

PARSLEY LEAVES (*Petroselinum Sativum*) AS CORROSION INHIBITORS OF STEEL DIN 2391 ST 37-4 IN ACID MEDIUM 5% H₂SO₄

ABSTRACT

In this article, the corrosion inhibition of steel DIN 2391 St 37-4 in acidic medium 5% H₂SO₄ with and without the presence of eco inhibitors of leaf extract (*Petroselinum Sativum*) was examined. Inhibitory properties of parsley leaves (*Petroselinum Sativum*) on steel DIN 2391 St 37-4 were examined by potentiodynamic polarization - Tafel extrapolation, and FTIR method in order to categorize the oxide layer. The test was performed in static medium and with stirring at 600 rpm. By Tafel extrapolation based on changes in corrosion potential, the inhibitor behaves as mixed. Increasing the concentration of inhibitors increases the efficiency of inhibition. Corrosion processes are inhibited by adsorption of organic matter on the surface of steel DIN 2391 St 37-4, forming a film. The obtained results indicate that parsley leaf extract (*Petroselinum Sativum*) is an effective eco inhibitor for the tested steel in 5% sulfuric acid.

Keywords: DIN 2391 St 37-4, Tafel extrapolation, Petroselinum Sativum, FTIR, 5% H₂SO₄

INTRODUCTION

Costs incurred as a result of corrosion processes increase from year to year. Most often, these are corrosion processes that lead to the conversion of a large number of useful metals into materials and compounds that are not useful. Steel is the material most used in the construction of various structures. Corrosion reduces the use value of steel, shortens the duration of structures, increases their maintenance, causes losses in production, downtime, etc. Procedures for protection of materials against corrosion include the application of corrosion-resistant materials, construction and technological protection measures, electrochemical protection methods (cathodic and anode protection), protection against corrosion inhibitors, and coating protection. Corrosion inhibitors are chemical compounds that are added in small concentrations to an aggressive environment to slow down or prevent corrosion.

Raising environmental awareness reduces the use of chemical-based inhibitors, and increases researchers' interest in eco-inhibitors. The use of eco inhibitors has its advantages not only in biodegradability but also in the ease of preparation as well as the lower cost of preparations that are available in natural resources.

Many research studies discuss the possibility of using natural plant extracts as green corrosion inhibitors for metals in various aqueous media (17,18,19). There is still a limitation in the choice of the appropriate solvent that could be used for the extraction of bioactive ingredients from plant biomass (8). Miralrio and Espinoza Vázquez (9) and Tamalmani and Husin (10) believe that the type of solvent affects its diffusion into plant tissues in order to dissolve and extract bioactive ingredients.

Corrosion inhibitors based on plant extracts have been successfully used to inhibit steel corrosion in various media.

All flavonoid-rich plant extracts can take on the function of eco-inhibitors, but each potential inhibitor must be thoroughly tested in different media and methods and, if it has a satisfactory inhibitory effect, released into commercial use. Parsley (*Petroselinum Sativum*) is rich in antioxidant components such as: alkaloids, flavonoids, flavonoid glycosides, carotenoids, proteins, amino acids, etc. (12), (13) and is therefore considered a promising corrosion inhibitor. The aim of this paper is to examine the properties and efficacy of inhibitors using electrochemical methods of Tafel extrapolation, and methods of characterization of inhibitors by FTIR method in 5% H₂SO₄.

MATERIALS AND METHODS

The tests were performed on DIN 2391 St 37.4 prepared before the measurement. The electrode surface was mechanically cleaned with P600 WBB grinco and P1200 WBB grinco sandpaper (Waterproof abrasive paper), then washed with a stream of distilled water, then ultrasonically degreased in ethanol, then washed again with distilled water and immersed in electrolyte solution. The chemical properties of the material are shown in Table 1.

Table 1. Chemical properties DIN 2391 St 37.4 and X5 CrNi 15-10

| Sample | Fe | C | Si | Mn | P max | S max |
|------------------|---------------|-------|-------|-------|-------|-------|
| DIN 2391 St 37.4 | 99,39 –99,63% | ≤0,17 | ≤0,04 | ≥0,35 | 0,04 | 0,04 |

To perform the experimental part of the inhibition of said steel, an eco inhibitor was used: parsley (*Petroselinum Sativum*) in an acidic medium of 5% H₂SO₄.

The dried leaves of *Petroselinum Sativum* (parsley) are ground and ground into a fine powder. The inhibitor was added directly to the prepared 5% H₂SO₄ solution of 500 ml in amounts of 0.5 g; 1 year and 3 years.

Electrochemical measurements were performed on a Potentiostat/Galvanostat Model 263A and a corrosion cell model K47. The corrosion cell is composed of saturated calomel electrodes as reference electrodes, graphite electrodes as counter-electrodes and steel (DIN 2391 St 37.4) as the working electrode.

The electrochemical nature of the corrosion process allows the application of various electrochemical techniques to determine the corrosion rate. The direct current method (DC - method) was used for testing and measuring efficiency. The value of the corrosion current is obtained from the extrapolation of the linear parts of the anode and cathode polarization curve to the corrosion potential, and b_a and b_k are calculated from the slope of the linear parts. This method has certain limitations in the case of interfering electrochemical processes, e.g. occurrence of passivity at high anodic polarizations, in which the sample surface changes. Another consequence is the appearance of an unequal distribution of current density over the surface. The Tafel extrapolation method is based on the Butler-Volmer equation.

$$i = i_0 \cdot \left[\exp\left(\frac{\alpha_A n F}{RT} \eta\right) - \exp\left(-\frac{\alpha_C n F}{RT} \eta\right) \right]_1$$

FT-IR spectroscopy technique (Fourier Transform Infrared Spectroscopy Technique) was used to characterize the tested eco inhibitor. The main characteristic of FTIR is sensitivity to functional groups.

¹ The Butler-Volmer equation

By combining the basic vibrations and rotations of different functional groups in a molecule and the interaction of these groups with other atoms in the molecule, a unique, complex IR spectrum for each functional group is obtained.

The FTIR spectrum of *Petroselinum Sativum* (parsley) was measured on a Nicolet iS10 FTIR Spectrophotometer-Thermo Fisher Scientific.

RESULTS AND DISCUSSION

Measurements in sulfuric acid solution (5% H₂SO₄) were performed to determine the concentration-dependent inhibitor efficacy. In the acid medium, the tests were performed in a steady state and with stirring at a speed of 600 rpm.

Examination of the corrosive behavior of steel in H₂SO₄ solution showed that parsley shows inhibitory properties at concentrations of 0.5g and 1g, while further increasing the concentration to 3g begins to act as a corrosion activator. The diagram of the corrosive behavior of steel in H₂SO₄ solution without inhibitors and with the addition of primrose as an eco-corrosion inhibitor is shown in Figure 1.

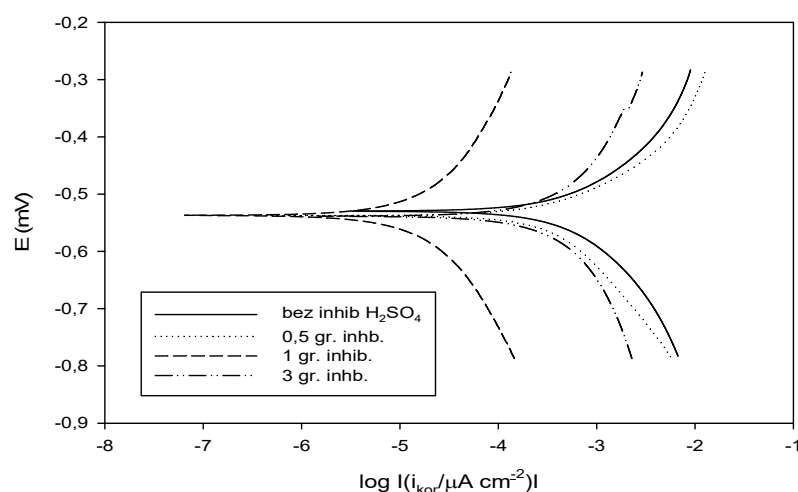


Figure 1. Diagram of the corrosion behavior of steel in H₂SO₄ solution without inhibitors and with the addition of primrose as an eco-corrosion inhibitor.

The results obtained by measurement are shown in Table 2.

Table 2. Results obtained for inhibitor efficiency and corrosion rate of steel in H₂SO₄ solution without mixing with and without inhibitors

| | E _{corr} (mV) | Corrosion rate (mm / year) | IE% |
|--------------|------------------------|----------------------------|-------|
| Without inh. | -529.711 | 11.62 | - |
| 0,5 g. | -537.530 | 8.121 | 30.11 |
| 1 g. | -537.155 | 0.4402 | 96.21 |
| 3 g. | -538.651 | 17.85 | - |

By examining the behavior of steel in H₂SO₄ solution with stirring, it was found that the corrosion rate decreases, which means that the effectiveness of primrose as an inhibitor increases. The corrosive behavior of steel in H₂SO₄ solution with stirring is shown in Figure 2.

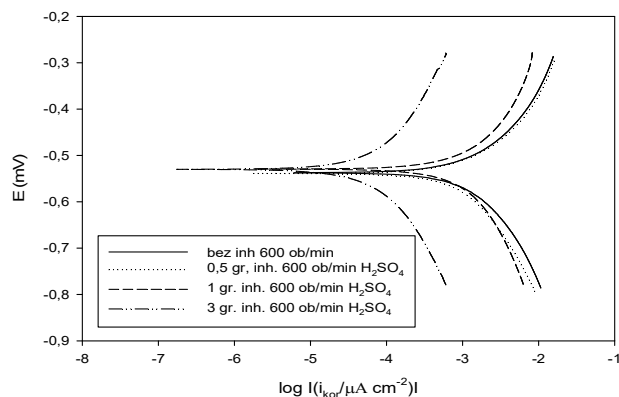


Figure 2. Diagram of the corrosive behavior of steel in H₂SO₄ solution without inhibitors and with the addition of primrose as an eco-corrosion inhibitor (with mixing).

The results obtained by measurement are shown in Table 3.

Table 3. Results obtained for inhibitor efficiency and corrosion rate of steel in H₂SO₄ solution with mixing with and without inhibitors.

| | E_{corr} (mV) | Corrosion rate (mm / year) | IE% |
|--------------|-----------------|----------------------------|-------|
| Without inh. | -537.305 | 27.56 | - |
| 0,5 gr. | -538.947 | 22.90 | 16.91 |
| 1 gr. | -529.038 | 21.83 | 20.79 |
| 3 gr. | -530.100 | 1.602 | 94.19 |

FTIR (Fourier transform infrared spectroscopy) was used to characterize *Petroselinum Sativum* (parsley) which was used as a corrosion inhibitor. The aim of the analysis was also to characterize the oxide layer. Inhibitor spectra are shown in Figure 3.

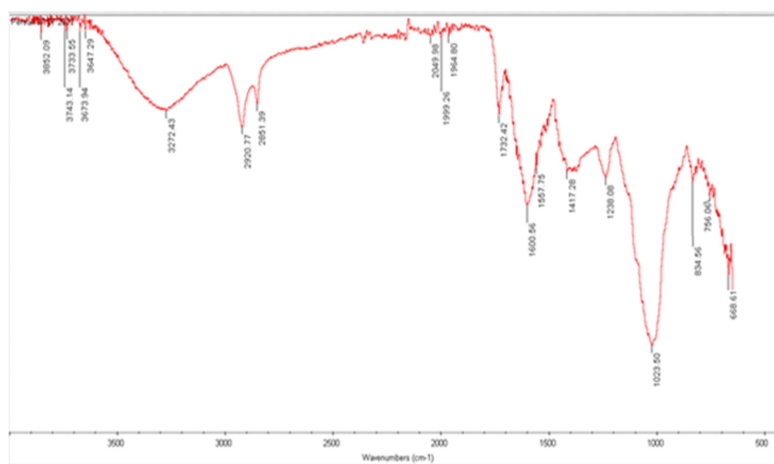


Figure 3. FTIR spectrum of *Petroselinum Sativum* (parsley)

The FTIR spectrum of *Petroselinum Sativum* (primrose) has several bands characteristic of the functional groups it possesses. Peak identification shown in Table 4.

Table 4. Identification of peaks *Petroselinum Sativum* (parsley)

| Wave number (peak position) (cm ⁻¹) | Identification |
|---|---|
| 3272.43 | –O–H tensile vibrations in alcohol / phenol molecules |
| 2920.17 | asymmetric –C–H vibrational stretching of aliphatic –CH ₂ and –CH ₃ group |
| 2851.39 | symmetric –C–H vibrational stretching of aliphatic –CH ₂ and –CH ₃ group |
| 1732.42 | –C=O tensile vibrations (carbonyl group of aldehydes, ketones, esters and / or carboxylic acids) |
| 1600.56 | <ul style="list-style-type: none"> • –C=C– tensile vibrations in conjugated alkenes and/or • –C–C– tensile vibrations (in the plane) in aromatic components |
| 1417.28 | This peak is a bit wider, so it can originate from: <ul style="list-style-type: none"> • –C–H bending vibrations in –CH₂ and –CH₃ group and/or • –C–C– tensile vibrations (flat) in aromatic components and/or • –O–H bending vibrations in alcohol and/or carboxylic acid molecules |
| 1238.08 | <ul style="list-style-type: none"> • –C–O tensile vibrations in ethers and / or esters • –C–C– stretching vibrations in the carbohydrate structure (if carbohydrates are present) |
| 1023.50 | This peak with a maximum at 1023.50 cm ⁻¹ is also characterized by the presence of "shoulders" in the range towards a larger wave number (up to about 1200 cm ⁻¹ , so that this whole range corresponds to –C – O tensile vibrations in ethers and/or esters, primary , secondary and tertiary alcohols |
| 1000-650 | <ul style="list-style-type: none"> • –C=C– bending vibrations in alkenes and/or • –C–H bending vibrations |

FTIR results of *Petroselinum Sativum* (parsley) are given in Figure 3 and their corresponding FT-IR peaks are given in Table 4. The presence of functional groups –OH, –COOH containing oxygen atom with lone pairs acting as adsorption centers in order to reduce corrosion rates.

CONCLUSION

Surface modification with corrosion inhibitors is a very important approach in preventing and reducing corrosion problems. For this reason, finding new environmentally friendly inhibitors and examining the mechanism of their action is the subject of much research today.

Based on the tests of primrose samples and the results obtained in this paper, it can be concluded that the effectiveness of primrose as an eco-corrosion inhibitor is exceptional on steel DIN 2391 St 37-4 in H₂SO₄ solution and with mixing.

By increasing the concentration of inhibitor in the static electrolyte, the corrosion rate was significantly reduced to the amount of inhibitor 1 g, where the effect of inhibition was 96.21%. At a 3g inhibitor concentration with electrolyte mixing of 5% H₂SO₄, which was the highest concentration tested, the corrosion rate decreased from an initial 27.56 mm/year in solution without inhibitor to only 1.6

mm/year. The inhibition efficiency obtained was 94.19%. Polarized curves show that the eco inhibitor behaves as a mixed inhibitor.

FTIR results of *Petroselinum Sativum* (parsley) indicate the presence of functional groups -OH, -COOH containing an oxygen atom with solitary pairs acting as adsorption centers in order to reduce the corrosion rate.

This research has shown that at certain concentrations *Petroselinum Sativum* (parsley) can be used as a very effective inhibitor and that further research, bio-based inhibitors will certainly be able to replace certain inhibitors that have proven to be toxic, and thus contribute to environmental protection.

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