Inhibition of Copper Corrosion in NaCl Solution by Propolis Extract

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This study investigates the possibility of corrosion inhibition of copper by propolis extract in 0.51 mol dm^{-3} NaCl solution. The influence of propolis extract concentration and temperature on corrosion behaviour of copper was studied using electrochemical methods. The protective effect of propolis coating deposited on the electrode surface and dried in air was also examined. The results of the study showed that with increasing propolis extract concentration in the solution there was a slight increase in open circuit copper potential to positive values, an increase in polarization resistance, and a decrease in the corrosion current density. A significantly more prominent change of all three of these parameters was observed in the case of propolis coating. Potentiodynamic measurements indicate that propolis extract acts as a mixed corrosion inhibitor, which is adsorbed on the electrode surface according to Langmuir's isotherm. The decrease in inhibition efficiency with increasing temperature indicates physical adsorption. Adsorption of propolis on the electrode surface was confirmed by the spectrophotometric method.

Keywords:
copper, propolis, corrosion, adsorption

Introduction

Because of its very good constructional properties, high electrical and thermal conductivity, and its relatively noble properties, copper is widely used in various industries. Research has shown that copper corrodes in chlorine-containing media[1–3]. The corrosive effect of aggressive components in electrolytes in practice can be reduced in many ways, but most often with the use of inhibitors. The use of environmentally harmful chemicals, including many effective corrosion inhibitors, has been reduced drastically in recent years. Therefore, many alternative natural products, eco-friendly or green corrosion inhibitors have been developed[4]. Apart from herbal extracts, honey and propolis are natural products, which can also be used as corrosion inhibitor for metals and alloys. Previous research has shown that ethanol extract of propolis significantly inhibits corrosion of steel[5–7] and copper alloys[8] in sulphate and chloride solutions.

Propolis is a resinous substance, the composition of which depends on vegetation, time, and collection area. The colour of this substance varies from yellow green to dark brown, depending on the source and age. It is accepted that propolis consists of 50 % resin, 30 % bees wax, 10 % essential and aromatic oils, 5 % pollen, and 5 % other substances, usually flavonoids[9,10]. In addition, propolis contains minerals, such as iron and zinc, and vitamins A, B1, B2, B6, C, and E. Apart from medical purposes, propolis is also used in industry. It is considered that some organic substances in propolis capable of inhibiting corrosion. Namely, flavonoids are substances with very good antioxidative properties. The following flavonoids have been found in propolis: galangin, quercetin, kempferol, apigenin, pinocembrin, and pinobanksin. All of them contain polyphenol and phenol groups (Scheme 1). Owing to such composition, the inhibition effect of propolis is based on adsorption and formation of a protective layer on the surface of the metal.

The aim of this work was to investigate the inhibition effect of propolis extract as a new and non-toxic inhibitor of copper corrosion in a 0.51 mol dm^{-3} NaCl solution. The experiments were performed by electrochemical methods and UV-VIS spectroscopy.

Experimental

Materials preparation

Cylindrical copper samples (purity 99.99 %) were soldered beforehand to insulated copper wires in order to achieve good electrical contact, and in-

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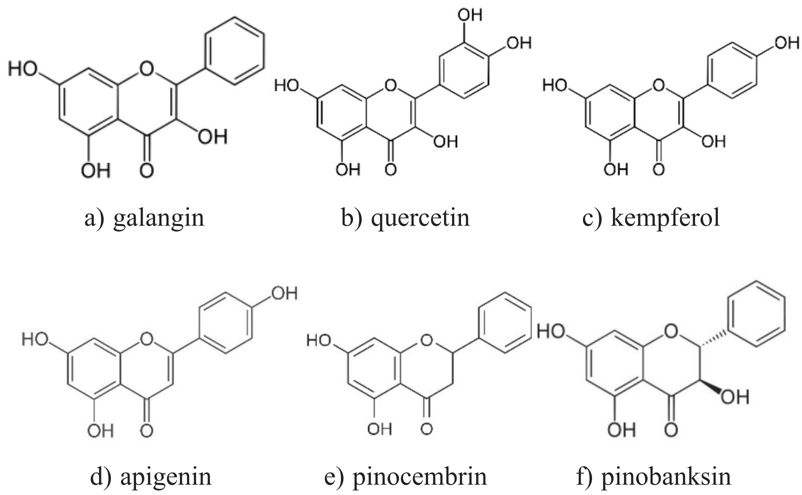

Scheme 1 – *Structural formulas of flavonoids, present in propolis*[6]

sulated with polymeric mass (Simgal- R paste) on all sides. The working surface of the electrode was 1 cm^2. Before electrochemical measurements, the electrode surface was cleaned mechanically with abrasive sanding papers of fineness 400, 600 and 1200. After that, the surface was washed with ethanol and distilled water.

The electrode with the solid coating of propolis was prepared by applying alcoholic propolis extract to the electrode surface. The obtained coating was air-dried.

The measurements were carried out in an 0.51 mol dm^{-3} NaCl solution, which was prepared by the dissolution of the solid NaCl, p.a. purity, in distilled water.

A commercial alcohol extract of propolis, insoluble in an aqueous NaCl solution, was used in experimental measurements. Therefore, the calculated amounts of commercial extract were diluted with 30 cm^3 of ethanol and added to 200 cm^3 of 0.51 mol dm^{-3} NaCl solution. Thus, solutions of different concentrations of commercial propolis extract (350–3500 mg dm^{-3}) were obtained. The solutions were constantly mixed in order to fully dissolve the propolis extract.

Electrochemical experiments

Potentiostate-Galvanostate 273 analyzer model PAR – 325II interfaced with software was used for the corrosion investigations. Polarization experiments were carried out in a special three-electrode glass cell with a cylindrical graphite counter electrode and a saturated calomel electrode (SCE) as reference.

The time dependence of the open circuit potential for Cu in 0.51 mol dm^{-3} NaCl solution was measured in duration of 30 minutes at temperature of 25 ºC in solutions with and without the addition of various propolis extract concentrations. Linear polarization method was recorded in the potential range of ± 20 mV relative to corrosion potential. Potentiodynamic measurements were performed in the potential range from –250 mV to +500 mV relative to open circuit potential, with continuous monitoring of current between the working and counter electrode.

Spectrophotometric measurements

Adsorption behaviour of organic molecules from propolis was interpreted by spectrophotometric method. UV – VIS spectra of propolis extract solution (concentration of 3500 mg dm^{-3} in 0.51 mol dm^{-3} NaCl) were analysed before and after immersion of copper sample in the solution for 48 hours. Recording of the spectrum was performed by the 105 UV-VIS Spectrophotometer BUCK Scientific.

Results and discussion

Open circuit potential measurements

The dependence of the open circuit potential for Cu in 0.51 mol dm^{-3} NaCl solution in the absence and presence of propolis extract as a function of time is shown in Fig. 1.

It can be observed that the changes in the copper corrosion potential with the addition of propolis extract are not significantly expressed in relation to the corrosion potential of Cu in the non-inhibited solution (Fig. 1). Corrosion potential values shifted to negative values during the first ten minutes of open circuit potential measurements, and then achieved a constant value. This behaviour is at-

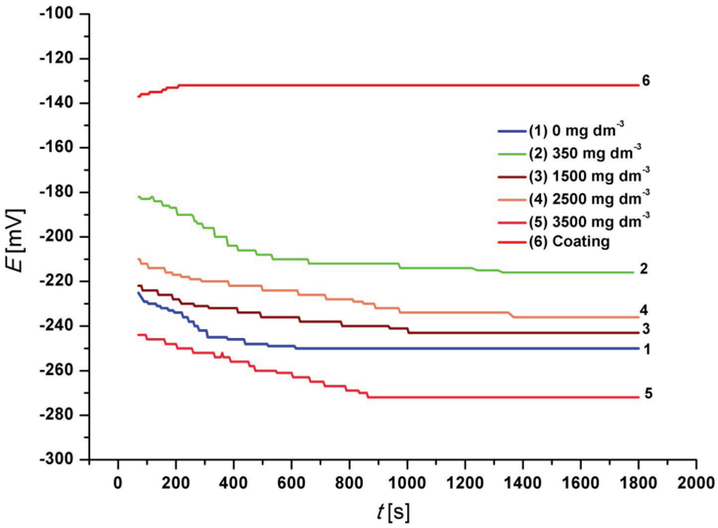

Fig. 1 – *Dependence of corrosion potential for Cu in 0.51 mol dm^{-3} NaCl solution in the absence and presence of propolis extract as a function of time*

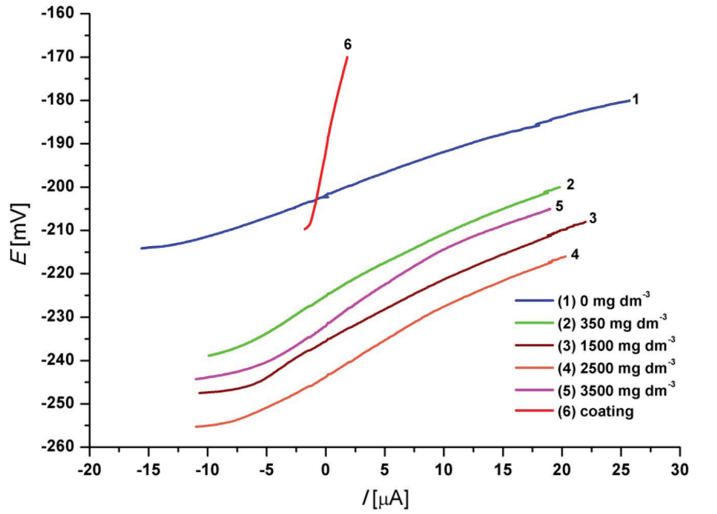

Fig. 2 – *Linear polarization curves for copper in 0.51 mol dm^{-3} NaCl solution without stirring as a function of various propolis extract concentrations*

tributed to the formation of the adsorbed layer on the copper surface, since there was no protective film to prevent metal dissolution at the moment of electrode immersion in the test solution[11]. In such cases, it is considered that cathode processes are dominant in relation to anode processes[12]. Generally, if the displacement in corrosion potential is higher than 85 mV in the presence of inhibitor with respect to corrosion potential of the blank, the inhibitor can be classified as a cathodic or anodic type[13]. No significant changes in open circuit potentials in chloride solution with propolis extract compared to blank solution suggest a mixed type of inhibitor.

Potential of electrode with propolis coating is much more positive than corrosion potential for the copper in the blank NaCl solution. This potential slowly shifted towards positive values with time. Such behaviour indicates a predominant inhibition effect of propolis coating.

Polarization measurements

After 30 minutes of monitoring open circuit potential, polarization resistance was determined by the linear polarization method. Having establishing stable corrosion potential, the working electrode polarized cathodically and anodically ± 20 mV relative to the corrosion potential. Linear polarization curves for copper in 0.51 mol dm^{-3} NaCl solution without stirring at 25 ºC as a function of various concentrations of propolis extract are shown in Fig. 2.

The slope of the linear part of the curve increased with increasing propolis extract concentration, indicating an increase in polarization resistance, i.e., increased corrosion resistance of copper. The copper electrode with propolis coating had the highest corrosion resistance (Fig. 2).

Values of polarization resistance were determined from the slope of linear part of the curves. Based on these values, degree of surface coverage (θ) and inhibition efficiency (η) were calculated according to equation (1):

$$\eta = \theta \cdot 100 = \left(\frac{(R_p)_{\text{inh}} - R_p}{(R_p)_{\text{inh}}} \right) \cdot 100 \qquad (1)$$

where R_p and $(R_p)_{\text{inh}}$ are the values of polarization resistance in the absence and presence of inhibitor.

The values of polarization resistance, degree of surface coverage, and inhibition efficiency determined by linear polarization method are shown in Table 1. It is evident that, with increasing propolis concentration, the inhibition efficiency increased, as well as that the highest efficiency was achieved with solid propolis coating.

Table 1 – *Linear polarization parameters for copper corrosion in 0.5 M NaCl in the presence of various concentrations of propolis extract at temperature 25 ºC*

C [mg dm^{-3}]	j_{corr} [μA cm^{-2}]	R_p[kΩ]	θ	η [%]
0	24.53	0.885	–	–
350	16.17	1.341	0.3408	34.08
1500	15.73	1.381	0.3587	35.87
2500	14.11	1.539	0.4248	42.48
3500	12.37	1.756	0.5364	53.64
coating	1.875	11.58	0.9236	92.36

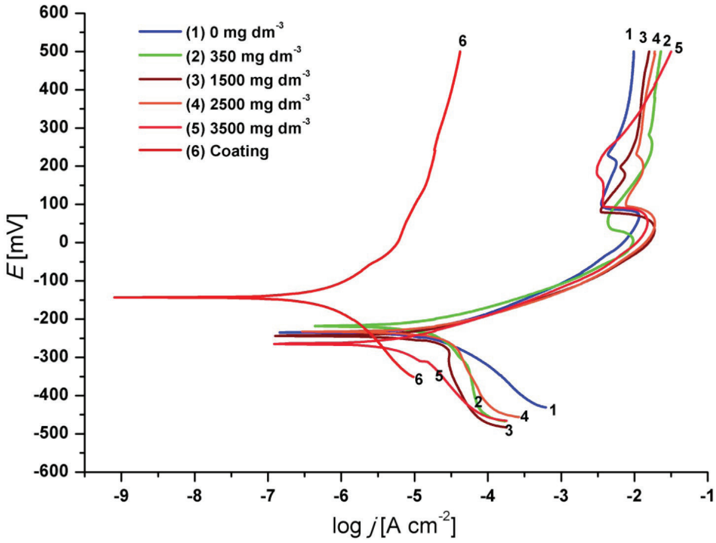

Fig. 3 – *Potentiodynamic polarization curves in 0.51 mol dm^{-3} NaCl solution as a function of various propolis extract concentrations*

Potentiodynamic polarization curves of copper in 0.51 mol dm^{-3} NaCl solution as a function of various propolis extract concentrations are shown in Fig. 3. Corrosion parameters were determined from the polarization curves, while inhibition efficiency was calculated using equation (2):

$$\eta = \frac{j^o_{corr} - j_{corr}}{j^o_{corr}} \cdot 100 \qquad (2)$$

where j_{corr} and j^o_{corr} are the values of corrosion current density with and without inhibitor, respectively.

The addition of propolis extract in NaCl solution led to a decrease in corrosion current density and displacement of corrosion potential in cathodic and anodic direction. Decrease in the corrosion current density indicates the inhibitory effect of propolis, which is consistent with the data obtained with the previous two methods. The value of the corrosion potential significantly increased, while cathodic and anodic currents decreased for the sample with propolis coating. Considering that the displacement in corrosion potential is not higher than 85 mV in the presence of inhibitor with the respect to corrosion potential of the blank, propolis can be classified as a mixed type of inhibitor with a more pronounced impact on the cathode reaction[6,13,14].

The inhibition efficiency of propolis extract on copper corrosion in 0.51 mol dm^{-3} NaCl solution increased with increasing propolis extract concentration, reaching a value of 72.69 % at a concentration of 3500 mg dm^{-3}, while the inhibition efficiency of the propolis coating was 98.54 %.

The slight change in the value of Tafel's slopes with increasing propolis extract concentration indicates that addition of propolis does not change the copper dissolution mechanism, meaning that propolis exhibits its inhibitory effect only by adsorption on the electrode surface.

Adsorption models

The process of metal corrosion inhibition is based on the adsorption of organic inhibitor molecules on the metal surface. Adsorption of the organic inhibitor can be physical adsorption or chemisorption. In order to examine the adsorption mechanism closely, it is important to determine the adsorption isotherm that best fits the experimental results. Effective adsorption of organic inhibitors can be considered as a process of substitution, which takes place at the electrode electrolyte boundary phase according to equation[15]:

$$Org_{inh_{(aq)}} + xH_2O_{(ads)} \rightleftarrows Org_{inh_{(ads)}} + xH_2O_{(aq)} \qquad (3)$$

where $Org_{inh(aq)}$ and $Org_{inh(ads)}$ are the molecules of organic inhibitors in the solution and molecules adsorbed on the metal surface, respectively. $H_2O_{(ads)}$ represents water molecules adsorbed on the metal surface, and x is the number of water molecules, which is substituted with one molecule of organic inhibitor.

Results of examination showed that adsorption of propolis on the copper surface can be best described by Langmuir's adsorption isotherm (Fig. 4). Langmuir's adsorption isotherm was given by the following equation[16]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (4)$$

where K_{ads}– is the equilibrium constant of adsorption process; θ – degree of surface coverage; C – is the inhibitor concentration. Dependence (C/θ) as a function of C is straight line with the slope equal to the unit and ordinate intercept $-K_{ads}^{-1}$.

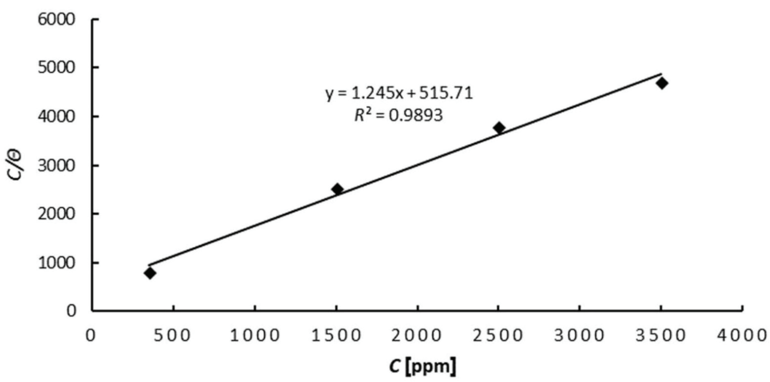

Fig. 4 – *Langmuir's adsorption isotherm for propolis adsorption process on the copper surface in NaCl solution*

High value of R^2, which amounts 0.9893, indicates that adsorption process can be described by Langmuir's isotherm[6,8]. Langmuir's isotherm assumes that the solid surface contains a fixed number of adsorption sites, and each site holds one adsorbed species, indicating monolayer adsorption[17].

On the basis of obtained straight line, the value of adsorption constant K_{ads} = 1.93 mol^{-1} dm^3 was calculated. The value of the given constant indicates that propolis is easily and strongly adsorbed on the surface of metal[18].

Equilibrium constant of adsorption process was related to free energy of adsorption by equation[19]:

$$K_{ads} = \frac{1}{55.55}\exp\left(-\frac{\Delta G_{ads}}{RT}\right) \quad (5)$$

where ΔG_{ads} – Gibbs free energy of adsorption (kJ mol^{-1}); 55.55 (mol dm^{-3}) – molar concentration of water in solution.

The value of free Gibss energy of adsorption (ΔG_{ads}) at temperature 25 ºC calculated from equation (5) was –11.582 kJ mol^{-1}. The obtained value ΔG_{ads} indicates the spontaneity of adsorption of propolis on the surface of copper electrode[20], as well as strong physical adsorption[5,21]. Therefore, inhibitory effect of propolis on the surface of copper electrode is the consequence of the formation of a protective film. This film physically blocks attention of aggressive ions from NaCl solution.

Influence of temperature on copper corrosion in 0.51 mol dm^{-3} NaCl was examined in the temperature range of 25 ºC – 55 ºC. The results of examination (Table 2) show that corrosion rate in the uninhibited and in the inhibited NaCl solution increases with temperature. A quantitative relationship between temperature and corrosion rate is given by Arrhenius's equation[22]:

$$j_{corr} = A\exp\left(\frac{-E_a}{RT}\right) \quad (6)$$

where: j_{corr} is current density, which is directly proportional to the corrosion rate, A is Arrhenius's pre-exponential factor, E_a is the apparent activation energy, R is the universal gas constant (8.314 J K^{-1} mol^{-1}), T is the absolute temperature (K). Dependence $\ln j_{corr} = f(1/T)$ is given by equation (7):

$$\ln j_{corr} = -\frac{E_a}{RT} + \ln A \quad (7)$$

A plot of $\ln j_{corr}$ versus $1/T$ for 0.51 mol dm^{-3} NaCl solution with and without inhibitor is presented in Fig. 5.

Obtained straight lines have slope ($-E_a/R$) from which the values of activation energy were calculated: 23.69 kJ mol^{-1} in the inhibitor-free solution, and 36.18 kJ mol^{-1} in the presence of inhibitor. The higher value of E_a in the presence of inhibitor indicates physical adsorption of propolis on the copper surface[5,15,23].

Table 2 – *Corrosion parameters and inhibition efficiency for copper in 0.51 mol dm^{-3} NaCl solution in the absence and presence of propolis extract at different temperatures*

C [mg dm^{-3}]	E_{corr} [V]	j_{corr} [µA cm^{-2}]	b_a [V dec^{-1}]	b_k [V dec^{-1}]	η [%]
		T = 25 °C			
0	–0.246	30.25	0.070	–0.125	–
350	–0.214	17.18	0.056	–0.106	43.21
1500	–0.243	12.97	0.061	–0.075	57.12
2500	–0.236	11.75	0.051	–0.054	61.15
3500	–0.276	7.78	0.066	–0.080	74.28
coating	–0.137	0.44	0.071	–0.055	98.54
		T = 35 °C			
0	–0.258	42.35	0.065	–0.120	–
3500	–0.283	12.89	0.054	–0.090	69.56
		T = 45 °C			
0	–0.263	53.85	0.062	–0.123	–
3500	–0.292	19.75	0.056	–0.105	63.33
		T = 55 °C			
0	–0.261	75.38	0.006	–0.130	–
3500	–0.295	32.56	0.056	–0.120	56.81

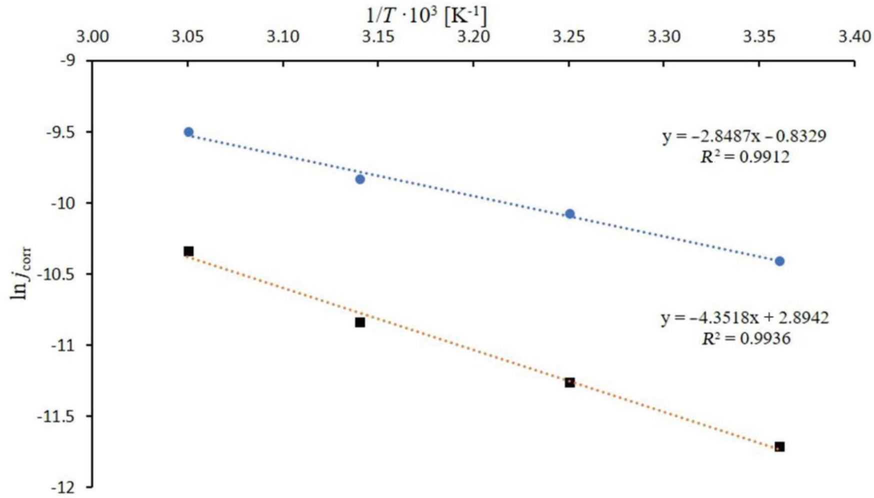

Fig. 5 – *Arrhenius's plots for Cu in 0.51 mol dm^{-3} NaCl: in the absence (●), and in presence of propolis extract (■) in concentration of 3500 mg dm^{-3}*

UV-visible spectroscopy

Inhibition of corrosion of copper in NaCl solution by propolis was explained by mechanism of molecular adsorption, and confirmed by UV spectroscopy (Fig. 6). Spectra, which were obtained in the propolis solution before and after immersion of copper samples, have the same position of absorption maximum, with noticeable change in absorbance value. The change in the position of absorption maximum or change in the value of absorbance indicate the formation of a complex between two species in solution[24,25]. On the basis of the change in the value of absorbance, it can be concluded that organic compounds, in the propolis composition, were adsorbed on the copper surface and formed a protective film of inhibitor. This conclusion is in accordance with the increase in coverage degree with increasing propolis extract concentration, which was confirmed by electrochemical methods.

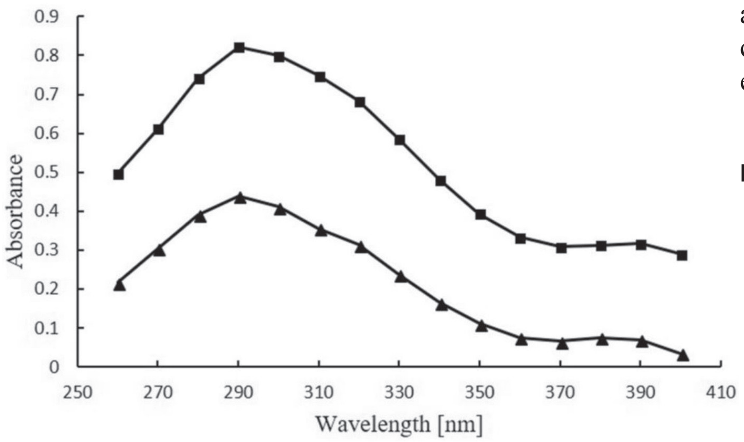

Fig. 6 – *UV-Visible spectra of test solution with propolis extract (3500 mg dm^{-3}): before immersion (■), and after 48 hours immersion (▲) of copper samples in solution*

Conclusion

The results confirmed that propolis can be used as a corrosion inhibitor for copper in NaCl solution. Thus, it can be concluded that inhibition efficiency of propolis increases with its concentration, and the highest efficiency was achieved with propolis coating on the electrode surface. Based on the change in corrosion potential in the presence of inhibitor as compared to the corrosion potential in NaCl solution without inhibitor, propolis can be classified as a corrosion inhibitor of mixed type. Inhibitory action of propolis was explained by mechanism of adsorption in accordance with Langmuir's isotherm. The value of free adsorption energy indicates the spontaneity of adsorption process, which has character of physical adsorption. Addition of propolis increases activation energy of the adsorption process, indicating physical adsorption. The results of UV-VIS spectroscopy confirm the conclusion about adsorption of organic compounds of propolis on copper surface. Propolis can be used as an eco-friendly inhibitor of copper corrosion.

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