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PROOF

Nigella sativa: an alternative solution for the corrosion of mild steel in hydrochloric acid medium

R. Souli[1, 2, 3*], E. Triki[1], P. Berçot[2], M. Rezrazi[2], B. Jaouad[3], A. Derja[3], L. Dhouibi[1]
[1]*Equipe COPROMET, Unité de Recherche Mécanique-Energétique, ENIT, Université de Tunis El-Manar, Tunis1002, Tunisie.*
[2]*Institut UTINAM, CNRS UMR 6213, Université de Franche-Comté, 16 route de Gray, 25030 Besançon Cedex, France*
[3]*Laboratoire Physico-Chimie des Matériaux et Environnement, FSSM, Université Cady Ayyad, Maroc*

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[*]*Corresponding Author. E-mail: rania.souli@gmail.com; Tel (+21696734827)*

Abstract

The use of plants presents a new field to explore in order to prevent the pollution caused by the employment of synthetic chemical compounds especially in corrosion inhibition. In fact, efficient inhibitors available are toxic and harmful for both human and environment. As a result, studies were conducted to extract molecule with protective ability against the corrosion of metal. Extract of tobacco, mangoes, coffee... were used to protect efficiently the steel from corrosive attacks of the media. The object of this work is the study of the inhibitor power of seeds of Nigella sativa from the corrosion of mild steel in acidic media by different electrochemical technique. This research has revealed that the aqueous extract of Nigella sativa can be used as an inhibitor of the mild steel corrosion in acidic media. It offers a good protection and its efficiency increases with the concentration.

Keywords: Green inhibitor, Corrosion, Mild steel, Nigella sativa, EIS

1. Introduction

Corrosion is the deterioration of the metal while placed in an aggressive medium. Such as phenomena causes tremendous financial lost to the industrial sector. Thus, numerous ways to protect the metal are installed, and since few decades anew brunch of studies was directed to plants and natural products as safe environmental friendly and efficient inhibitors of corrosion. Corrosion inhibition of the extract of black paper [1], Chamomile, Halfabar [2], Azarticaindica [3] were studied as corrosion inhibitors in HCl and H_2SO_4 medium. Abdallah and al investigate the effect of Nigella on the acidic corrosion of Nickel and found that it provides a good protection against pitting corrosion [4]. Nigella sativa is considered by many traditional medicines as an efficient treatment for various diseases. Studies showed that the chemical composition of the seeds can be affected by different elements [5]. But, in general, the qualitative study of the Nigella sativa extract had shown an interesting percentage of vitamin B including: thiamine (B1), riboflavin (B2), pyridoxine (B6), niacin (B3) and folic acid (B9) and a good antioxidant power [6-8]. However, there are no records of the inhibition of the mild steel corrosion in HCl media by Nigella S. extract.

The objective of the present work is to study the inhibitive action of Nigella Sativa seeds extract using electrochemical techniques.

2. Materials and methods

2.1. Apparatus

The samples of 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%))were mounted into glass tubes of appropriate diameter by epoxy resin leaving a free surface area (0.28 cm^2) to contact the solution. The metallic electrodes were abraded successively with fine grade emery papers (400, 600, 800 and 1200 grit), then the metal surface was rinsed with distillated water degreased in absolute ethanol, dried prior to each use. The aggressive solution (0.5 M HCl) was prepared by the dilution of analytical chemical grade HCl (37%) solution in bi-distilled water.

The Nigella extract (NE) was obtained by infusing the grounded seeds in the HCl (0.5 M) solution. The solution was filtered and added to0.5M HCl solution to prepare the desired concentrations in a range from 0.05g/L to 0.5g/L.

2.2. Methods

The electrochemical measurements were conducted in a conventional three-electrode electrolytic cell, with the mild steel samples as working electrode, a platinum foil of 1 cm^2 as counter electrode, and a saturated calomel electrode as the reference one at room temperature in non stirred solution. The polarization curves were obtained while potential was scanned from -0.65 V to -0.35 V with the scan rate set at 1 mVs^{-1}.The impedance spectra were measured starting from open circuit potential in the frequency range from 100 kHz to 50 mHz with a sine wave perturbation of 10 mV amplitude.. The studies were carried out using radiometer VOLTALAB PGZ 201 potentiometer. The impedance plots were fitted with a compatible electronic equivalent circuit using Zsimpw in software.

All experiments were performed in duplicate, and where discrepancy was observed, additional experiments were performed.

3. Results and discussions

3.1. Open circuit potential measurements

Changes in the corrosion potential values (E_{corr}) with the addition of an inhibitor are often a useful indication of whether the cathodic or the anodic reaction is the most affected. Fig.1shows the variation of the open circuit potential (OCP) of mild steel with time in 0.5 M HCL without and with the addition of various concentrations of NE.

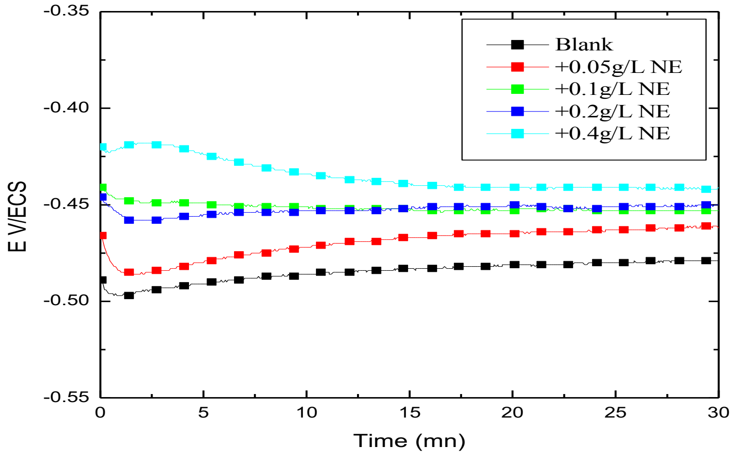

Figure 1: Evolution of the open circuit potential (OCP) vs. exposure time in 0.5 M HCl for mild steel in the absence and in the presence of NE.

For the three first concentrations (0.05g/L, 0.1 g/L and 0.2 g/L) and the blank, the OCP development is similar; it increases to more anodic values, then stabilizes. Although, for the fourth selected concentration (0.4g/L), the OCP increases for few seconds then decreases and finally stabilizes. As first approximation, this trend indicates that the addition of NE affects the corrosion rate within time as a result of the adsorption of NE molecules on the metallic surface [9].

3.2. Potentiodynamic polarization

The polarization measurement was made to evaluate the inhibition efficiency of the NE. The values of the electrochemical corrosion kinetic parameter, i.e. corrosion current densities (j_{corr}), corrosion potential (E_{corr}), the anodic and cathodic Tafel slopes (β_a, β_c) and corrosion rate (V_{corr}) as function of NE concentration were calculated from the Tafel extrapolation of the polarization curves of Fig.2and presented in table.1. Table 1 included also the inhibition efficiency (τ%). which is expressed by the following equation:

$$\tau\% = \frac{J_{corr} - J_{corr(i)}}{J_{corr}} \times 100 \qquad (1)$$

Where J_{corr} and $J_{corr(i)}$ are the corrosion current densities in the absence and the presence of inhibitor.

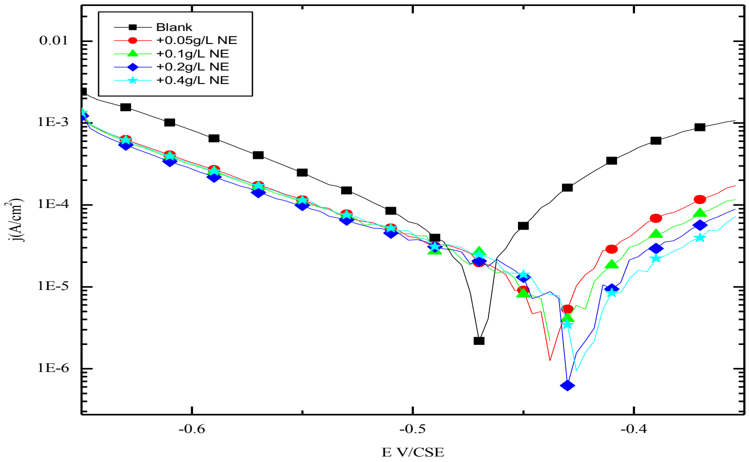

Figure 2: Polarization curves of the mild steel immersed in 0.5 M HCl in the absence and presence of different concentrations of the NE

Table 1: Kinetic Electrochemical parameters of mild steel

	E_{corr} mV/SCE	J_{corr} µA/cm^2	β_a mV/dec	β_c mV/dec	V_{corr} µm/Y	τ%
Blank	-483	147.4	65	-95	1724	
+0.05g/L	-451	45.3	68	-111	530	69.2
+0.1g/L	-446	42.5	77	-115	497	71.2
+0.2g/L	-438	35.6	73	-121	417	75.9
+0.4g/L	-433	38.2	78	-123	446	74.0

Experimental data indicates that the addition of NE reduces prominently anodic dissolution and retarded hydrogen evolution reaction, and resulted in significant decrease in corrosion current densities. As was shown in the OCP measurements, the presence of NE shift the corrosion potential (E_{corr}) to anodic region and hence, as reported in literature [10-12], if the displacement is **Δ**E<85 mV(maximum shift value recorded was 50mV) the inhibitor can be considered as a mixed-type inhibitor in 0.5 M HCl. The anodic Tafel slopes are slightly displaced, whereas the change in cathodic Tafel slopes are larger which means that NE molecules are adsorbed on both sites but under cathodic control affecting the mechanism of hydrogen evolution reaction due to a diffusion or barrier effect [13-14].The highest inhibition detected is obtained with a 0.2g/L concentration of the NE. However, the increase of the concentration does not improve the inhibition efficiency meaning that the NE had an optimum concentration.

3.3. Electrochemical impedance

EIS experiments have been employed to evaluate the adsorption and the performance of corrosion inhibitors. Fig. 3 shows the Nyquist and bode plot of mild steel immersed in 0.5M HCL in the absence and presence of different concentrations of the NE after 30 min immersion. In the presence and absence of the NE, the Nyquist diagrams display a capacitive loop. Although, in the presence of the inhibitor, the semi-circles are larger than in the blank case. These curves show that the corrosion process was mainly charge transfer controlled [15]. The depressed loop can be explained by the surface heterogeneity of structural or interfacial origin, such as found in adsorption process [16]. The equivalent circuit diagrams are given in Fig.3.

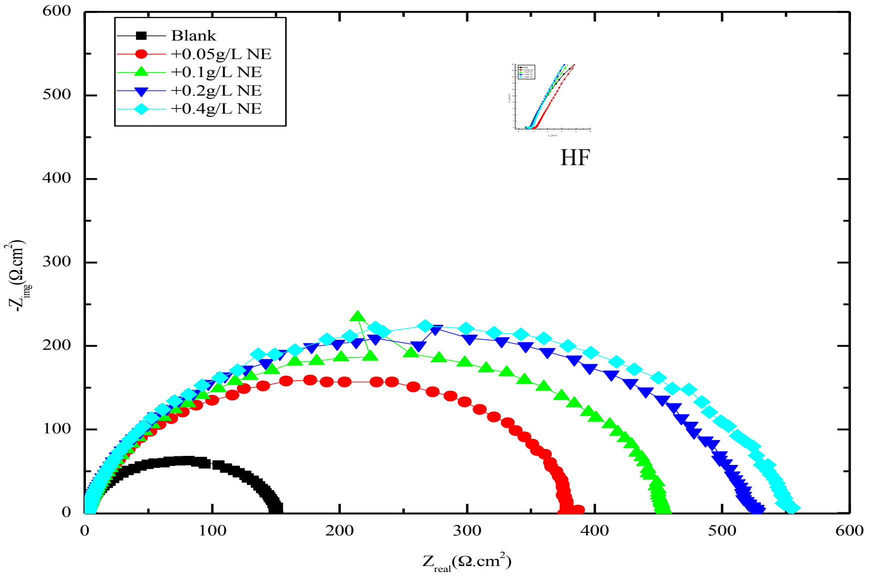

Figure 3: Nyquist plots of the immersed mild steel with and without NE in 0.5M HCl

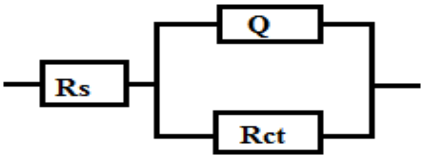

Figure 4: Equivalent circuit model

The electrical equivalent circuit includes the electrolyte resistance R_s, the charge transfer resistance R_{ct} and a constant phase element CPE (Q)in order to take into consideration the electrode surface heterogeneity resulting from surface roughness, dislocations, impurities, inhibitors adsorption and porous layer formation [17]. The impedance function of the CPE is as follows:

$$Z_{CPE}=\frac{1}{Q}\times\frac{1}{(j\omega)^n} \qquad (2)$$

Where Q is the CPE coefficient, n the CPE exponent ($0<n<1$), ω the angular frequency ($\omega=2\pi f$,f is the AC frequency) and $j= -1^{1/2}$. If n =1, the CPE is considered to behave as an ideal double-layer capacitance (C_{dl}) [15]. In our case (CPE in parallel with a resistance), Hsu and Mansfield [18] have established a relation to calculate the ideal capacitance C_{dl} using the following equation:

$$C_{dl} = Q\,(\omega_{\max})^{n-1} \qquad (3)$$

Where$\omega_{\max} = 2\pi f_{\max}$. $f_{\max}$ is the highest frequency at the top of the depressed loop. The impedance parameters (R_s, R_{ct}, Q, n, C_{dl}, and τ%) are gathered in table 4. The inhibition efficiency is calculated using the following relation:

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

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

Table 2: EIS parameter obtained by fitting the Nyquist plots shown in Fig 3. with the equivalent circuit shown in fig 4 for mild steel in 0.5M HCl solution in absence and presence of NE

	R_e Ω.cm²	Q µF/cm²	N	R_{tc}Ω.cm²	C_{dl} µF/cm²	τ%
Blank	1.63	268.1	0.8897	150.2	180.9	
+0.05g/L	2.37	151.5	0.8692	386.7	96.5	61.1
+0.1g/L	1.45	129.6	0.8654	460.1	85.2	67.3
+0.2g/L	15.8	117.3	0.8737	522.1	79.1	71.23
+0.4g/L	17.4	120	0.8774	547.5	81.9	72.56

The addition of the NE to the HCl medium increases the R_{ct} values. This augmentation is generally due to a slower corroding system [19].

The recorded parameters show clearly that the increase of the NE concentration decreases the C_{dl} values, and according to Helmholtz model this means that the thickness of the electrical double layers had increased or/and attributed to a decrease in local dielectric constant. However, as was indicated for the polarization results, the values reach an optimum point (for the 0.2g/L) then decreases (0.4g/L).

3.4. Adsorption isotherm

The adsorption of the organic molecules is the first phase of corrosion inhibition. This process depends on the molecule's chemical composition, the temperature and the electrochemical potential of the metal/solution interface. In order to get further information about the adsorption mode, the experimental data have been tested with different adsorption isotherm. In order to obtain the isotherm, a linear correlation between degree of surface coverage ($\boldsymbol{\theta}$) values and inhibitor concentration (C) must be found.

In this case, the best fit is obtained from the Langmuir isotherm [20-23]. The relation between and C is given by: $\frac{C}{\theta} = \frac{1}{K} + C$ (5)

Where K is the adsorption constant and the surface coverage$\theta = \frac{J_{corr}-J_{corr(i)}}{J_{corr}}$ obtained from the polarization curves data.

The choice of the best fit was made according to the correlation coefficient R^2, and since $R^2>0.99$, the adsorption obeys to the Langmuir isotherm. The relation between C/$\boldsymbol{\theta}$ and C is shown in Fig. 5. The plot is linear with a slope slightly higher than the unity (1.33); this could be explained by the occupation of the active sites. The adsorption constant K is related to $\boldsymbol{\Delta}G_{ads}$ by the following equation:

$$K = \frac{1}{C_{solvant}} \times exp\left(\frac{\Delta G_{ads}}{RT}\right) \qquad (6)$$

Where $c_{solvent}$ represents the molar concentration of the solvent, which is in the case of water is 55.5 M [24], R is the gas constant and Tis the absolute temperature. Since the molecular mass of the NE is unknown, the following results were given as an approximation. The high value of K (240.9) suggests a strong adsorption on the mild steel surface in 0.5 M HCl.

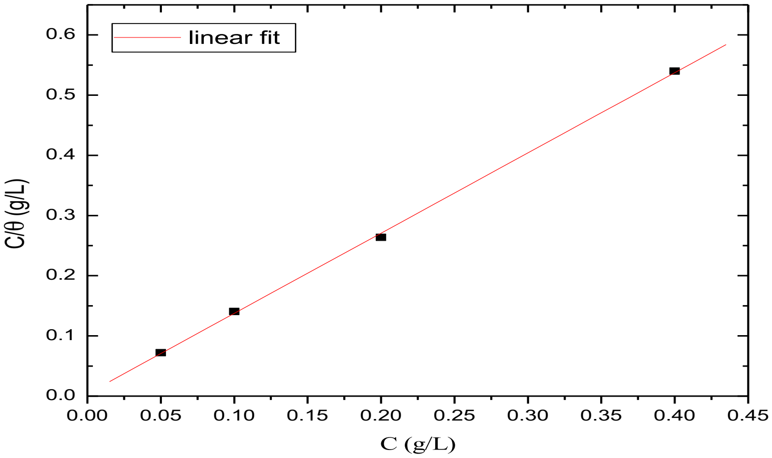

Figure 5: Langmuir's isotherm for adsorption of NE on the mild steel surface in 0.5 M HCl

The value and sign of K lead to a negative value of **Δ**G_{ads} are consisting with the spontaneity of the adsorption process and the stability of the adsorbed layer on the mild steel surface. Since we use an extract containing infinite components at various contents, we limit our study to the qualitative study; and we introduce that the inhibition of corrosion occurs by a synergistic effect of intermolecules of the natural extract [25-27].

3.5. Surface Analysis

Scanning electron micrographs (SEM) of mild steel surface immersed24 hours in 0.5M HCl and 0.5M HCl containing 0.2g/L plant extract are shown in fig 6. A rough surface was noticed for mild steel in the blank solution. In the case of the addition of the plant extract, a smooth surface was noticed. This shows that this inhibits corrosion of mild steel in 0.5 M HCl solution.

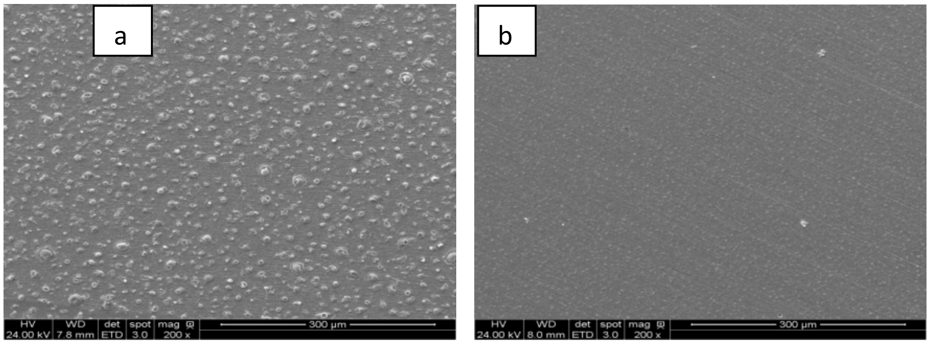

Figure 6: SEM graphs of mild steel immersed in 0.5 M HCl without (a) and with (b) the plant extract

Conclusion

The NE extract show good inhibition proprieties of the corrosion of mild steel in 0.5 M HCl. The inhibition efficiency increases with the NE concentration but reach an optimum point at a 0.2g/L. Tafel polarization data show that the NE acts as a mixed type inhibitor. Based on the EIS diagrams an electrical equivalent circuit was selected to fit the experimental data. The inhibition efficiencies obtained by polarization and EIS are in good agreement. The adsorption of the NE on the mild steel/0.5M HCl interface obeys the Langmuir adsorption isotherm model. The negative value of the **Δ**G_{ads} indicates that the adsorption is spontaneous and due to physic bound.

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