



RESEARCH ARTICLE

STABILITY STUDY OF NIGELLA SATIVA LAYER FORMED ON THE STEEL SURFACE IN NEUTRAL SOLUTION

^{*,1,2}Rania Souli, ¹Dhouibi Leila, ²Patrice Berçot, ²El Mustafa Rezrazi and ¹Ezzeddine Triki

¹U.R. Mécanique-Energétique, Equipe de Recherche COPROMET, ENIT, BP 37 1002 Belvédère, Tunis, Université de Tunis El-Manar, Tunisie

²Institut UTINAM, CNRS UMR 6213, 16 route de Gray 25030, Besançon CEDEX, Université de Franche-Comté, France

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ABSTRACT

The inhibition of corrosion of mild steel in an aerated 0.5 M NaCl solution was studied using electrochemical impedance spectroscopy in the presence of different amounts of extract of *Nigella Sativa* seeds. The previous work we proved that presence of this mixture in the solution decreases the corrosion current density. Long term immersion showed that lower amounts are more efficient than higher ones. And the inhibitor layer is more stable for smaller amount after 19 hours of immersion. The surface examination and analyses confirm that a layer is formed on the metal surface.

Key words:

Corrosion, EIS, *Nigella Sativa*, Mild steel, Inhibition.

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INTRODUCTION

Carbon steel is a constructional metal used in several industries. It presents excellent affordable mechanical proprieties. However, this industrial process is very corrosive, especially in aggressive aqueous solution. Therefore there is an urgent need for developing corrosion inhibitors. The Use of synthetic chemical compounds has proved to be highly efficient. Nevertheless, it presents a health and environmental hazard with high toxicity rates (Diamantino *et al.*, 2000). As a result, studies were conducted to extract safer molecules with protective ability against metal corrosion from natural products (Benmoussoud *et al.*, 2013). Researchers such as Barannik and Putilova (Barannik and Putilova, 1945) noticed that the inhibitor molecules in the plant extracts are usually alkaloids with other organic nitrogen bases as well as carbohydrates, proteins and their acid hydrolysis products, availability of lone pairs and π electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal, forming a coordinate

covalent bond. Extract of *tobacco*, *eggplant*, *coffee*... were used to protect efficiently the steel from corrosive attacks of the media (Akalezi *et al.*, 2012; Loto *et al.*, 2011; Ibrahim and Habbab, 2011). Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of *Hibiscus Subdariffa* has been evaluated (Ec Hosary *et al.*, 1972). An aqueous extract of *Curcuma Longa L.* powder has been used as a corrosion inhibitor for carbon steel (Izni Kairi and Kassim, 2013). *Nigella Sativa* seeds are used as treatment in several countries for many diseases (Tennekoon *et al.*, 1991; Topozada *et al.*, 1965; Turkdogan *et al.*, 2003; Wichtl and Anton, 2003). Along with *Thymiquinone*, the seeds contain vitamins, phenols and minerals (Jassir, 1992; Nergiz and Otles, 1993). *Nigella Sativa* seeds oil has been reported to inhibit nickel and steel corrosion in acidic and neutral media (Takruri and Dameh, 1998; Abdallah *et al.*, 2010; El Mounsi *et al.*, 2015; Ahamad *et al.*, 2010). However, to the best of our knowledge, there is no reported work on the inhibitive proprieties of the aqueous *Nigella* extract (NE) on the corrosion of carbon steel in NaCl solution. The aim of this paper is the study of the stability of the inhibitor layer from *Nigella Sativa* extract on carbon steel corrosion in 0.5 M NaCl solution after a long term immersion by electrochemical impedance spectroscopy and the aspect of the layer by different surface analysis.

*Corresponding author: ^{1,2}Rania Souli,

¹U.R. Mécanique-Energétique, Equipe de Recherche COPROMET, ENIT, BP 37 1002 Belvédère, Tunis, Université de Tunis El-Manar, Tunisie.

²Institut UTINAM, CNRS UMR 6213, 16 route de Gray 25030, Besançon CEDEX, Université de Franche-Comté, France.

Experimental

Materials preparation

The work electrode is made from mild steel (C (0.18%), Mn (0.59%), Si (0.16%), S (0.032%), P (0.012%), Cr (0.03%), Cu (0.253%), V(0.006%), Mo(0.004%), Fe (98.654%)). The substrate was embedded in an epoxy resin leaving a free surface area (0.28 cm²) to contact the solution. The specimen were polished successively using SiC papers of decreasing grit size (180-800), washed with distilled water and degreased with ethanol prior each experiment. The *Nigella* extract (NE) was prepared by infusing the dried seeds into boiling 0.5 M NaCl solution. The solution is, then, cooled in room temperature and filtrated to remove the non-soluble powder. The amount of the main solution was determined by evaporating 10 mL of the filtrate and weighing the deposit. Prior each experiment, the main extract was diluted with appropriate quantities of 0.5 M NaCl solution to obtain the required concentration of the extract. The solution with or without the different NE concentrations at any point of the electrochemical tests was unstirred.

Electrochemical study

Impedance spectroscopy was carried out after various periods of stabilization. The EIS experiments were performed on the specimen with a sine wave perturbation of 10 mV amplitude. The frequency interval was from 100 kHz to 10 mHz, data analysis was made by Zsimpwin software. All experiments were carried out at ambient temperature and in unstirred solution.

Surface analysis

In order to analyze the influence and nature of inhibitive molecules on the steel surface, Scanning Electron Microscopy (SEM) was carried out using a JEOL type 5600 associated to an energy dispersive spectroscopy (EDS) and was recorded after 19 h immersion in 0.5 M NaCl solution without and with NE. Also, the dried residue was scratched with a glass rode and the resultant powder was mixed with KBr and prepared as pellets for IR studies (KBr pellet method) and an IRRAS SPECTRA of the surface with and without NE were drawn. The IR study was performed by using a Bruker VERTEX 70/70v FT-IR spectrometer in the spectral region between 4000 and 500 cm⁻¹.

RESULTS AND DISCUSSION

Electrochemical impedance

As a first approach, electrochemical impedance spectroscopy was performed after 30 minutes immersion for different amounts of the extract. The Nyquist plots are given in Fig.1. As shown in Fig.1. the significant increase in the diameter of Nyquist semi-circles with the augmentation of NE concentrations suggest that the presence of the NE changed the corrosion kinetics on the electrode surface. The graphical calculation revealed that for the blank solution one time constant was identified and attributed to the charge transfer process. The Nyquist diagrams resume the reported corrosion behavior of mild steel in 0.5 M NaCl (fig.1.(a)). Its corrosion is initiated through two mechanisms: formation and build-up of an iron oxide layer and partial destruction of this layer by

pitting (20-21). As for the results recorded after the addition of the NE extract, the diagrams show two time constants. The time constant calculated at the high frequencies can be referred to inhibitor layer on the metal surface, and the second one was attributed to the charge transfer process. The fitting of this behavior is simulated by the electrical equivalent circuits shown in Fig.3a for the 0.5 M NaCl solution and Fig.3b after the addition of the NE. The deviation of the semicircles from perfect circular shape is often referred to the frequency dispersion of interfacial impedance. This behavior is usually attributed to the metal surface inhomogeneity and roughness (Souli *et al.*, 2015). In this case it is commonly accepted to replace the capacitive element by a constant phase element (CPE) in the equivalent circuit. The graphical methods presented by Orazem *et al.* were used to obtain CPE parameters α et Q (Orazem *et al.*, 2006; BenSalah *et al.*, 2014) and the log ($|Z_{img}|$) vs log (f) plots were drawn (Fig.2). The CPE exponent α is calculated from the log ($|Z_{img}|$) vs log (f) as the slope of the linear line from the following relation:

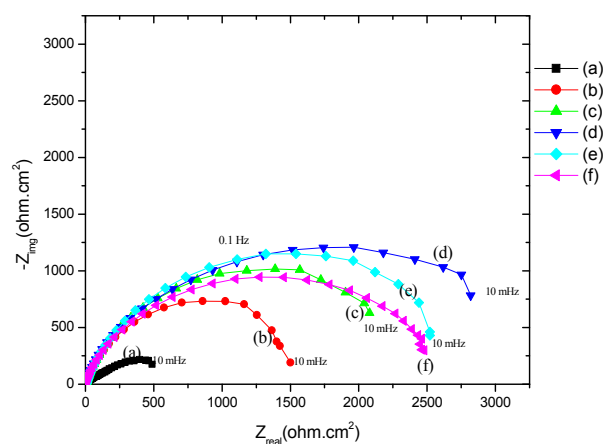


Fig.1. Impedance diagrams of the mild steel immersed in 0.5 M NaCl solution containing different NE concentrations; a: 0 g.L⁻¹, b: 0.07 g.L⁻¹, c: 0.35 g.L⁻¹, d: 0.7 g.L⁻¹, e: 1.4 g.L⁻¹, f: 2.1 g.L⁻¹

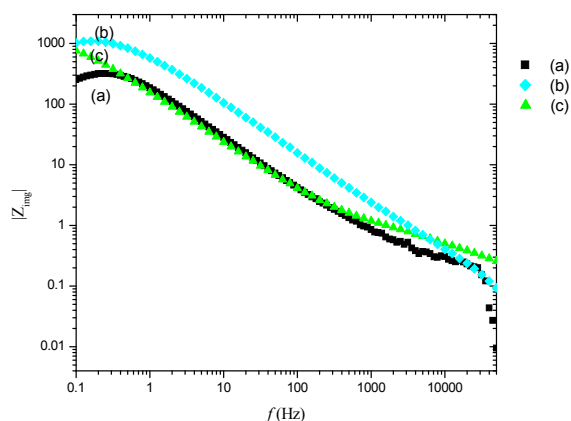


Fig.2. The log ($|Z_{img}|$) vs log (f) plots of the immersed steel in 0.5 M NaCl solution in absence and presence of different NE concentrations a: 0 g.L⁻¹, b: 0.07 g.L⁻¹, 0.35 g.L⁻¹, c: 0.7 g.L⁻¹, 1.4 g.L⁻¹, 2.1 g.L⁻¹

$$Z_{img} = \sin\left(\frac{\alpha\pi}{2}\right) \times \frac{-1}{(2\pi f)^{\alpha} Q_{eff}} \quad \dots\dots\dots (2)$$

Where Q_{eff} is the CPE coefficient, α the CPE exponent ($0 < \alpha < 1$), and f the frequency. If $\alpha = 1$, the CPE is considered to behave as an ideal double-layer capacitance (C_{dl}) (Behpour *et al.*, 2012). Hsu and Mansfield (25) have established a relation to calculate the ideal capacitance C_{dl} using the following equation:

$$C_{dl} = Q_{eff} (\omega_{max})^{\alpha-1} \dots\dots\dots(3)$$

where $\omega_{max} = 2\pi f_{max}$ and f_{max} is the highest frequency at the top of the depressed loop.

The inhibition efficiency τ (%) based on the charge transfer resistance is calculated by:

$$\tau\% = \left(1 - \frac{R_{ct}}{R_{ct(inhib)}}\right) \times 100 \dots\dots\dots(4)$$

Where R_{ct} et $R_{ct(inhib)}$ are the charge transfer resistance values in the absence and presence of the NE, respectively.

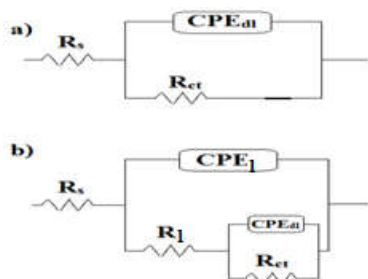


Fig. 3. Equivalent electrical circuits for mild steel in 0.5 M NaCl solution. containing different amounts of Nigella Sativa aqueous extract; a: 0 g.L⁻¹ and 0.07 g.L⁻¹. 0.35 g.L⁻¹. b: 0.7 g.L⁻¹, 1.4 g.L⁻¹, and 2.1 g.L⁻¹

As is seen from Table I the results suggest that:

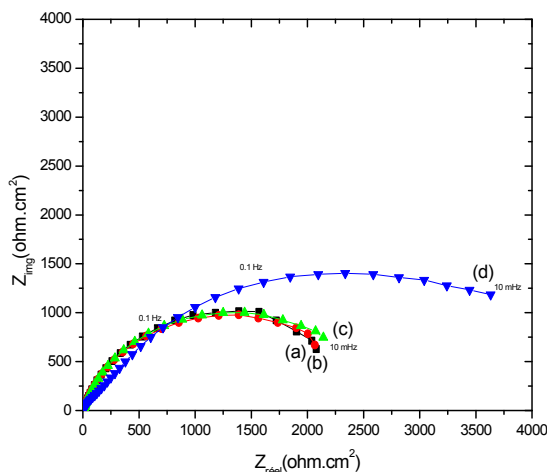
- The R_1 increases with the augmentation of NE concentration. This implies the increase of the inhibition efficiency. The evolution of R_1 and CPE_1 is due to the change of the layer density (Hsu and Mansfield, 2001).
- The C_{dl} values decrease with the increase of the NE concentration which confirmed that the inhibitor molecules are adsorbed on the active sites on the metal surface. The α_2 coefficient is higher than the one recorded in the blank solution revealing that the addition of NE homogenizes more the solution/layer/metal interface (Laamari *et al.*, 2010).
- The inhibition efficiency increases with the concentration to reach an optimum with 91 % at a 0.7g.L⁻¹ concentration.

In order to investigate the stability of the inhibitor layer, two groups of impedance diagrams were recorded with an amount of 0.07 and 2.1 g.L⁻¹ for a duration varying between 30 minutes and 19 hours. The Nyquist diagrams are reported in Fig. 4.

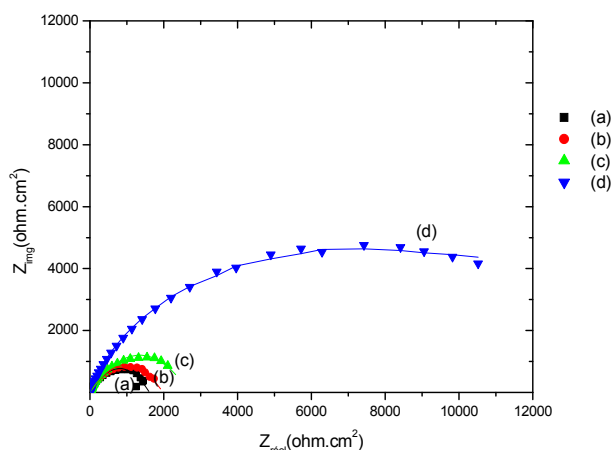
The graphic investigation of the figure shows that:

- For 0.07 g.L⁻¹. the extended immersion time enhance the protection of the metal much better than for 1.4 g.L⁻¹.

- For a duration inferior to 2 hours, the size of the semicircle increases progressively for 0.07 g.L⁻¹ and is fixed for 2.1 g.L⁻¹. This could indicate that for highest amount, the protective layer is stable. As for the lower amount the buildup of this layer is a continuous process.
- Past 2 hours. the protective layer is more efficient for smaller amounts than for the higher ones.



(A)



(B)

Fig.4. Impedance diagrams of the mild steel immersed in 0.5 M NaCl solution containing (A) 1.4 g.L⁻¹ and (B)0.07 g.L⁻¹ ; a: 30 min. b: 1h. c: 2 h. d: 19 h

EDS and SEM observation

A surface morphology examination of carbon steel electrodes kept at open-circuit in an aerated 0.5 M NaCl solution with and without the extract in an aerated 0.5 M NaCl solution with and without the extract was conducted using SEM after 19 h of immersion. The corresponding images are shown in Fig.5. It can be clearly seen that in the absence of the extract (Fig.5a) some pits become distinguishable. The EDS spectrum (Fig.6a) shows that the surface contains iron, oxygen, chloride and sodium atoms. The addition of the extract (Fig.5b) forms a uniform porous and dense layer covering the surface. This layer (Fig.6b) is composed of iron, oxygen, chloride, sodium, phosphates and carbons atoms. This suggests that the extracted molecules are incorporated into the oxide layer.

Table 1. EIS parameters obtained by fitting the EIS spectra shown in Fig.1.

	$R_s, \Omega.cm^2$	$CPE_{dl} \Omega^{-1}.cm^{-2}.s^{\alpha} \times 10^{-4}$	α_1	$R_1, \Omega.cm^2$	$(Q_{eff}) CPE_{dl} \Omega^{-1}.cm^{-2}.s^{\alpha} \times 10^{-4}$	$C_{dl}, \mu F.cm^{-2}$	α_2	$R_{ct}, \Omega.cm^2$	$\tau (%)$
0.5 M NaCl	4.5	-	-	-	17	2573	0.80	322	-
+0.07g.L ⁻¹	5.7	-	-	-	10	1189	0.85	1721	81
+0.35 g.L ⁻¹	1.8	-	-	-	5	637	0.85	2695	88
+0.7g.L ⁻¹	3.2	6.8	0.76	6.5	1.4	164	0.90	3550	91
+1.4 g.L ⁻¹	2.6	3.0	0.80	11.0	1.4	146	0.80	2738	88
+2.1 g.L ⁻¹	1.9	3.6	0.75	3.0	9.6	1927	0.8	2653	87

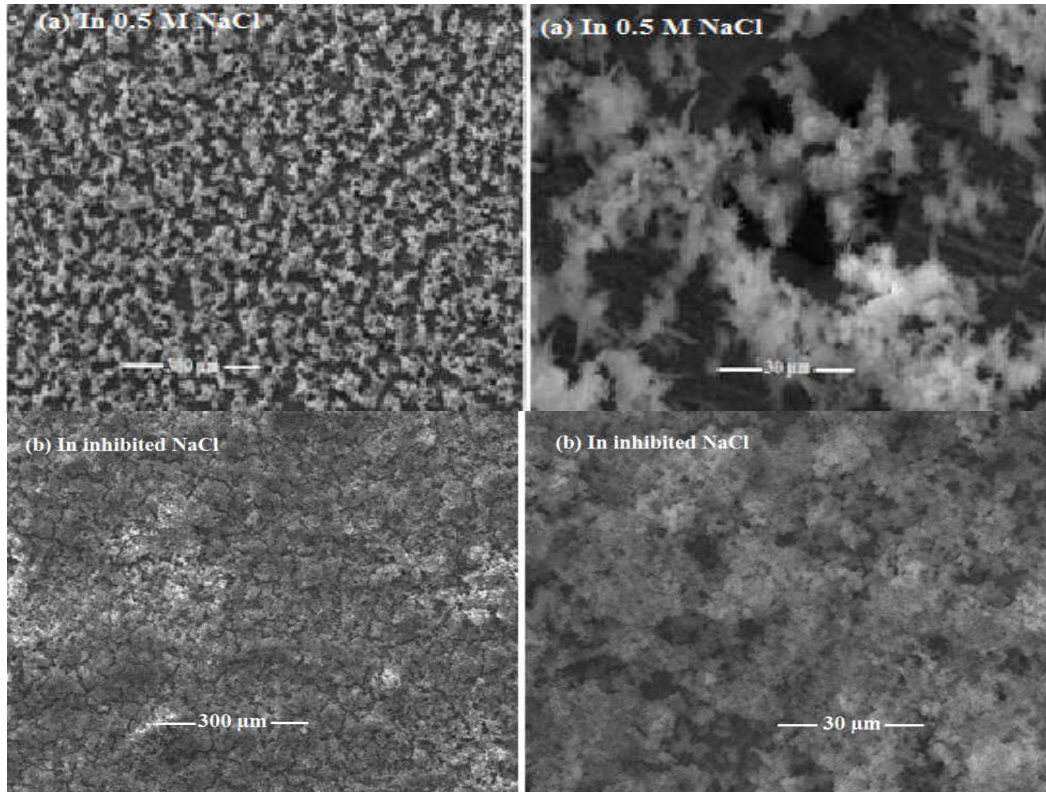


Fig.5. SEM observation of metal surface immersed into (a) the 0.5 M NaCl solution containing (b) inhibitor extract

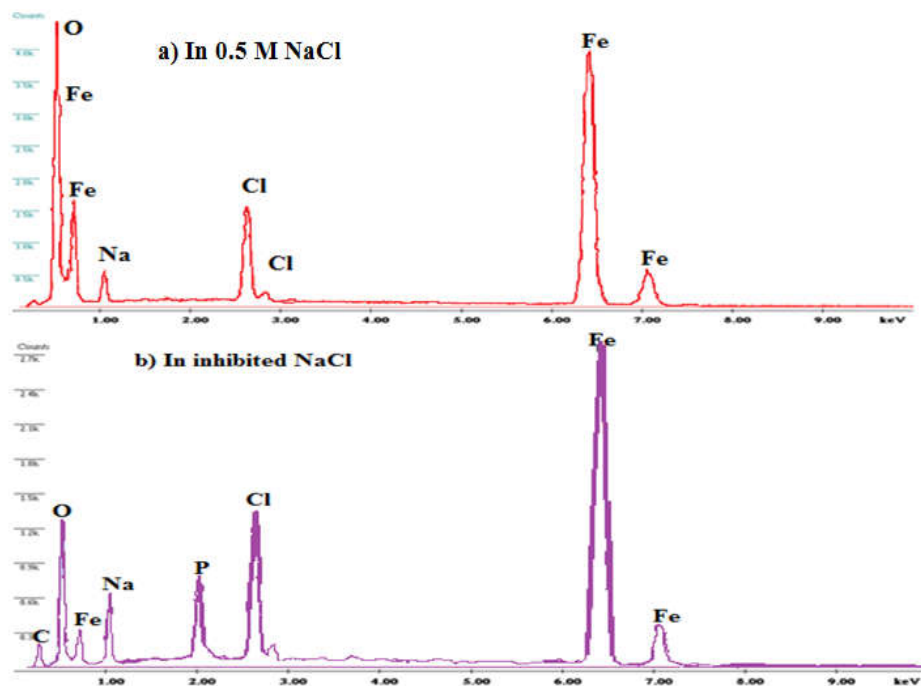


Fig. 6. EDS spectra of immersed steel in 0.5 M NaCl solution (a) without and (b) with the NE extract

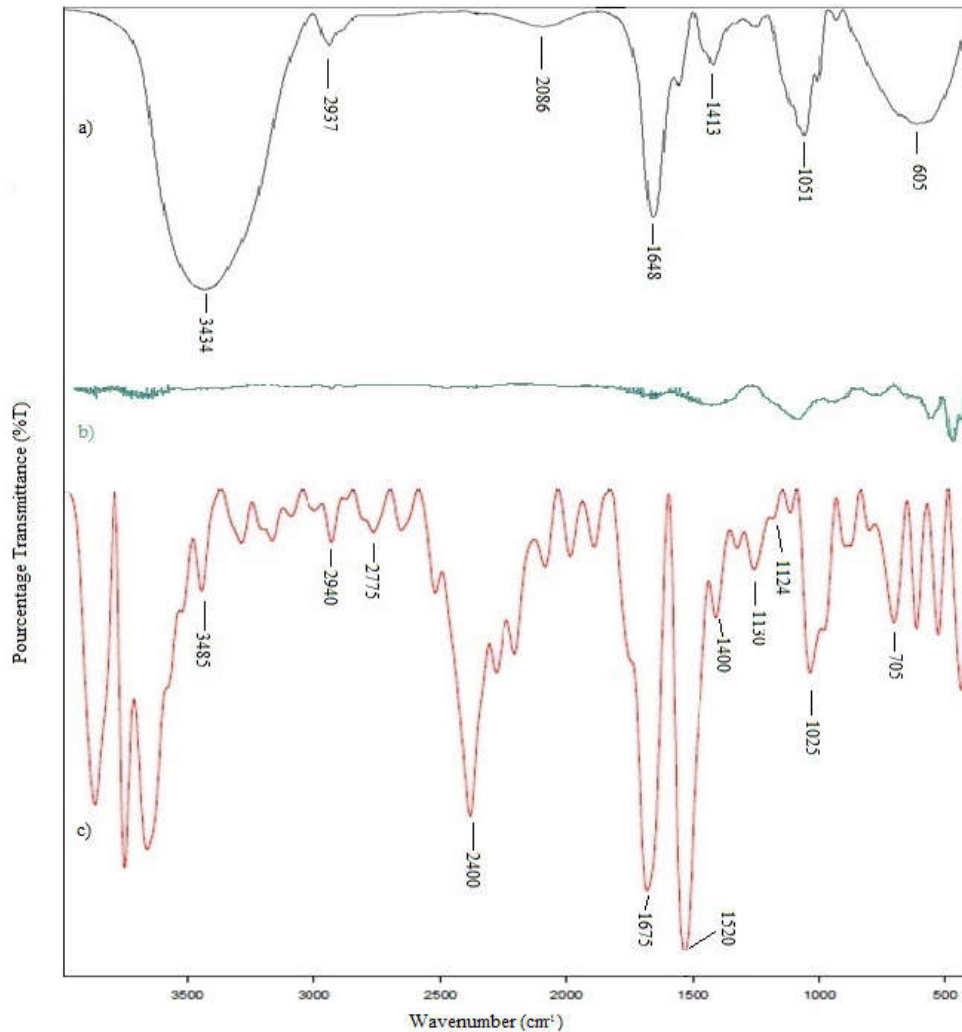


Fig.7. FT-IR spectrum of (a) *Nigella sativa* residue, (b) IRRAS spectrum of steel immersed in 3% NaCl and (c) containing NE

IR analysis

IR spectrum (KBr pellet method) of the *Nigella sativa* residue is displayed in Fig.7.a. The IR studies shows that the plant extract contains alcohols (O-H) or amides (N-H) (3434 cm^{-1}), alkynes (2086 cm^{-1} , and 605 cm^{-1}) and ketones (1648 cm^{-1}). The Fig.7.c shows the IRRAS spectrum of mild steel immersed in 0.5 M NaCl solution containing the NE. The bands at 3485 cm^{-1} and 2400 cm^{-1} can be attributed to the O-H and/ or N-H stretching vibration the peak appearing on 1675 cm^{-1} is attributed to the ketones. The band at 2940 cm^{-1} is due to the $\text{CH}_3\text{-Fe}$ asymmetric stretching. While the band at 2775 cm^{-1} can be attributed to the $\text{CH}_3\text{-Fe}$ symmetric stretching, bands appearing at 1400, 1130 and 705 cm^{-1} are attributed to asymmetric, symmetric $\text{CH}_3\text{-Fe}$ vibration and rocking vibration (Socrates, 2001). The bands between 1025 cm^{-1} and 1124 cm^{-1} are attributed to the of phosphor fixation on the metal surface (Houmane *et al.*, 1986). Comparison between FT-IR spectrum of dried residue Fig.7.a. steel surface immersed in NaCl, without Fig.7.b and with the NE Fig.7.c, shows that various chemical compounds are adsorbed on the metal surface assuring its protection.

Conclusion

The SEM and EDS results indicate the presence of a dense adsorptive layer over the mild steel surface composed of corrosive products and inhibitive molecules detected by IR.

The EIS study shows a quick adsorption of corrosive products and inhibitive molecules on the metal surface and a rise of inhibitive properties with the NE amounts. Long term immersion revealed that lower amount are more efficient than higher ones due to a more stable protective layer.

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