

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 (20). 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. According to the mechanism of action, inhibitors are divided into: anodic

inhibitors, cathodic inhibitors, mixed inhibitors (3). Corrosion inhibition usually begins with the

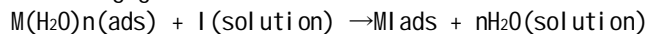
adsorption of inhibitors on the metal surface. The adsorption process depends on the state of the metal surface, the conditions prevailing in the corrosion environment (temperature and pressure), and

the physical and chemical properties of the inhibitor. The main types of interaction between the inhibitor and the metal surface are physical adsorption and chemisorption.

Physical adsorption is the result of electrostatic attractive forces between inhibiting organic molecules

or dipoles and the electric charge of the metal surface (21).

Chemisorption is a process that involves the transfer of charge from an inhibitor molecule to a metal surface, resulting in a coordinative type of bond. During the chemisorption of inhibitors on the metal surface, simultaneous desorption of water molecules occurs, which can be represented by the following general reaction:



where n is the number of water molecules that are displaced from the metal surface with each molecule of adsorbed inhibitor.

The effectiveness of the inhibition is expressed through the relationship to the degree of adsorption,

i.e. the covering of the metal surface with the inhibitor. The degree of coverage θ is calculated according to the equation (22):

$$\theta = \frac{I_{\dots} - I_{\dots}}{I_{\dots}}$$

where is:

I_{kor0} - corrosion current in an uninhibited system

I_{kor} - corrosion current in the inhibited system

While the Inhibitor Efficiency is expressed as a percentage and is obtained from the degree of coverage, according to the equation:

$$\eta = \theta \cdot 100\%$$

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% H_2SO_4 .

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

surface of the electrode on which the measurements were performed was 1 cm².

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: leaf extract

(*Petroselinum Sativum*) in an acidic medium of 5% H₂SO₄.

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

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. Measurements were made at a temperature of 25°C. The results obtained by anodic and cathodic polarization in a wide range of potentials from the corrosion potential ($E = E_{\text{corr}} \pm 250$ mV) are

displayed graphically in semi-logarithmic form ($E - \log j$).

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.

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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.

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 0.5gr and 1gr, while further increasing the concentration to 3gr begins

1 The Butler-Volmer equation

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.

log I (i_{kor} / A cm⁻²)
 -8 -7 -6 -5 -4 -3 -2 -1
 E (mV)
 -0,9
 -0,8
 -0,7
 -0,6
 -0,5
 -0,4
 -0,3
 -0,2
 bez inh H₂SO₄
 0,5 gr. inh.
 1 gr. inh.
 3 gr. inh.

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)	i _{corr} (mm / year)	IE%
Without inh.	-529.711	11.62
0,5 g.	-537.530	8.121
1 g.	-537.155	0.4402
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.

log I (i_{kor} / A cm⁻²)
 -8 -7 -6 -5 -4 -3 -2 -1
 E (mV)
 -0,9
 -0,8
 -0,7
 -0,6
 -0,5
 -0,4
 -0,3
 -0,2
 bez inh 600 ob/min
 0,5 gr. inh. 600 ob/min H₂SO₄
 1 gr. inh. 600 ob/min H₂SO₄
 3 gr. inh. 600 ob/

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)	i _{corr} (mm / year)	IE%
Without inh.	-537.305	27.56
0,5 gr.	-538.947	22.90
1 gr.	-529.038	21.83
3 gr.	-530.100	1.602

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* (parsley) has several bands characteristic of the functional groups it possesses. Peak identification shown in Table 4.

Table 4. Identification of peaks *Petroselinum Sativum* (parsley) (23)

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

-CH₂ and -CH₃ group

2851.39

symmetric -C-H vibrational stretching of aliphatic

-CH₂ and -CH₃ group

1732.42

-C=O tensile vibrations (carbonyl group of aldehydes,

ketones, esters and / or carboxylic acids)

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:

• -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

• -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

• -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 parsley 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 gr, where the effect of inhibition was 96.21%. At a 3gr 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%. The change in corrosion potential is not greater than 85 mV, which indicates that the inhibitor can be classified as cathodic or anodic with

respect to corrosion potential. 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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