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Rosemary as ecologically acceptable corrosion inhibitor of steel

Ćatić, S.[a,*], Obralić, E.[b], Bratovčić, A.[a]

[a] *University od Tuzla, Faculty of Technology, Univerzitetska br. 8, 75.000 Tuzla,*
[b] *Solana d.d. Tuzla, Ulica soli br. 3, 75 000 Tuzla*

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***Corresponding author:**
E-mail: sead.catic@untz.ba
Phone: +387(0)35 320 778

Abstract: In recent years, due to increasing interest and attention of the world towards environmental protection, there has been a complete reduction or use of a certain number of corrosion inhibitors. Corrosion inhibitors are substances which, added in small quantities in aggressive media, may greatly reduce the rate of corrosion of metals. In the development of corrosion inhibitors, it is necessary to pay special attention to their toxicity and impact on environmental pollution. The research of plant extracts have become a great area of interest in the study of corrosion inhibitors. Testing the ability to protect steel was performed with plant material (*Rosmarinus officinalis* L.). In order to determine the basic parameters that show the effectiveness of green inhibitors, electrochemical measurements of corrosion rate were carried out. Results obtained by DC techniques (method of Tafel extrapolation) showed that the corrosion rate decreases in the presence of the tested corrosion inhibitor. Studies have shown that, in a certain concentration, rosemary (*Rosmarinus officinalis* L.) has the effectiveness of the protection of steel in 3% NaCl, and as such, it is considered an acceptable corrosion inhibitor.

INTRODUCTION

Corrosion is a natural process by which physical-chemical interactions of metals and the environment result in the shift of metals to the thermodynamically favorable state ie. it comes to the oxidation of metals, which results in a loss of its functionality. The corrosion effect of aggressive components in the electrolyte in practice is very often reduced by using metal′s corrosion inhibitors. Within the method of protection from corrosion, the inhibitors occupy a special place, both by the specificity of protection and by the widespread application. There are several classifications of inhibitors. According to the electrochemical nature of the corrosion process, inhibitors can be classified as anodic, cathodic, or mixed.

According to the chemical nature, inhibitors are further categorized into substances of organic and inorganic origin. Finally, according to the chemical properties: oxidizing and non-oxidizing compounds and further divisions according to the pH value of the solution in which they are applied: for acidic, neutral and alkaline solutions. The main characteristics of inhibitors are: the ability to protect the metal surface, a big activity in small concentrations, low price, easy handling and storage, and low toxicity. The process of adsorption of metal surfaces is to be coated with the inhibitor, which slows down the corrosion of metals. The reduction or termination of the use of certain corrosion inhibitors has arisen due to their impact on environmental pollution. In recent years, the focus of research has shifted to the inhibitory activity of biological molecules or mixtures of natural compounds. The aim of this paper is to examine the corrosion resistance of steel in 3% NaCl solution, with the use of non-toxic "green inhibitor" (*Rosmarinus officinalis* L.). The relationship between the reaction rate, current and potential, is characteristic for the electrochemical reaction and it is an important data in the analysis of the corrosion process by electrochemical methods on the tested system.

EXPERIMENTAL

In electrochemical corrosion, the testing process of corrosion of DC method polarization method of measurement (potentiostatic and galvanostatic) is used. The objective of measurement is to record the wrong/curved polarization of current/current polarization - voltage. For electrochemical testing of corrosion rate, the following equipment is being used - a system that consists of:

- ✓ Poteciostat/galvanostat model 263A
- ✓ PowerCorr DC Corrosion software version 2.47, PowerPulse Electroanalytical software version 1.07
- ✓ Corrosion cell K 0047, with standard, saturated calomel electrode, auxiliary electrode-graphite, and Flat Specimen Holder Kit model K0105.

Potentiostat/galvanostat is used to transfer data from a computer to a cell. The obtained data are returned from the cell to the computer. The cell is a glass container, in which auxiliary electrodes, standard calomel electrode and a working electrode with a sample are located (Figure 1). The saturated electrode is placed in Lugin capillaries, in which a saturated solution of KCl is placed.

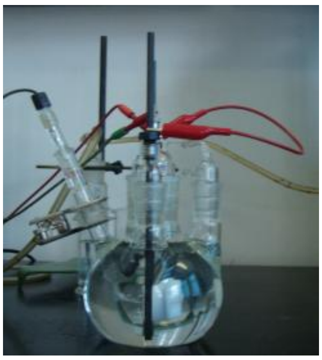

Figure 1. Corrosion cell Model K 47

In order to determine corrosion parameters, the method Tafel extrapolation, based on Butler - Volmer equation that gives the relationship between the current and overvoltage, was applied.

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

All measurements were performed in 3% NaCl solution, to which an inhibitor of plant origin has been added (*Rosmarinus officinalis* L.) at various concentrations. Work surface of tested materials (steel) is mechanically cleaned before each measurement (abrasive paper of different fineness), degreased in alcohol and washed with distilled water, chemically treated in HCl and washed with distilled water.

RESULTS AND DISCUSSION

Corrosion behavior of steel S235JR and X5CrNi18-10 has been presented experimentally by the obtained Tafel diagrams (Figure 2). Based on the curves obtained by Tafel extrapolation the corrosion parameters have been determined (Table 1).

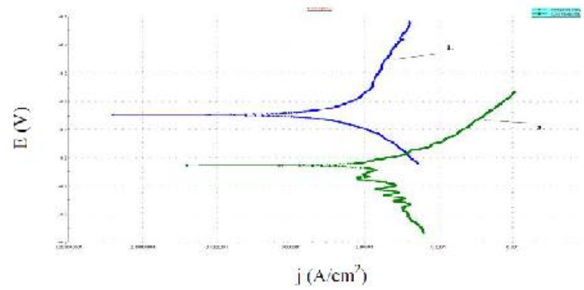

Figure 2. Tafel diagrams in 3% NaCl solution: X5CrNi18-10 (1) and S235JR (2)

Table 1. Data obtained by Tafel extrapolation

Type of steel	Electrolyte 3% NaCl		
	Corrosion potential (mV)	Corrosion current (μA)	Corrosion rate (mm/year)
X5CrNi18-10	-447	15,32	1,832
S235JR	-626	3,48	0,4166

For tested steel S235JR were used three different concentrations of rosemary extracts as a corrosion inhibitor. The results are shown in Figure 3, and the corrosion parameters have been presented in Table 2.

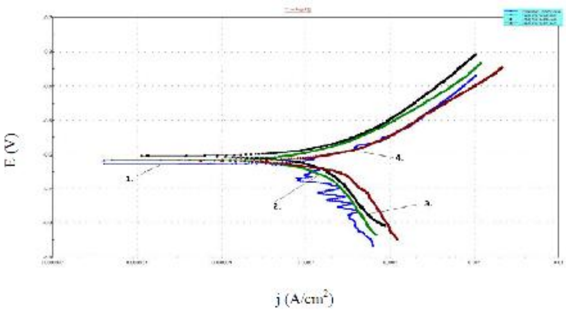

Figure 3. Tafel diagrams for steel S235JR in 3% NaCl solution with different concentrations: (1) steel without inhibitor; (2) 0.005 mg / ml;(3) of 0.01 mg/ml (4) of 0.1 mg/ml inhibitor

Table 2. Corrosion indicators for the plant extract of rosemary as an ecologically acceptable corrosion inhibitors for steel S235JR in 3% NaCl solution.

c_{inh} (mg/ml)	j_{corr} (μA/cm²)	B_k (mm/year)	E_{corr}	Z_{inh} (%)
Without inhibitor	3,48	0,4166	-626	-
0,005	2,27	0,2712	-616	34,90
0,01	3,20	0,3831	-604	8,04
0,1	8,03	0,9608	-616	-

As it can be seen from the diagram (Figure 3), polarization curve is shifted towards the left (curve 2),

which means that the presence of the inhibitor at a concentration of 0.005 mg/ml reduces the corrosion rate.
On the basis of certain corrosion parameters by Tafel extrapolation method (Table 2), it can be seen that in the investigated concentration range the lowest rate of corrosion is at the concentration of inhibitors of 0.005 mg/ml and it amounts to 0.2712 mm/year and its effectiveness amounts to 34.90%. By further increasing of the concentration to 0.01 mg/ml inhibitory effect continues, because the corrosion rate (0.3831 mm/year) is still lower than the rate of corrosion of the examined steel without the presence of the inhibitor (0.4166 mm/ year). At a concentration of 0.1 mg/ml inhibitor functions as an activator because the corrosion rate is higher than the rate of corrosion without inhibitor.
Figure 4. shows the anodic and cathodic polarization curves X5CrNi18-10 in the electrolyte with inhibitor addition (rosemary) in different concentrations (Table 3). The polarization curve shifts to the left (curve 2, 3, 4, 5) ie. the presence of inhibitor at the concentration of 0,01 mg/ml; 0,1 mg/ml; 0,3 mg/ml and 0,4 mg/ml reduces the corrosion rate. On the basis of certain corrosion parameters by Tafel extrapolation method in Table 3 we can see that in the investigated concentration range the lowest rate of corrosion is at the concentration of inhibitors of 0.3 mg/ml and it amounts to 0.03642 mm/-year, and its efficiency amounts to 98.01%.

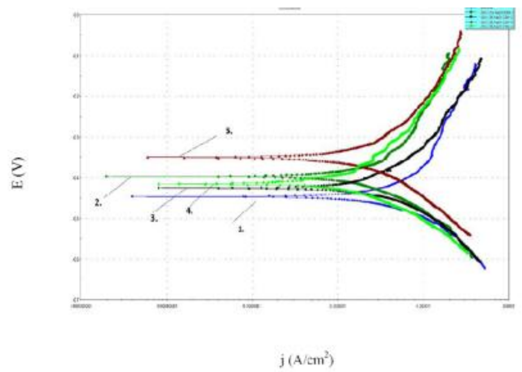

Figure 4. Tafel diagrams for steel X5CrNi18-10 in 3% NaCl solution (1) steel without inhibitor (2) 0.01 mg / ml; (3) 0.1 mg / ml; (4) 0.3 mg / ml; (5) 0.4 mg / ml;

Table 3. Corrosion indicators for plant extract of rosemary as an ecologically acceptable corrosion inhibitors for steel X5CrNi18-10 in 3% NaCl solution.

c_{inh} (mg/ml)	j_{corr} (μA/cm^2)	B_k (mm/year)	E_{corr}	Z_{inh} (%)
Without inhibitor	15,32	1,832	-447	-
0,01	6,35	0,07597	-398	95,85
0,1	5,82	0,06965	-425	96,20
0,3	3,04	0,03642	-419	98,01
0,4	5,0	0,05983	-347	96,73

CONCLUSION

As the obtained results have shown, rosemary (*Rosmarinus officinalis* L), as the "green inhibitor", can be applied in order to reduce the corrosion rate. For steel S235JR, examined by Tefal extrapolation in 3% NaCl solution with the addition of rosemary, the best results were obtained with the inhibitor concentration of 0.005 mg/ml.
It has been proven that the applied "green inhibitor" has better properties with regard to decreasing of corrosion rate for steel X5CrNi18-10. Based on the corrosion parameters obtained by Tafel extrapolation method in the investigated concentration range of rosemary as a corrosion inhibitor, it has been shown that the lowest rate of corrosion is at a concentration of 0.3 mg/ml.
Test results have shown that rosemary has a high efficiency for the protection of steel X5CrNi18-10 in 3% NaCl solution (98.01%) at a concentration of 0.3 mg/ ml.
Results obtained by DC techniques (by Tafel extrapolation method) have shown that the investigated inhibitor of certain concentration can be used as a "green inhibitor" of corrosion for both steels tested in this paper.

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Summary/Sažetak

Posljednjih godina, zbog većeg interesa i pozornosti svijeta prema zaštiti okoliša dolazi do potpunog smanjenja odnosno upotrebe određenog broja korozionih inhibitora. Inhibitori korozije su tvari koje dodane u maloj količini u agresivni medij mogu u velikoj mjeri smanjiti brzinu korozije metala. Pri razvoju korozonih inhibitora potrebno je posebnu pažnju obratiti na njihovu toksičnost te uticaj na onečišćenje okoliša. Istraživanje ekstrakata biljaka u zadnje vrijeme je područije visokog interesa kada je riječ o inhibitorima korozije. Ispitivanje mogućnost zaštite čelika je vršeno sa biljnim materijalom (*Rosmarinus officinalis* L.*)*. U cilju određivnja osnovnih parametara koji pokazuju efikasnost zelenih inhibitora izvršena su elektrohemijska ispitivanja brzine korozije. Rezultati dobiveni DC- tehnikama (metodom Tafelove ekstrapolacije) pokazali su da se brzina korozije smanjuje u prisustvu ispitivanih inhibitora korozije. Istraživanja su pokazala da ružmarin (*Rosmarinus officinalis* L.*)* ima pri određenoj koncentraciji djelotvornost zaštite čelika u 3% NaCl-u, te kao takvom se smatra prihvatljivim inhibitorom korozije.