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Study of an Anthocyanins as a Corrosion Inhibitor for Aluminum Alloy EN AW-2024 in acidic media

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Abstract. **The paper presents the results from a study of the possibility to use Bilberries anthocyanins as a corrosion inhibitor for aluminum alloy EN AW-2024 in 1 M solution of HCl. In this study the model system between Bilberries anthocyanins and metal was investigated. The inhibitory effect of Bilberries anthocyanins on the corrosion of aluminum alloy EN AW-2024 in 1M HCl was investigated by electrochemical methods and mathematical analysis to validate the results. The absorption was determined from 25 °C. The results show that Bilberries anthocyanins exhibits a good inhibitory effect on the corrosion of the aluminium alloy EN AW-2024 in 1M HCl. The reason for the good inhibitory effect is the adsorption of the inhibitor molecules on the surface of the aluminum alloy.**

Keywords: corrosion inhibition, aluminum alloy, mathematical model, anthocyanins.

I. Introduction

Aluminum alloys are widely used in the industrial industry and are often in contact with process media that destroy them. There are various methods of protecting metals from corrosion, one of them being the use of environmental corrosion inhibitors.

Depending on their chemical composition, environmental inhibitors are divided into inorganic (rare earth compounds [1]-[3] and organic environmental inhibitors (organic acids, amino acids, biopolymers, plant extracts and essential oils [4]-[5]. The use of plant extracts of Aloe vera [6], Lavandula angustifolia [7] and Rosmarinus officinalis [8]-[10] are common as environmental corrosion inhibitors in various corrosive environments.

Bilberry is one of the richest natural sources of anthocyanins, which are polyphenolic, glycoside-containing compounds coloring plant parts red, purple, and brown [11]. The two major anthocyanins in the composition of bilberries are malvidin-3-glucoside and malvidin-3-galactoside.

These compounds contain aromatic nuclei in their structure that can be bonded to metal surfaces by π-π electronic reaction.

This property of anthocyanins makes them suitable for use as corrosion inhibitors [12].

In the present paper, the feasibility of using bilberry extract as an environmental corrosion inhibitor of EN AW-

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2024 aluminum alloy in 1M HCl was investigated by spectrophotometric study to establish the inhibitory effect of the two major anthocyanins in the composition of bilberry and electrochemical measurement to determine the corrosion parameters. The existence of a correlation relationship between corrosion rate [µm/h] and inhibitor concentration [µpy] was also investigated using SPSS 25.0 using correlation and regression analysis methods.

II. Materials and methods

The materials used were HCl; the pigment anthocyanins from bilberries; aluminum alloy EN AW-2024.

Plant materials were prepared from fresh fruits from bilberries were put in polyethylene bags, frozen immediately and stored at – 18°C until extracted.

Extraction, purification and determination of anthocyanins carry out frozen bilberries was thawed. The homogenised purée was extracted overnight at 4°C using ethanol acidified with hydrochloric acid (1%, v/v) .

Spectrophotometric measurements were performed with UV-Vis spectrophotometer SPEKOL 11. The absorption spectra of model solutions were measured from 400 to 700 nm. The study was conducted at 25°C.

Electrochemical measurements were carried out using a Princeton Applied Research potentiostat/galvanostat (model 263A) at room temperature. The obtained data were processed with the PowerSuite program. A three-electrode cell composed of a working electrode of the investigated EN AW 2024 aluninium alloy, an auxiliary electrode of platinum wire and a reference electrode of saturated Ag/AgCl electrode was used.

The area of the working electrode was 1 cm^2 and the rest of its surface was coated with varnish.

The open circuit potential (OCP) measurement was performed after immersing the working electrode in the test solution of 1 M HCl without and in the presence of bilberry extract at a concentration from 0,00008 to 0,00048 mM (until steady state was reached (200 seconds). Potentiodynamic polarization was performed at an autotonic potential change from -0.250 V to +0,250 V, relative to open circuit potential, at a scan rate of 0,16 mV/s.

Correlation and regression analysis

We will check whether the model is adequate at the significance level of the F criterion. Adequate models are those in which Sig. < 0.05, and then the statistically significant values of the regression coefficients are interpreted.

The relationship between two phenomena (factors) Y and X is investigated using single-factor regression models. Most often, Y is the dependent variable (effect) and X is the explanatory factor. The general form of the single-factor regression model is represented by the formula:

$$Y_i = f(X_i, \varepsilon_i),$$

where:
Y_i is the dependent variable or the effect variable
X_i is the explanatory variable or factor
ε_i is the random component in the model.

In the course of data analysis, the following statistical tables were obtained:

TABLE 1 ANOVA

ANOVA[a]

Model		Sum of Squares	df	Mean Square	F	Sig.
1	Regression	25,457	1	25,457	20,280	,046[b]
	Residual	2,511	2	1,255		
	Total	27,968	3			

a. Dependent Variable: CR[mpy].E-06
b. Predictors: (Constant), c [mM]

TABLE 2 COEFFICIENTS

Coefficients[a]

Model		Unstandardized Coefficients		Standardized Coefficients			Correlations			Collinearity Statistics	
		B	Std. Error	Beta	t	Sig.	Zero-order	Partial	Part	Tolerance	VIF
1	(Constant)	13,776	2,323		5,929	,027					
	c [mM]	-28205,250	6263,264	-,954	-4,503	,046	-,954	-,954	-,954	1,000	1,000

a. Dependent Variable: CR[mpy].E-06

TABLE 3 COLLINEARITY DIAGNOSTICS

Collinearity Diagnostics[a]

Model	Dimension	Eigenvalue	Condition Index	Variance Proportions	
				(Constant)	c [mM]
1	1	1,970	1,000	,01	,01
	2	,030	8,172	,99	,99

a. Dependent Variable: CR[mpy].E-06

TABLE 4 MODEL SUMMARY

Model Summary

Model	R Square	Adjusted R Square	Std. Error of the Estimate
,954	,910	,865	1,120

1

In Table 4 Model Summary, the correlation analysis values are calculated. The value of the correlation coefficient (R) is equal to 0.954, which means that there is a correlation relationship between the factor (independent variable) X, which in this case is inhibitor concentration [mM] and the effect (dependent variable) Y (corrosion rate CR [mpy]). The value of the coefficient ranges from 0 to 1, from which it follows that a unidirectional correlation relationship is observed between X and Y.

The second tool of correlation analysis is the coefficient of determination (of determinacy) - R square, whose value measures the strength of influence of the factor X on the consequence Y. In this case, the value of the coefficient of determination is 0,910(91%), which means that 91% of the differences in the corrosion rate CR [mpy] are due to different values of the inhibitor concentration factor C[mM].

The third tool of correlation analysis is the coefficient of indeterminacy (of uncertainty), whose value is obtained by the rule: 100%- R square. In this case, the value of the coefficient of indeterminacy is 100%-91%= 9%. The resulting value measures the strength of the influence on the consequence Y of factors other than the factor X. The 9% value indicates that 9% of the variation in corrosion rate CR[mpy] is under the influence of factors other than inhibitor concentration C[mM].

From the table containing the values of the model parameters, it is clear that the parameters of the linear model are statistically significant since the sig. values are less than 0,05 and the model used (linear) is adequate to investigate the relationship between the variables. Column B of Table 2 contains the values of the unstandardized regression coefficients for the trait factor, which value carries information about how much the corrosion rate CR[mpy] would change if the inhibitor concentration factor C [mM] were increased by one. Only those regression coefficients whose significance level sig. in the Coefficients table is less than the selected level of agreement $\boldsymbol{\alpha}$(<0,05) are interpreted.

The function defining the relationship between the explanatory variables and the outcome variable has a general form:

$$Y = b_0 + b_1 x_1 + \varepsilon_i$$

where:
Y is the dependent variable;
b_0 - a constant that has no clear scientific interpretation;
b_1 - a coefficient that carries information about the correlation of a factor X_1;
ε_i - accidental error;

The dependency has the form:
Corrosion rate CR [mpy] = 13,776 - 28205,25* Inhibitor concentration C [mM] $+\varepsilon i$

III. Results and Discussion

Spectrophotometric measurements

From the study it was found that the absorption of the ethanolic extract of anthocyanins reaches a maximum value at a wavelength of 525 nm, after which it decreases (fig. 1).

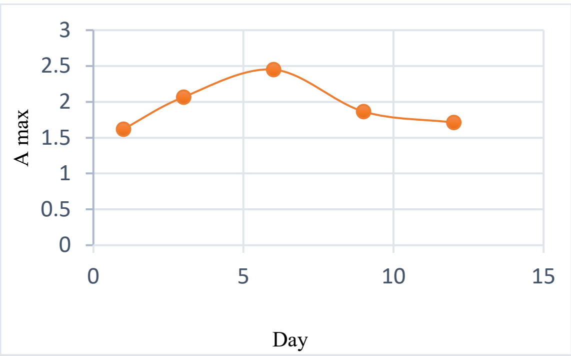

Fig. 1. The variation of absorbance with time at maximum wavelength and temperature 25 ^{0}C.

Electrochemical measurements

The open circuit potential of EN AW-2024 aluminium alloy in 1M HCl in the absence and presence of ethanolic extract of bilberry is shown in Figure 2. On comparing the E_{OCP} values of the studied alloy, it is observed that with increasing inhibitor concentration from 0,00008 to 0,00048 mM, the E_{OCP} values shift in more positive direction as its value remains relatively constant (between -0,550 V and -0,553 V) compared to the E_{OCP} values without inhibitor (-0,566 V). This deviation of E_{OCP} is probably due to the inhibitory action of bilberry extract and is related to the decrease in the degradation of the alloy studied. The shift of the potential value in a more positive direction after obtaining bilberry extract indicates the good adsorption of the inhibitor molecules on the surface of the aluminium alloy. By forming a protective, inhibitory layer on the metal surface, bilberry extract reduces the degradation of the alloy.

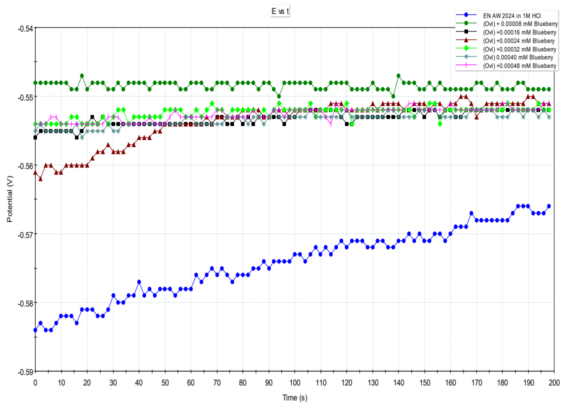

Fig. 2. Open circuit potential of EN AW 2024 alloy in 1 M HCl in the absence and in the presence of Bilberry.

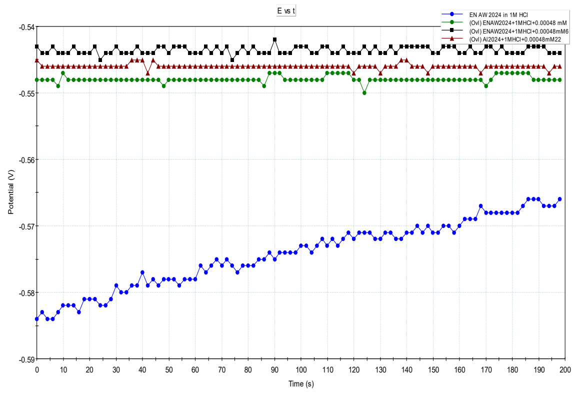

Fig. 3. Open circuit potential of EN AW 2024 alloy in 1 M HCl in the absence and in the presence of 0,000 48 mM Bilberry after 6 and 22 days.

Figure 3 presents the results of measuring the open circuit potential of EN AW-2024 aluminium alloy in 1M HCl in the absence and presence of ethanolic extract of bilberry at a concentration of 0,00048 mM by tracking the effect of the inhibitor over time 2, 6 and 22 hours. It is observed that over the time studied, the E_{OCP} value of aluminium alloy EN AW-2024 in 1M HCl presence of bilberry extract remains constant and is more positive compared to the E_{OCP} values without inhibitor, indicating that bilberry extract retains its inhibitory action and continues to protect the metal surface from the destructive action of hydrochloric acid.

Table 5 presents the corrosion current (Icorr), corrosion rate (CR), surface coverage (θ) and inhibition effect (η %) values of aluminium alloy 2024 in 1 M HCl without and in the presence of an inhibitor, ethanol extract of bilberry.

The inhibitory effect (η %) was calculated using the following equation:

$$\eta\ \% = \frac{I_{corr} - I'_{corr}}{I_{corr}} \cdot 100 \quad (1)$$

where Icorr and I'corr the value of corrosion current in the absence and presence of inhibitor, respectively.

TABLE 5 ELECTROCHEMICAL PARAMETERS OF EN AW 2024 IN 1 M HCL IN THE ABSENCE AND IN THE PRESENCE BILBERRY

c, mM	I_{corr} (μA)	CR(mpy)	θ	η %
blank	7,377	9.852	-	-
0,00024	5,894	7,872	0,2021	20,21
0,00032	2,726	3,641	0,6250	62,50
0,00040	1,583	2,114	0,7896	78,96
0,00048	0,644	0,8596	0,9127	91,27

Data showed that the magnitude of the corrosion current decreased significantly with increasing concentration of bilberry extract, probably due to the formation of a barrier film on the alloy surface. At the same time, the inhibitory effect increased with increasing the concentration of bilberry extract and the maximum was 91,27% at 0,00048 mM concentration of bilberry extract.

Mathematical model

Interpretation of the obtained values of the regression coefficients:

$\boldsymbol{b0}$ = 13,776 - no clear scientific interpretation, but its inclusion in the model is justified for the following reasons:

- contains unaccounted for influences of existing factors;
- contains measurement errors;
- contains biases due to the use of inadequate models.

The $\boldsymbol{b1}$ = - 28205,25 carries information about the sought correlation relation between the factor X and the consequent Y. This value is different from 0, which means that a correlation relationship exists between the factor (independent variable) X, which in this case is inhibitor concentration C [mM] and the consequence (dependent variable) Y (corrosion rate). The value of the coefficient is greater than 0, from which it follows that as the value of the factor (independent variable) X increases for Y the consequence (dependent variable) Y (corrosion rate) will exhibit a unidirectional correlation relationship (fig. 4).

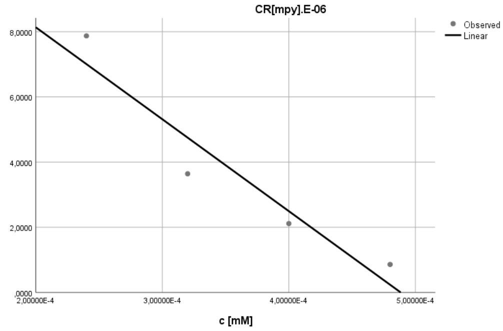

Fig.4. Corrosion rate graph = f (Inhibitor concentration)

The value of the regression coefficient also indicates by how many units the theoretical value of the outcome variable changes if the factor variable is increased by one unit. It is an average change because the relationship is correlational and not functional.

IV. CONCLISIONS

Based on the data obtained, it can be concluded that the ethanol extract of bilberry demonstrated a good inhibitory effect on the corrosion of EN AW-2024 aluminum alloy in hydrochloric acid (91,27%). The results obtained in this study indicate that with increasing concentrations of the inhibitor, the values of corrosion current and corrosion rate of the studied alloy decreased. There is a strong correlation relationship between the inhibitor concentration factor C [mM] and the consequent (dependent variable) Y corrosion rate, and increasing the inhibitor concentration C [mM] by 1, the theoretical value of corrosion rate CR [mpy] decreases by 28205,25 E-06.

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REFERENCES

[1] M. Arenas, M. Bethencourt, F. Botana, J. Damborenea, M. Marcos, "Inhibition of 5083 aluminium alloy and galvanized steel by lanthanide salts," Corr. Sci., 43, pp. 157-170, 2001.

[2] M.Bethencourt,F. Botana,J. Calvino,M.Marcos, M.Rodriguez-Chacon," Lanthanide compounds as environmentally-friendly corrosion inhibitors of aluminium alloys," Corr. Sci.40, pp. 1803-1819,

[3] J.De Damborenea, A. Conde,M. Arenas, "3 - Corrosion inhibition with rare earth metal compounds in aqueous solutions Rare Earth-Based," Woodhead Publishing, pp. 84-116,2014.

[4] A.El-Azaly, "Influence of Soybean (Glycine Max) plant extract on corrosion of aluminum in 1M HCl," Int. J. Electrochem. Sci.,14, 2714-2731,2019.

[5] J.Wysocka, S. Krakowiak, J.Jacek, Ryl, K. Darowicki. Citric acid as corrosion inhibitor for aluminium alloys in aqueous alkaline environments. Conference: 7th Kurt-Schwabe-Symposium At: University of Applied Sciences. Mittweida, Germany,2016.

[6] A.Al-Turkustani, S. Arab, R. Aldahiri, "Aloe plant extract as environmentally friendly inhibitor on the corrosion of aluminum in

hydrochloric acid in absence and presence of iodide ions," Mod. Appl. Sci 4, pp. 105-124,2010.

[7] J.Halambek, K. Berkovii, J. Vorkapid-Furat, "The influence of Lavandula angustifolia L. oil on corrosion of Al-3Mg alloy," Corr. Sci.,52, pp. 3978-3983, 2010.

[8] J.Radošević, M. Kliškić, A.Višekruna, "Inhibition of corrosion of the Al-2.5Mg alloy by means of the third acidic phenolic subfraction of aqueous extract of Rosemary," Kem. Ind., 2001, 50, pp. 537–542, 2001.

[9] M.Kliškić, J.Radošević, S. Gudić, V.Katalinić, "Aqueous extract of Rosmarinus officinalis L. as inhibitor of Al–Mg alloy corrosion in chloride solution," J. Appl. Electrochem., 30, pp. 823-830, 2000.

[10] M.Deyab, "Corrosion inhibition of aluminum in biodiesel by ethanol extracts of Rosemary leaves," J. Taiwan Inst. Chem. Eng., 58, pp. 536-541, 2016.

[11] T.Thornthwaite, P.Seth Thibado, A. Kyle, "Thornthwaite. Bilberry anthocyanins as agents to address oxidative stress, " Pathology, Oxidative Stress and Dietary Antioxidants. (17), pp. 179-187, 2020.

[12] Y.Teng , W. Zhang , M. Wang, C. Yu, Y. Ma, J. Bian , X. Yang, D. Zhang. "Anthocyanin as sustainable and non-toxic corrosion inhibitor for mild steel in HCl media: Electrochemical, surface morphology and theoretical investigations," J. Mol. Liqs, " pp.344,2021.