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Der Pharma Chemica, 2015, 7(10):350-356
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

Hexane extract of *Nigella sativa* L as eco-friendly corrosion inhibitor for steel in 1 M HCl medium

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ABSTRACT

*This work is devoted to examine the effectiveness of the hexane extract of Nigella Sativa L **(SH NS)** on corrosion of mild steel in 1 M HCl solution using the weight loss measurement at various concentration effects. Polarization curves and electrochemical impedance spectroscopy (EIS) methods were employed to evaluate corrosion rate and inhibition efficiency. The inhibition efficiency was found to increase with inhibitors content to attain 98% (at 0.5g/L). Data obtained from EIS studies were analyzed to determinate the model inhibition process through appropriate equivalent circuit model. Inhibition efficiency E (%) obtained from the various methods is in good agreement. The associated activation energy has been determined. The adsorption of natural products on the steel surface was found obey to Langmuir's adsorption isotherm.*

Key words: Mild steel, Nigella Sativa L, Hexane Extract, HCl, Corrosion, Green inhibitor

INTRODUCTION

Mild steel is an important material which finds wide applications in industry due to its excellent mechanical properties and low cost. It is extensively used in various industries as construction material for chemical reactors, heat exchanger and boiler systems, storage tanks, and oil and gas transport pipelines. It is also used in chemical and allied industries in handling acids, alkalis and salt solutions. Corrosion inhibitors synthetic chemicals are widely used to protect metals against corrosion, but most of them are not environment friendly due to their toxicity levels, bioaccumulation, and/or biodegradability [1]. Hence, the research of new corrosion inhibitors non-toxic, ecofriendly, natural, at low environmental impact are desired [2]. Plant extract is a rich source of naturally synthesized chemical compounds, readily available at low cost and eco-friendly, and can be obtained through simple extraction process with low cost as well as biodegradable [3]. The advantages of using plant extracts for steel corrosion control under acidic media are that the inhibitor is readily soluble and becomes their corresponding acid salt which leads to both economic and environmental benefits.

The encouraging results obtained by naturally oils and extracts as corrosion inhibitors of steel in acid solutions permit to test more extracts and oils [4]. The purpose of this paper is to evaluate as corrosion inhibitor Hexane extract of Nigella Sativa L for mild steel in 1M HCl solution by gravimetric method and electrochemical techniques such as potentiodynamic polarisation, linear polarisation and impedance spectroscopy (EIS). The adsorption and inhibition efficiency of these inhibitors were investigated and the thermodynamic parameters in absence and presence of these inhibitors were calculated.

MATERIALS AND METHODS

2.1. Materials and solutions

Coupons were cut into 1.5× 1.5 × 0.05 cm3 dimensions having composition (0.09%P, 0.01 % Al, 0.38 % Si, 0.05 % Mn, 0.21 % C, 0.05 % S and Fe balance) used for weight loss measurements. Prior to all measurements, the exposed area was mechanically abraded with 180, 400, 800, 1000, 1200 grades of emery papers. The specimens are washed thoroughly with bidistilled water degreased and dried with ethanol. The aggressive solutions of 1.0 M HCl were prepared by dilution of an analytical grade 37% HCl with double distilled water. The concentration range of inhibitor employed (**SH NS)** was 0.5 - 5 (g/L).

2.2. Preparing sample of Hexane extract of Nigella Sativa L (SH NS):

Nigella sativa L. seeds samples were purchased from a local market at Oujda (Morocco). Harvesting of Nigella sativa seeds was performed in Saudi Arabia in the month of October 2010 which is characterized by its warm, dry climate in this season. After collection, the seeds are stored in the dark at room temperature until use.

The seeds of Nigella sativa previously cleaned and crushed (m_{seeds} = 50 g). The Soxhlet extraction is started at first with hexane, then the hexane was evaporated in rota evaporator (extract **SH NS**).

RESULTS AND DISCUSSION

Mild steel corrosion behavior in 1 M HCl was investigated in the absence and presence of hexane extract of Nigella Sativa L **(SH NS)** with the help of weight loss and electrochemical techniques. It was seen that mild steel dissolution rate was very high in 1 M HCl alone but presence of inhibitor significantly decreased the corrosion rate of mild steel.

3.1 Weight Loss Measurements

The weight loss data made primarily at 6 hours of immersion at room temperature (308 K) were given in Table 1, where the inhibition efficiency was calculated using the following equation (1):

$$\text{Ew}\ \% = \frac{V0-V}{V0}\ \text{X}\ 10 \qquad \mathbf{(1)}$$

where V_0 and V are the values of corrosion rate without and with inhibitor, respectively.

It is clear that with the rise in hexane extract of Nigella Sativa L **(SH NS)** concentration, corrosion rate decreased and then the inhibition efficiency increased. The highest inhibiting efficiency attained 98% at 0.5g/L.

Table 1. ***Corrosion rate and inhibition efficiency in the absence and presence of (SH NS) in 1.0 M HCl solution at 308K***

Inhibitors	Concentration (g/l)	V (mg.cm^{-2} h^{-1})	Ew (%)
1M HCl	-	0.82	---
Hexane extract of Nigella Sativa L **(SH NS)**	0,5	0.011	98.66
	1	0.003	99.63
	2	0.002	99.76
	3	0.001	**99.88**
	5	0	**100.00**

Those data reveal that the rate of mild steel corrosion is greatly reduced upon the addition of the Hexane extract of Nigella Sativa L (SH NS) and decreases with the inhibitor concentration due to the fact that the adsorption coverage increases, which shields the steel surface efficiently from the acid solution. In acidic media, the corrosion rate decreases sharply with an increase in Hexane extract of Nigella Sativa L (SH NS) samples concentrations. From weight loss measurement, we can conclude that SH NS is the excellent inhibitor.

3.2. Polarisation results

The electrochemical study was carried out using a potentiostat PGZ100 piloted by Voltamaster soft-ware. This potentiostat is connected to a cell with three electrode thermostats with double wall. A saturated calomel electrode (SCE) and platinum electrode were used as reference and auxiliary electrodes, respectively. Anodic and cathodic potentiodynamic polarization curves were plotted at a polarization scan rate of 0.5mV/s. Before all experiments, the potential was stabilized at free potential during 30 min. The polarisation curves are obtained from −800 mV to −200 mV at 308 K. The solution test is there after de-aerated by bubbling nitrogen. Inhibition efficiency (Ep%) is defined as Equation 2, where $i_{corr(0)}$ and $i_{corr(inh)}$ represent corrosion current density values without and with inhibitor, respectively.

$$Ep\% = \frac{\mathrm{icor(0)-icor(inh)}}{\mathrm{icor(0)}} \text{ x } 100 \quad \mathbf{(2)}$$

Anodic and cathodic polarization curves for mild steel in 1.0 M HCl with and without various concentrations of used inhibitor are shown in Figures 4.

Various corrosion parameters such as corrosion potential (Ecorr), corrosion current density (I_{corr}) and the inhibition efficiency (E%) were determined by Tafel extrapolation method [5] and are given in Table 2.

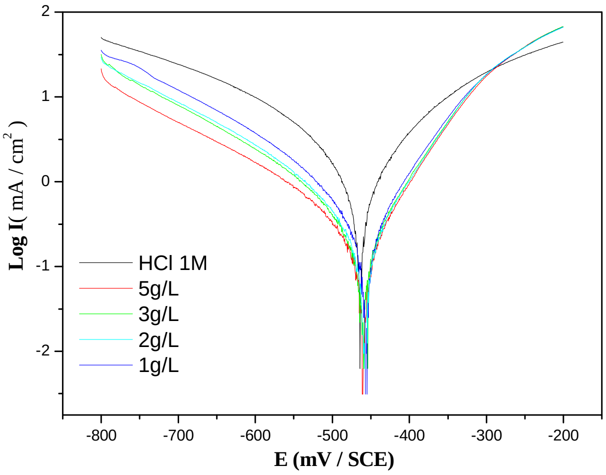

Figure 4. Tafel plot of mild steel with different concentrations of (SH NS) in 1M HCl solution

The analyse of the data in Table 2 revealed that the corrosion current density (i_{corr}) decreases considerably with increasing Hexane extract of Nigella Sativa L (SH NS) concentration, while no definite trend was observed in the shift of E_{corr} values. The cathodic Tafel slope (βc) show slight changes with the addition of Hexane extract of Nigella Sativa L (SH NS), which suggests that the inhibiting action occurred by simple blocking of the available cathodic sites on the metal surface, which lead to a decrease in the exposed area necessary for hydrogen evolution and lowered the dissolution rate with increasing Hexane extract of Nigella Sativa L

(SH NS) concentration. The dependence of E(%) versus the inhibitor concentration of Hexane extract of Nigella Sativa L (SH NS) is also presented in Table 2. The obtained efficiencies indicate that (SH NS) acts as effective inhibitor. Indeed, the values of E (%) increase with inhibitor concentration, reaching its maximum value, 97%, at 5g/L.

Table 2. ***Polarization parameters and corresponding inhibition efficiency for the corrosion of the mild steel in 1M HCl without and with addition of various concentrations of*** **(SH NS)** ***at 308K***

Inhibitor	**Concentration** (g/L)	**-E_{corr}** (mV/ECS)	**I_{corr}** (µA/cm^2)	**-$β_c$** (mV/dec)	**E_P** (%)
1M HCl	-	**454**	**1205**	**184**	**--**
Hexane extract of Nigella Sativa L **(SH NS)**	0,5	**455**	**279**	**128**	**77**
	1	**461**	**230**	**128**	**81**
	2	**463**	**182**	**135**	**85**
	3	**460**	**97**	**152**	**92**
	5	**477**	**29**	**148**	**97**

3.3. Electrochemical impedance spectroscopy (EIS)

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system, which included a digital potentiostat model Voltalab PGZ100 computer at Ecorr after immersion in solution without bubbling. After the determination of steady-state current at a corrosion potential, sine wave voltage (10 mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 0.5 hour of exposure at 308 K. The impedance diagrams are given in the Nyquist representation. Inhibition efficiency (E_{Rt}%) is estimated using the equation 4, where $R_t(0)$ and Rt(inh) are the charge transfer resistance values in the absence and presence of inhibitor, respectively:

$$ER\% = \frac{\mathrm{Rt(inh)} - \mathrm{Rt(0)}}{\mathrm{Rt(inh)}} \mathrm{x}\, 100 \qquad \textbf{(3)}$$

Electrochemical impedance spectroscopy (EIS) is commonly used technique in corrosion researches to explain the mechanisms and adsorption phenomena [6, 7]. Especially, in inhibition studies, a single semi-circular shape is observed for mild steel in acidic media. As in previous studies [8, 9], the parallel results were detected in EIS data. The EIS results and equivalent circuit were presented in Figs. 5 and 6, respectively**.**

It is the diameter of Nyquist plot shows the difference in real impedance at lower and higher frequencies. The CPE is the constant phase element which is used in place of double layer capacitance (C_{dl}) to give non-ideal capacitive behavior [10]. In Fig. 5, Nyquist plots for mild steel in 1 M HCl solution with, and without different concentrations of the Hexane extract of Nigella Sativa L (SH NS) were seen. The Nyquist plots were detected as one part of a semicircle.

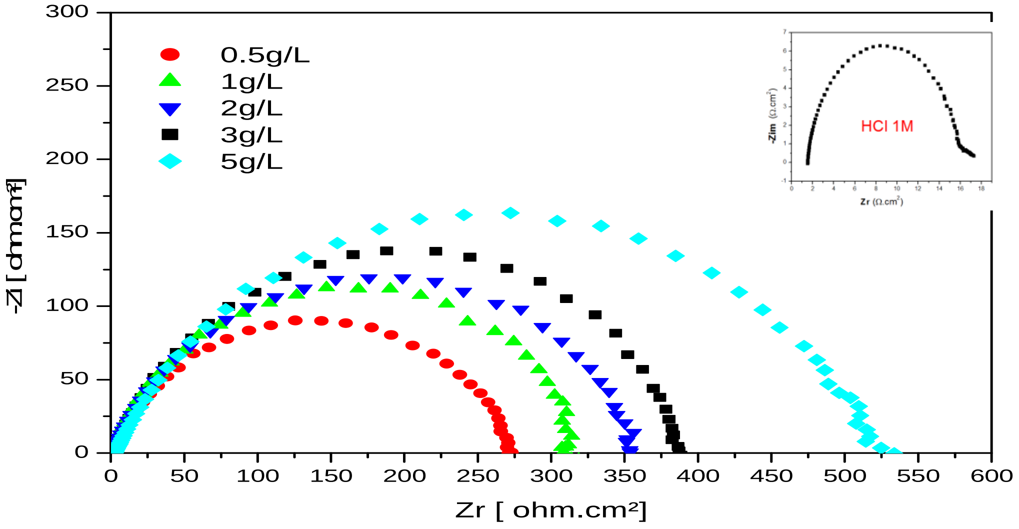

Figure 5: Nyquist plot at different concentrations of Hexane extract of Nigella Sativa L (SH NS) in 1M HCl solution

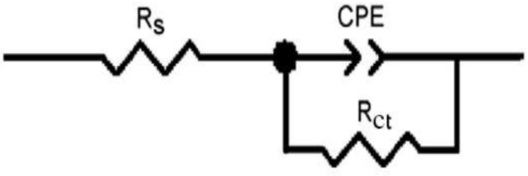

Figure 6: Electrical equivalent circuit model used for the modeling metal/solution

In this equivalent circuit, RS is the solution resistance, Rct is the charge transfer resistance and CPE is a constant phase element. The impedance function of the CPE is as follows:

$$Z_{CPE} = Y^{-1} (j\omega)^{-n} \qquad (4)$$

Where Y is the magnitude of CPE, ω is the angular frequency ($2\pi f_{max}$), and the deviation parameter n is a valuable criterion of the nature of the metal surface and reflects microscopic fluctuations of the surface. For n = 0, Z_{CPE} represents a resistance with $R = Y^{-1}$; n = -1 an inductance with $L = Y^{-1}$, n = 1 an ideal capacitor with C = Y [11].

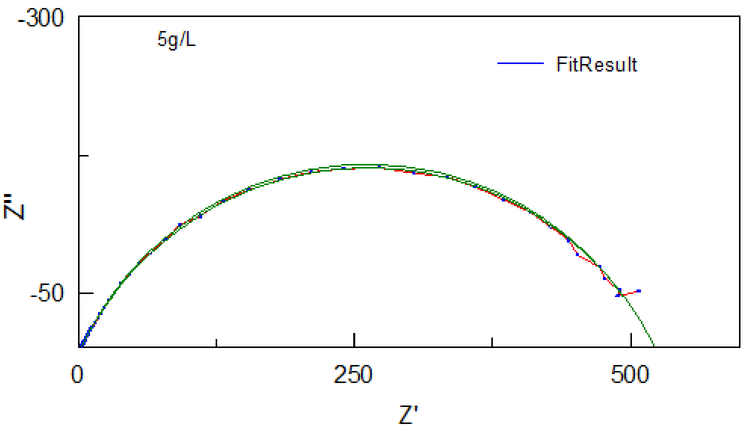

Figure 7a: EIS Nyquist plot for mild steel /1M HCl+1g/L Nigella Sativa L interface: -----experimental data -----calculated

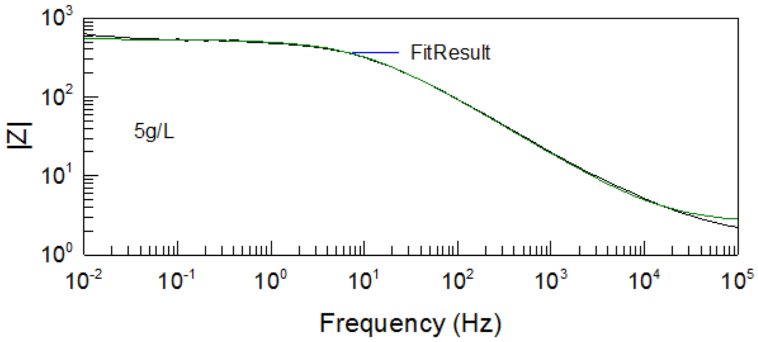

Figure 7b: EIS Bode plot for mild steel /1M HCl+1g/L Nigella Sativa L interface: -----experimental data -------calculated

The measured and simulated data fit very well. It is observed that the fitted data follow almost the same pattern as the original results along the whole diagrams, with an average error about 1% in all cases.

A quick examination of the electrochemical and EIS parameters indicates that the values of the corrosion potential, anodic and cathodic Tafel slopes vary slightly in the presence of Nigella Sativa L concentration. These results suggest that the action of molecules of Nigella Sativa L act by pure geometric blocking of the electrode surface. Results obtained show that R_t increases and C_{dl} tends to decrease when the concentration of inhibitor increases. A decrease in the Cdl values, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the Hexane extract of Nigella Sativa L (SH NS) function by adsorption at the metal solution/interface [12, 13].

Table 3. Impedance parameter values for the corrosion of mild steel in 1M HCl

Inhibitor	**Concentration (M)**	**R_t (Ω cm^2)**	**C (µf/cm^2)**	**E_{Rt} (%)**
1M HCl	-	**14.57**	**200**	--
Hexane extract of Nigella Sativa L **(SH NS)**	0,5	270	83.8	94.60
	1	310	47.1	95.30
	2	350	40.94	95.84
	3	379	36.31	96.16
	5	557	28.55	**97.38**

3.4. Adsorption isotherm

Additional information about the properties of the tested compounds may be provided from the kind of adsorption isotherm. Several adsorption isotherms were tested and the Langmuir adsorption isotherm was found to provide best description of the adsorption behaviour of the investigated inhibitor. The Langmuir isotherm is given by the equation (5) [14]:

$$C/\theta = 1/K_{ads} + C \qquad \textbf{(5)}$$

$$\Theta = E/100 \qquad \textbf{(6)}$$

The degree of surface coverage of each inhibitor at a given concentration can be calculated using the above equation (6). The strong correlation (R^2=0.99) of the Langmuir adsorption isotherm for Hexane extract of Nigella Sativa L **(SH NS)** was observed. Fig.7. depicts the graph of the Langmuir adsorption isotherm for the studied compound.

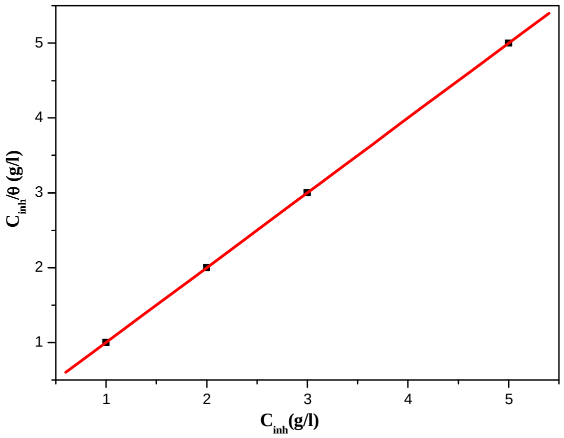

Figure 7: Experimental results at 308 K according to the Langmuir adsorption isotherm for Hexane extract of Nigella Sativa L (SH NS) at calculated by gravimetric method

Plotting of C vs. C/θ results in a linear correlation, shown in Fig. 7. The standard free energy of adsorption ($\Delta G°_{ads}$) was estimated by the following equation:

$$K = \frac{1}{55.5}\exp\left(\frac{\Delta G^0 ads}{RT}\right) \qquad (7)$$

Where 55.5 is the molar concentration of water in the solution expressed in molarity units (M) [15].

As shown in Table 4, the negative $\Delta G°_{ads}$ value (-39.57) obtained indicates that the adsorption process of SH NS to the surface is spontaneous and the interaction of the adsorbed layer with the steel surface is stable [16]. Meanwhile, it could be deduced that inhibitor **SH NS** adopts both electrostatic-adsorption and chemisorptions on the mild steel surface in 1 M HCl with the latter being privileged [17, 18].

Table 4. The calculated value of K_{ads} and $\Delta G°_{ads}$ for mild steel in 1 M HCl containing SH NS at 308K

Inhibitor	R^2	Slope	K (M^{-1})	$\Delta G°_{ads}$($Kj.mol^{-1}$)
SH NS	0.999	1.01	94.39 10^3	-39.57

3.5. Explanation for inhibitions

The steel surface charges positive in acid solution so it is difficult for these protonated compounds to approach the positively charged steel surface due to the electrostatic repulsion. Nigella Sativa L sample extract is composed of numerous naturally occurring organic compounds containing many O and N atoms in functional groups (O–H, C=O, C–O, N–H) and O-heterocyclic rings, and they act as reaction centers leading to the formation of film on the surface of the alloy. These compounds could be protonated in the acid solution; accordingly, the inhibitive action could be attributed to the adsorption of its components on the steel surface [19]. The corrosion inhibition property of plant extract is normally due to the presence in their composition of complex organic species such as tannins, alkaloids and nitrogen bases, carbohydrates, amino acids, and proteins as well as hydrolysis products. These organic compounds contain polar functions with N, S, and O atoms as well as conjugated double bonds or aromatic rings in their molecular structures, which are the major adsorption centers [20]. Also, the anticorrosion activity is attributed to the presence of heterocyclic constituents such as alkaloids, flavonoids, tannins, cellulose, and others which form an adsorbed film on the metal surface [21].

CONCLUSION

The following results can be drawn from this study:

✓Hexane extract of Nigella Sativa L **(SH NS)** successfully retarded mild steel corrosion in HCl solutions, and the efficiency of inhibition increases with increased inhibitor concentration.

- ✓ Tafel polarization curves advocated that **SH NS** restricted mild steel corrosion via reducing mild steel dissolution, which the impedance study suggested was occurred through molecular adsorption of organic moieties of the extracts on steel surface.
- ✓ Thus, it is clear from the study that Hexane extract of Nigella Sativa L **(SH NS)** can be used as an effective solution of steel corrosion in acid media.

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