3.3. Fatty acid composition of seeds *Nigella Sativa L.*

The results of fatty acid analysis are summarized in Table 3.

Table 3: Fatty acid composition of seeds *Nigella Sativa L.*

Fatty acid	[20]	The present study
Myristic $C_{14:0}$	0,5	--
Palmitic $C_{16:0}$	12,5	12,32
Palmitoleic $C_{16:1}$	--	--
Margaric $C_{17:0}$	--	1,20
Stearic $C_{18:0}$	3,4	3,35
Oleic $C_{18:1}$	23,4	22,70
Linoleic $C_{18:2}$	55,6	55,84
Linolenic $C_{18:3}$	0,4	0,59
Arachidic $C_{20:0}$	--	--
Eicosenoic $C_{20:1}$	--	--
Inecosanoic $C_{21:0}$	--	2,73
Behenic $C_{22:0}$	3,1	--

The gas chromatography shows that the seed oil of Moroccan *Nigella Sativa L.* is a rich fatty acids oil with long unsaturated chains (oleic and γ-linoleic acids). Also, the results presented in Table 3 show little difference between the analyzed sample and the one reported in the literature [20].

3.4. Physico-chemical characteristics of the seed oil of *Nigella Sativa L.*

The physico-chemical characteristics of this oil are: refractive index, density, the saponification, the unsaponifiable matter content and the acid value were determined according to the French Standard, respectively [21], the Table 4 gives the physico-chemical characteristics of the seed oil of *Nigella Sativa L.*

Table 4: Physico-chemical characteristics of the seed oil of *Nigella Sativa L*

Physico-chemical parameters	
Refractive index at 20 ° C	1,4697
Density at 20 ° C	0,895
Saponification index (mg of KOH/g)	196
Insaponifiable matter content in %	0,77
Acid index (mg of KOH/g)	6,89

3.5. Gravimetric measurements

We comparatively report the values of the corrosion rate and the inhibitory efficiencies by measuring weight loss and the method of analysis ICP in order to establish an analogy between the two methods.

3.5.1. Gravimetric study

The corrosion rate of iron is determined by weight loss, after 24 hours immersion in 3% NaCl medium, in the absence and presence of different concentrations of FBN. The inhibition efficiency (IE %) is determined by the following relationship:

$$IE\% = \frac{W_o - W_{inh}}{W_o} \times 100$$

Where W_0 and W_{inh} respectively represent the values of the rate of iron corrosion after immersion in the absence and presence of the FBN formulation. The values of corrosion rate (W) and the percentage of the inhibition efficiency (% IE) determined by the gravimetric method for different concentrations of FBN, as presented in Table 5.

Table 5: Inhibition efficiency and corrosion rate determined at various concentrations of formulation FBN

Concentration of FBN (ppm)	Corrosion rate (mg cm^{-2} j^{-1})	IE (%)
Blank	0.68	--
250	0,23	66
500	0,14	79
1000	0,06	91
2000	0,03	95

The Table 5 shows that the formulation FBN has excellent corrosion inhibiting properties of the tested iron in 3% NaCl medium. We note, the corrosion rate decreases while the efficiency of the protection of iron increases with the concentration of the inhibitor reaching a maximum value of 95% at 2000ppm of inhibitor.

Also we wish to clarify that 2000ppm formulation FBN is soluble in solution.

3.5.2. ICP technique Analysis

The ICP technique allowed us to dose the ferrous and ferric ions immersed in the solution during 24 hours in the absence and presence of FBN formulation at different concentrations. The results are summarized in Table 6.

Table 6: Determination of iron passed in solution by ICP technique and inhibition efficiency at different concentrations of FBN.

Concentration of FBN (ppm)	C_m (Fe) (ppm)	IE (%)
Blank	0,933	--
250	0,280	70
500	0,069	92
1000	0,063	93
2000	0,033	96

According to the Table 6, it can be seen that the inhibitor concentration increases as the concentration of dissolved iron in solution decreases. This can be explained by the substrate protection by a film formed by the formulation FBN.

The inhibition efficiency increases with the concentration to attain a maximum value of 96% to 2000ppm of FBN. This result is in agreement to that obtained by the gravimetric method. The evaluation of the inhibiting efficiency determined by the weight loss does not enable the approach of the mechanisms involved in corrosion. However, electrochemical techniques are a more effective method for the determination of instantaneous corrosion rates.

The electrochemical methods used in this study can be classified into two categories: stationary (plots of current-potential curves) and transitory methods such as electrochemical impedance measurement methods.

To confirm the results obtained through these measurements, we used the surface analysis SEM coupled with EDX.

3.6. Stationary electrochemical measurements

This method tends to impose a potential variation between the working electrode and the reference and to record the variation of the current intensity between the working electrode and the auxiliary electrode. Theses curves able us to estimate the instantaneous corrosion rate and to understand the film formation inhibitor. Indeed, the presence of a film formed can be characterized on the curves from the decreasing values of current densities over a wide range of over voltages applied. The polarization curves after 30 minutes of immersion with a scan rate of 1 mV/s are shown in Figure 1.

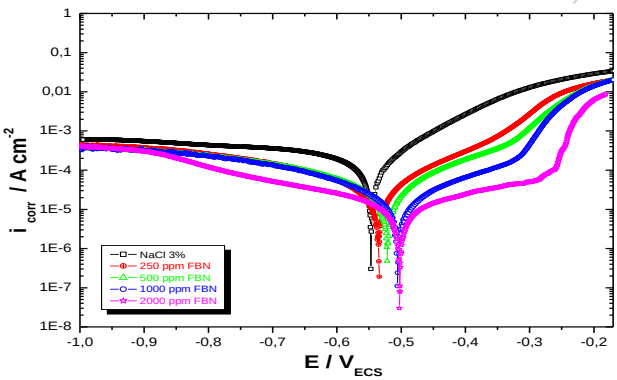

Figure 1: Polarization curves of iron in a 3% NaCl medium without and with the addition of different concentrations of FBN.

The analysis of this figure shows that, in the witness case, the cathodic current density increases with the voltage. This increase was fast and attained the current limit diffusion level.

The current plateau is attributed to the diffusion limit of the current dissolved oxygen [22]. The addition of the inhibitor to a corrosive medium changes the electrochemical behavior of iron in the medium. Also, we notice the appearance of a linearity range in the cathodic area, the current bearing is not affected by addition of the inhibitor, and the corrosion potential is shifted towards higher values. This displacement of E_{corr} is more pronounced at 2000ppm and attained a value of $-0.5V_{ECS}$. It is in the range of $-0.547V_{ECS}$ in absence of inhibitor. On the other hands, in the anodic area with the absence of FBN, the current density increases exponentially with the potential. This shows the dissolution of iron under control of pure load transfer kinetics. We also note that in this area, the addition of the inhibitor is accompanied by a decrease in density values of anodic currents higher than the concentration of FBN. The anodic action is more pronounced in the vicinity of the corrosion potential.

At high anodic voltages, the inhibitor does not appear to affect the characteristics of iron. There is also a brutal increase in current from $-0.3V_{ECS}$. This could be interpreted by three principal hypotheses:

-The oxidation manifested by degradation of the inhibiting film formed by maintaining the corrosion potential.

-The oxidation potential of the water is moved to a negative potential, which causes an evolution of oxygen contributing to the degradation of the inhibiting film.

- In $-0.3V_{ECS,}$ we reach the field of pitting iron which causes a degradation of the inhibiting film.

We notice that, in the anodic area, a passivity level is apparent. Indeed, at 2000ppm FBN, the passivity formed by the addition of inhibitor is kept at about - 0.430 V_{ECS}.

These results reveal the mixed character of the FBN inhibitor.

The values of the current density corrosion I_{corr}, the corrosion potential E_{corr}, the Tafel slopes of cathodic b_c and anodic b_a and the inhibiting efficiency (IE %) for different concentrations of FBN are shown in Table 7.

The inhibitory efficiency was calculated as follows:

$$EI\% = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \times 100$$

Where i_{0corr} and i_{corr} are the values of current density corrosion of iron determined after the immersion in 3% NaCl medium without and with addition of formulation respectively.

Table 7: Electrochemical parameters and inhibition efficiency of iron corrosion in 3% NaCl with and without addition of FBN.

Concentration of FBN (ppm)	E_{corr} (mVvs.ECS)	I_{corr} ($\mu A.cm^{-2}$)	$-b_c$ ($mV.dec^{-1}$)	b_a ($mV.dec^{-1}$)	IE (%)
Blank	-547	31,77	88	80	--
250	-534	19,06	85	96	40
500	-520	18,51	81	97	42
1000	-505	12,06	115	111	62
2000	-501	4,61	83	89	86

In the light of results presented in Table 7, we note that the inhibitory efficiency increases with the concentration of FBN and attain a maximum value of 86% at 2000ppm of formulation.

3.7. Electrochemical impedance spectroscopy

Electrochemical impedance measurements consist in studying the response of the electrochemical system, following a disturbance which is usually a low amplitude AC signal [23, 24]. The advantage of this technique in comparison with the previous one is to differentiate the reaction phenomena by their relaxation time. Only fast processes are characterized by high frequency, when the applied frequency decreases. The contributions the slower steps appear as transport phenomena or as diffusion solution [25].

In the case of inhibition corrosion studies, the electrochemical impedance spectroscopy allows to determine the mode of action of the product. It can act either by a simple adsorption on the substrate or through the formation of a three dimensional film interface [26].

3.7.1. Effect of the concentration of FBN

The Nyquist diagrams are performed in 3% NaCl aerated medium at 25°C in the presence and absence of the inhibitor after the immersion of one hour in an open circuit potential.

The shape of the Nyquist diagrams obtained is shown in Figure 2.

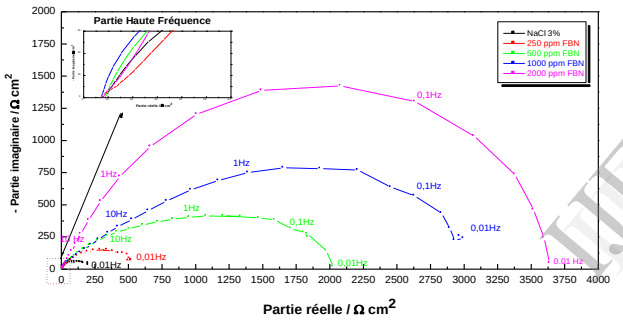

Figure 2: The Nyquist diagrams of iron in 3% NaCl solution in the absence and presence of different concentrations of FBN.

The impedance diagrams obtained are not centered on the real axis. This can be attributed to the frequency dispersion of the interfacial impedance [27,28]; usually due to surface heterogeneity which may result from its roughness, impurities, dislocations, adsorption of the inhibitor and the formation of porous layers of corrosion products [29,30]. In all concentrations used, we note the presence of a single capacitive loop corresponding to the charge transfer resistance. From these diagrams carried out by the abandonment potential, we managed to get access to the values of charge transfer resistance R_t, and of the capacity C and consequently of the inhibiting efficacy of FBN in the operating conditions.

The values of charge transfer resistance are calculated by the difference of impedance at high and low frequencies on the real axis, as suggested by Haruyama and Tsuru [31]. The capacity C is determined at the frequency for which the imaginary part of the impedance is maximum ($-Z^{max}_{imag}$) from the equation:

$$f(-Z^{max}_{imag}) = \frac{1}{2\pi C R_t}$$

The corrosion inhibiting efficiency of iron is calculated by the resistance of the charge transfer according to the relationship:

$$\mathbf{EI}(\%) = (1 - \frac{R_t}{R'_t}) \times 100$$

Where R_t and R'_t respectively represent the values of charge transfer resistance in the presence and absence of the inhibitor.

The related parameters to electrochemical impedance measurements of iron in 3% NaCl medium with and without FBN are shown in Table 8.

Table 8: Parameters and inhibition efficiency of the corrosion of iron in a 3% NaCl solution at different concentrations of the formulation FBN.

Concentration of FBN (ppm)	R_t ($\Omega.cm^2$)	f_{max} (Hz)	C ($\mu F.cm^{-2}$)	IE (%)
Blank	201,6	1,00	789,85	-
250	522,3	0,631	483,16	59
500	2023	0,398	197,77	89
1000	2996	0,251	177,40	92
2000	3638	0,398	109,97	94

Analyzing these results, we notice that the R_t values increase significantly with the increase the concentration of the inhibitor whereas the calculated capacity decreases to a value of 109.97µF.cm^{-2}. This value is greater than normally attributed to the double layer (20µF.cm^{-2}) [32].

The decrease of the capacity C is due to the adsorption of the inhibitor on the surface of iron which has the effect of reducing the active surface of the electrode.

The inhibiting efficiency increases with the concentration of the inhibitor to attain a maximum value of 94% at 2000 ppm of formulation. This result is in good agreement with those found by stationary electrochemical measurements and gravimetric measurements. To evaluate the resistance of the inhibiting film formed with the time of immersion, we studied the effect of the latter on the appearance of electrochemical impedance diagrams in the presence of the best concentration. These results accord with those obtained by the stationary measurements. To confirm these results we studied the effect of immersion time on electrochemical impedance diagrams in the presence of 2000ppm in the inhibitor.

3.7.2. Effect of immersion time

The evolution of electrochemical impedance diagrams in corrosion potential for a concentration of 2000ppm of FBN at the level of immersion time is shown in Figure 3.

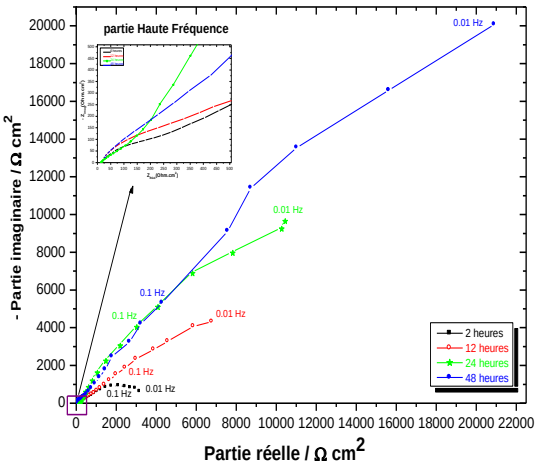

Figure 3: Effect of immersion time in a concentration of 2000ppm FBN determined on archaeological iron interface/3% NaCl.

The electrochemical impedance diagrams show a significant increase of the polarization resistance according to the immersion time. This increase appears to be linear at low frequencies. After 12 hours of immersion, we are shown that R_p tends to become infinite, reflecting the importance of the barrier of the inhibiting film and hence reducing the rates of the interface reactions.

3.8. Surface analysis

The results of the surface analysis by the SEM coupled with the EDX analysis of iron without and with 2000ppm of formulation in 3% NaCl solution after 24 hours of immersion are illustrated in Figure 4.

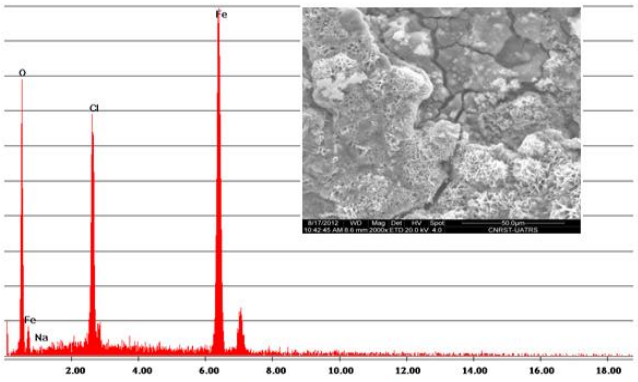

Figure (a): Without FBN (Blank)

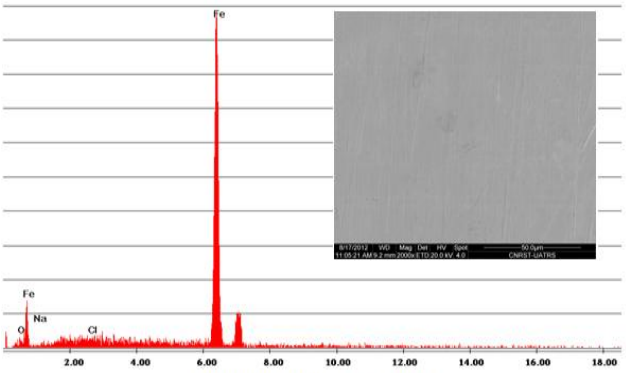

Figure (b): Addition 2000ppm of FBN

Figure 4: The SEM photos coupled with EDX analysis of a sample of iron in the absence (a) and in the presence 2000ppm (b) of FBN.

The analysis of these results shows that the surface of the two samples of iron studied in 3% NaCl solution in the absence and presence of the inhibitor shows a large difference between the state of the surface without and in the presence of formulation.

We note that a thick and totally fissured layer of corrosion products is clearly apparent in the case of the witness, whereas in the presence of the inhibitor, the surface is clean without any apparent corrosion.

The EDX spectra shows a high percentage of oxygen and the presence of chloride ions at the surface in the case of the witness; which promotes an accelerated corrosion on the whole metal surface.

In the presence of inhibitor, the surface is exempt of corrosion products, thus showing the inhibitory effect revealed by a low percentage of chlorine and oxygen, which characterizes the protective effect of the inhibitor in the presence of aggressive ions.

IV. CONCLUSION

We have shown that the formulation FBN is an appropriate inhibitor of iron corrosion in 3% NaCl medium. The gravimetric study shows that the corrosion rate decreases while the efficiency of the protection increases with the concentration of the inhibitor. The formulation FBN acts by reducing the current densities both in the cathodic and anodic area. This result highlighted the mixed character of the inhibitor used in the immediate vicinity of the corrosion potential. According to the study of the electrochemical impedance spectroscopy, the inhibitor acts by changing the kinetics of the corrosion process at the interface iron/3% NaCl. This is a promising and reliable system of protection in view of its efficiency, but also by its «ecological » property, which will certainly save at least the Moroccan if not the Mediterranean archeological heritage. Its inhibiting efficiency increases with the immersion time, providing a significant protection of the metal surface, by the formation of a film whose presence has been confirmed by surface analysis SEM / EDX.

The comparison of fatty acid seed oil of *Nigella Sativa L.* has shown that it contains many oleic and linoleic acids. The

evaluation of the physico-chemical properties of the oil showed that it is a long carbonized chain.

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