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Corrosion Inhibition of API 5L Carbon Steel by Nettle Leaves Hydroalcoholic Extract in a 0.5 M H_2SO_4 Solution

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Abstract

In this work, electrochemical methods such as Tafel polarization and electrochemical impedance spectroscopy (EIS) were used to study the inhibition efficiency of Nettle leaves hydroalcoholic extract as a green corrosion inhibitor of API 5L carbon steel in 0.5 M H_2SO_4 solution. The results showed that the inhibition efficiency was increased with increasing the concentration of the extract and the maximum inhibition efficiency in the concentration of 6 g/L was 96%. The negative sign ΔG^0_{ads} absorption of inhibitor on the steel surface was spontaneous and the value ΔG^0_{ads} represented the physical absorption of the inhibitor which followed the Langmuir isotherm.

Keyword: API 5L carbon steel; Nettle extract; EIS; Langmuir isotherm.

1. Introduction

Despite the various methods of preventing corrosion, one of the most effective methods of protecting metals in acidic media is the use of corrosion inhibitors [1)]. Most of the used inhibitors are organic compounds whose inhibition efficiency depends their absorption ability on the metal surface [2–4)]. Due to the toxicity of these synthetic compounds, the use of them is limited due to environmental regulations and recent research has been focused on the use of natural products such as plant extracts. These affordable natural products can be characterized as green corrosion inhibitors. Generally, the use of natural products as corrosion inhibitors can be traced back to the 1930s, when plant extracts of Celandine and for the first time, other plants were used in sulfuric acid pickling baths. Inhibitors in this group are those that are eco-friendly and can be obtained from natural products such as plant extracts [5)].

The effect of Chenopodium Ambrosioides extract on the corrosion behavior of steel was studied in sulfuric acid solution. The results showed that inhibition efficiency depended on the concentration of the inhibitor and maximum of the inhibition efficiency was 94% in the concentration of 4 g/L [6)]. The effect of watermelon rind extract on mild steel corrosion was studied in acidic environments HCL and H_2SO_4. The results showed that watermelon rind extract acted as a mixed inhibitor and followed rind adsorption isotherm [7)]. By using electrochemical methods, Siparuna Guianensis extract inhibiting effect on the corrosion behavior of the carbon steel in the acidic solution was evaluated. The results showed that the inhibition efficiency was increased with adding the concentration of extract and absorption of the extract followed the Langmuir isotherm [8)]. By using weight loss method and Quantum chemical, the inhibitory effect of Nicotiana Tabacum leaves extract for the mild steel was studied in sulfuric acid solution. The experimental results of the weight loss method showed that with increasing the concentration of inhibitor, surface coverage and inhibition efficiency were increased. Quantum chemical calculations confirmed the experimental results too [9)].

Given these positive results, we decided to study Nettle leaves hydroalcoholic extract as a green corrosion inhibitor in a solution of 0.5 M H_2SO_4. Some advantages of this compound as corrosion inhibitor are the free solvent, inexpensiveness, availability, nontoxiity and easy production. It is noteworthy that the water extract of Nettle has been studied in a solution of HCl [10, 11)].

Nettle (Urtica dioica L.) is a plant of the Urticaceae family, which is commercially used for medicinal purposes. Nettle extract is effective in the treatment of diseases like eczema, rheumatism and allergic rhinitis. Nettle root is used in the treatment of diseases such as benign prostatic hyperplasia. A wide range of metabolites and Nettle species having flavonoids and phenylpropanoids components can be seen in Fig. 1 [12)].

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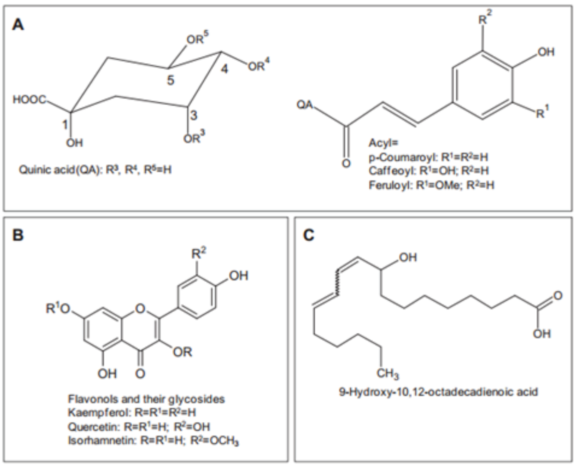

Fig. 1. Major classes of natural products; (A) phenolic acids, (B) flavonoids and (C) fatty acids.

The aim of this study was to investigate the inhibitory effect of Nettle leaves hydroalcoholic extract as green corrosion inhibitor for API 5L carbon steel in a 0.5 M H_2SO_4 solution using different electrochemical methods.

2. Material and Methods

2.1. Preparation of Nettle extract

Nettle leaves hydroalcoholic extract was prepared by the maceration method. To do this process, the cut plant was put in a glass jar and some water-ethanol (4:1 v/v) mixture was poured on it. In order to avoid chemical interactions of radiation with plant material, extraction was done in a place protected from direct sunlight and fastening the lid of the jar of extraction prevented the evaporation of the solvent.

The process of extraction was continued by repeated shaking and mixing for 5 days at a temperature of 25 °C. Then the resulting extract filter and the remainder of plant were put under pressure with press machine. Finally, the extracts were combined and to settle the resulting sediments, they were held for 5 days at a temperature of less than 15 °C; then they were carefully filtered through the filter paper to prevent the evaporation of the solvent.

2.2. Electrochemical measurements

API 5L Carbon steel samples with an area of 0.4 cm^2 were used as the working electrode. Their chemical composition is displayed in Table 1. Before performing any test, specimens were polished with sandpaper to the grit 2000 and then washed with distilled water and dried in warm air. Electrochemical tests were done in a three-electrode cell with glazed glass. Saturated calomel electrode was used as counter electrode and platinum electrode was employed as the reference electrode in the given cell. Before each test, 100 ml of 0.5 M H_2SO_4 solution was poured in the cell and then Nettle hydroalcoholic extract was added to it.

To obtain a steady state condition, immersion of the working electrode in test solution was carried out for 1800 s. Tafel polarization was done with the sweep rate of 1 mV/s and the range –0.25 to +0.25 V, rather than the corrosion potential. EIS tests were measured over the frequency range of 10 kHz to 10 mHz and with a 10 mV amplitude. Also, NOVA software was used for modeling the EIS data.

3. Results and Discussion

3.1. Electrochemical measurements

By immersing the working electrode in 0.5 M H_2SO_4 solution with and without the Nettle extract for 1800 seconds, open-circuit potential (OCP) was stabilized and electrochemical tests were carried out (Fig. 2).

Tafel cathodic and anodic polarization curves and electrochemical parameters of API 5L carbon steel samples in different concentrations of the Nettle extract are displayed in Fig. 3. The potentidynamic polarization parameters were extracted by Tofle extrapolation method and these parameters included corrosion potential (E_{corr}) and corrosion current density (i_{corr}), as illustrated Table 2. Changes in corrosion potential (E_{corr}) can be a useful parameter to identify the inhibition effect on each anodic or cathodic reaction. Iron reaction in an acid solution containing a cathode reaction and the anode reaction is as follows [13]:

$Fe \rightarrow Fe^{2+} + 2e^-$

Anodic reaction (Oxidation reaction)(1)

$2H^+ + 2e^- \rightarrow H_2$

Cathodic reaction (Reduction reaction)(2)

As shown in Table 2, E_{corr} is changed only a few millivolts, from -0.418 V in the acid solution without the inhibitor to –439 mV in the acidic solution with 6 g/L Nettle extract. Thus increasing the concentration of extract could lead to maximum changes in E_{corr}, equal to 21 mV. Changes of corrosion potential in a positive or negative direction and less than 85 mV and the decrease in cathodic and anodic current density mean that the inhibitory effect of both cathode and anode reactions is one of a mixed inhibitor [10].

Table 1. Chemical composition of API 5L carbon steel.

Elements	C	Mn	P	Ti	Fe
API 5L carbon steel/ wt. %	0.28	1.20	0.30	0.04	Bal

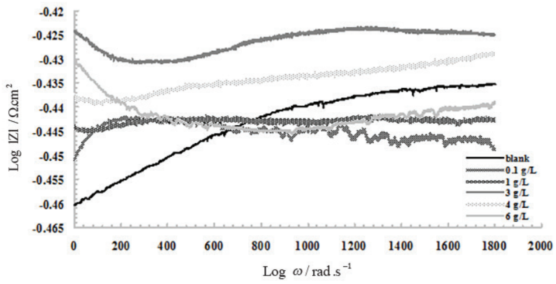

Fig. 2. Variation of the OCP as a function of time, re corded for API 5L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of Nettle extract.

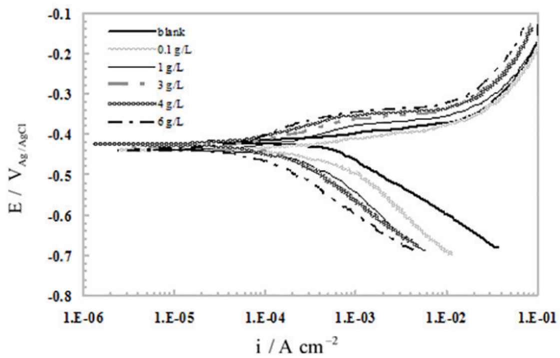

Fig. 3. Tafel polarization curves of API 5L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of the Nettle extract.

Table 2. Electrochemical parameters derived from Tafel plots of API 5L carbon steel sample immersed in 0.5 M H_2SO_4 with and without the Nettle extract inhibitor.

C (g/L)	i_{corr} (μA cm^{-2})	E_{corr} (V)	η(%)
0	424.2	-0.418	-
0.1	212.0	-0.438	50
1	98.9	-0.439	77
3	60.1	-0.430	86
4	55.3	-0.423	87
6	41.7	-0.439	90

Inhibition efficiency (η) given in Table 2 can be achieved by Eq. (3) 14):

$$\eta = \frac{i^0_{corr} - i_{corr}}{i^0_{corr}} \qquad \text{(Eq. 3)}$$

, where i_{corr} is corrosion current density in the presence of the inhibitor and i^0_{corr} is the value of corrosion current density in the absence of the inhibitor. According to Table 2, reducing the corrosion current density increased the efficiency of inhibition with increasing the concentration of the Nettle extract in the 0.5 M H_2SO_4 solution. The maximum inhibition efficiency achieved was 90 % when the concentration of extract was 6 g/ L. Loss of corrosion current density was obtained by the absorption of extract on the metal surface. In fact, with increasing the concentration of extract, greater coverage was created on surface, resulting in less corrosion and increasing the efficiency of inhibition [13].

EIS was another powerful careful tool used to study the corrosion behavior. Impedance curves obtained from API 5L carbon steel in the 0.5 M H_2SO_4 solution, in concentrations of 0.1 to 6 g/L Nettle extract, have been shown in Fig. 4. As be seen, the Niquist curves illustrated a semi-circle (the depressed capacitive loop) and as a result, had one time constant. The depressed capacitive loop showed the presence of micro roughness and the metal surface inhomogeneities in corrosive solutions [10]. In low frequencies, there was an induction loop that was related to adsorption ions such as H^+_{ads} and SO_4^{2-} [15].

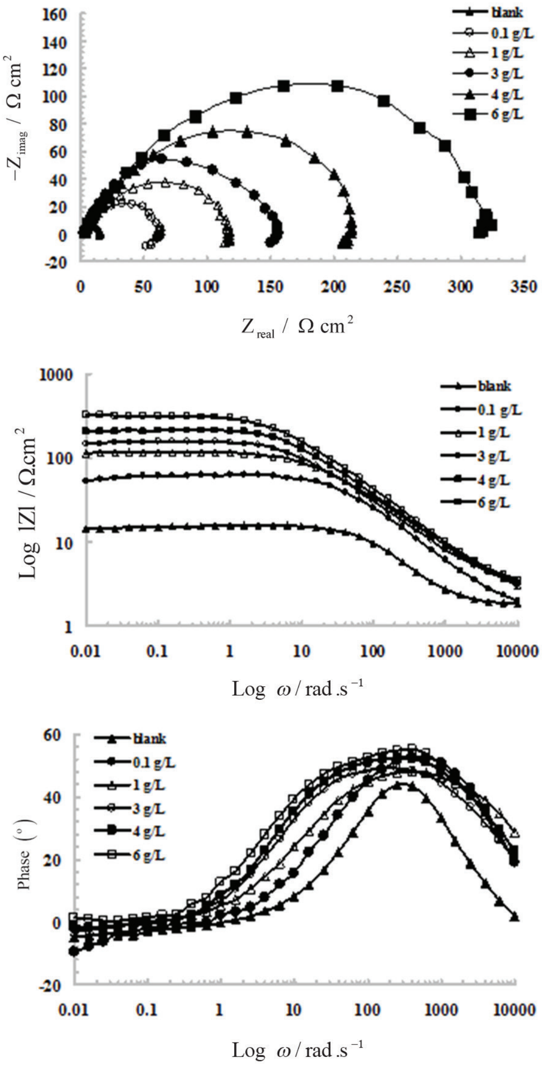

Fig. 4. EIS plots of API 5L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of the Nettle extract exemplified as: (a) Nyquist, (b) bode modulus, and (c) bode phase angle plots.

This equivalent circuit was used to fit the impedance data using the NOVA software shown in Fig. 5. In this equivalent model, R_S and R_{ct} represent solution resistance and charge transfer resistance and CPE is the constant phase element, respectively [16-18]. It should be noted that this equivalent circuit is the best fit for the impedance data, fitting the entire frequency range, but with the use of inductors, physical importance was not clear [19].

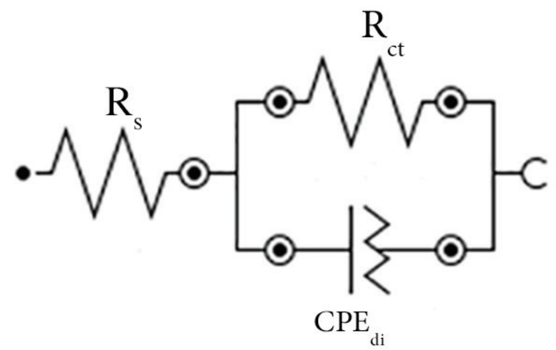

Fig. 5. The best equivalent circuit used to model the experimental EIS data of API 5L carbon steel in 0.5 M H_2SO_4 in the absence and presence of different concentrations of Nettle.

Double layer capacitance (C_{dl}) in a circuit containing constant phase element (CPE) can be obtained by Eq. (4) [11]:

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \qquad \text{(Eq. 4)}$$

, where f_{max} is the maximum frequency of the imaginary impedance component. The obtained impedance parameters, including C_{dl}, R_S and R_{ct}, are illustrated in Table 3. These parameters showed that with increasing the concentration of the Nettle extract in the solution of 0.5 M H_2SO_4, R_{ct} was increased, while the C_{dl} was reduced. Reduction of C_{dl} can be attributed to the inhibitor absorption in the steel surface and changes in the characteristics of the double layer at the surface [14, 15]:

$$C_L = \frac{\varepsilon\varepsilon_0}{d} S \qquad \text{(Eq. 5)}$$

, where d is the thickness of the layer, S stands for the surface of the electrode, ε_0 represents the permittivity of the air, and ε is the local dielectric constant in Eq. (5), respectively. The decrease of C can be attributed to the increase in the thickness of a double layer at electrode surface and/or the decrease of local dielectric constant as result of the increase in the inhibitor concentration. Accordingly, the corrosion resistance was increased. The value of inhibition efficiency was obtained using Eq. (6) [14]

$$\eta = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \qquad \text{(Eq. 6)}$$

, where R_{ct} and R_{ct}° were charge transfer resistance in the presence and absence of Nettle extract, respectively. Nettle extract inhibition efficiency maximum in the 0.5 M H_2SO_4 solution was 96%, in the concentration of 6 g/L. These results confirmed those obtained by Tafel polarization curves.

In studies conducted on 43 species of Nettle plant by using UPLC-Q-TOF-MS [12], phenolic compounds and fatty acid derivatives were identified as the main constituent of the plant. During the survey, it was observed that there was significant photochemical difference between different types of Nettle species. Nettles studied were classified into two groups: one with a high content of hydroxy fatty acids and the other one with a high content of phenolic acids. π-electrons and pair of electrons caused the adsorption of herbal extract compounds on the metal surface. In fact, polar functions in the presence of atoms of oxygen, nitrogen and sulfur and π-electrons in organic compounds cause the reaction of extract with the metal surface and prevent corrosion [20]. All compounds of Nettle extract (Fig. 1) have oxygen and as a result , the inhibition corrosion of API 5L carbon steel in the 0.5 M H_2SO_4 solution can be attributed to the absorption of these compounds on the metal surface.

However, identifying the most effective plant part in inhibiting corrosion is difficult due to different and complex combinations of herbal extracts. More detailed analysis is required using surface analysis techniques to identify active compounds and elements in the layer created by the extract on the metal surface.

3.2. Adsorption mechanism of corrosion inhibition

Data obtained from EIS curves were used to check the process of inhibitor absorption. Langmuir and Temkin adsorption isotherms were studied according to formulas 7 and 8 and the Langmuir isotherm model was selected as the most suitable one [11].

$$\frac{C}{\theta} = \frac{1}{K} + C \qquad \text{(Langmuir)} \qquad \text{(Eq. 7)}$$

$$\exp(-2a\theta) = KC \qquad \text{(Temkin)} \qquad \text{(Eq. 8)}$$

In this formula, θ is the created surface coverage obtained from impedance, *a* is the parameter of absorption interaction, C is the concentration of inhibitor and K_{ads} is the absorption-desorption equilibrium constant. By drawing $\frac{C}{\theta}$ in C, a straight line is obtained, as shown in Fig. 6. The R^2 value was 0.999, suggesting that the inhibitor absorption followed the Langmuir isotherm. Standard free energy (ΔG_{ads}°) of the inhibitor absorption on the metal surface was obtained according to the following formula:

$$\Delta G_{ads}^0 = -RT \ln(55.5 \times K_{ads}) \qquad \text{(Eq. 9)}$$

, where T is the absolute temperature and R is the gas constant. Value (ΔG_{ads}°) was -16 KJ/mol, which represented the physical absorption of the inhibitor on the surface of the steel in H_2SO_4 0.5 M solution. Negative value (ΔG_{ads}°) represents the spontaneous

Table 3. Electrochemical parameters derived from EIS plots of API 5L carbon steel sample immersed in 0.5 M H_2SO_4 with and without the Nettle extract inhibitor.

C (g/L)	R_S (Ω cm²)	R_{ct} (Ω cm²)	C_{dl} (μF cm⁻²)	η (%)	θ
0	1.80	14.00	131.91	-	-
0.1	1.61	62.43	58.13	78	0.78
1	1.78	127.02	72.63	89	0.89
3	2.43	176.01	50.34	92	0.92
4	2.34	238.54	87.41	94	0.94
6	3.71	341.04	81.81	96	0.96

inhibitor absorption. If the absolute value (ΔG°_{ads}) is less than or equal to 20, physical adsorption occurs, and when the absolute value (ΔG°_{ads}) is greater than or equal to 40, chemical absorption occurs and whenever it is between these two values, mixed absorption will be created between the inhibitor and the metal surface [21]. Physical adsorption occurs by electrostatic forces between the inhibitor molecule and the metal surface and chemical adsorption containing the transfer of the charge and charge sharing between the inhibitor molecule and the metal surface [22].

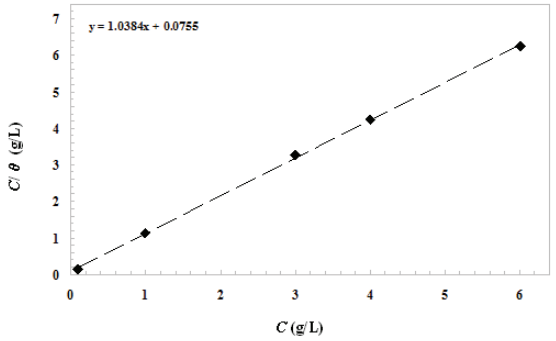

Fig. 6. Langmuir adsorption isotherm for API 5L carbon steel in the absence and presence of the Nettle extract in 0.5 M H_2SO_4.

4. Conclusions

The effect of Nettle leaves extract (as a green corrosion inhibitor) on the corrosion behavior of API 5L carbon steel in the 0.5 M H_2SO_4 solution was studied. The results showed that Nettle leaves extract had a significant effect on reducing the rate of the corrosion of API 5L carbon steel in the 0.5 M H_2SO_4 solution. Also, the results revealed that Nettle leaves extract acted as a mixed type inhibitor. Absorption of this inhibitor on the API 5L carbon steel surface followed the Langmuir isotherm. The value of indicated that the adsorption of the present inhibitor on API 5L carbon steel surface was physical.

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