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Application of Tafel extrapolation when testing the effects of eco-inhibitor Mimosa tannin and Pectin C on St 37-4 in acidic medium 3.5% HCL

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ABSTRACT :*In this study, the inhibition of corrosion of St 37-4 steel in acidic medium of 3.5% HCl with and without the presence of the eco-inhibitors Mimoza tannin and Pectin C was tested. The methods used for analysis are a mass loss (gravimetric method) and electrochemical method, Tafel extrapolations. Mimosa tannin is a condensed tannin that has a polymeric structure that contains, on average, four flavonoid units. Pectin is a polysaccharide made up of galacturonic acid units, and it differs in polymer chain length, complexity, as well as the structure of the monosaccharide unit. Tafel extrapolation based on changes in corrosion potential inhibitors behave more like cathodic rather than anodic inhibitors.Increasing the inhibitor concentration leads to an increase and inhibition efficiency. Corrosion processes are inhibited by the adsorption of organic substances on the steel surface St 37-4, forming a film. The results obtained by gravimetric method and electrochemical measurements indicate that Pectin C and Mimoza tannin are effective eco-inhibitors for the tested steel in 3.5% hydrochloric acid.*

KEYWORDS: *St 37-4, Tafel's extrapolation, Mimosa tannin, Pectin C, 3.5% HCl*

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I. INTRODUCTION

With the development of industry and the necessity of using large quantities of different materials under the influence of external factors, the degradation of the metal surface, ie corrosion, occurs. In order to prevent or reduce the degradation of the metal surface, corrosion inhibitors occupy a special place. Demand for inhibitors has been increasing over the past few years. The increase for 2012 was 26.6% divided to oil refineries; gas production 16.7%, chemical industry 15.3%: metals 9.5%, cellulose, and paper 7.1%; and other 8%, and in 2017 American demand was estimated to rise 4.1% annually to 2.5 billion USD. [2]

Corrosion inhibitors are substances which can greatly reduce the rate of corrosion of metals when added in a small amount to an aggressive medium. Today, environmentally friendly corrosion inhibitors are gaining more importance. Their development requires knowledge of the legislation of a particular country, testing the impact on the environment and excellent corrosion protection under test conditions. An important requirement set on the environmentally friendly inhibitors is that they are not retained in the environment after the action and they decompose into harmless and degradable products. The inhibitor concentration may vary from several g/l. The inhibitory activity in acidic solutions has been attributed to the adsorption of the inhibitor to the metal-electrolyte phase boundary. Ions or neutral polar molecules can be absorbed. The interaction between ions or neutral polar molecules in an electric bilayer changes its properties and structure. The adsorbed inhibitors in the acidic solution act in the manner of stopping the cathodic hydrogen emission reaction or the anodic dissolution of the metal, or both, what is the result of the effect on the electrical bilayer, the reduction of metal reactivity, the partial precipitation of the inhibitor and the formation of a physical barrier. Reduction of metal reactivity implies adsorption of the inhibitor to the active sites of the electrode rather than the entire surface. The densities of corrosion currents decrease but the slopes of Tafel directions do not change. The dissolution of the metal takes place with the formation of an intermediate that absorbs to the surface. For iron in an acidic medium, the adsorbed intermediate is FeOH and with the addition of an organic inhibitor, the [(FeHO) Inh] complex is formed. This complex can alter the reaction mechanism, acting to reduce or increase the slope of the Tafel direction. Some inhibitors create multi-molecular layers on the metal surface. The formed surface films created characterize the chemisorption bonds, π electron interactions, and lateral attractive interactions. Plants are a rich source of natural compounds of complex molecular structure and various chemical, biological and physical properties.

II. MATERIALS AND METHODS

The material used for the test is St 37-4 and the chemical composition is shown in Chart 1.

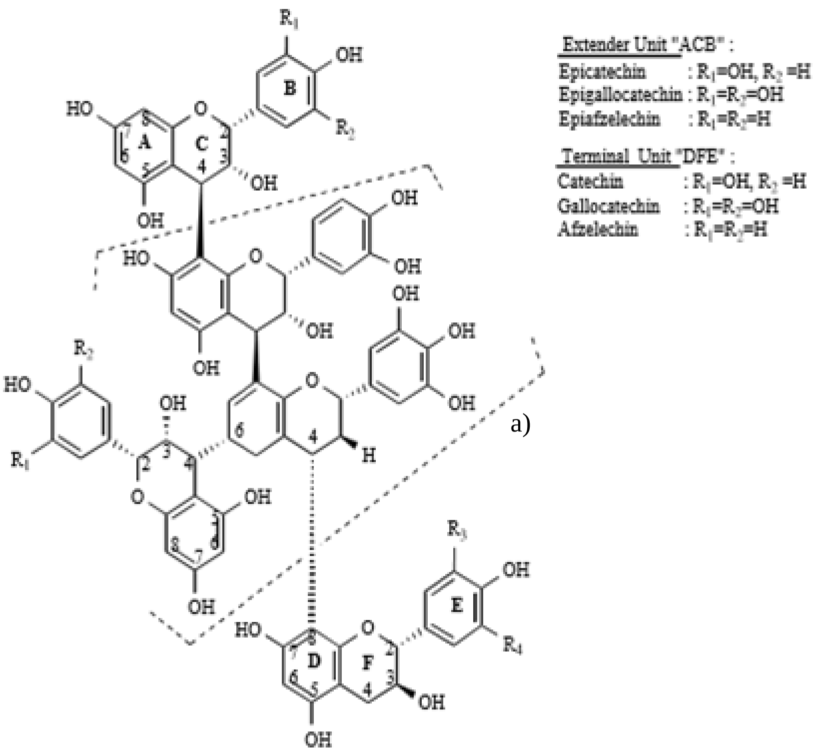
Chart 1. Chemical composition St 37 – 4

Sample	Fe	C	Si	Mn	P max	S max	Cr	Ni
St 37-4	99,39 –99,63%	≤0,17	≤0,04	≥0,35	0,04	0,04	-	-

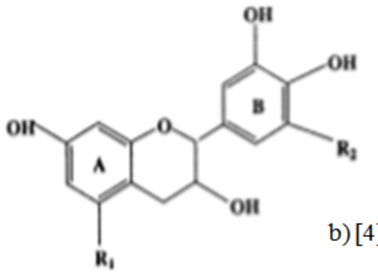
The requirement for conducting and the accuracy of the analyzes depends on the surface preparation of the tested steels. Steel was prepared by a mechanical and chemical process.

In order to perform the experimental part, in addition to the above steel, the eco-inhibitors Mimoza tannin and Pectin C in acidic medium of 3.5% HCL were used.

Tannins are non-nitrogenous polyphenolic compounds, which can be separated into two types: hydrolyzing (pyrogenic) and condensed (catechin) tannins. In addition to the above, there are mixed tannins, which represent a mixture of these two types. Hydrolyzing tannins are polyesters of gallic acid and the central sugar molecule (most often glucose), while condensed tannins are often formed by the condensation of two or three molecules of flavan 3-ols (catechin, epicatechin) or flavan 3,4 diol (protoanthocyanide or leukoanthocyanide). Tannins are very widespread in the plant world, and are found in the cytoplasm of paranchymal cells of different organs. They are made from oak, cherry, ash, walnut and other bark of trees and fruits. The use of tannins when protecting from corrosion in the development of the industry and their use in the formulation of pigments in coatings of dyes, flocculants, viscosity modifying agents, iron-based deposits cleaners increasing are pointing to the growing importance in relation to the industrial raw materials of synthetic phenols.



a)



b) [4]

Figure 1. Structure of a) condensed tannin [8] and b) mimosa tannins

Pectin is a polysaccharide made up of galactouronic acid units. Pectins differ in the length of the polymer chain, the complexity as well as the structure of the monosaccharide unit itself. Pectins compose of one-third of the dry cell wall, and the highest pectin concentrations are in the middle lamina of the cell wall gradually decreasing through the primary wall toward the plasma membrane. Most of the commercial pectin is derived from the lemon peel or apple pomace. Apple pomace contains 10-15% of pectin based on dry substance, and the citrus peel contains 20-30%. [10]

According to the chemical structure shown in Figure 2, pectin has a large amount of related residues of D-galacturonic acid. D-galacturonic acid is a cyclic monosaccharide with one carboxylic acid on the lateral side and four hydroxyl groups. A small proportion of the carboxyl groups in the D-galacturonic residues is esterified and on the lateral varnishes, the residue can be deprotonated and form anions.

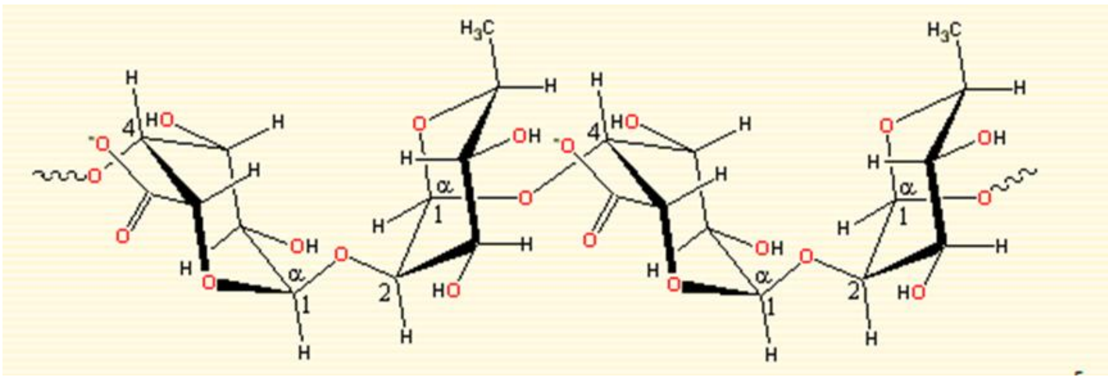


Figure 2. Chemical structure of Pectin C

Analytical and electrochemical methods were used to determine the corrosion behavior of St37 - 4 steel in 3.5% HCl without and in the presence of inhibitors. The weight-loss method (gravimetric method) was applied from the analytical methods. The gravimetric method is time-consuming and limited to systems that create adhered layers of corrosion products. Electrochemical methods are based on Faraday's law, which link the amount of substance per surface unit and time unit with the amount of elapsed current.

Gravimetric methods are based on measuring the change in mass of a sample exposed to an aggressive medium. In order to determine the corrosion behavior of steel, the measurement was performed in accordance with standard ASTM G 31-72 (1990).

$$\upsilon = \frac{m_1 - m_2}{S\,(t_2 - t_1)} = \frac{\Delta m}{S \Delta t} \quad [3]$$

By calculating the corrosion rate, the inhibition efficiency of the used inhibitor can be determined:

$$\eta = \frac{\upsilon_0 - \upsilon_{inh}}{\upsilon_0} \cdot 100 \ [\%] \ [6]$$

Where are: v_0 (corrosion rate without inhibitors) i v_{inh} (corrosion rate with inhibitor)

Electrochemical testing measures the time change of potential between the electrodes of a galvanic cell using a device with a high electrical resistance through which a minimum electrical current passes. In order to determine the electrode potential, it is necessary to measure the electromotive force between the working electrode and the reference electrode of known and constant potential.

Measurements were made in accordance with the norms and standards on the Potentiostat / Galvanostat PAR Model 263A device using PowerCorr DC Corrosion software version 2.47, PowerPulse Electroanalytical software version 1.07. and corrosion cell K47 with Flat Specimen Holder Kit model K0105 with saturated calomel electrode as the reference electrode, graphite electrode as the counter electrode and steel (St 37-4) as the working electrode.
The applied technique to determine the corrosion rate is the DC method, the graphical determination of the corrosion current density, the corrosion potential and the Tafel slope:

Tafel's extrapolation method is based on the Butler-Volmer equation, the basic equation of electrochemical kinetics: [3]

$$j = j_0 \{\exp[(1-\alpha)zF\eta / RT] - \exp[-\alpha zF\eta / RT]\}$$

III. RESULTS AND DISCUSSION

The potentiodynamic polarization curves of St 37-4 steel in a solution of 3.5% HCl without and in the presence of different concentrations of Mimose tannin inhibitors are shown in Figure 3, and the corrosion parameters are shown in Chart 2.

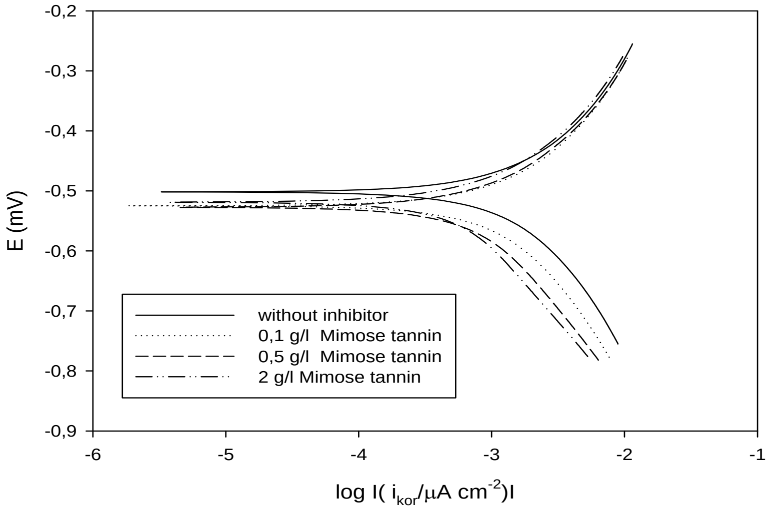


Figure 3. Potentiodynamic polarization curves in the presence of different concentrations of Mimose tannin in a solution of 3.5% HCl

Chart 2. Corrosion parameters of St 37-4 steel in 3.5% HCl solution without and in the presence of different concentrations of inhibitors

Inhibitor Concentration	E (mV)	I (μA)	Corrosion rate (mm / god)	IE%
-	-501.612	2.717e+003	31.56	-
0,1 g/l	-524.930	2.1988e+003	25.53	19.11
0,5 g/l	-527.292	1.447e+003	16.81	46.74
2 g/l	-518.812	1.156e+003	13.43	57.44

The corrosion parameters obtained from the polarization curves shown in Chart 2 show that by the presence of the Mimose tannin inhibitor it results in the shift of the corrosion potential towards the more negative values, and the cathode part of the polarization curve to the lower values of the current density.
In addition to testing the effect of Mimose tannin as an eco-inhibitor, the effect of Pectin C was also tested, as it is shown in Figure 4.

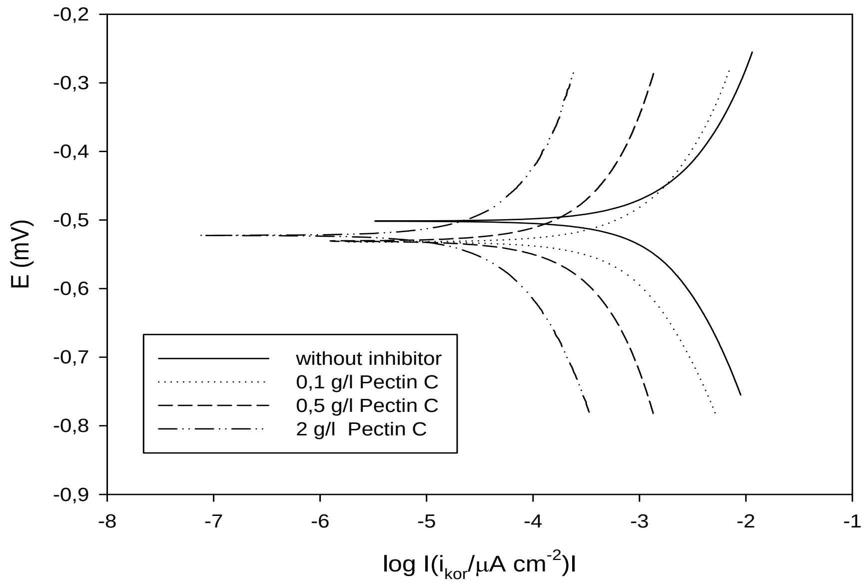


Figure 4. Potentiodynamic polarization curves in the presence of different concentrations of Pectin C in 3.5% HCl solution

Chart 3. Corrosion parameters of St 37-4 steel in 3.5% HCl solution without and in the presence of different concentrations of Pectin C inhibitor

Inhibitor Concentration	E (mV)	I (µA)	Corrosion rate (mm/god)	IE%
-	-501.612	2.717e+003	31.56	-
0,1 g/l	-532.109	1.521e+003	17.67	44.01
0,5 g/l	-530.739	1.121e+003	13.02	58.75
2 g/l	-522.212	7.280e+001	0.8457	97.32

In the solution of 3.5% HCL, the corrosion parameters presented in Table 3. and the polarization curves presented in Figure 4. show that the presence of the Pectin C inhibitor results in a shift of the corrosion potential towards more negative values, and the cathodic part of the polarization curve towards smaller values of current density.

Tables 2 and 3 show that the change in corrosion potential does not exceed 85 mV, suggesting that the inhibitor can be classified as cathodic or anodic in relation to the corrosion potential. By analyzing Figures 3 and 4, it can be seen that Mimose tannin and Pectin C inhibit corrosion by acting on the cathodic reaction and thus can be categorized as a cathodic inhibitor.

Chart 4. Results of gravimetric determination corrosion rateof steel St 37-4 in 3.5% HCl with Pectin C inhibitor

Steel and inhibitor concentrations	Corrosion rate (g/cm^{2}per day)	Inhibitor effectiveness (%)	Corrosion rate (g/cm^{2}per day)	Inhibitor effectiveness (%)
	2 days		7 days	
Without inhibitor	0,00532	-	0,00242	-
0,1 g/l	0,00097	81,77	0,000844	65,12
0,5 g/l	0,00347	34,77	0,00112	53,72
1 g/l	0,00317	40,42	0,00059	75,62
2 g/l	0,00028	94,74	0,00018	92,56

Chart 5. Results of gravimetric determination corrosion rate of St 37-4 steel in 3.5% HCl with Mimoza tannin inhibitor

Steel and inhibitor concentrations	Corrosion rate (g/cm^{2}per day)	Inhibitor effectiveness (%)	Corrosion rate (g/cm^{2}per day)	Inhibitor effectiveness (%)
	2 days		7 days	
Without inhibitor	0,00532	-	0,0242	-
0,1 g/l	0,00161	69,74	0,0198	18,18
0,5 g/l	0,00286	46,24	0,00614	74,63
1 g/l	0,00442	16,92	0,00829	65,74
2 g/l	0,00037	93,05	0,000235	99,03

The inhibition efficiency increases with the concentration increase of both inhibitors, and in connection to the aforementioned, the effect of the inhibitor can be explained by simple adsorption on the surface of the electrode which further affects on the decrease of the corrosion rate.

IV. CONCLUSION

Based on the made measurements, Mimoza tannin and Pectin C in the medium of 3.5% HCL acid show inhibitory effects on the tested St 37-4 steel, however, a higher degree of efficiency based on Tafel's extrapolation is seen at Pectin C at a concentration of 2 g/l which is 97.32 %. The change in corrosion potential is not greater than 85 mV, suggesting that the inhibitor may behave as cathodic or anodic in relation to the corrosion potential, however, by analyzing the diagram, it can be seen that Mimoza tannin and Pectin C inhibit corrosion by acting on the cathodic reaction, and can, therefore, be classified as cathode inhibito

The inhibition efficiency increases with increasing concentration in the test acid medium. The action of the inhibitor can be explained by simple adsorption on the electrode surface which further affects the corrosion rate decrease. The results obtained by gravimetric and electrochemical methods indicate the possibility of use/application of Mimose tannin and Pectin C as an effective inhibitor for St 37-4 in a solution of 3.5% HCl.

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