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Effect of aqueous extract of *Nigella sativa* seeds on the mild steel corrosion in chloride media

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Abstract: The inhibition of corrosion of mild steel in an aerated 0.5 M NaCl solution was studied by using potentiodynamic polarisation in the presence of different concentrations of extract of *Nigella Sativa* seeds. The presence of this mixture in the solution decreases the corrosion current density. *Nigella* extract presents an efficient inhibitor of corrosion. It acts as a mixed-type inhibitor and adsorbs on the metal surface according to the Langmuir isotherm model. The values of thermodynamic parameters suggest that the adsorption of inhibitor molecules on the metal surface is chemical.

Key words: Corrosion, *Nigella sativa*, mild steel, inhibition, NaCl

INTRODUCTION

Carbon steel is a constructional metal used in several industries. It presents excellent mechanical proprieties at a low cost. Some industrial process causes the metal corrosion, especially in aggressive aqueous solution. Thus, it becomes a common interest to develop corrosion inhibitors. In fact, many synthetic chemical compounds were used; they assure a high efficiency but with huge toxicity level for both human and environment [1]. Hence, studies were conducted to extract safer molecules with protective ability against the corrosion of metal from natural products [2]. Barannik and Putilova [3] noticed that the inhibitors molecules in the plant extracts are usually alkaloids and 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[4,6]. Corrosion inhibition of carbon steel in low chloride media by an aqueous extract of *Hibiscus Subdariffa* has been evaluated[7]. An aqueous extract of *Curcuma Longa L.* powder has been used as a corrosion inhibitor for carbon steel [8].

Nigella Sativa seeds are used as treatment in several country for many diseases [9-12]**.** Seeds contain vitamins, phenols and minerals. The major compound detected is thymoquinone[13-15]. *Nigella Sativa* seeds oil and aqueous solution has been reported to inhibit nickel and steel corrosion, respectively, in acidic media[15-16].

However, to the best of our knowledge, there is no reported work on the inhibitive proprieties of the *Nigella* aqueous extract (NE) on the corrosion of carbon steel in NaCl solution. The aim of this paper is to investigate the inhibiting behavior of *Nigella Sativa* extract on carbon steel corrosion in 0.5 M NaCl solution (the concentration of chloride in sea water). The first part of the results regroups the extract and surface characterization by Scanning Electron Microscopy, Infra-Red Spectroscopy and Atomic Absorbance Spectroscopy study. The second part is dedicated to the study of corrosion inhibition mechanism of the mild steel in

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Table I : Amount of metals contained in the plant extract by SAA

	Zn		**Cu**	
	Absorbance	**C (mg/L)**	**Absorbance**	**C (mg/L)**
70g/L	0.072	0.73	0.034	0.081
100g/L	0.105	1.14	0.038	0.092

0.5 M NaCl solution by the *Nigella Sativa* extract (NE), OCP, polarization, EIS and thermodynamic studies was conducted. Adsorption and temperature studies are also described to apprehend the inhibition mechanism.

EXPERIMENTAL

1. Materials preparation

The working 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 cm^2) to contact the solution. The specimens 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, filtrated to remove the non-soluble powder. 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. During the electrochemical tests, the solution was unstirred.

2. Electrochemical study

The potentiodynamic polarization was performed using a radiometer VOLTALAB PGZ 100 all-in-one potentiometer in a three-electrode conventional electrochemical cell, with a platinum auxiliary electrode and a saturated calomel electrode as a reference electrode. The sample was polarized from -0.9 V/SCE to -0.2V/SCE in the anodic direction at a rate of 1 mV/s after 30 minutes of stabilization at open circuit potential.

3. Extract analyze

To determine the amount of some metals in the plant extract, a flame atomic absorption spectroscopy was used via the ICE 3000 series AA thermo scientific spectrometer. The analyze was conducted under a 0.9 $mL.min^{-1}$ flow and acetylene-air flame.

RESULTS AND DISCUSSIONS

1. Atomic absorption spectrometry

Studies show that the *Nigella Sativa* seeds contains an interesting amount of metal [15]. The main solution was analyzed to detect copper and zinc in the extract with a concentration of 70g/L and 100 g/L. The results are gathered in the table I. The standard range was chosen from 0.2 mg/L to 2 mg/L.

The SAA analysis shows that the plant extract contained an amount of Zn and Cu. The presence of such element in the extract solution may influence the metal dissolution [20].

2. Electrochemical study

2.2. Polarization curves

Figure 2 illustrates the polarization curves of mild steel in 0.5 M NaCl solutions containing different concentration of NE extract at room temperature. The inhibition efficiency can be calculated by the following relation [23]:

$$\tau(\%) = 100 \times \left(1 - \frac{J_{cor\ inhib}}{J_{corr}}\right) \qquad (1)$$

Where J_{corr} and $J_{corr\ inhib}$ are the current densities, respectively, without and with the inhibitive extract determined by extrapolation of the Tafel lines to the corrosion potential.

A first analyze of the polarization curves of the mild steel shows that the presence of the extract shifts the corrosion potential E_{corr} to further anodic values. Nevertheless, as the amount of the introduced extract into the corrosive solution increases the E_{corr} approaches the potential recorded in the 0.5 M NaCl. This shift may be due to the synergetic action between organic compound and metal (zinc, copper) contained into the plant extract [24-25]. The presence of the extract affects

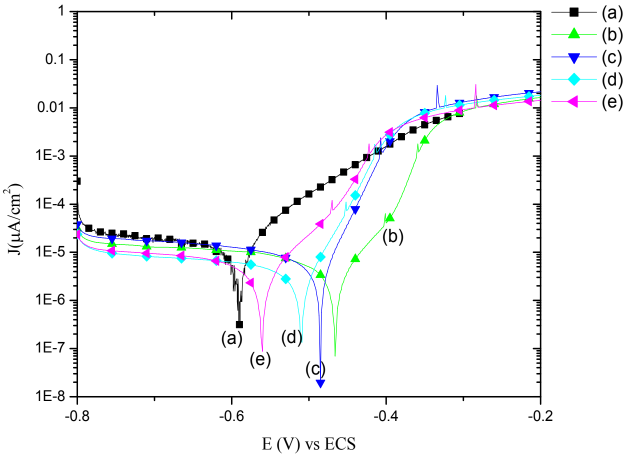

Figure 2: Polarization curves for mild steel in 0.5 M NaCl containing different concentrations of the plant extract at 303 K, a: 0 g.L^{-1}, b: 0,35 g.L^{-1}, c: 0,7 g.L^{-1}, d: 1,4 g.L^{-1}, e: 2,1 g.L^{-1}

the anodic branches leading to a remarkable decrease in the corrosion rate. The parameters derived from the polarization curves in Figure 2 are given in table II. The inhibition efficiency τ increases with increasing the NE extract concentration. The Tafel slopes β_a decrease obviously upon addition of NE extract, which may mean that inhibitive molecules are adsorbed at both anodic and cathodic sites. Since the change of E_{corr} are less than 85 mV, the NE extract acts as a mixed type inhibitor for the corrosion of mild steel in 0.5 M NaCl solution [6].

As reported in literature, corrosion inhibitors adsorption blocks the active sites and modifies the activation energy of the corrosion process [26-27]. The shifting of E_{corr} is the way to distinguished which effect is more important. In this case, the NE extract acts like a mixed type inhibitor and shifts the E_{corr}, so the energy effect is more important than the geometric blocking effect.

3. Adsorption isotherm

In general, inhibitors can function either by physical (electrostatic) adsorption or chemisorption with the metal. To obtain more information about the interaction between the inhibitor molecules and the metal surface, different adsorption isotherms were tested. The degree of surface coverage, *θ*, at different concentrations of the plant extract in chloride solutions was determined from the corresponding electrochemical polarization measurements according to the equation:

$$\theta = \frac{J_{corr} - J_{corr\ inhib}}{J_{corr}} \qquad (5)$$

The Langmuir isotherm, Eq. (6), which is based on the assumption that all adsorption sites are equivalent and that molecule binding occurs independently from nearby sites being occupied or not, was verified [28]:

$$KC = \frac{\theta}{1-\theta} \qquad (6)$$

Where C is the concentration of inhibitor, *θ* is the fractional surface coverage and K is the adsorption equilibrium constant related to the free energy of adsorption ΔG_{ads} as [26]:

$$K = \frac{1}{C_{solvent}} \times \exp\frac{-\Delta G_{ads}}{RT} \qquad (7)$$

Where $C_{solvent}$ represents the molar concentration of the solvent, which is in the case of water is 55.5 mol/L. But, since our concentration is expressed in g/L the $C_{solvant}$ will be equal to 1000g/L [38], R is the gas constant and T is the thermodynamic temperature. The Langmuir isotherm [29-32], Eq. (6), can be rearranged to obtain the following expression:

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad (8)$$

Table II: Electrochemical parameters for mild steel in 0.5 M NaCl containing different plant extract concentrations

Media	**E_{corr} mV vsECS**	**j_{corr} μA/cm^2**	**β_a mV dec^{-1}**	**τ (%)**
0,5 M NaCl	-591	52	83	-
+0,35 g/L	-470	9.3	54.9	82
+0,7 g/L	-490	4.6	30	91
+1,4 g/L	-515	6.1	36.3	89
+2,1 g/L	-565	8.7	59.5	85

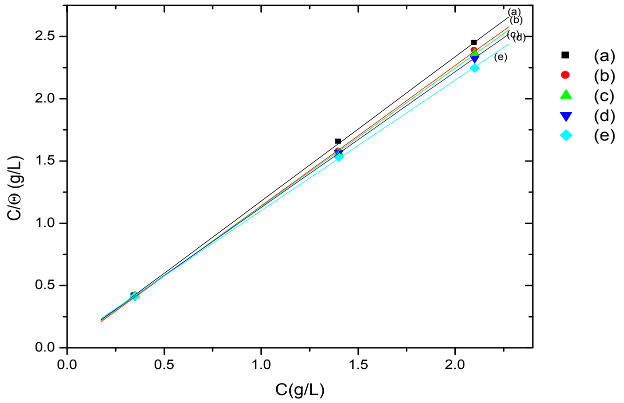

Figure 3: Langmuir adsorption isotherm for the mild steel in 0.5 M NaCl with various amount of plant extract at a: 283 K , b: 293 K , c: 303 K , d: 313 K, e: 323K

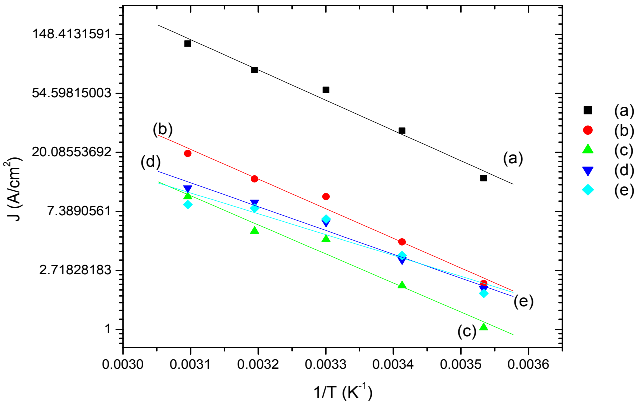

Figure 4: Arrhenius Law for mild steel in 0.5 M NaCl without and with NE
a: 0 g.L^{-1}, b: 0,35 g.L^{-1}, c: 0,7 g.L^{-1}, d: 1,4 g.L^{-1}, e: 2,1 g.L^{-1}

To get a fitting a linear-relationship should be obtained on plotting C/θ as a function of C, with a slope of unity. In Figure 3, the proposed relation is plotted for the adsorption of inhibitor molecules on mild steel and the free energy of adsorption and the adsorption constant are calculated.

The lines' slopes are slightly lower than 1 (~0.94). This deviation can be explained by the multilayer inhibitor formation on the surface of the steel [21, 33,34].

Even thought, the concentration considered is in g/L and not mol/L, the ΔG_{ads} values are significant and representative of the system "metal surface/inhibitor molecules". The negative value of ΔG_{ads} (-60 kJ/mol) confirm the spontaneous adsorption of the molecule on the metallic surfaces. However, since that value is superior to 20 kJ/mol in absolute value, the adsorption mechanism is chemical [35].

4. Activation energy calculations

The variation of the corrosion courant density of the steel immersed in 0.5 M NaCl solution in presence and absence of NE was plotted against temperature (10°C, 20°C, 30°C, 40°C and 50°C) for calculation of activation energy (Figure 4). The activation energy E_a was calculated from the relation [36]:

$$\ln J_{corr} = \ln A - \frac{E_a}{RT} \qquad (9)$$

In our case, as the concentration rises the activation energy decreases $E_{a\ inhib(2.1)} < E_{a\ inhib(1.4)} < E_{a\ inhib(0.7)} < E_{a\ inhib(0.35)} < E_a$ (table III). This result shows that the inhibition efficiency increases with the temperature. The bands between inhibitor molecules and metallic surface are stronger at higher temperature. This results confirm that the adsorption has a chemical nature [37].

CONCLUSION

The NE extract act as an efficient mixed inhibitor for the corrosion of mild steel in 0.5 M NaCl solution. It affects the energy activation of the corrosion/inhibition process.

The adsorption of the NE on the mild steel surface obeys the Langmuir adsorption isotherm and is a spontaneous process.

The calculation of the energy of activation and the adsorption free enthalpy confirms that the adsorption is chemical. The organic molecules form a strong bound with the metallic surface.

Table III: Activation energy for the system NE/ NaCl/Metal

	0.5 M NaCl	**0.5 M NaCl + 0.35 g/L NE**	**0.5 M NaCl +0.7 g/L NE**	**0.5 M NaCl +1.4g/L NE**	**0.5 M NaCl +2.1g/L NE**
Ea kJ.mol^{-1}	42.7	41.7	40.9	33.5	29.3

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