

The Inhibition Effect of Mad Honey on Corrosion of 2007-Type Aluminium Alloy in 3.5% NaCl Solution

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The inhibition effect of mad honey on corrosion of 2007-type aluminium alloy in 3.5% NaCl solution was investigated by Tafel extrapolation (TP), electrochemical impedance spectroscopy (EIS) and dynamic electrochemical impedance spectroscopy (DEIS). All the studied parameters exhibited good anti-corrosive properties against corrosion of 2007-type aluminium alloy in the test solution; the corrosion rates decreased with the increase of the mad honey concentration. The surface morphology of the alloy was examined under scanning electron microscopy (SEM) in the absence and presence of the inhibitor. The inhibitory adsorption processes of mad honey on the 2007-type aluminium alloy surfaces conformed to the Langmuir adsorption isotherm.

Keywords: aluminium, corrosion, inhibitor, mad honey

1. Introduction

Aluminium is a lightweight metal (density = 2.71 g/cm³) having good electrical and thermal conductivity combined with good atmospheric corrosion resistance as well as corrosion resistance to many aqueous media¹. Despite its cost, this remarkable combination of qualities makes aluminium a highly popular choice for many critical applications in the fields of aerospace, automotives, food handling, construction, heat exchange, and electrical transmission². The importance of aluminium alloys, especially in the automotive and aviation industries, has been growing in recent years. The automotive industry is greatly interested in using aluminium alloys because of their potential to reduce fuel consumption and exhaust emissions³. For every kg of aluminium used as structural material in a car, the CO₂ (eq) emissions are reduced by 19 kg during the life-cycle of the vehicle⁴.

An alternative to chromate-based coatings for the protection of aluminium alloys is greatly needed⁵⁻⁷, and the development of a natural and non-toxic type of corrosion-resistant material would be very desirable⁸⁻¹⁰. Corrosion inhibitors are presently added to cooling systems, refinery units, chemicals, oil and gas production units, boilers, etc. These inhibitors function by adsorption of ions or molecules on metal surfaces, thus reducing the corrosion rate of the metals¹¹.

Natural honey offers interesting possibilities for corrosion inhibition because it is safe, inexpensive, readily available and highly soluble in water¹². The corrosion inhibition properties of honey have been investigated with different types of materials in various environments¹³⁻¹⁵. However, the use of "mad honey" as a corrosion inhibitor for any metal or alloy has not been reported in the literature.

"Mad honey", or toxic honey, has been known since ancient times. This honey is produced by honeybees from nectar collected from the flowers of *Rhododendron* species¹⁶. From as early as 400 BC, mad honey has been produced from the nectar of *Rhododendron ponticum* which grows on the mountains of the Eastern Black Sea Region of Turkey, as well as in Japan, Nepal, Brazil and some parts of North America and Europe¹⁷.

The leaves, flowers, pollen and nectar of many *Rhododendron* species contain toxic diterpenoids (grynanotoxins), found only in Ericaceae plants¹⁸, and these are the main compounds responsible for poisoning¹⁹. The acknowledged toxic effects of honey poisoning include bradycardia, cardiac arrhythmia, hypotension, nausea, vomiting, sweating, salivation, dizziness, weakness, loss of consciousness, fainting, blurred vision, chills, cyanosis, and convulsions²⁰.

Due to these dangerous health effects, the Turkish Ministry of Food, Agriculture and Livestock has published a circular letter to stop the consumption of this honey²¹. The aim of this present study was to compensate for the economic loss brought about by the prohibition of the sale of this honey by proposing an alternative use for the product, and thus to make a contribution to the local people and to the country.

The inhibition effect of mad honey on corrosion of 2007-type aluminium alloy in 3.5% NaCl solution was investigated by Tafel extrapolation (TP), electrochemical impedance spectroscopy (EIS) and dynamic electrochemical impedance spectroscopy (DEIS). The surface morphology of the alloy under study was examined with scanning electron microscopy (SEM), and the correlations between these methods were applied.

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2. Experimental Approach

2.1. Materials

All electrochemical measurements were carried out in a three-electrode type cell with separate compartments for the reference electrode (Ag/AgCl), and the counter electrode, which consisted of a platinum (Pt) plate. The working electrode was a cylindrical disc cut from a specimen of Al-2007 having the chemical composition of (wt. %) 3.5 Cu, 1.3 Mg, 0.9 Pb, 0.19 Cr, 0.8 Mn, 0.42 Fe; and the remainder of Al. This metal disc was coated with epoxy resin with the exception of the 0.20 cm² area on its bottom surface. Electrical conductivity was provided by a copper wire. The working electrode was first prepared using 400-2000-grade abrasive paper and following this procedure, it was rinsed with distilled water and degreased with acetone. Before each measurement, the sample was immersed in the corrosion cell and allowed to stabilise for 2 h. For all applied methods (EIS, TP, SEM) every experiment was repeated at least seven times in order to obtain the most accurate agreement. The mad honey was easily dissolved at room temperature in double-distilled water and solutions at 100 ppm, 500 ppm, 1000 ppm and 1500 ppm were prepared in 3.5% NaCl. The NaCl was purchased from Merck and the mad honey was obtained from the Duzce University Bee Keeping Research, Development and Application Centre²² in Yigilca, Turkey.

2.2. Mad honey analysis

The total phenolic content and the antiradical, antioxidant and antimicrobial activities of mad honey have previously been reported¹⁶. In addition to these analyses, a CHNS-Analyzer (Loco, USA) was used to calculate the CHNS content (wt. %) of the mad honey. This analysis showed the presence of carbon (30.70%), hydrogen (6.72%), nitrogen (0.062%), sulphur (0.016%) and oxygen (62.51%).

The sugar content of the mad honey was determined by Laboratory Analytical Procedures (LAP) from the National Renewable Energy Laboratory (NREL)²³. The honey was analysed using the Agilent 1200 HPLC system equipped with a Shodex SC1011 column (mobile phase: 5 mM H₂SO₄, flow rate: 0.5 ml/min, column temperature: 60 °C) and a refractive index detector. The proline content was measured by the Official Method 979.20, using a Perkin Elmer / Lambda 25 spectrometer (Table 1).

The transmission vibrational spectrum of mad honey is depicted in Figure 1 and its respective FT-IR peaks are given in Table 2. The broad peak at 3400-3300 cm⁻¹ (Figure 1) indicates the presence of a strong hydroxyl group²⁴, the peak at 3350-3360 cm⁻¹ is attributed to the N-H stretch²⁵, the bands at 3000-2900 cm⁻¹ are aliphatic C-H^[26], the peak at 1700-1500 cm⁻¹ is attributed to the stretching mode of (C=O) and (C=C)^[27], and the bands at 1100-1000 cm⁻¹ are assigned to the C-O bending modes of saccharides²⁸. These results show that the FT-IR spectroscopy is more intense in the 1200-800 cm⁻¹ wave number regions. The presence of these regions is considered very reliable according to previous studies^{29,30}, thus making this method a quick tool for identifying carbohydrate-based additives for food authentication.

2.3. Method

2.3.1. Potentiodynamic polarisation measurements

Potentiodynamic polarisation measurements were performed using the Gamry Instrument Potentiostat/Galvanostat/ZRA, and polarisation curves were recorded at a constant sweep rate of 1 mV/s at a -300 to +300 mV interval with respect to open circuit potential (E_{corr}). Corrosion current density values, I_{corr} , were calculated by using the Tafel extrapolation method and by taking an extrapolation interval of ± 250 mV around the E_{corr} value, once stable³¹. The polarisation resistance (R_p) from the Tafel extrapolation method was calculated using the Stern-Geary Equation (Equation 1)³², where β_a and β_c are anodic and cathodic Tafel slopes, respectively.

$$I_{\text{corr}} = \frac{\beta_a \beta_c}{2.303(\beta_a + \beta_c)} \frac{1}{R_p} \quad (1)$$

2.3.2. Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) was performed using the Gamry Instrument Potentiostat/Galvanostat/ZRA, and measurements were carried out at open E_{corr} by using an amplitude signal of 10 mV in the frequency range of 100 mHz to 1MHz.

Table 1. Some compounds in mad honey.

Compound	g/L*
Glucose	552.47
Fructose	662.10
Proline	1.99

*Values are average of duplicate measurements.

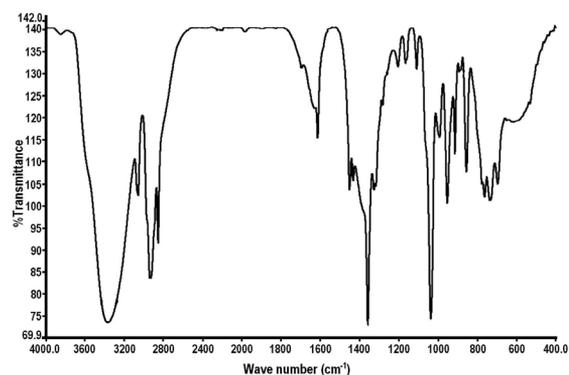


Figure 1. FT-IR transmittance spectra of mad honey.

Table 2. FT-IR transmittance spectrum of mad honey and its identification.

Peaks From FT-IR spectrum ν (cm ⁻¹)	Possible groups
1100-1000	C-O stretch
1700-1500	C=O or C=C stretch
3000-2900	C-H stretch
3300-3250	N-H stretch
3400-3300	-OH group

2.3.3. Dynamic electrochemical impedance spectroscopy (DEIS)

In the DEIS technique, a system under investigation is perturbed with a set of sine voltage or current signals having the same or different amplitude and different frequencies. This method is general and allows the analysis of impedance spectra in a joint time–frequency domain. The perturbation and response signals are registered continuously during the measurement. The analysing window function is employed to cut a fragment out of the recorded register. In the next step, this segment is subjected to the regular Fourier transformation and an instantaneous spectrum is determined. The spectrum is averaged over the time range equal to the length of the analysing window³³.

Generation of the current perturbation was performed with a National Instruments Ltd. PCI-4461 digital-analog card. The same card was used to measure the current and voltage signals. Slepski Galvanostat equipment was used to supply the galvanostatic condition as well as a current-voltage converter. The perturbation signal was a package composed of current sinusoids of the frequency range from 4.5 kHz to 700 MHz. The lowest frequency of the perturbation signal must be higher than the rate of the investigated process. In other words; the low frequency limit depends on the time scale of the analysis performed. The sampling frequency was 12.5 kHz^[34,35].

2.3.4. Surface analysis

The surface analysis of the Al-2007 alloy was investigated by means of a SEM (JEOL SEM5800) equipped with an EDS probe (accelerator voltage 20 keV) after 2 h of immersion in the corrosive medium without and with 1500 ppm of mad honey.

3. Results and Discussion

3.1. Potentiodynamic polarisation measurements

The polarisation behaviour of the Al-2007 alloy in 3.5% NaCl in the absence and presence of different concentrations of mad honey is given in Figure 2. Various electrochemical corrosion parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), anodic (β_a) and cathodic (β_c) Tafel constants and polarisation resistance (R_p), are shown in Table 3.

The inhibition efficiencies (IE %) were calculated for the Al-2007 alloy in 3.5% NaCl solutions containing 100 ppm, 500 ppm, 1000 ppm and 1500 ppm of mad honey from the Tafel plots in Table 3. The IE% values were obtained from I_{corr} data using Equation 2.

$$IE(\%) = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100 \quad (2)$$

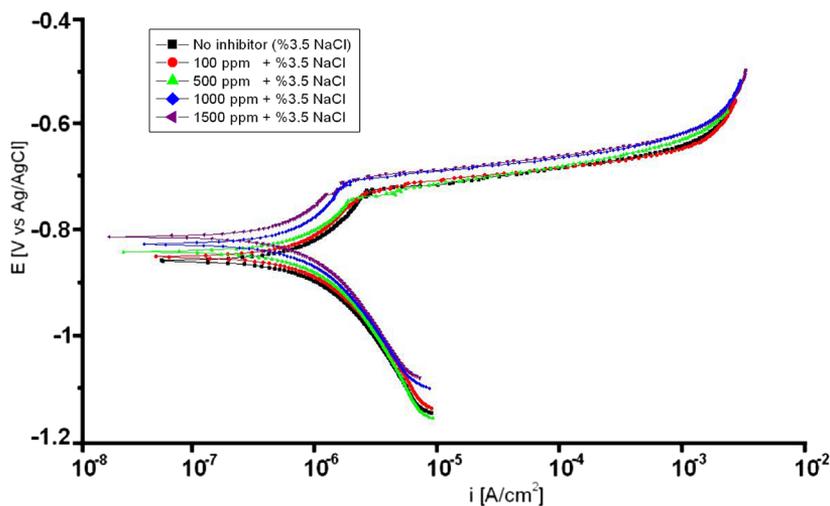


Figure 2. Potentiodynamic polarisation curves for Al-2007 alloy in 3.5% NaCl at various concentrations of mad honey.

Table 3. Kinetic parameters of Al-2007 alloy in 3.5% NaCl medium containing different concentration of mad honey.

Concentration	β_a (mVdec ⁻¹)	β_c (mVdec ⁻¹)	I_{corr} (μAcm^{-2})	E_{corr} (mV)	R_p (Ωcm^2)	IE%
No inhibitor	178	92	1.07	-857	24530	-
100 ppm	137	87	0.56	-849	41250	47
500 ppm	123	90	0.48	-838	46562	55
1000 ppm	111	82	0.39	-824	53527	63
1500 ppm	97	77	0.29	-810	62954	73

where I_{corr} is the corrosion current density measured in solutions without the inhibitor and $I_{corr(inh)}$ is the same parameter determined in solutions containing the inhibitor.

Table 3 illustrates that mad honey acts as an inhibitor for the corrosion of Al-2007 alloy in 3.5% NaCl solution. Better performances are seen when 1500 ppm mad honey was used. All the additions of mad honey concentrations decreased the anodic and cathodic current densities; this means that the additive affected both anodic and cathodic processes and shows that mad honey acts as a mixed-type corrosion inhibitor. It was found that I_{corr} values decreased with increasing inhibitor concentration, while E_{corr} values changed direction to anodic. This change in E_{corr} is assumed to be related to the growth of a passive layer on the electrode surface³⁶.

In aerated or oxygenated Cl^- solutions, the presence of oxygen enhances the cathodic reaction due to oxygen reduction in addition to the water reduction, as seen in Equation 3³⁷.



The anodic reaction is shown in Equation 4-6:



The final reaction being:



Then this aluminium hydroxide, $Al(OH)_{3(ads)}$, transforms to aluminium oxide:



The high passivity, which is normally associated with aluminium, comes from the highly adherent oxide barrier of Al_2O_3 that forms on the surface. In aqueous environments, a greater thickness of this protective oxide is formed and, as long as there is oxygen present, it will continue to re-passivate if flaws are created³⁸. However, the action of an aggressive environment such as a 3.5% NaCl medium will cause a breakdown of the passive film and hinder its repair³⁹.

Since the polarisation range was limited to ± 300 mV versus open circuit potential, pitting corrosion was not observed. Thus, the reduction of general corrosion of the Al-2007 alloy in the 3.5% NaCl solution was observed with the presence and absence of the mad honey inhibitor under study⁴⁰. The DEIS results confirmed the proposed idea concerning general corrosion of the Al-2007 alloy in a 3.5% NaCl solution.

3.2. Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of Al-2007 alloy in a 3.5% NaCl solution in the absence and presence of mad honey was investigated using EIS. Nyquist plots are given in Figure 3, and it is clear from these that the impedance response changes with the addition of the inhibitor additives. In general, all the plots display a single capacitive loop. Impedance parameters and the equivalent circuit diagram are given in Table 4 and Figure 4, respectively. The circuit consists of a constant phase element (CPE) Q , in parallel with charge-transfer resistance (R_{ct}). The use of a CPE-type impedance has been extensively described in accordance with previous reports^{41,42}.

Equation 7 provides information about the degree of non-ideality in capacitance behaviour. Where j is an

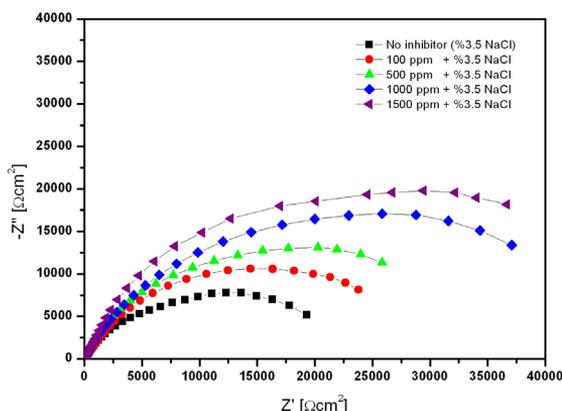


Figure 3. Nyquist plots for Al-2007 alloy in 3.5% NaCl media in the absence and presence of different concentrations of mad honey.

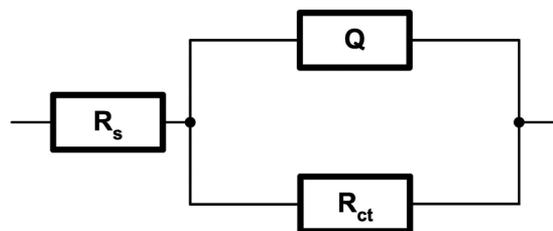


Figure 4. Model of an $R(QR)$ electrical circuit. Key: R_s : Resistance of electrolyte in bulk. R_{ct} : Charge transfer resistance at the metal surface. Q : Constant phase element (CPE).

Table 4. EIS Data for Al-2007 alloy in 3.5% NaCl in the absence and presence of different concentration of mad honey.

Concentration	R_{ct} (Ωcm^2)	Q ($Q/S s^n cm^{-2}$)	n	IE %
No inhibitor	23600	4.34E-5	0.72	-
100 ppm	35780	4.22E-5	0.77	34
500 ppm	38980	3.92E-5	0.79	40
1000 ppm	50070	3.03E-5	0.80	53
1500 ppm	57220	2.62E-5	0.81	59

imaginary number, Q is the frequency independent real constant, $\omega=2\pi f$ is the angular frequency (rad/s), f is the frequency of the applied signal, and n is the CPE exponent. Its value makes it possible to differentiate between the behaviour of an ideal capacitor ($n = 1$) and of a CPE ($n < 1$)^[43].

$$Z_{\text{CPE}} = [Q(j\omega)^n]^{-1} \quad (7)$$

In this sense, n serves as a measure of surface heterogeneity. The low values of Q correspond to high values of the n parameter, as can be seen from Table 4. In addition, low values of the Q parameter indicate that water molecules were possibly replaced by inhibitor molecules. Therefore, it can be assumed that a layer of the inhibitor was formed at the metal/solution interface, thus improving corrosion inhibition⁴⁴.

The Nyquist plots from EIS and DEIS were analysed with the ZSimpwin 3.10 program⁴⁵ which provides accurate information about the circuit. The measure of goodness of fit of the model is the χ^2 parameter; during the analysis, χ^2 did not exceed 1×10^{-4} , attesting to a very high fit of received impedance spectra to the proposed electrical equivalent circuit³⁴.

The EIS results indicate that the R_{ct} values increased with increasing additive concentration. The percentage of inhibition efficiency (IE %) was calculated from the charge transfer resistance (R_{ct}) values by using Equation 8.

$$\text{IE}(\%) = \frac{(R_{\text{ct}})^{-1} - (R_{\text{ct}(\text{inh})})^{-1}}{(R_{\text{ct}})^{-1}} \times 100 \quad (8)$$

where $R_{\text{ct}(\text{inh})}$ and R_{ct} are the charge transfer resistance values with and without the inhibitor, respectively. Calculated IE% values are shown in Table 4.

3.3. Dynamic electrochemical impedance spectroscopy (DEIS)

Figures 5 and 6 display the DEIS results obtained for the Al-2007 alloy in 3.5% NaCl solution without and with 1500 ppm mad honey, respectively. The DEIS results obtained undoubtedly indicate that the investigated system was in a stationary state during the time of examination. Therefore, it can be seen that the studied time, potential and frequency were able to measure general corrosion of Al-2007 in a 3.5% NaCl solution. Previous research^{46,47} on pitting corrosion confirms this claim. Over a 2-h period, the Nyquist plots obtained from DEIS were similar to those of EIS. Thus, the same circuit model was used to analyse DEIS results.

Figures 7 and 8 shows the evaluation of R_{ct} and n values respectively, as a function of time, after exposure of Al-2007 samples in a 3.5% NaCl solution in the presence of 1500 ppm mad honey. The changes in R_{ct} and n values versus time were small, and this indicated that the system was stationary⁴⁸ and the results were similar to each other. Table 5 shows the change of R_{ct} and IE% values for the corrosion of Al-2007 alloy in 3.5% NaCl in the presence of 1500 ppm mad honey after 1 and 2 h. It can be seen that the IE% values decreased with time; however, this change in such an aggressive environment (3.5% NaCl)

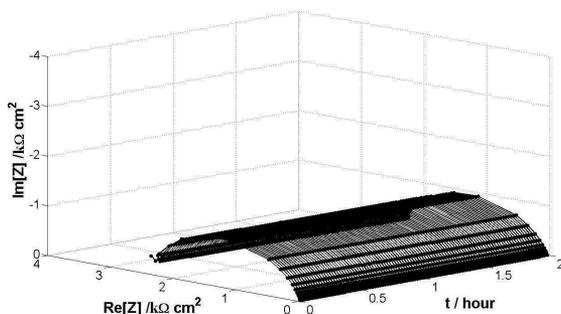


Figure 5. DEIS result of Al-2007 alloy in 3.5% NaCl solution.

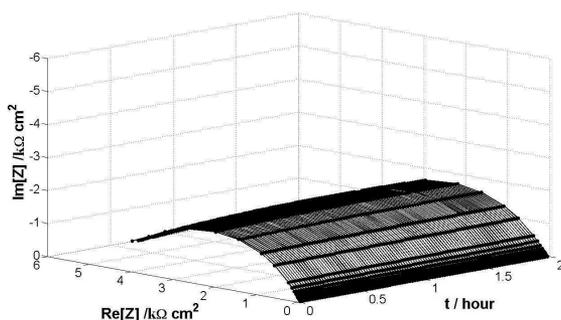


Figure 6. DEIS result of Al-2007 alloy, with 1500 ppm mad honey in 3.5% NaCl solution.

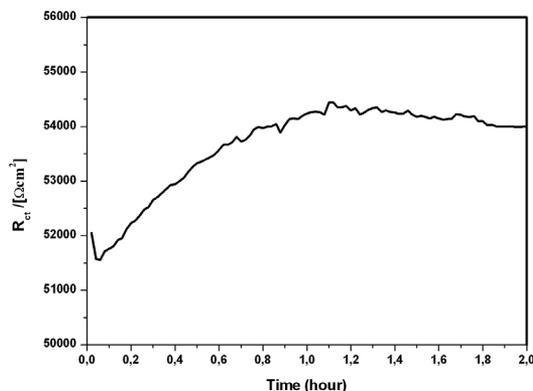


Figure 7. Charge transfer resistance evaluation vs. time of exposure in 1500 ppm mad honey in 3.5% NaCl solution, based on the DEIS results.

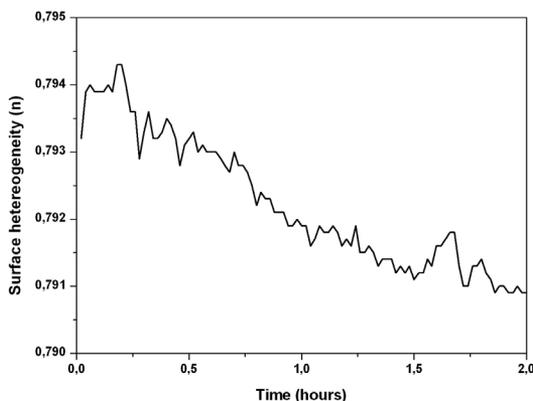


Figure 8. Surface heterogeneity (n) vs. time of exposure in 1500 ppm mad honey in 3.5% NaCl solution, based on the DEIS results.

Table 5. Change of R_{ct} and IE% values for the corrosion of Al-2007 alloy in 3.5% NaCl in the presence of 1500 ppm mad honey after 1 and 2h.

Concentration	After 1 h		After 2 h	
	R_{ct} (Ωcm^2)	IE%	R_{ct} (Ωcm^2)	IE%
No inhibitor	25030	-	24800	-
1500 ppm	54240	54	53590	53

was very small. According to potentiodynamic polarisation measurements, DEIS and EIS were non-destructive AC techniques. Thus, the IE% values obtained from DEIS were very close to the EIS results. The small differences between DEIS-EIS arose from the character of the measurements, as DEIS was made in galvanostatic, whereas EIS was made under potentiostatic conditions.

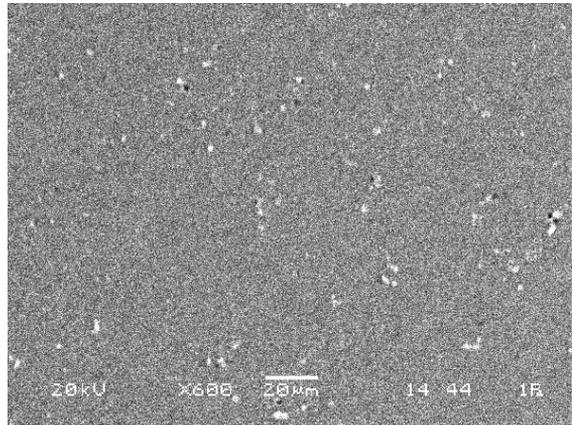
3.4. SEM investigation and EDS analysis

Figure 9 shows the SEM photographs of the Al-2007 alloy surface. It can be seen from Figure 9a that the aluminium samples seemed smooth before immersion. After immersion in an uninhibited 3.5% NaCl solution for 2 h, the aluminium surface appears to be under an aggressive attack by the corroding medium, as shown in Figure 9b. By contrast, Figure 9c illustrates that there was much less damage on the aluminium surface in the presence of 1500 ppm of mad honey, further confirming its inhibition ability. In addition, it is possible that an adsorbed film had formed on the aluminium surface which is not seen in Figure 9c. Accordingly, it might be concluded that the adsorption film was able to efficiently retard the corrosion of the aluminium.

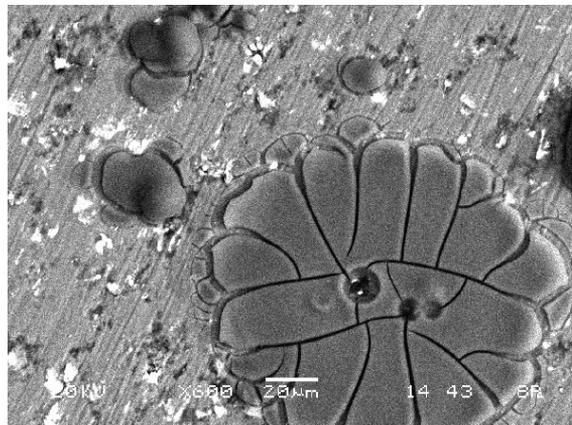
The EDS analysis showed that the oxide percentage of the alloy surface before the experiment was 5.8%, as seen in Figure 10a, whereas the alloy surface exposed to 3.5% NaCl solution was 19.70%, as seen in Figure 10b. However, Figure 10c shows that the EDS analysis of the medium containing 1500 ppm of mad honey in 3.5% NaCl was 12.30%. The low oxygen percentage in 3.5% NaCl containing 1500 ppm of mad honey indicates that mad honey had an influence on the Al-2007 metal surface, and thus inhibited the formation of Equation 6. This decrease in the quantity of oxygen could also be the result of anodic dissolution of the Al-2007 through surface adsorption (Equation 4). This results in the formation of a small amount of aluminium oxide.

3.5. Adsorption isotherms

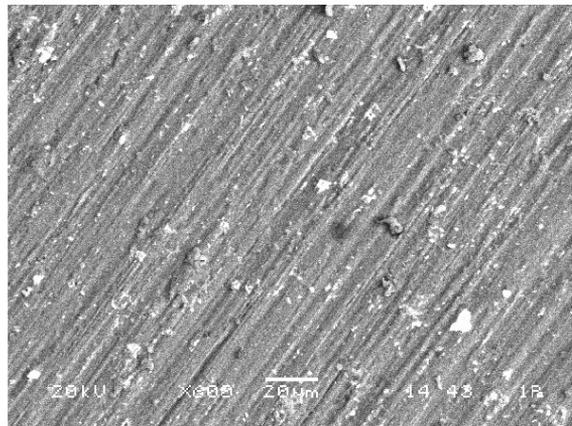
The nature of corrosion inhibition has been deduced in terms of the adsorption characteristics of the inhibitor⁴⁹. A metal surface in aqueous solution is always covered with adsorbed water dipoles. Therefore, the adsorption of inhibitor molecules from an aqueous solution is a quasi substitution process^{25,50}. The data obtained from Potentiodynamic polarisation measurements and EIS were tested with several adsorption isotherms. A correlation between surface coverage (θ) and the concentration (C) of the inhibitor in the electrolyte can be represented by the Langmuir adsorption



(a)



(b)



(c)

Figure 9. SEM micrographs of Al-2007 alloy surface: (a) before immersion; (b) after 2 h of immersion at 20 °C in 3.5% NaCl solution; (c) after 2 h of immersion at 20 °C in 3.5% NaCl with 1500 ppm mad honey.

isotherm. According to this isotherm, the surface coverage (θ) is related to the equilibrium adsorption constant (K) and concentration (C) via Equations 9-11.

$$\theta = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} ; \theta = 1 - \frac{(R_{ct})}{(R_{ct(\text{inh})})} \quad (9)$$

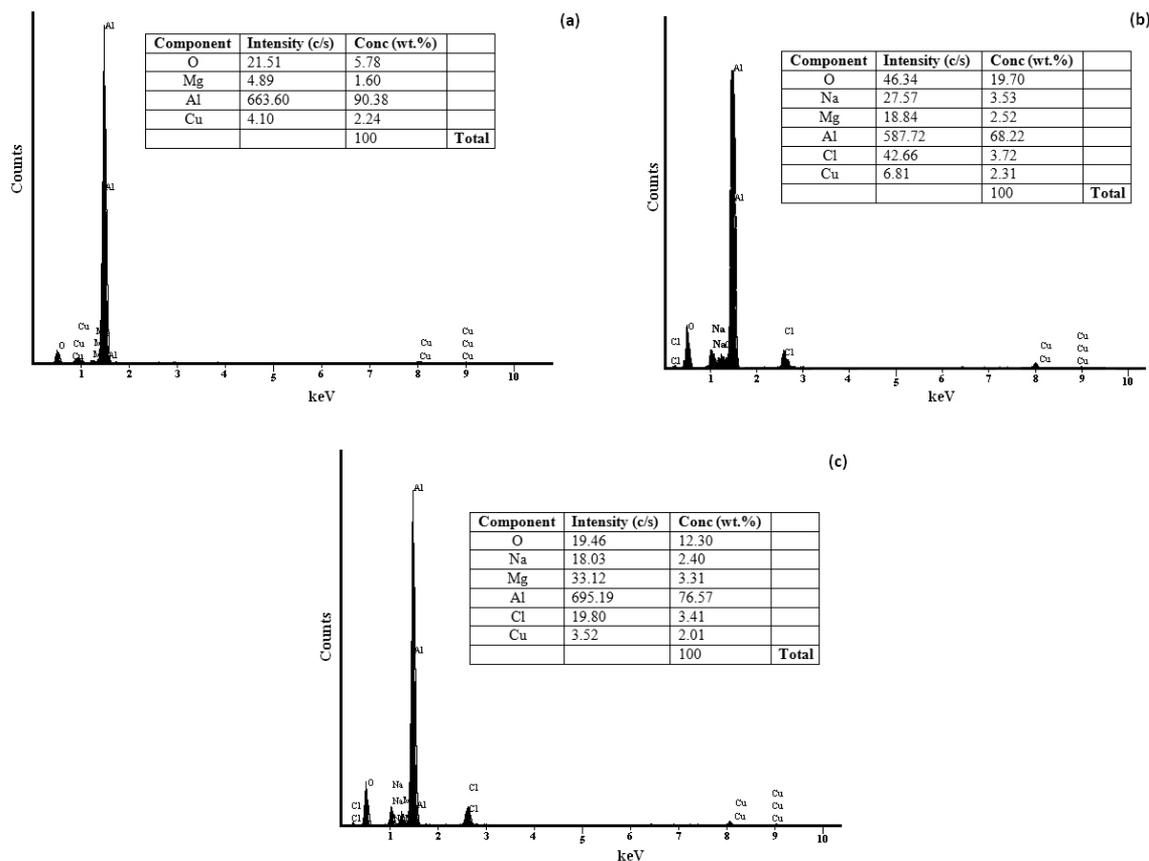


Figure 10. EDS spectrum of Al-2007 alloy surface: (a) before immersion; (b) after 2 h of immersion at 20 °C in 3.5% NaCl solution; (c) after 2 h of immersion at 20 °C in 3.5% NaCl with 1500 ppm mad honey.

$$\theta = \left(\frac{KC}{1 + KC} \right) \tag{10}$$

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^0}{RT}\right) \tag{11}$$

where 55.5 is the concentration of water in the solution in mol.dm⁻³, *K* is the equilibrium adsorption constant, *R* is the universal gas constant and *T* is the thermodynamic temperature.

The equilibrium adsorption constant (*K*) and standard free energy of adsorption (ΔG^0_{ads}) were calculated from the Langmuir plots displayed in Figure 11 and indicated in Table 6.

As can be seen from Table 6, the values of ΔG^0_{ads} for the Al-2007 alloy in 3.5% NaCl solution with TP and EIS were in the range of $-26.57 < \Delta G^0_{ads} < -19.60$ kJ mol⁻¹. The negative values of ΔG^0_{ads} show the spontaneity of the adsorption process and stability of the adsorbed layer on the metal surface. Since the value of the ΔG^0_{ads} of -40 kJ mol⁻¹ is usually accepted as a threshold value between chemisorption and physisorption, the values obtained of the adsorption free energy, ΔG^0_{ads} , may be indicative of physical adsorption^{51,52}.

3.6. Constituents responsible for inhibition

It is well known that honey provides inhibition to different types of alloys in various environments¹²⁻¹⁵.

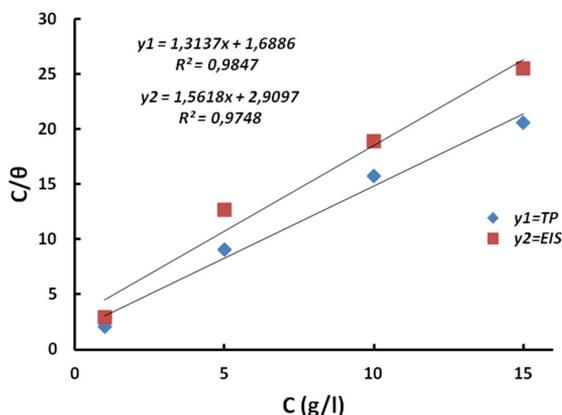


Figure 11. Langmuir adsorption plot for Al-2007 alloy immersed in a 3.5% NaCl medium containing different concentrations of mad honey obtained by using surface coverage values calculated from Tafel polarisation and EIS methods.

However, the characteristics of the constituents that provide the inhibition are still unclear. To identify the probable constituents responsible for the inhibition, the chemical composition of the mad honey was investigated. Studies have shown that sugar-containing compounds can be used as corrosion inhibitors^{14,15,53}. One of the main amino acid molecules in honey is proline⁵⁴, which has been reported as

Table 6. Thermodynamic parameters of Langmuir plots obtained from TP and EIS.

Alloy	Tafel Polarisation		EIS	
	K_{ads} (l/mg)	$-\Delta^0$ (kJ mol ⁻¹)	K_{ads} (l/mg)	$-\Delta G^0$ (kJ mol ⁻¹)
AA-2007	48.82	19.60	812.27	26.57

Table 7. Impedance parameters of Al-2007 alloy in 3.5% NaCl media, 1500 ppm mad honey and the quantity of the studied compounds in 1500 ppm mad honey in 3.5% NaCl media.

Concentration	R_{ct} (Ω cm ²)	Q (Ω S s ⁿ cm ⁻²)	n	IE %
No inhibitor	23600	4.34E-5	0.72	-
Proline (0.0017 g/L)	31450	3.76E-5	0.73	25
Glucose (0.4735 g/L)	46770	3.56E-5	0.78	49
Fructose (0.5675 g/L)	48580	3.21E-5	0.79	51
1500 ppm mad honey	57220	2.62E-5	0.81	59

a corrosion inhibitor^{55,56}; therefore, this molecule was also investigated as an inhibitor in the present study.

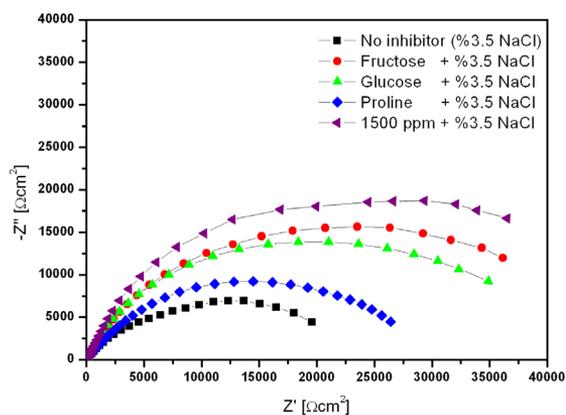
The sugar and proline contents of mad honey are shown in Table 1. According to the results of these analyses, commercial fructose, glucose and proline compounds (Sigma-Aldrich, Slovakia) were used to measure corrosion in the Al-2007 alloy in 3.5% NaCl with EIS (as described in 3.2) and these results were analysed using the same electrical circuit model (Figure 5). Results are given in Figure 12 and Table 7.

The density of mad honey was measured as 1.75 mg/L, and 1500 ppm of mad honey was used as a reference to measure the amount of the constituents. From the analytic formulations (Density = Mass/Volume), the quantity of the compounds in 1500 ppm of mad honey are shown in the first column of Table 7.

The constituent molecules of the mad honey contain oxygen atoms in functional groups (O–H, C–H, C–O, C=O), which meet the general consideration of typical corrosion inhibitors. The adsorption of these compounds on the Al surface reduces the surface area that is available for the attack of the aggressive ion from the 3.5% NaCl solution⁴⁰.

These results suggest that the inhibition behaviour of all mad honey constituents inhibits corrosion of the Al-2007 alloy in 3.5% NaCl media. The inhibitive action for these constituents increases in the following order: fructose > glucose and proline. Fructose has the highest inhibition efficiency among the other constituents. The inhibition behaviour of proline versus the concentration of this compound in mad honey is very good, indicating that much more attention should be paid to this amino acid. The data for the Al-2007 alloy in the 3.5% NaCl medium obtained from the EIS studies show that the inhibition effect of 1500 ppm of mad honey is close to the inhibition effect of fructose.

It is well known that corrosion is a major problem in various industries. The presence of gyanotoxin molecules in mad honey renders it a waste product with no economic value. This research supports results showing that monosaccharides can be used as corrosion inhibitors. Moreover, due to the synergistic effect, it may be possible to enhance the inhibition effect of mad honey by the addition of halide ions. Thus, mad honey can be valuable as a non-chromate, non-phosphate inhibitor in closed circuit systems.

**Figure 12.** Nyquist plots of Al-2007 alloy in 3.5% NaCl media, 1500 ppm mad honey and the quantity of the studied compounds in 1500 ppm mad honey in 3.5% NaCl media.

4. Conclusions

1. The data obtained from microscopic observation and electrochemical methods (TP, EIS and DEIS) confirm that by increasing the concentration of mad honey, the inhibition efficiency on the Al-2007 alloy in a 3.5% NaCl medium was increased;
2. The adsorption of mad honey on the Al-2007 alloy surface in 3.5% NaCl was found to obey the Langmuir adsorption isotherm, and physisorption is proposed as the mechanism for the corrosion inhibition;
3. The Tafel polarisation studies indicated that mad honey is a mixed-type inhibitor for the Al-2007 alloy in a 3.5% NaCl medium;
4. The results have further demonstrated the influence of monosaccharides on the corrosion mechanism of aluminium alloys in a 3.5% NaCl medium.

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