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# Parsley Leaves (*Petroselinum Sativum*) as Corrosion Inhibitors of Steel DIN 2391 St 37-4 in Acid Medium 5% H<sub>2</sub>SO<sub>4</sub>

Ema Obralić<sup>a\*</sup>, Amra Odobašić<sup>a</sup>, Sanja Panić<sup>b</sup> and Marijana Tadić<sup>c</sup>

<sup>a</sup> Department of Physical Chemistry and Electrochemistry, Faculty of Technology, University of Tuzla, Bosnia and Herzegovina.

<sup>b</sup> Faculty of Technology, University of Novi Sad, Serbia.

<sup>c</sup> Euroaquaind D.O.O. Tuzla, Bosnia and Herzegovina.

### Authors' contributions

This work was carried out in collaboration among all authors. All authors read and approved the final manuscript.

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Original Research Article

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## ABSTRACT

In this article, the corrosion inhibition of steel DIN 2391 St 37-4 in acidic medium 5% H<sub>2</sub>SO<sub>4</sub> with and without the presence of eco inhibitors of leaf (*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 (*Petroselinum Sativum*) is an effective eco inhibitor for the tested steel in 5% sulfuric acid.

Keywords: DIN 2391 St 37-4; tafel extrapolation; leaf of *Petroselinum sativum*; FTIR; 5% H<sub>2</sub>SO<sub>4</sub>.

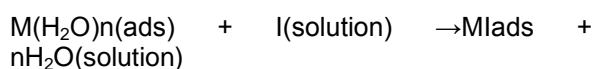
\*Corresponding author: E-mail: [ema.obralic@gmail.com](mailto:ema.obralic@gmail.com);

## 1. 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 [1]. 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 [2-5]. According to the mechanism of action, inhibitors are divided into: anodic inhibitors, cathodic inhibitors, mixed inhibitors [6]. 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 [7].

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 [8,9]. 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  $\theta$  is calculated according to the equation [10]:

$$\theta = \frac{I_{kor^0} - I_{kor}}{I_{kor^0}}$$

where is:

$I_{kor^0}$  - 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 [11-15].

Many research studies discuss the possibility of using natural plant extracts as green corrosion inhibitors for metals in various aqueous media [16,17,18]. 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 [19]. Miralrio and Espinoza Vázquez [20] and Tamalmani and Husin [21] 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. Leafs of parsley (*Petroselinum sativum*) is rich in antioxidant components such as: alkaloids, flavonoids, flavonoid glycosides, carotenoids, proteins, amino acids, etc. [22], [23] 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<sub>2</sub>SO<sub>4</sub>.

## 2. 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 cm<sup>2</sup>.

The chemical properties of the material are shown in Table 1.

To perform the experimental part of the inhibition of said steel, an eco-inhibitor was used: leaf of parsley (*Petroselinum Sativum*) in an acidic medium of 5% H<sub>2</sub>SO<sub>4</sub>.

The dried leaves of *Petroselinum Sativum* (parsley) are ground into a fine powder. The inhibitor was added directly to the prepared 5% H<sub>2</sub>SO<sub>4</sub> 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<sup>0</sup> C. The results obtained by anodic and cathodic polarization in a wide range of potentials from the corrosion potential ( $E = E_{\text{corr}} \pm 250 \text{ mV}$ ) 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  $i_a$  and  $i_c$  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. 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 leafs *Petroselinum Sativum* (parsley) was measured on a Nicolet iS10 FTIR Spectrophotometer-Thermo Fisher Scientific.

## 3. RESULTS AND DISCUSSION

Measurements in sulfuric acid solution (5% H<sub>2</sub>SO<sub>4</sub>) 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 H<sub>2</sub>SO<sub>4</sub> solution showed that leafs of parsley shows inhibitory properties at concentrations of 0.5 gr and 1 gr, while further increasing the concentration to 3 gr begins to act as a corrosion activator. The diagram of the corrosive behavior of steel in H<sub>2</sub>SO<sub>4</sub> solution without inhibitors and with the addition of primrose as an eco-corrosion inhibitor is shown in Fig. 1.

The results obtained by measurement are shown in Table 2.

By examining the behavior of steel in H<sub>2</sub>SO<sub>4</sub> 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 H<sub>2</sub>SO<sub>4</sub> solution with stirring is shown in Fig. 2.

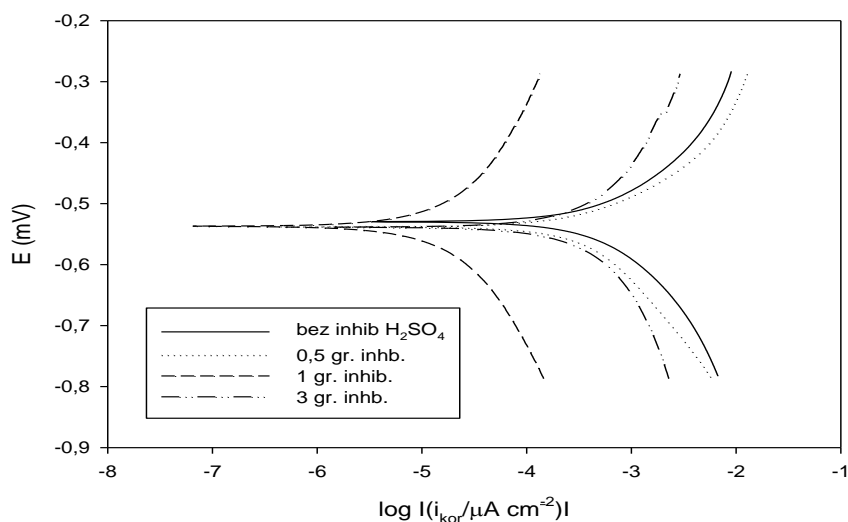
The results obtained by measurement are shown in Table 3.

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<sup>1</sup> The Butler-Volmer equation

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

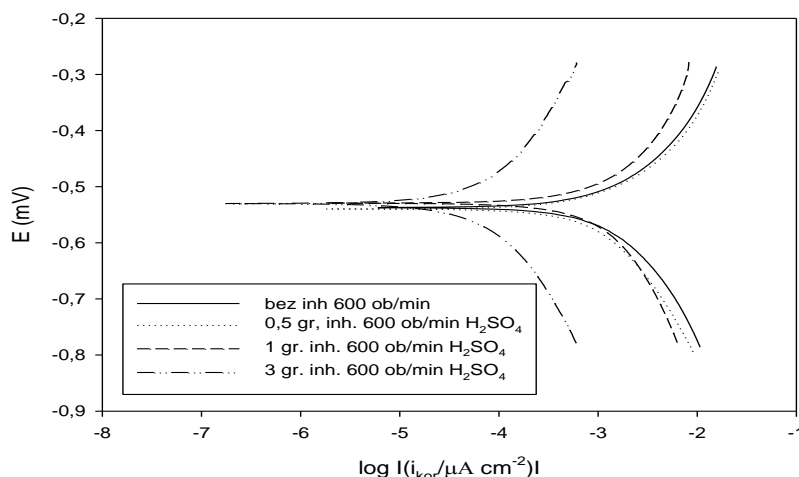
Sample	Fe	C	Si	Mn	P max	S max
DIN 2391 St 37.4	99,39 –99,63%	≤0,17	≤0,04	≥0,35	0,04	0,04



**Fig. 1. Diagram of the corrosion behavior of steel in H<sub>2</sub>SO<sub>4</sub> solution without inhibitors and with the addition of primrose as an eco-corrosion inhibitor**

**Table 2. Results obtained for inhibitor efficiency and corrosion rate of steel in H<sub>2</sub>SO<sub>4</sub> 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	30.11
1 g.	-537.155	0.4402	96.21
3 g.	-538.651	17.85	-



**Fig. 2. Diagram of the corrosive behavior of steel in H<sub>2</sub>SO<sub>4</sub> solution without inhibitors and with the addition of primrose as an eco-corrosion inhibitor (with mixing)**

**Table 3. Results obtained for inhibitor efficiency and corrosion rate of steel in H<sub>2</sub>SO<sub>4</sub> solution with mixing with and without inhibitors**

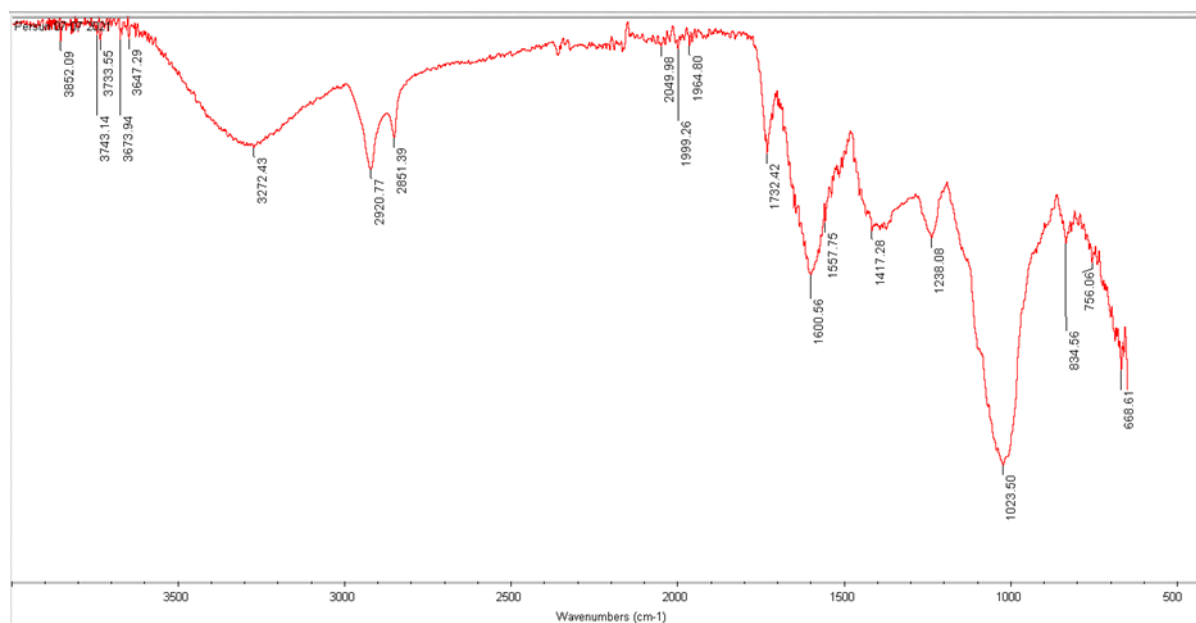
	<b>E<sub>corr</sub> (mV)</b>	<b>i<sub>corr</sub> (mm / year)</b>	<b>IE%</b>
Without inh.	-537.305	27.56	-
0,5 gr.	-538.947	22.90	16.91
1 gr.	-529.038	21.83	20.79
3 gr.	-530.100	1.602	94.19

FTIR (Fourier transform infrared spectroscopy) was used to characterize leaves of *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 Fig. 3.

The FTIR spectrum of leaves *Petroselinum Sativum* (primrose) has several bands

characteristic of the functional groups it possesses. Peak identification shown in Table 4.

FTIR results of leaves *Petroselinum Sativum* (parsley) are given in Fig. 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.



**Fig. 3. FTIR spectrum of *Petroselinum sativum* (parsley)**

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

<b>Wave number (peak position) (cm<sup>-1</sup>)</b>	<b>Identification</b>
3272.43	–O–H tensile vibrations in alcohol / phenol molecules
2920.17	asymmetric –C–H vibrational stretching of aliphatic
	–CH <sub>2</sub> and –CH <sub>3</sub> group
2851.39	simmetric –C–H vibrational stretching of aliphatic
	–CH <sub>2</sub> and –CH <sub>3</sub> 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"> <li>• –C=C– tensile vibrations in conjugated alkenes and/or</li> <li>• –C–C– tensile vibrations (in the plane) in aromatic components</li> </ul>

Wave number (peak position) (cm <sup>-1</sup> )	Identification
1417.28	This peak is a bit wider, so it can originate from: <ul style="list-style-type: none"> <li>• –C–H bending vibrations in –CH<sub>2</sub> and –CH<sub>3</sub> group and/or</li> <li>• –C–C– tensile vibrations (flat) in aromatic components and/or</li> <li>• –O–H bending vibrations in alcohol and/or carboxylic acid molecules</li> </ul>
1238.08	<ul style="list-style-type: none"> <li>• –C–O tensile vibrations in ethers and / or esters</li> <li>• –C–C– stretching vibrations in the carbohydrate structure (if carbohydrates are present)</li> </ul>
1023.50	This peak with a maximum at 1023.50 cm <sup>-1</sup> is also characterized by the presence of "shoulders" in the range towards a larger wave number (up to about 1200 cm <sup>-1</sup> , 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"> <li>• –C=C– bending vibrations in alkenes and/or</li> <li>• –C–H bending vibrations</li> </ul>

#### 4. 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 examination of parsley leaf samples and the results obtained in this work, it can be concluded that the effectiveness of parsley leaves as an eco-corrosion inhibitor is exceptional on DIN 2391 St 37-4 steel in H<sub>2</sub>SO<sub>4</sub> solution and with stirring.

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% H<sub>2</sub>SO<sub>4</sub>, 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 leaves 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 leaves *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.

#### COMPETING INTERESTS

Authors have declared that no competing interests exist.

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