

CORROSION INHIBITION MILD STEEL IN NaCl SOLUTION IN THE PRESENCE OF PROPOLIS EXTRACT

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This work studies the corrosion inhibition of X52 5L carbon steel in a 0.51 mol dm⁻³ sodium chloride solution in the presence of propolis extract. The inhibition efficiency of propolis extract was tested by its addition to the working solution and by making a solid propolis coating on the electrode surface. The results of potentiodynamic polarization method shown that propolis extract acts as a corrosion inhibitor of the anodic type whose efficiency increases with increasing temperature and with stirring of the solution. Electrochemical impedance spectroscopy confirmed the formation of a protective layer by adsorption of propolis extract on the electrode surface. The results of Fourier transform infrared spectroscopy, scanning electron microscopy and energy-dispersive X-ray spectroscopy surface tests are consistent with the results of electrochemical testing.

Keywords: carbon steel; propolis; corrosion; inhibition efficiency

ИНХИБИЦИЈА НА КОРОЗИЈА НА МЕК ЧЕЛИК ВО РАСТВОРОТ НА NaCl ВО ПРИСУСТВО НА ЕКСТРАКТ НА ПРОПОЛИС

Во оваа студија е извршено истражување на инхибицијата на корозија на јаглеродниот челик X52 5L во раствор на натриум хлорид во присуство на екстракт на прополис. Ефикасноста на инхибицијата со екстрактот на прополис беше испитана со додавање работен раствор и со образување цврст слој прополис на електродната површина. Резултатите на методот на потенциодинамичка поларизација покажуваат дека екстрактот на прополис дејствува како инхибитор на корозијата од аноден тип чијашто ефикасност се зголемува со покачување на температурата и со мешање на растворот. Електрохемиската импедансна спектроскопија потврди дека се образува заштитен слој со адсорпција на екстрактот на прополис на електродната површина. Резултатите на Фуриеовата трансформациона инфрацрвена спектроскопија, скенирачката електронска микроскопија и рендгенска дифракција со дисперзија на енергијата на површината се во согласност со резултатите од електрохемиските тестирања.

Клучни зборови: јаглероден челик; прополис; корозија; ефикасност на инхибиција

1. INTRODUCTION

Carbon steel, as a construction material, is often in contact with aggressive media, such as sea water. Since iron ions with chloride, unlike other metals, do not form hard soluble salts, steel

corrodes in environments where chloride ions are present [1]. One way of stopping or reducing corrosion is the use of inhibitors. Most synthetic inhibitors, despite their high efficiency, are toxic and not used. Therefore, natural products, which are non-toxic, biodegradable and readily availa-

ble, are increasingly becoming used. Previous research indicates the possibility of using different plant extracts as corrosion inhibitors for carbon steel [2–8]. Their inhibition activity is attributed to the presence of complex organic compounds in their composition such as: polyphenols, alkaloids, flavonoids, carbohydrates and amino acids. These compounds contain polar functional groups (with S, N or O atoms), multiple bonds, or aromatic rings that are responsible for the adsorption of inhibitors on the metal surface. In addition to herbal extracts, bee products were used as efficient inhibitors of metal and alloy corrosion [9–17]. Propolis is a bee product of complex composition that varies depending on the time and place of collection [18].

In this study, the possibility of inhibiting carbon steel corrosion by propolis extract in a 0.51 mol dm⁻³ NaCl solution in flow conditions and at different temperatures was investigated. The tests were performed by electrochemical methods, namely, a potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS). Furthermore, in order to obtain more detailed information regarding the steel surface in inhibited and uninhibited systems. Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were performed.

2. EXPERIMENTAL

2.1. Materials

Corrosion tests were performed on carbon steel X52 5L, with a composition in mass fractions of elements, w/%, of C 0.26, Si 0.40, Mn 1.40, P 0.03, S 0.03 and the remainder is Fe. Cylindrical steel samples were soldered beforehand to insulated copper wires in order to achieve good electrical contact and insulated by polymeric mass (Simgal-R paste) on all sides, except the base of the cylinder, which was directly exposed to the electrolyte.

2.2. Solution preparation

The measurements were carried out in a 0.51 mol dm⁻³ NaCl solution in the absence and in the presence of commercial alcoholic propolis extract. The NaCl solution was prepared by dissolution of a weighed amount of solid NaCl (p.a. purity) in redistilled water.

A commercial propolis alcohol extract, which is insoluble in an aqueous NaCl solution,

was used in the experimental measurements. Therefore, the calculated amounts of commercial extract were diluted with 30 cm³ of ethanol and added to a 200 cm³ of 0.51 mol dm⁻³ NaCl solution. The solution was constantly mixed in order to fully dissolve the propolis. After that, the working electrode was immersed in a prepared solution and left for 24 h at stirring rate of 250 rpm and electrochemical tests were then performed. For the purpose of comparing the results, the behavior of the steel in the pure electrolyte solution after 24 h of electrolyte and electrode contact was monitored.

In addition to examining the possibility of corrosion inhibition by propolis extract added to the electrolyte solution, the inhibition efficiency of a propolis coating was also investigated. The electrode with the solid coating of propolis was prepared by applying alcohol propolis extract to the electrode surface. The obtained coating was dried in air for 24 h.

2.3. Methods

A Potentiostat-Galvanostat 273 analyzer model PAR-325II, interfaced with software for the corrosion investigations, was used for electrochemical tests in the 0.51 mol dm⁻³ NaCl solution. A conventional thermostated three-electrode cell, employing a steel carbon disc as the working electrode, super graphite as the counter electrode, and saturated calomel electrode as the reference electrode, was used for the measurements. The potentiodynamic polarization experiments were performed at a scan rate of 1 mV s⁻¹ in the potential range ± 150 mV relative to the open circuit potential.

The measurements were carried out in a temperature range of 35–65 °C. For flow system simulation, the electrolyte was mixed with a magnetic stirrer.

In order to examine the properties of the oxide layer in the absence and in the presence of an inhibitor, the FTIR spectra were recorded using a Perkin Elmer Spectrum One spectrometer. The spectra were obtained in the range from 450 to 4000 cm⁻¹, with a scan resolution of 4 cm⁻¹. Pellets used as samples were obtained in a mold using a hydraulic press. Samples were made by removing corrosion products from the steel plate surface by rubbing with KBr (350 g), which is a carrier.

EIS was applied to obtain information of the nature of the electrochemical system. The excitation amplitude of 10 mV peak-to-peak in the

frequency range from 50 mHz to 10 kHz, at open circuit potential, was used.

3. RESULTS AND DISCUSSION

3.1. Polarization curves

The influence of stirring on corrosion behavior of the steel in 0.51 mol dm^{-3} NaCl solution after 24 h of electrode and electrolyte contact is shown in Figure 1. Solution mixing has a significant influence on the cathodic reaction by moving the cathodic polarization curves to higher current density values. This may be a consequence of faster oxygen diffusion, because the tested electrolyte was in contact with air during the entire measurement [19]. With the increase of stirring rate from 250 to 700 rpm, the current density value increases from 50.326 to $68.041 \mu\text{A cm}^{-2}$, while its value in the unmixed electrolyte is $11.237 \mu\text{A cm}^{-2}$.

Figure 2 shows the potentiodynamic polarization curves in the absence and in the presence of propolis in 0.51 mol dm^{-3} NaCl solution without stirring after 24 h of electrode and electrolyte contact (Fig. 2a), as well as at different stirring rates (Figs. 2 b and c).

The inhibition efficiency was calculated using equation (1):

$$\eta(\%) = \left(\frac{j_{corr}^0 - j_{corr}}{j_{corr}^0} \right) \cdot 100 \quad (1)$$

where j_{corr} and j_{corr}^0 are the values of corrosion current density in the presence and in the absence of inhibitor, respectively.

The corrosion parameters obtained from the polarization curves are shown in Table 1.

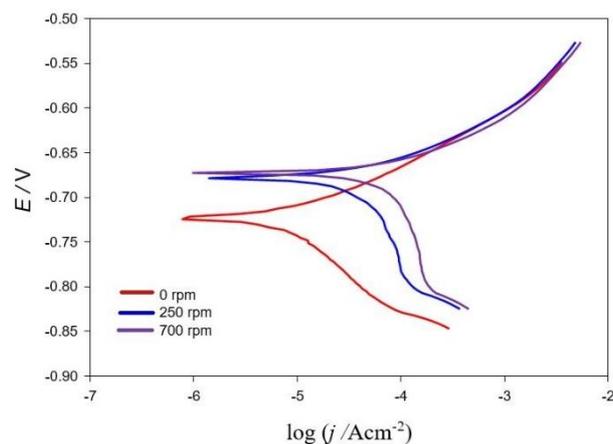


Fig. 1. Potentiodynamic polarization curves of steel in 0.51 mol dm^{-3} NaCl solution at different stirring rates after 24 h of electrode and electrolyte contact

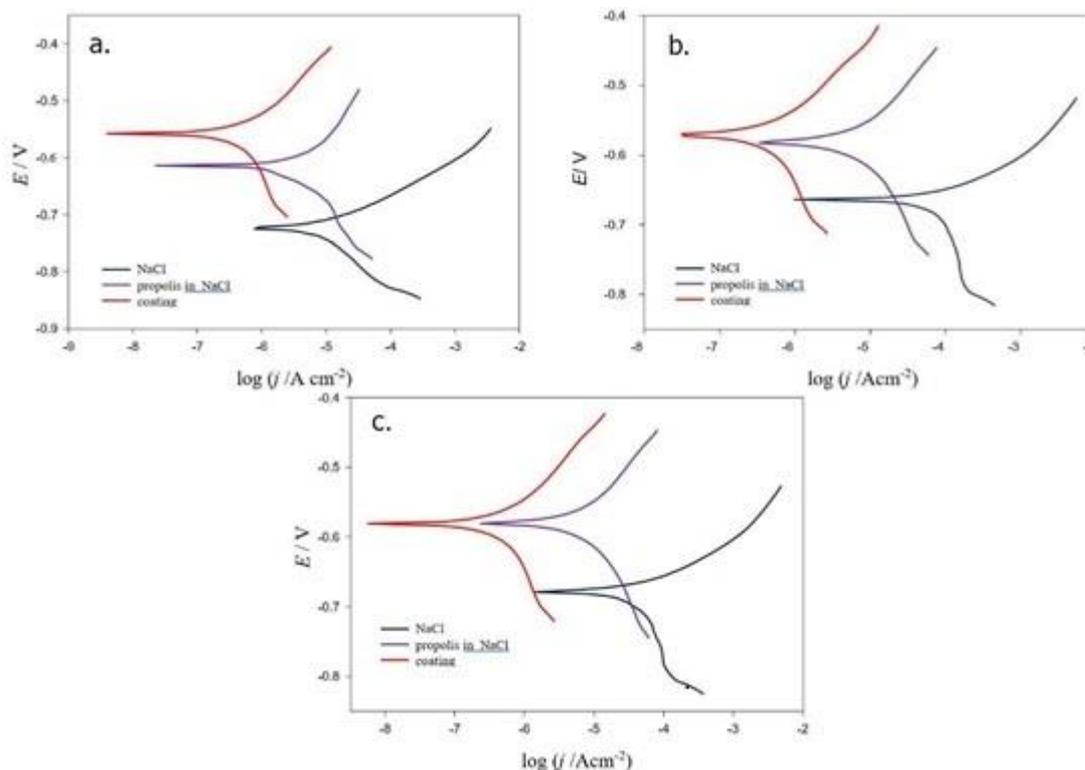


Fig. 2. Potentiodynamic polarization curves in the absence and in the presence of propolis in 0.51 mol dm^{-3} NaCl solution: a) without stirring after 24 h of electrode and electrolyte contact and at different stirring rates of: b) 250 and c) 700 rpm.

Table 1

Corrosion parameters obtained from polarization curves (Figures 1 and 2) for steel in 0.51 mol dm⁻³ NaCl solution

	$I_{corr}/\mu\text{A}$	$j_{corr}/\mu\text{A cm}^{-2}$	E_{corr}/mV	$b_a/\text{mV dec}^{-1}$	$b_c/\text{mV dec}^{-1}$	$\eta/\%$
0.51 mol dm⁻³ NaCl						
0 rpm	1.412	11.237	-723.71	40.75	-96.10	
250 rpm	6.324	50.326	-678.29	54.38	-220.34	
700 rpm	8.550	68.041	-664.14	48.39	-278.23	
0.51 mol dm⁻³ NaCl + 1 cm³ propolis extract						
0 rpm	0.329	2.618	-613.5	88.76	-76.05	76.7
250 rpm	0.693	5.515	-580.91	93.73	-151.47	89.04
700 rpm	0.871	6.931	-579.77	89.92	-156.16	89.81
Propolis coating in 0.51 mol dm⁻³ NaCl						
0 rpm	0.045	0.358	-557.09	69.69	-185.38	96.81
250 rpm	0.052	0.414	-569.77	90.40	-213.18	99.18
700 rpm	0.057	0.454	-580.5	91.75	-117.28	99.33

The values in Table 1 show the decrease in the current density with the addition of propolis extract in solution without stirring, as well as in the stirring solution. These results indicate the ability of propolis extract to reduce the corrosion rate due to its adsorption on the steel surface.

Corrosion potential, in the presence of propolis extract, is shifted towards more positive values, as well as the cathodic current density being reduced in solution without stirring and in the stirring solution. The propolis extract can be classified as an anodic type of inhibitor due to the displacement in corrosion potential, which is more than 85 mV [16, 20].

The inhibition efficiency of propolis extract depends on the stirring rate and propolis extract application. It is evident that the efficiency is greater in flow conditions and by applying propolis extract to the electrode surface. The highest efficiency (99.33%) was achieved after a 24-h exposure of the electrode with the propolis coating to the electrolyte at a stirring rate of 700 rpm.

3.2. Influence of temperature

The influence of temperature on the corrosion behavior of carbon steel in a 0.51 mol dm⁻³ NaCl solution containing propolis extract was examined in the temperature range of 308–338 K by recording potentiodynamic curves. The current values and the corresponding efficiencies are shown in Table 2.

The data presented in Table 2 show that with increasing temperature, the corrosion current density increases in the 0.51 mol dm⁻³ NaCl solution.

The increase of the corrosion rate with increasing temperature is present to a lesser degree in the uninhibited system, and therefore at higher temperature provides a higher efficiency of protection. This indicates that the propolis extract is chemisorbed on the steel surface, because in the case of physical adsorption at the examined temperatures, organic molecules would break down. In the case of chemisorption, with increasing temperature, reinforcement of the bonds is achieved, so there is no decrease in the protection efficiency [21, 22].

Table 2

Corrosion current and inhibition efficiency on carbon steel in 0.51 mol dm⁻³ NaCl solution at different temperatures

T /K	$j_{corr}/\mu\text{A cm}^{-2}$	$j_{corr}^0/\mu\text{A cm}^{-2}$	$\eta/\%$
308	34.412	16.406	52.32
318	57.828	21.777	62.34
328	86.896	31.509	63.73
338	100.462	36.768	63.40

3.3. Activation energy and thermodynamic parameters of inhibition process

A quantitative relationship between temperature and corrosion rate is given by Arrhenius' equation:

$$j_{corr} = A \exp\left(-\frac{E_A}{RT}\right) \quad (2)$$

where: j_{corr} is the current density that is directly proportional to the corrosion rate, A is the Arrhe-

nus' pre-exponential factor, E_A is the apparent activation energy, R is the universal gas constant and is equal to $8.314 \text{ J K}^{-1} \text{ mol}^{-1}$, T is the absolute temperature in K.

A plot of $\ln j_{\text{corr}}$ versus $1/T$ for the 0.51 mol dm^{-3} NaCl solution in the absence and in the presence of propolis is presented in Figure 3. The ob-

tained straight lines have slope $(-E_A/R)$ and intercept of $\ln A$, from which E_A and A were calculated and then listed in Table 3. The correlation coefficients (R^2) show values close to unity, which indicates that the corrosion of the carbon steel in a 0.5 mol dm^{-3} NaCl solution is well described by the Arrhenius' equation.

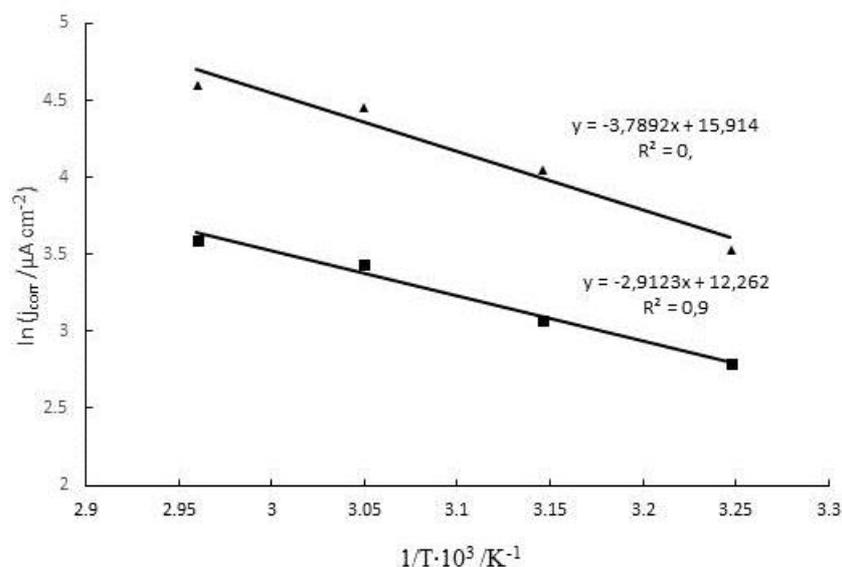


Fig. 3. Arrhenius' plot of $\ln j_{\text{corr}}$ versus $1/T$ for carbon steel in a 0.51 mol dm^{-3} NaCl solution without propolis (▲) and with propolis (■)

Table 3

Activation parameters of carbon steel corrosion in 0.51 mol dm^{-3} NaCl in the absence and in the presence of propolis extract

	$E_a^\circ / \text{KJ mol}^{-1}$	$A / \mu\text{A cm}^{-2}$	$\Delta H_{a^\circ} / \text{KJ mol}^{-1}$	$\Delta S_{a^\circ} / \text{J mol}^{-1} \text{ K}^{-1}$
0.51 mol dm⁻³ NaCl	31.5248	$82.1049 \cdot 10^5$	31.4211	- 113.145
Propolis extract in 0.51 mol dm⁻³ NaCl	24.3177	$2.1951 \cdot 10^5$	21.5299	- 151.781

Literature data suggest that if the activation energy is higher in the presence of an inhibitor, physical adsorption is performed [23, 24], while the reduction of apparent activation energy indicates chemisorption [25, 26]. The results presented in Table 3 show that the values of E_A are lower in the presence of the corrosion inhibitor than those obtained in the inhibitor free solution. This indicates chemisorption of the propolis on the carbon steel surface. The lower value of activation energy in the presence of the inhibitor can be explained by the fact that the reaction occurs on the surface covered by inhibitor' molecules, which results in a lower reaction rate than on the uncovered metal surface [27].

It can be seen from equation 2 that at lower corrosion current values, the value of the Arrhenius' pre-exponential factor is lower, and the apparent activation energy values are higher. Therefore, it can be concluded that the reduction of the corrosion rate in the case of propolis extract inhibition is determined by the reduction in the Arrhenius' pre-exponential factor.

The two important thermodynamic parameters of corrosion were also calculated, namely: the activation enthalpy (ΔH_{ads}°) and activation entropy (ΔS_{ads}°), using the equation of transition state [12]:

$$j_{\text{corr}} = \frac{RT}{Nh} \exp\left(\frac{\Delta S_{ads}^\circ}{R}\right) \exp\left(-\frac{\Delta H_{ads}^\circ}{RT}\right) \quad (3)$$

where: N is Avogadro's number, and h is Planck's constant.

A plot of $\ln(j_{\text{corr}}/T)$ versus $1/T$ is the straight line with the slope $(-\Delta H_{\text{ads}}^0/R)$ and intercept $[(\ln$

$(R/Nh)) + (\Delta S_{\text{ads}}^0/R)]$ (Fig. 4). The activation parameters of the carbon steel corrosion in the 0.51 mol dm^{-3} NaCl solution in the absence and in the presence of propolis extract are presented in Table 3.

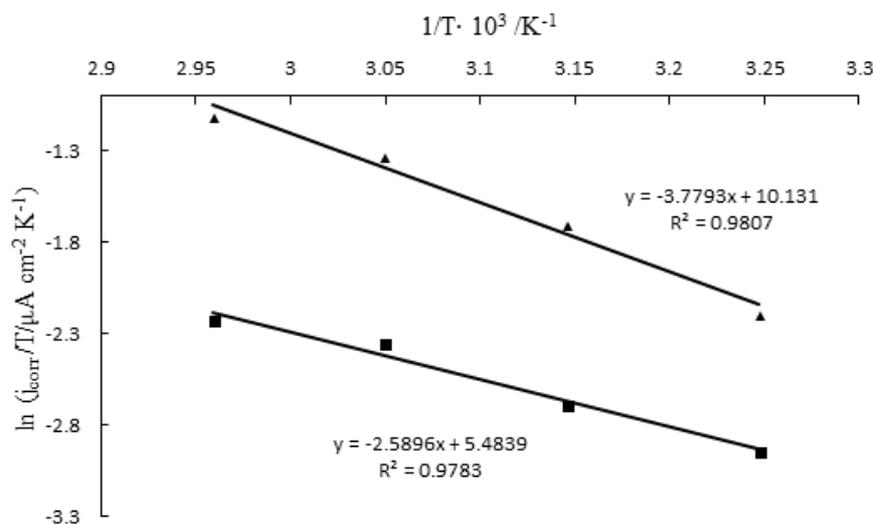


Fig. 4. Plot of $\ln(j_{\text{corr}}/T)$ versus $1/T$ in 0.51 mol dm^{-3} NaCl solution: without propolis (▲) and with propolis (■)

Positive values of activation enthalpy reflect an endothermic corrosion process. The negative values of the activation entropy (ΔS_{ads}^0) both in the absence and in the presence of propolis extract imply that the activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disordering takes place on going from reactants to activated complex [28].

EIS measurements at open-circuit potential were carried out to determine the kinetic parameters for electron transfer reactions at the steel/electrolyte interface and simultaneously regarding the surface properties of the investigated system. The shape of the impedance diagram will provide mechanistic information. The Nyquist and Bode impedance plots obtained for the steel electrode in the absence and in the presence of propolis extract in the 0.5 mol dm^{-3} NaCl solution are shown in Figures 5 and 6. The experimentally obtained Nyquist plots are marked by the points on the diagram, while the lines represent the simulated Nyquist curves, which correspond to the constructed electric circuit model (Fig. 7). The obtained results show good correlation between the experimental and simulated curves, indicating that the proposed model is good.

The presence of the inhibitor causes a change in the dependence of the frequency as a function of phase angle in all frequency domains in

relation to the measurement without the inhibitor (Fig. 5). This phenomenon indicates that propolis molecules form a barrier on the steel surface and thus protect it from corrosion [29]. The deviation of the maximum of Nyquist curve from the ideal semicircle could be due to the imperfection of the electrode surface or inhibitor adsorption [30, 31].

The equivalent circuit proposed (Fig. 7) to fit the experimental data consists of an electrolyte resistance R_s connected with two time constants. The first time constant, observed in the high frequency region, is the result of the fast charge-transfer process in the steel dissolution reaction in the NaCl solution. In this case, R_1 represents the charge transfer resistance and CPE_1 represents the constant phase element and replaces the capacity of the electrochemical double layer [14]. To account for the surface layer in the low frequency range, additional equivalent circuit parameters were introduced, such as R_2 for the surface layer resistance and CPE_2 for the constant phase element of the surface layer, which replaces the capacity of the surface layer.

The calculated equivalent circuit parameters for carbon steel in neutral chloride solutions without and with propolis extract are presented in Table 4. The CPE is a special element whose admittance value is a function of angular frequency (ω), and the phase is independent of the frequency.

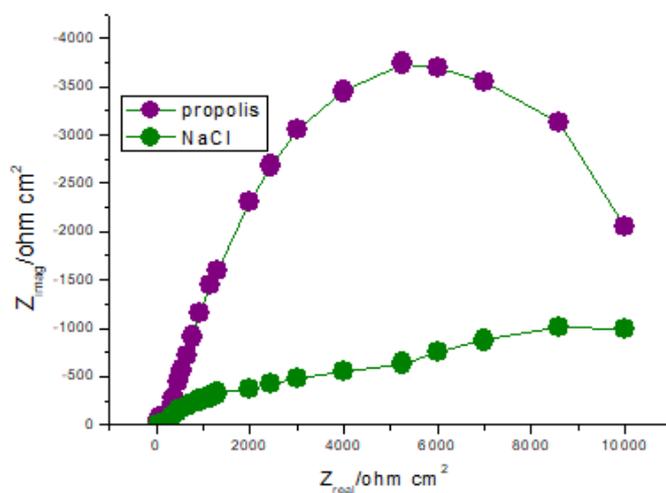


Fig. 5. Nyquist plots for carbon steel in 0.51 mol dm⁻³ NaCl solution in the absence and in the presence of propolis extract

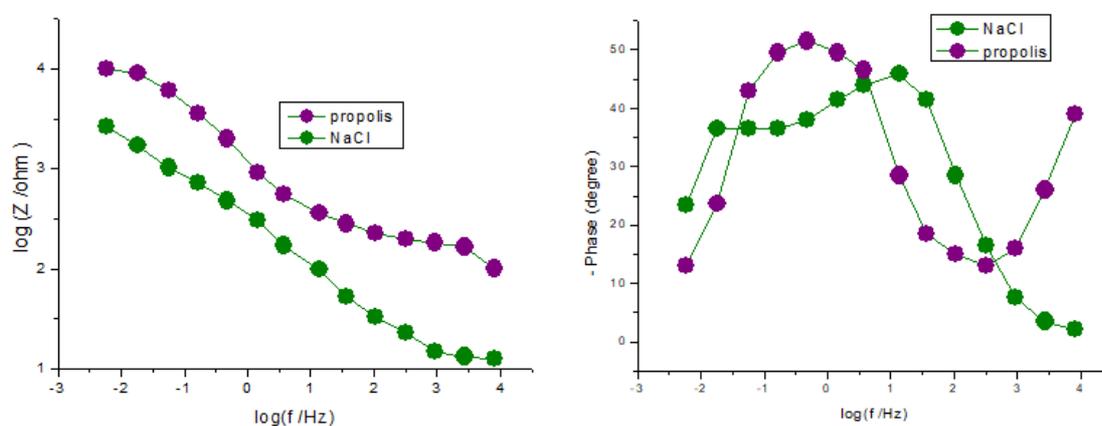


Fig. 6. Bode plots for carbon steel in 0.51 mol dm⁻³ NaCl solution in the absence and in the presence of propolis extract

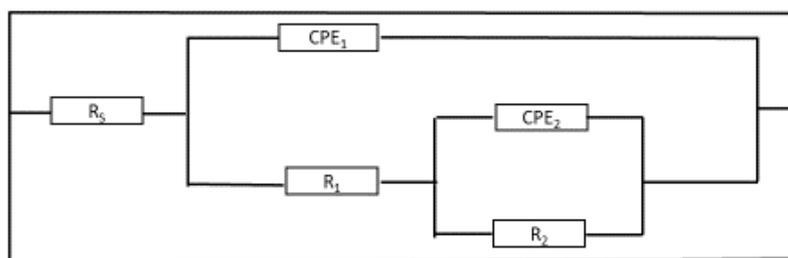


Fig. 7. Equivalent circuit used in fitting the impedance spectra

Table 4

Equivalent circuit parameters in Figure 7 required for fitting the EIS for carbon steel in 0.51 mol dm⁻³ NaCl solution in the absence and in the presence of propolis extract

	R_s/Ω	$CPE_1/S\ s^{-n}$			R_1/Ω	$CPE_2/S\ s^{-n}$			R_2/Ω
		$Q \cdot 10^6$	n	$C/\mu F$		$Q \cdot 10^5$	n	$C/\mu F$	
NaCl	22.12	433.97	0.74	233.46	395.50	156.44	0.56	6795.46	4218
Propolis extract	11.78	2.61	0.73	0.175	229.00	23.66	0.72	353.64	11711

The Nyquist plots show depressed semicircles with their centers below the real axis. This phenomenon, which is known as the frequency dispersion effect, is typical for solid metal electrodes [32]. For these reasons, the electrochemical double layer capacity in the electric circuit was replaced by a constant phase element to make the model better suited to the experimental results. The constant phase element is used to quantify various physical phenomena, such as inhomogeneity of the electrode surface due to roughness, oxide layers formation or adsorption of the inhibitor. CPE consists of a constant Q and a component n [33]. The rise of value n in the presence of the inhibitor indicates a decrease in inhomogeneity of the surface due to adsorption inhibitor [34].

The exponent value n is used to determine the degree that controls the electrochemical reaction rate. A value of n less than 0.7 indicates that the electrochemical reaction is controlled by a diffusion process. The value of n in the range from 0.7 to 0.9 indicates that slow reaction degree is charge transfer. The values in Table 4 indicate that the carbon steel corrosion rate in the chloride solution without propolis extract is controlled by diffusion, while in the system with propolis it is controlled by charge transfer [35].

The double layer capacity value is calculated according to:

$$C = (QR_{ct}^{1-n})^{\frac{1}{n}} \quad (4)$$

There is a decrease in the double layer capacity value (Table 4) in the presence of the inhibitor, which can be explained by the inhibitor adsorption on the electrode surface. The decrease in C is due to an increase in the electrochemical double layer thickness, which is due to the reduction of the local dielectric constant. This was due to the gradual replacement of the water molecule by the inhibitor molecules at the electrode/electrolyte interface [36]. Increasing resistance R indicates a corrosion rate reduction.

FTIR analysis was carried out in order to investigate the properties of the adsorbed propolis layer, which causes a reduction in the corrosion rate (Fig. 8).

The peaks appearing at 3436 cm^{-1} can be attributed to surface-bound water [37]. The peaks at 544 , 630 , 897 , 1123 and 1161 cm^{-1} indicate the presence of iron oxide and oxyhydroxide (α phase) as corrosion products on the steel surface [38–40]. The FTIR spectrum of the surface film on carbon steel formed after exposure to inhibited solution

showed a displacement of peak from 3436 to 3430 cm^{-1} , as well as the absence of bonds characteristic for oxides and iron hydroxides. The peaks at 1031 and 1166 cm^{-1} are characteristic for the C-O bond, while the peaks at 1632 and 1527 cm^{-1} can be attributed to C=C and the C=C aromatic ring [41]. Peaks characteristic for N-O, nitro N=O and nitrile C≡N bonds were observed in the spectrum of the sample in NaCl solution with propolis extract [42].

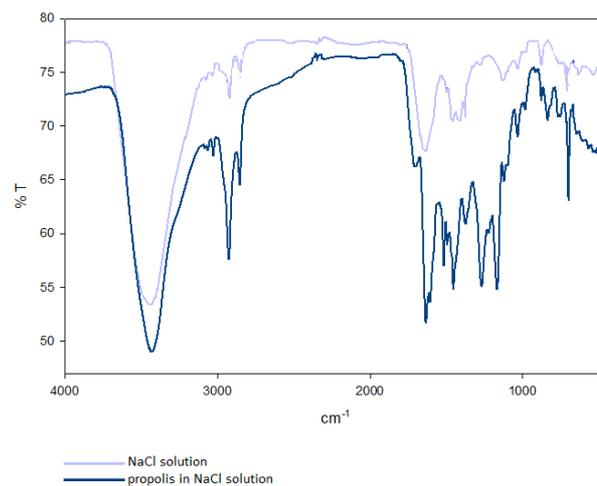


Fig. 8. FTIR spectra of corrosion products of X52 L5 steel after exposure to NaCl solution in the absence and in the presence of propolis extract

The microstructures of the steel surface analyzed by SEM-EDX before exposure to the electrolyte, as well as after 24 h of immersion in electrolyte in the absence and in the presence of propolis extract, are shown in Figure 9. The microstructure of the steel surface before exposure to the electrolyte shows a smooth surface with scratches left behind after grinding, but without corrosion damage.

Small quantities of carbon, oxygen and mostly iron are presented on the steel before exposure to the electrolyte, while large amounts of iron and oxygen and small quantities of sodium, chlorine and carbon are determined on the surface of steel exposed to NaCl. These results indicate that the surface is covered with corrosion products i.e. iron oxides and iron chlorides (Fig. 9b). The results of this analysis on the sample from the inhibited system (Fig. 9c) show mostly the amount of carbon of $\sim 71\%$, which can be related to the chemisorption of propolis on the electrode surface. Oxygen, nitrogen, iron, chlorine and sodium are present in small percentages (Fig. 9c).

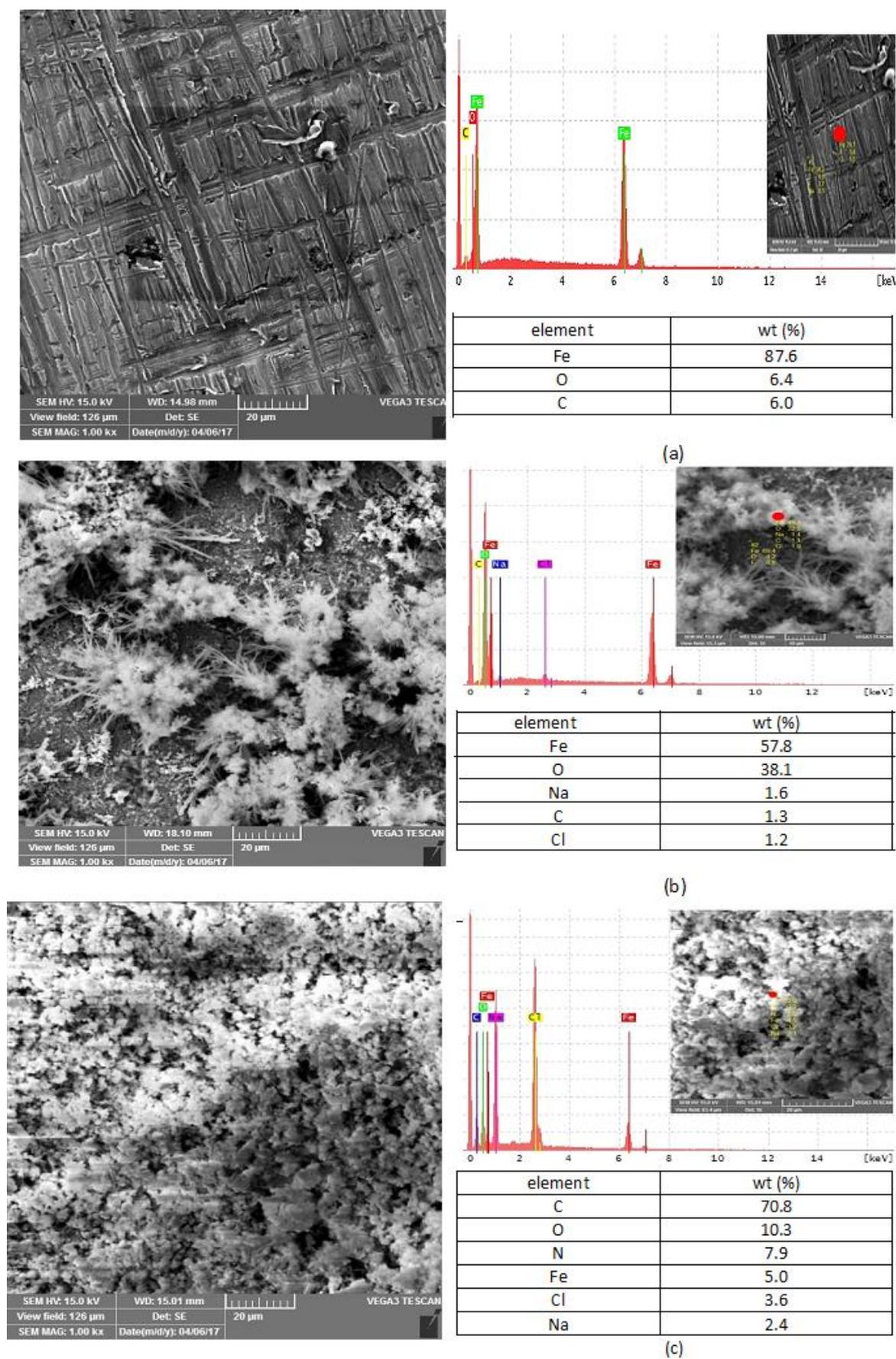


Fig. 9. SEM and EDX analysis of steel surface before exposure to electrolyte (a), after exposure of 0.51 mol dm^{-3} NaCl (b), and after exposure of 0.51 mol dm^{-3} NaCl in the presence of propolis (c)

4. CONCLUSIONS

On the basis of the performed examinations, it was found that the propolis extract acts as an anodic corrosion inhibitor of X52 L5 steel in 0.51 mol dm⁻³ NaCl solution. Its inhibition efficiency increases with increasing stirring rate, as well as with increasing temperature. The best inhibition efficiency is achieved using a propolis coating, which increases at higher stirring rates. The maximum efficiency of 99.33 % was obtained at a stirring rate of 700 rpm, after one day. Therefore, it is recommended using propolis as a steel inhibitor in flow systems. By analyzing the kinetic parameters, it was found that the propolis was chemisorbed on the electrode surface. The results of the EIS show that in the presence of propolis extract there is a decrease in the charge transfer resistance. According to FTIR analysis, corrosion products of steel in uninhibited system are mainly oxides and iron hydroxides. The presence of bonds characteristic for organic compounds in the inhibited system confirms the adsorption of propolis on the steel surface, which is consistent with the results of electrochemical measurements. SEM and EDX analysis show the presence of mostly corrosive products on the electrode exposed to the uninhibited system while 71 % of the carbon is presented on the surface inhibited by propolis extract. Due to its high efficiency and environmental friendliness, propolis extract can be used as an inhibitor of steel corrosion in 0.51 mol dm⁻³ NaCl.

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