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Corrosion Inhibition of AA 5052 Aluminium Alloy in NaCl Solution by Different Types of Honey

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The inhibitive action of five different types of honey (oak honey (H1), coniferous honeydew honey (H2), winter savory honey (H3), alder buckthorn honey (H4) and carob tree honey (H5)) were tested as potential corrosion inhibitor of AA 5052 aluminium alloy in 0.5 M NaCl solution. Investigation was performed by electrochemical methods such as linear and potentiodynamic polarization and impedance spectroscopy measurements. The inhibition efficiency was found to increase with increase in honey concentration and inhibition efficiency changes in the following sequence: H3 < H5 < H4 < H2 < H1. Results of polarization behaviour have shown that all tested honeys act as mixed type inhibitors with a higher influence on anodic reaction, as expressed in particular for H1 and H2. The adsorption behaviour of investigated inhibitors can be described by the Langmuir adsorption isotherm and the values determined for standard free adsorption energy indicate physical adsorption of organic compounds from honey on the surface of AA 5052 aluminium alloy in NaCl solution.

Keywords: honey, aluminium alloy, corrosion, electrochemical techniques, Langmuir adsorption isotherm

1. INTRODUCTION

The unique combinations of properties provided by aluminium and its alloys make aluminium one of the most versatile, economical and attractive metallic materials for a broad range of uses - from soft, highly ductile wrapping foil to the most demanding engineering applications [1]. Al-Mg alloys have found wide application in shipbuilding, chemical and food industry. Therefore, aluminium alloy AA 5052 have been use for production of pressure vessels, fan blades, tanks, automotive parts, chemical equipment, cooking utilities, food packaging, etc. [1]. However, despite their apparent advantages, the applications of aluminium alloys sometimes were hampered by their corrosion in aggressive environments, especially in media containing chloride ions.

In efforts to mitigate corrosion of aluminium alloys, the main strategy is to effectively isolate the metal from corrosive agents, which can be achieved by the use of corrosion inhibitors [2]. Some effective corrosion inhibitors, such as chromates, nitrates, arsenates, etc., have a negative influence on the environment and for these reasons are nearly forbidden for practical use in various countries [3,4]. As a consequence, this problem has stimulated an active search for alternative, ecologically safe corrosion inhibitors. Some investigators focus their research on natural products as potential corrosion inhibitors [5-13]. Natural honey is relatively healthy and easy digestible foodstuff which contains a range of nutritiously important complementary organic compounds such as saccharides, organic acids, amino acids, polyphenols, aromatic substances and vitamins [14]. Honey is also relatively cheap and readily available, so it fulfils the requirements for the nontoxic corrosion inhibitors. El-Etre published first papers on the topic of metal corrosion inhibition using honey [15-16]. Investigations of Rosliza and associates have shown that natural honey is a mixed-type corrosion inhibitor for Al–Mg–Si alloy in seawater [17]. The influence of natural honey with black radish juice, on the corrosion of tin in aqueous and sodium chloride solutions was studied by Radojčić et al. [18]. It was found that the addition of black radish juice increased the inhibition efficiency of honey. Emad and Al-Rasheedi found that natural honey is effective corrosion inhibitor for copper in cooling water system [19].

The present work is devoted to study the inhibitive properties of five different types of natural honey as safe and environmentally friendly corrosion inhibitors for aluminium alloy AA 5052 in 0.5 M NaCl solution. In this paper, for the first time, a possible corrosion inhibition effect of honeydew honey is examined. Unlike floral honeys, which derive from the nectar of flowering plants, honeydew honey is obtained by secretions of living parts of plants or excretions onto them produced by sap-sucking insects [20]. Along with honeydew honey, four different types of floral honey, which are distinguish by their color, were examined as potential corrosion inhibitors for aluminium alloy AA 5052 in 0.5 M NaCl solution.

2. EXPERIMENTAL

Electrochemical measurements were performed in a conventional three-electrode glass cell (equipped with saturated calomel electrode (SCE) as reference and platinum sheet as a counter electrode) using a potentiostat/galvanostat (PAR M273A) and "lock-in" amplifier (PAR M5210) connected with personal computer.

A cylindrical sample of AA 5052 aluminium alloy with the composition of 97.20% Al, 2.50% Mg and 0.25% Cr was used as working electrode. Sample was isolated with Polirepar S resin leaving exposed alloy surface area of 0.5 cm^2.

Before being used, aluminium alloy were abraded with a series of emery papers with different grades (400 – 1000). In order to remove the surface oxide layer and optionally the entered impurities, electrode was immersed for 1 minute in 0.1 M NaOH solution (T = 40 °C) washed with deionised water and placed in the electrochemical cell.

For all measurements in this study as a main electrolyte was used 0.5 M NaCl solution. The solution was prepared by dissolving of analytical grade purity NaCl salt in deionized water. The following types of honey were tested as potential corrosion inhibitor of Al alloy: oak honey (H1), coniferous honeydew honey (H2), winter savory honey (H3), alder buckthorn honey (H4) and carob tree honey (H5). Honey solutions (from H1 to H5) was prepared by dissolving of 0.4, 0.6, 0.8, 1.0 and 1.2 g honey in the electrolyte (0.5 M NaCl) to achieve honey concentrations: 400, 600, 800, 1000 and 1200 ppm. All measurements were performed on 20 ^{o}C, with deaeration by purging pure argon into the solution.

Corrosion behaviour of AA 5052 aluminium alloy was investigated by potentiodynamic polarization method, linear polarization method and electrochemical impedance spectroscopy measurements (EIS).

The potentiodynamic polarization measurements were performed in potential region of ± 250 mV vs. E_{OC}, with the scanning rate of 0.5 mV s^{-1}. The polarization resistance, R_p, was determined from the slope of polarization curves obtained by measurements in the potential range ± 20 mV vs. E_{OC}, with the scanning rate of 0.2 mV s^{-1}. Impedance measurements were carried out in the frequency range of 50 kHz to 30 mHz, with the perturbation signal amplitude of 10 mV.

All measurements were performed after 60 min electrode stabilisation on E_{OC} in NaCl solution without and with addition of honey.

3. RESULTS AND DISCUSSION

3.1. Potentiodynamic polarization measurements

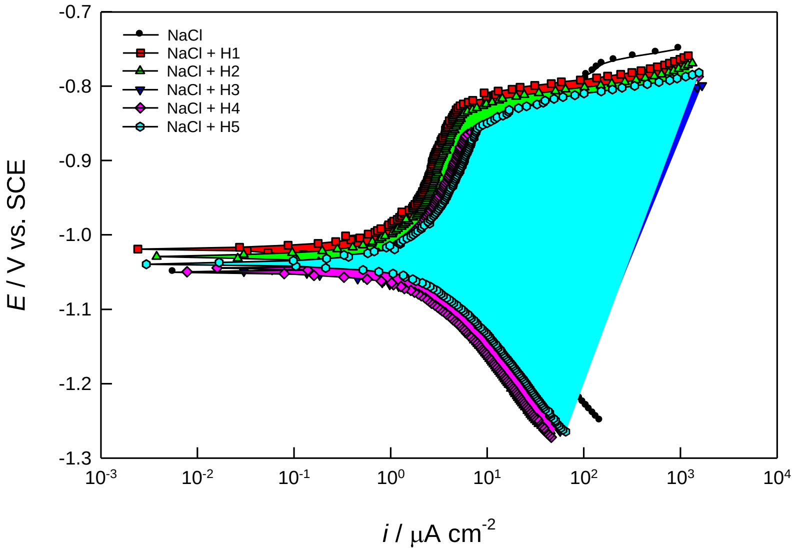

Figure 1. Potentiodynamic polarization curves for AA 5052 aluminium alloy in 0.5 M NaCl solution containing different types of honey in concentration of 1000 ppm

The nature of the corrosion inhibition process may be determined on the basis of polarization measurements. Thus, changes in the polarization curves after the addition of inhibitors typically are used as criteria for classification an inhibitor as cathodic, anodic or mixed type [21].

Typical potentiodynamic polarization curves for AA 5052 aluminium alloy in NaCl solution in the absence and presence of different types of honey in concentration of 1000 ppm are shown in Fig. 1.

On the polarization curve for Al alloy in NaCl solution, a tight passive area is observed just above the corrosion potential in the potential range from ≈ -1.0 V to ≈ -0.8 V. In this potential area growth of the oxide layer takes place on the alloy surface. Anodic current slowly rises until a so-called breakdown potential is reached (≈ -0.77 V). Above breakdown potential a passive layer breakdown takes place due to the pitting corrosion and andic current rises sharply.

As the solution was deaerated by purging with argon, a cathodic part of the polarization curves probably represent hydrogen evolution reaction.

The presence of dissolved honey causes significant changes in the polarization behaviour of the Al alloy. Depending on the honey type, the reduction of the anodic and cathodic current density along with the slight changes the values of corrosion potential in the anodic side can be observed. Decreasing the catodic current density along with the changes of corrosion potential in cathodic direction are characteristic of cathodic corrosion inhibitors, while decreasing the anodic current density along with the changes of corrosion potential in positive direction is characteristic of anodic corrosion inhibitors. Mixed inhibitors act by reducing both the cathodic and anodic current densities without any significant changes of corrosion potential values [22,23]. Generally, an inhibitor can be classified as cathodic or anodic type if the shift of corrosion potential in the presence of the inhibitor is more than 85 mV with respect to E_{corr} in the absence of the inhibitor [24,25]. Small shift of corrosion potential along with decreasing the anodic and cathodic current densities in the presence of investigated honeys indicated their action as mixed type corrosion inhibitor for AA 5052 aluminium alloy in NaCl solution, with the higher influence on anodic reaction, which was especially pronounced for H1 and H2.

These results are in agreement with the results obtained by Rosliza et al. [17] and Wan Nik et al. [26] who have found that natural honey act as mixed corrosion inhibitor for Al-Mg-Si alloy and AA 7631 alloy in seawater.

Table 1. Corrosion parameters for AA 5052 aluminium alloy in NaCl solution in the presence of different types of honey in concentration of 1000 ppm, determined from potentiodynamic polarization curves

solution	E_{corr} **/ V**	$-b_{\mathrm{c}}$ **/ V dec^{-1}**	b_{a} **/ V dec^{-1}**	i_{corr} **/ μA cm^{-2}**	**Θ**	η **/ %**
NaCl	-1.05	0.157	0.311	6.34		
NaCl + H1	-1.02	0.163	0.310	1.16	0.8170	81.70
NaCl + H2	-1.03	0.165	0.320	1.35	0.7870	78.70
NaCl + H3	-1.05	0.163	0.331	2.51	0.6041	60.41
NaCl + H4	-1.04	0.162	0.287	1.88	0.7035	70.35
NaCl + H5	-1.03	0.165	0.296	2.07	0.6735	67.35

Table 1 shows the electrochemical polarization parameters for AA 5052 alloy in 0.5 M NaCl solution in the presence and absence of different types of honey. The parameters include the corrosion potential (E_{corr}), corrosion current density (i_{corr}), cathodic and anodic Tafel slopes (b_{c}, b_{a}) as well as surface coverage (Θ) and inhibition efficiency (η) which were determined using the relation (1):

$$\eta = \Theta \times 100 = \frac{i_{\mathrm{corr}} - \left(i_{\mathrm{corr}}\right)_{\mathrm{inh}}}{i_{\mathrm{corr}}} \times 100 \qquad (1)$$

where i_{corr} and $(i_{\mathrm{corr}})_{\mathrm{inh}}$ represent corrosion current densities in the absence and presence of inhibitor.

The cathodic and anodic Tafel slopes (b_{c}, b_{a}) were slightly changed (remain almost the same) in the presence of different types of honey. This means that there is no change of the mechanism of the inhibition in presence and absence of inhibitors and that inhibitors act by simply blocking the available surface area.

Inhibitor action can be explained by simple adsorption on the electrode surface and by blocking active sites on the surface, which leads to a reduction of corrosion. In general, the adsorption processes in the metal/solution interface resulting in separation of the solute in solution (inhibitor), and its concentration on the metal surface. This process takes place until the establishment of the dynamic equilibrium between the concentration of the residual solute in the solution and its concentration on the metal surface. Thus, in the adsorption process metal surface is covering with inhibitor which slows down the corrosion of metal.

According to the Table 1 it can be seen that surface coverage and inhibition efficiently increase in the order: H3 < H5 < H4 < H2 < H1. So, the best inhibition efficiency showed the oak honey (81.70% for the concentration of 1000 ppm).

3.2. Linear polarization method measurements

Linear polarization measurements were performed in order to determine the polarization resistance of AA 5052 aluminium alloy in 0.5 M NaCl solution, without and with addition of different types of honey in concentration of 1000 ppm.

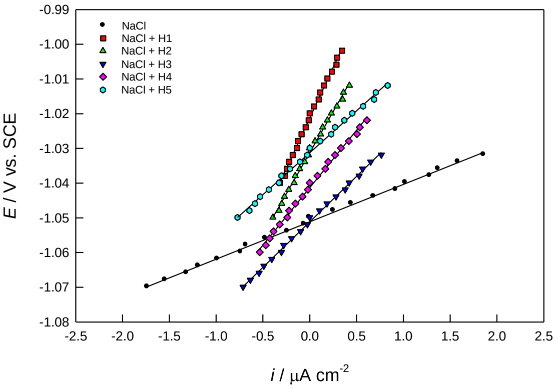

Figure 2. Linear polarization curves for polarization resistance determination of AA 5052 alloy in 0.5 M NaCl solution containing different types of honey in concentration of 1000 ppm

Results of these investigations are shown in Fig. 2. The addition of honey changes the slope of the linear curves, i.e. lead to a rise of curve slopes. The polarization resistance (R_p) can be defined by equation (2):

$$R_\mathrm{p} = \frac{\Delta E}{\Delta i} \tag{2}$$

Thus, increasing the slope of the linear part of polarization curve indicates an increase in the value of polarization resistance. Since the electrochemical theory assumes that $1/R_\mathrm{p}$ is directly proportional to the corrosion rate, the surface coverage (Θ) and inhibition efficiency (η) was calculated from R_p values using the equation (3) [27]:

$$\eta = \Theta \times 100 = \left(\frac{(R_\mathrm{p})_\mathrm{inh} - R_\mathrm{p}}{(R_\mathrm{p})_\mathrm{inh}} \right) \times 100 \tag{3}$$

where R_p i $(R_\mathrm{p})_\mathrm{inh}$ represent the values of polarization resistance in the absence and presence of inhibitor respectively. The values of polarization resistance and the inhibition efficiency for AA 5052 aluminium alloy in investigated honey solution were shown in Table 2.

Table 2. Corrosion parameters for AA 5052 aluminium alloy in 0.5 M NaCl solution in the presence of different types of honey in concentration of 1000 ppm, determined by linear polarization method

solution	R_p **/ kΩ cm^2**	Θ	η / %
NaCl	10.76		
NaCl + H1	58.23	0.8152	81.52
NaCl + H2	47.36	0.7728	77.28
NaCl + H3	26.17	0.5888	58.88
NaCl + H4	35.98	0.7009	70.09
NaCl + H5	30.89	0.6516	65.16

The values of polarization resistance as well as corrosion inhibition efficiency increase in order: H3 < H5 < H4 < H2 < H1. Again, the oak honey shows the best inhibition efficiency (81.52 % for concentration of 1000 ppm).

3.3. Electrochemical impedance spectroscopy measurements

Electrochemical characterization of tested systems Al alloy / NaCl (NaCl + inhibitor) were made using the EIS, and obtained results are shown on Fig. 3.

In Nyquist plot, which represents the ratio of the imaginary (Z_imag) and real (Z_real) components of the impedance, two more or less poorly separated time constants can be observed for all tested inhibitors: time constant or capacitive loop in the high frequencies range and time constant or other capacitive loop in the lower frequency range. Due to overlapping of time constants, based on this graphic display is hard to get a clear physical picture of the observed systems.

A more convenient method, which better shows the frequency dependence of the impedance data (and a clearer distinction between individual time constants) is the so-called Bode diagram, i.e. plots of logarithm of impedance, *Z*, and phase angle, respectively, *vs*. logarithm of frequency, *f*.

In this diagram for all examined systems it is possible to observe three characteristic regions:

- In the high frequency region (*f* > 1 kHz), the log |*Z*| values are low, tending towards constant values, while phase angle values fall rapidly towards 0^{o}. This is a classic resistive response, corresponding to the electrolyte resistance.
- In the medium frequency region (*f* < 10 kHz), the linear log |*Z*| *vs*. log *f* relationship with a slope close to -1 and a phase angle of ≈ -85^{o} mirror the capacitive behavior of the system.
- At the lowest frequencies (*f* < 1 kHz), the phase angle of ≈ -40^{o} and slope of the log |*Z*| vs. log *f* close to -0.5 point towards the presence of a slow diffusion process.

Generally, the overall impedance of the system increased with the honey addition, implying that the electrode surface was more protected.

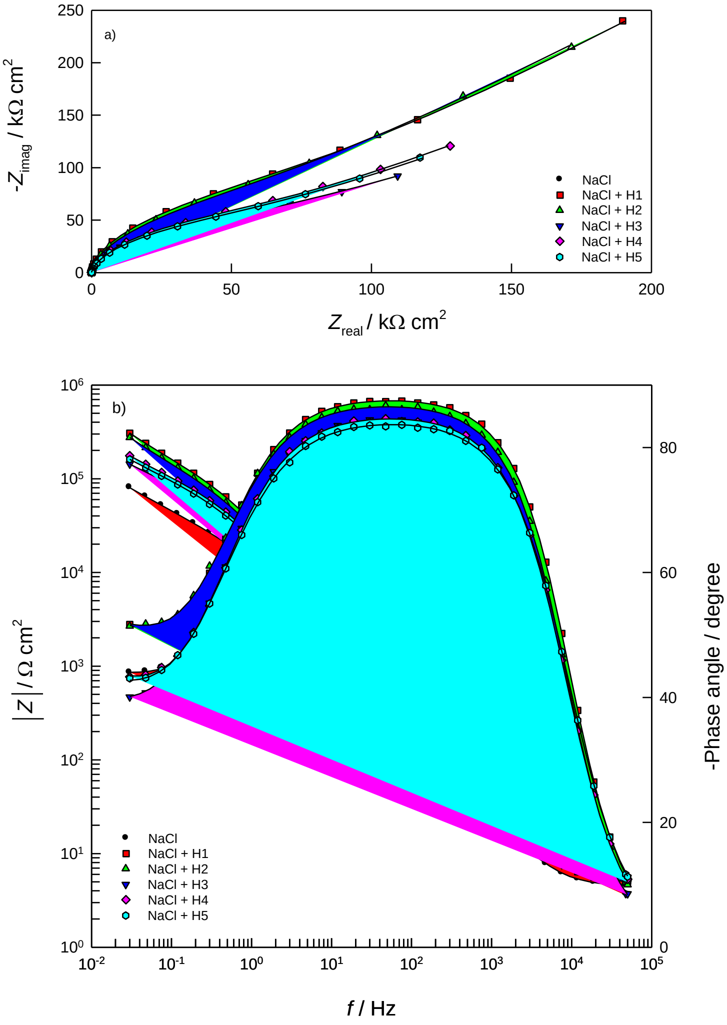

Figure 3. a) Nyquist and b) Bode plots for AA 5052 aluminium alloy alloy in 0.5 M NaCl containing different types of honey in concentration of 1000 ppm

The appearance of more than one time constant in the impedance spectra reflects the diversity of the interfacial phenomena in the systems under investigation. The high frequency time constant is the result of dielectric properties of surface film, while low frequency region of the diagram indicates that the experimental data processing must take into account the mass transfer through the surface layer.

The equivalent circuit proposed to fit the experimental data is shown in Fig. 4, and consists of the following elements: R_{el}, Q_1, R_1 and Q_2. In proposed circuit the R terms represents the ohmic resistance elements, while the Q terms represent constant phase elements (CPE).

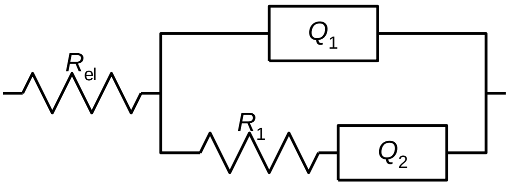

Figure 4. Proposed equivalent circuit for modeling the impedance data

The constant phase element describes the system deviation from ideal behavior. This behavior has not been completely explained physically, but the explanation may be related to non-homogeneity within the surface film mass and the fact that the electrode surface, seen at the microscopic level, is not ideally smooth but has a large number of surface defects, such as projections, cavities, local non-homogeneities of charge etc. [28-33]. The CPE's impedance (Z_{CPE}) corresponds to [29]:

$$Z_{\mathrm{CPE}} = \left[Q(j\omega)^n\right]^{-1} \qquad (4)$$

with $-1 \leq n \leq 1$, $j = \sqrt{-1}$ and $\omega = 2\pi f$, while Q is a frequency independent constant, having the features of pure capacitance when $n = 1$; resistance when $n = 0$; inductance when $n = -1$; while diffusion processes are characterized by $n = 0.5$.

According to the data given in the table 3, the n_1 values for Q_1 are about 0.94, whale the n_2 values for Q_2 are close to 0.51. Hence, Q_1 is a constant phase element (CPE) related to a series connection of double layer and surface film capacitances, while Q_2 represents diffusion process in the surface film. R_1 is the charge transfer resistance and R_{el} is the electrolyte resistance (≈ 5 Ω cm^2).

Table 3. Impedance parameters for the AA 5052 aluminium alloy in 0.5 M NaCl containing different types of honey

solution	**$Q_1 \times 10^6$ / Ω^{-1} s^n cm^{-2}**	**n_1**	**R_1 / kΩ cm^2**	**$Q_2 \times 10^6$ / Ω^{-1} s^n cm^{-2}**	**n_2**
NaCl	10.37	0.94	20.56	30.79	0.41
NaCl + H1	4.24	0.98	118.67	9.45	0.62
NaCl + H2	4.93	0.97	105.91	10.10	0.61
NaCl + H3	7.36	0.95	58.44	19.13	0.49
NaCl + H4	6.18	0.95	75.82	16.74	0.55
NaCl + H5	6.79	0.94	68.37	17.55	0.53

By comparing the different types of honey as corrosion inhibitors of AA 5052 aluminium alloy, it can be seen that the protective properties of the surface layer increase in order: H3 < H5 < H4 < H2 < H1. Namely, the charge transfer resistance (R_1) increase, while the capacity of the surface layer (Q_1) and the diffusion element (Q_2) decrease in the same order.

Furthermore, the decrease in Q_1 provides valid experimental evidence of adsorption of examined inhibitors on alloy surface. Such behavior has been associated with the plate capacitor model, according to which the surface film capacity is inversely proportional to its thickness. Therefore, the reduction of Q_1 in the indicated direction matches the corresponding increase in the thickness of the adsorbed inhibitor layer, which additionally indicated on increase of protective properties of surface layer.

3.4. Honey adsorption on AA 5052 surface

As the oak honey and coniferous honeydew honey proved to be the best corrosion inhibitors for AA 5052 aluminium alloy in NaCl solution, further investigations was focused is assessment of their adsorption on the surface of the alloy.

For this purpose, potentiodynamic and linear polarization measurements were carried out on AA 5052 alloy in NaCl solution in the absence and presence of oak honey (H1) and coniferous honeydew honey (H2) in different concentrations (from 400 to 1200 ppm). Corrosion parameters and inhibition efficiency obtain from potentiodynamic polarization measurements were shown in Table 4.

Table 4. Corrosion parameters for AA5052 aluminium alloy in NaCl solution in the presence of different concentration of oak honey and coniferous honeydew

c / ppm	E_{corr} / V	i_{corr} / μA cm^{-2}	Θ	η / %
0	-1.05	6.34		
		oak honey		
400	-1.04	2.30	0.6372	63.72
600	-1.03	1.84	0.7098	70.98
800	-1.01	1.48	0.7667	76.67
1000	-1.02	1.16	0.8170	81.70
1200	-1.00	0.91	0.8565	85.65
		coniferous honeydew honey		
400	-1.04	2.58	0.5931	59.31
600	-1.04	2.01	0.6830	68.30
800	-1.03	1.72	0.7283	72.83
1000	-1.03	1.35	0.7871	78.70
1200	-1.01	1.10	0.8265	82.65

It can be observed that increasing the concentration of oak honey and coniferous honeydew honey leads to a decrease in corrosion current densities and to change the values of corrosion potential in a positive direction. Values of surface coverage and inhibition efficiency also increased with increase in concentration of both inhibitors. Higher values of inhibition efficiency showed oak honey. Thus, for example, with the highest inhibitor concentration of 1200 ppm:

- oak honey showed inhibition efficiency of 85.65%,
- coniferous honeydew showed inhibition efficiency of 82.65 %.

Values of polarization resistance and inhibition efficiency obtained from linear polarization measurements are shown in Table 5. Generally, R_p values as well as inhibition efficiency increase with increasing honey concentration. Again, better inhibition efficiency shows oak honey (83.15 % for concentration of 1200 ppm).

Table 5. Values of polarization resistance, surface coverage and inhibition efficiency for AA 5052 aluminium alloy in NaCl solution in the presence of different concentration of oak honey and coniferous honeydew

c / ppm	R_p / kΩ cm^2	Θ	η / %
0	10.76		
oak honey			
400	28.22	0.6187	61.87
600	34.61	0.6891	68.91
800	42.07	0.7442	74.42
1000	58.23	0.8152	81.52
1200	63.87	0.8315	83.15
coniferous honeydew honey			
400	24.86	0.5672	56.72
600	29.70	0.6377	63.77
800	35.35	0.6956	6956
1000	47.36	0.7728	77.28
1200	51.97	0.7930	79.30

Equilibrium distribution of concentrations commonly displayed graphically by the adsorption isotherms, which describes the dependence of the surface concentration of the inhibitor or the surface coverage of the inhibitor concentration in the bulk solution. It should be noted that the data in these graphical representations are only valid for the same temperature, or isothermal conditions, since the change of temperature shifts the adsorption equilibrium [34].

To describe the adsorption equilibrium a different adsorption isotherms has been developed [33]. In defining the most favorable mechanism of absorption of honey oak and coniferous honeydew on the surface of AA 5052 aluminium alloy in 0.5 M NaCl, the best fit is achieved with the model of the Langmuir adsorption isotherm, which can be presented by the equation:

$$Kc = \frac{\Theta}{1-\Theta} \quad (5)$$

where c denotes the inhibitor concentration in bulk solution, Θ the surface coverage and K adsorption equilibrium constant. Langmuir adsorption isotherm can be rearranged in the form of line equation [35]:

$$\frac{c}{\Theta} = \frac{1}{K} + c \qquad (6)$$

Thus, the behavior in this model suggests a linear relationship between c and c/Θ, with unit slope and intercept on the ordinate in the amount of 1/*K* (Figs. 4 and 5).

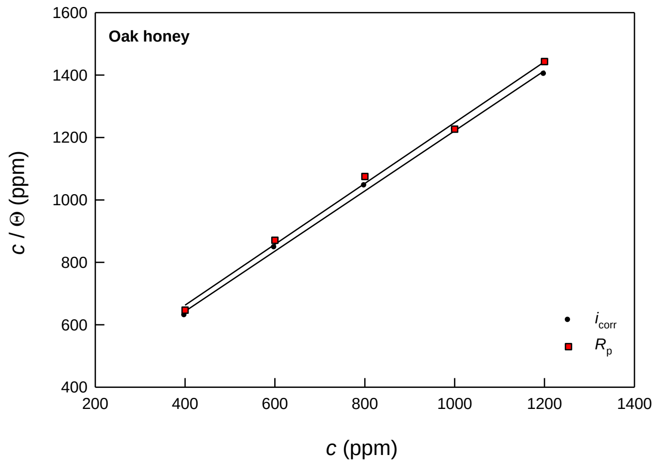

Figure 4. The Langmuir adsorption isotherm for AA 5052 alloy in 0.5 M NaCl at 20 ^{o}C in the presence of oak honey

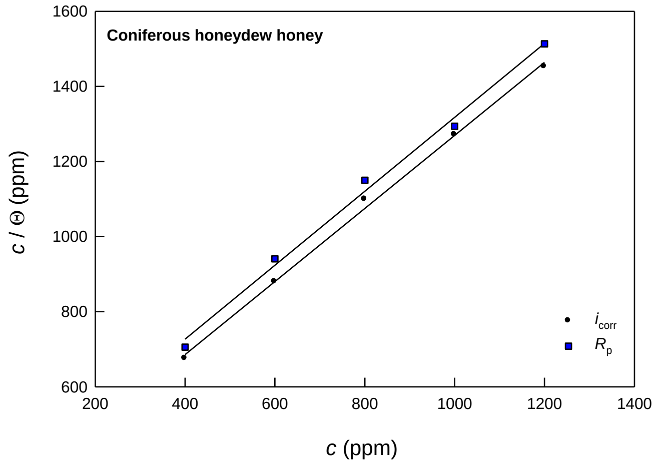

Figure 5. The Langmuir adsorption isotherm for AA 5052 alloy in 0.5 M NaCl at 20 ^{o}C in the presence of coniferous honeydew honey

The results in Figs. 4 and 5 show a linear c/Θ - c dependency, and the slope of the linear dependence was ~1 which confirms the good agreement between experimental results and Langmuir adsorption isotherms.

The equilibrium constant of adsorption, *K*, is linked with the free energy of adsorption ΔG^{o}_{ads} by the equation (7):

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G^{o}_{ads}}{RT}\right) \qquad (7)$$

Therefore, standard free energy of adsorption can be calculated by equation (8):

$$\Delta G^{o}_{ads} = -RT\ln(55.5K) \qquad (8)$$

The value of 55.5 is the concentration of water in the solution in mol dm^{-3}, R is the gas constant and T is the absolute temperature.

The values of adsorption equilibrium constant and free energy of adsorption are shown in Table 6.

Table 6. The values of adsorption equilibrium constant and free energy of adsorption

source	K	ΔG^{o}_{ads} / kJ mol^{-1}
	oak honey	
i_{corr}	3.87	-20.12
R_p	3.67	-19.99
	coniferous honeydew honey	
i_{corr}	3.38	-19.79
R_p	3.00	-19.50

The negative values of ΔG^{o}_{ads} ensures the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. According to the values of standard free energy it is possible to assess the mechanism of inhibitor adsorption on the metal surface. For physical adsorption the values of ΔG^{o}_{ads} are around -20 kJ mol^{-1} or lower, while for chemisorption the values of ΔG^{o}_{ads} are from -40 kJ mol^{-1} or higher and involve charge sharing or a transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond [36]. Calculated values of ΔG^{o}_{ads} (-20.12 kJ mol^{-1} and -19.99 kJ mol^{-1} for oak honey i.e. -19.97 kJ mol^{-1} and -19.50 kJ mol^{-1} for coniferous honeydew honey) indicate physical adsorption of oak honey and coniferous honeydew honey components on the surface of AA 5052 alloy in NaCl solution. Measurement method doesn’t have significant influence on the values of thermodynamic parameters.

It is very difficult to perform a complete chemical analysis of honey due to its very complex composition, which vary depending on the floral source, and external factors such as the season and environment [37-39]. More than 600 compounds were identified as honey volatiles in different chemical families originated from various biosynthetic pathways [39]. Therefore, most authors examined only pollen spectrum along with phisicochemical parameters of different types of honey, which include water content, electrical conductivity, pH values, free acidity, sugar content etc., without performing chemical analysis of honey organic compounds [40-43].

Due to the fact that honey is a mixture of various compounds containing oxygen as well nitrogen and sulphur (such as saccharides, organic acids, amino acids, polyphenols, mineral matter, aromatic substances, trace amounts of fat, enzymes and vitamins), which all potentially can be adsorbed on the corroded metal it is hard to decide which of these components is responsible for this inhibition.

In recent years many investigations were devoted to antioxidant properties of different honey types [44-47]. It was found that dark honeys have the highest level of total phenolic compounds and antioxidant activities [20,46,47]. In our investigation of corrosion inhibition properties of 5 different types of honey, we have found that dark honeys (coniferous honeydew honey and oak honey) showed better corrosion inhibition properties, which could be related due to high level of phenolic compounds in its composition.

4. CONCLUSIONS

Results of the corrosion inhibition investigation of AA 5052 aluminium alloy in 0.5 M NaCl solution by different types of honey (oak honey (H1), coniferous honeydew honey (H2), winter savory honey (H3), alder buckthorn honey (H4) and carob tree honey (H5)) have shown:

- The presence of honey lower corrosion attack on AA 5052 aluminium alloy in NaCl solution.
- Inhibition efficiency of different types of honey changes in the following sequence: H3 < H5 < H4 < H2 < H1. Increase in honey concentration leads to increase in inhibition efficiency. The best inhibition efficiency of (≈ 86 % for 1200 ppm) shows oak honey (H1).
- The results of impedance measurements have shown that in the presence of honey 3D layer formed on the surface of AA 5052 alloy consisting of an inhibitor and the corrosion products. This surface layer acts as a physical barrier and prevents direct contact of metal with the aggressive environment and thus the corrosion of metals. The protective properties of the surface layer increase in order: H3 < H5< H4 < H2 < H1.
- The adsorption behaviour of investigated inhibitors can be described by the Langmuir adsorption isotherm. The values determined for standard free adsorption energy were from -19.50 kJ mol^{-1} to 20.12 kJ mol^{-1} which indicate physical adsorption of organic compounds from honey on the surface of AA 5052 aluminium alloy in NaCl solution.

ACKNOWLEDGEMENTS
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