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Full Paper

Inhibitory Effect of Propolis against Corrosion Evaluated by Electrochemical Methods of Ti Grade 2 in Artificial Fluoride Saliva

Faiza Kakaa,[1] Mosbah Ferkhi,[1,*] and Mesbah Lahouel[2]

[1]*Laboratory of Interaction Materials and Environment (LIME), Mohamed Seddik Ben Yahia University, Ouled Aissa BP 98, Jijel, Algeria*
[2]*Laboratory of Molecular Toxicology, Department of Molecular and Cellular Biology, Faculty of Science, Mohamed Seddik Ben Yahia University, Ouled Aissa BP 98, Jijel, Algeria*

*Corresponding Author, Tel.:+213670351700
E-Mail: ferkhimosbah1@gmail.com

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Abstract-The objective of this work was to demonstrate the effect of fluoride and propolis extract on the corrosion behavior of commercially pur titanium (cp-Ti grade 2) in artificial saliva. The inhibition studies were approved out on cp-Ti as dental implant in Fusayama-Meyer with the propolis extract using potentiodynamic polarization and Electrochemical Impedance Spectroscopy (EIS). Parameters, such as concentration of the inhibitor, time of immersion were varied and optimized. The results showed that either the NaF or the presence of propolis extract in medium saliva had a significant influence on the corrosion rate (I_{corr}) and polarization resistance (R_p): the I_{corr} value increased and R_p decreased in medium containing fluoride, but the presence of propolis in media improved the corrosion resistance of this metal.

Keywords-Propolis; Titanium grade 2; Inhibition; Fusayama-Meyer; Electrochemical Impedance Spectroscopy

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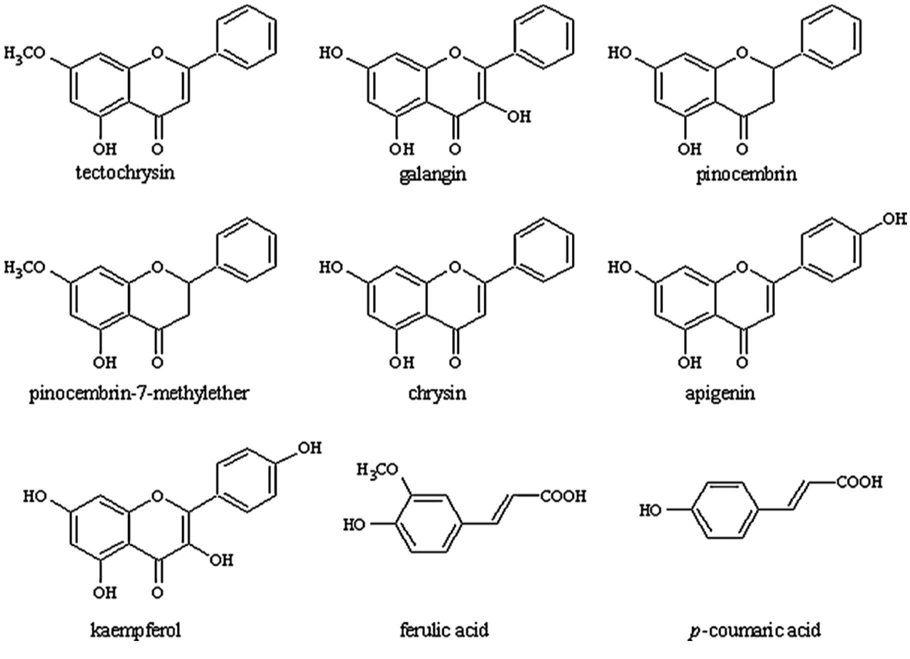
1. INTRODUCTION

Titanium and titanium alloys (such as Ti-6Al-4V) are frequently used as implant materials such as dental and orthopedic implants [1,2], for the reason that they present high corrosion resistance in physiological media, low toxicity and they have an excellent biocompatibility [3,4]. Commercially pure titanium (cp-Ti) has been used by the dental profession for a long time for the manufacture of crowns, bridges, etc. [3].

During dental caries treatment, doctors recommend that their patients utilize fluoride mouthwashes, specifically adolescents who do not always follow a good oral hygiene regime and present a high menace of dental caries. Fluoride promotes the formation of calcium fluoride globules that stick to the teeth and stimulate remineralization while protecting against acid aggression. Fluoride mouthwashes thus help prevent the development of caries and protect dental implants [5].

Propolis is a natural product resulting from the movement and activity of bees, based on substances taken from plants, trees, and flowers [6]. Propolis chemical composition and biological effects (anti-inflammatory, anti-oxidant, anti-bacterial, anti-tumor and also anesthetic and analgesic activities) is very variable and differs from environment, origin of plant species, time, vegetation of collection areas and type of bee flora [7]. It contains resins, composed of flavonoids and phenolic acids, waxes, essential oils, pollen and various organic compounds [8,9]. As the most important constituents, flavonoids and polyphenols contribute significantly to the biological and pharmacological actions of propolis [10-12]. Propolis extract have a broad range of pharmacological properties, counting anti-inflammatory, anti-oxidant, anti-bacterial, anesthetic and analgesic activities effects [7,13,14].



Scheme 1. Molecular Structure of flavonoids and phenolic acids present in propolis samples [15]

The aim of this study is to understand the mechanisms of corrosion damage and corrosion inhibition using biomaterials for the buccal environment to reduce tooth decay. Corrosion parameters, such as corrosion current density (**I_{corr}**), corrosion potential (**E_{corr}**) and polarization resistance (**R_p**), are used to adjust the experimental data and take out the parameters which describe the corrosion process. Electrochemical impedance spectroscopy (EIS) was performed to better understand the phenomena related to the substrate/solution system. We present results obtained by electrochemical measurements using commercially pure titanium (cp-Ti).

2. Materials and methods

2.1. Preparation of the samples

Pure titanium discs (1cm^2) (Mayitr, cp-Ti, ASTM B265, grade 2) were used as a working electrode. The way of cutting the samples was chosen as not modify the microstructure and corrosion test at the coupon surface, due to its low heat input and the absence of mechanical damage by avoiding heat affected areas. Pre-treatment of cp-Ti samples surfaces was approved out by polishing with on SiC abrasive paper from grade of 240 up to 2500 and then with 1µm alumina suspension, Ultrasonic cleaning procedure was used in acetone for 5 minutes, rinsing with bidistilled water and dried with compressed air at room temperature.

2.2. Electrochemical media

Artificial saliva type Fusayama-Meyer was a principal solution for preparing an electrochemical media for testing corrosion of titanium implant, the composition of solution is mentioned in Table 1 [16]. In the first time, addition of fluoride with different concentrations (100, 1000 and 12300 ppm) is necessary to know the effect of fluoride on the Ti surface. The second time, adding of propolis extract with different concentration is required to understand the effect of propolis extract against the corrosion of cp-Ti in fluorinated media.

Table1. Chemistry of the simulated artificial saliva type Fusayama-Meyer solution

Components	**KCl**	**NaCl**	**$CaCl_2.2H_2O$**	**$NaH_2PO_4.2H_2O$**	**$Na_2S.9H_2O$**	**Urea**
Concentration (g/L)	0.4	0.4	0.906	0.690	0.05	1

2.3. Propolis preparation

Propolis was collected with traps to minimize their contamination from beekeepers (Latitude N 36.755506, Longitude E 5.807074), located at Chaddia (Kaous-Algiers), 10 km in the South Eastern region of Jijel (Algeria) in September 2017. It was kept freezed and desiccated at -20°C. The extraction and composition process have been described previously by Lahouel et al [17]. Small pieces of propolis are immersed in a bath of alcohol 80° (1g / 10ml) for a period of 10 days, the solution is filtered and then passed through a rotary evaporator (Evaporator E100) at 69°C, the product extract is named; propolis extract. The final product was liophilised and the powder kept in the dark for testing in several fields: biological, electrochemical, etc.

2.4. Morphological analyses

Scaning electron microscopes (SEM) model VEGA3 TESCAN equipped with an Energy dispersive spectroscopy (EDS) analyzer was used to investigate the surface morphology and the chemical proportions of different elements.

2.5. Electrochemical study

The electrochemical study was carried out using a Voltalab PGZ 301 equipment piloted by voltamaster 4 connected to a usual three electrodes cell with a platinum as auxiliary electrode and a saturated calomel electrode as reference. The working electrode (WE) was in the cp-Ti and had the form of a disk with an exposed area of $1cm^2$. The polarization curves current-potential were recorded by varying the electrode potential from -450 to 100 mV/SCE, with a scanning rate of 1 mV/s. The next experimental data have been obtained by electrochemical measurements in present of propolis extract as corrosion inhibitors such with different concentrations (0.25, 0.5, 0.75 and 1 mg/ml) that have been added to the simulated artificial saliva solution with 12300 ppm F^-. Inhibition efficiencies (**EI** %) were determined from corrosion parameters values calculated by Tafel extrapolation method.

The resistance of polarisation (R_p), calculated from traces of the polarization curve at ±10 mV versus E_{OCP}, $\mathbf{R_p}$ was determined using the Stern-Geary equation [18]:

$$\mathbf{R_p} = \frac{\beta_a \beta_c}{2.3\, I_{corr}\, (\beta_a + \beta_c)} \tag{1}$$

The electrochemical impedance spectroscopy (EIS) measurements are approved out with the same electrochemical system to obtain the corrosion parameters in solution with and without propolis extract. After the determination of steady-state current at a corrosion potential, an amplitude of 10 mV was applied in a frequency area between 10^5 and 10 mHz. Computer programs automatically controlled the measurements performed at rest potentials after 24, 48 and 72 hours of exposure at 37 °C. The impedance diagrams are shown on the Nyquist plan.

3. RESULTS AND DISCUSSION

3.1. Morphological analysis

Morphological surface of Ti (SEM-EDS images) of titanium immersed in Fusayama-Meyer containing 12300 ppm F^- with and without propolis extract inhibitor (1mg/ml) for duration of 72-hours are shown in Figures (1b and 1c).

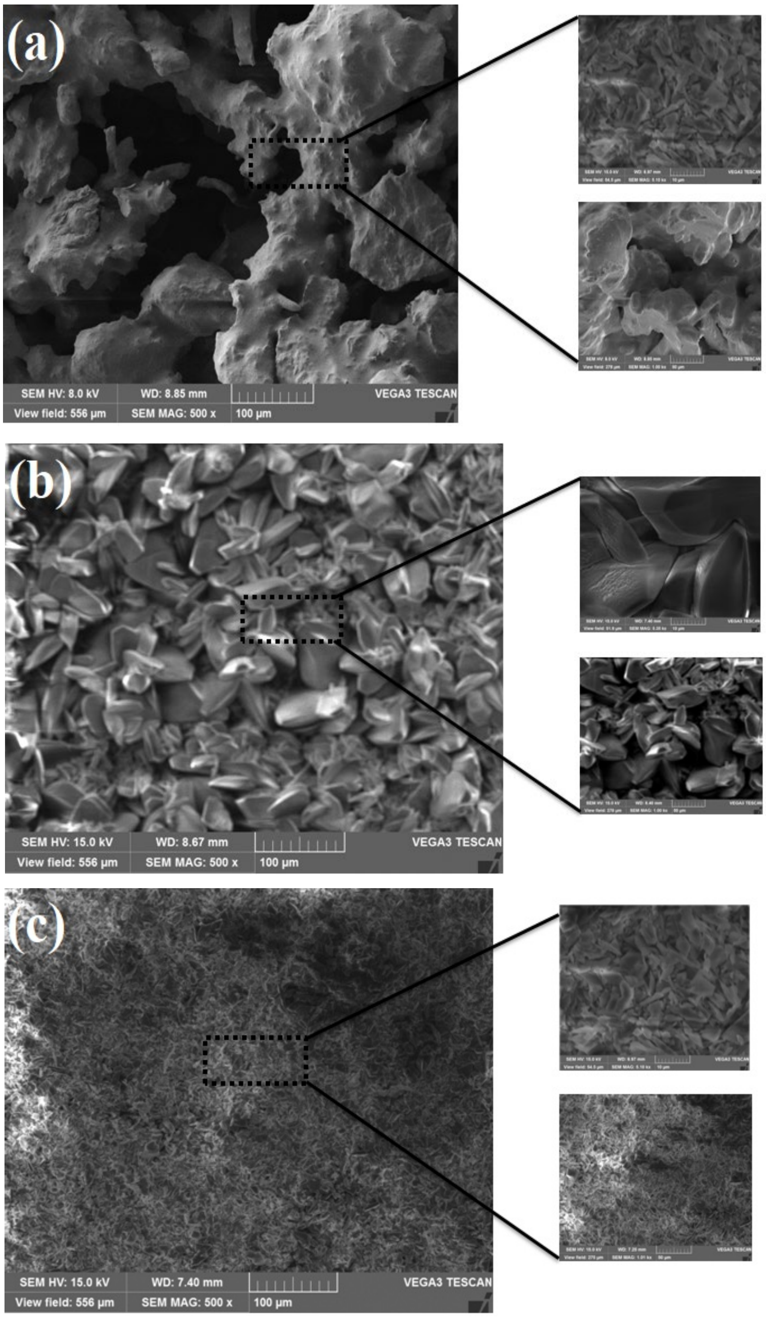


Fig. 1.SEM images for **(a):** propolis extract product, **(b):** cp-Ti in artificial saliva containing 12300 ppm F^- without propolis extract, **(c):** cp-Ti in artificial saliva containing 12300ppm F^- with 1mg/ml propolis extract after 72 hours immersion

In absence of inhibitor, it is very remarkable that a general corrosion phenomenon occurs on surface of subtract (attack by F$^-$ ions) causing the rough surface of titanium oxide layer TiO_2. EDS analyzes (Fig. 2a) of the surface confirm this result where the atomic percentages of Ti and O (41%, 59%, respectively) are high.

On the other hand, after adding 1mg/ml of inhibitor, a layer of propolis, generally, covers all surfaces of titanium electrodes, which indicates a good adhesion of inhibitor. EDS analyzes (Fig 2b) show a low oxygen atomic percentage (23 %) representing the composition of propolis inhibitor. The atomic percentage of Ti (60%) does not correspond to the TiO_2 layer; but rather the titanium substrate..

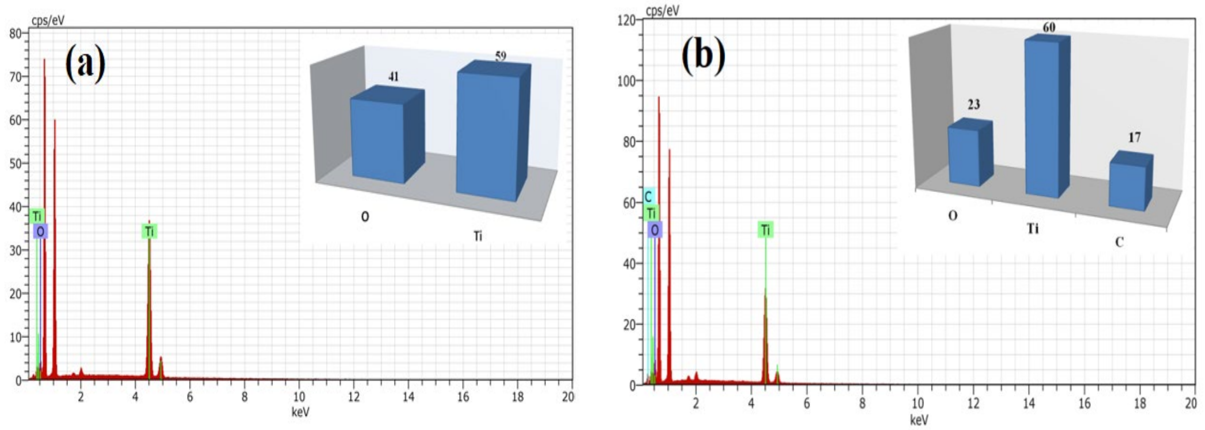


Fig. 2. EDS analysis for **(a):** cp-Ti in Fusayama-Meyer with 12300 ppm F$^-$ in absence of propolis and **(b):** cp-Ti Fusayama-Meyer with 12300ppm F$^-$ with 1mg/ml propolis after 72 hours of immersion

3.2. Electrochemical measurement

3.2.1. Effect of fluoride ions

a. Linear polarization curves

Fig. 3, shows the voltammograms obtained for cp-Ti after 24-hours immersion in Fusayama-Meyer with 12300 ppm of F$^-$ ions. The corrosion parameters I_{corr}, E_{corr} as well as the cathodic and anodic Tafel slopes (βc), (βa) are illustrated in Table 2.

According to these curves; if the F$^-$ ions concentrations values decreases, the corrosion current density for Ti increases slightly from 0.33 to 7.69 µA/cm^2 and polarization resistance decreases from 488 to 21 MΩ.cm^2. The value of E_{corr} tends towards the anodic values.

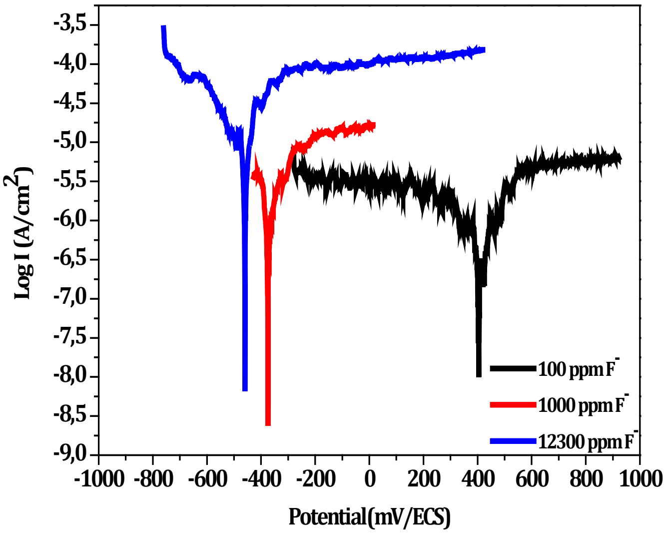


Fig.3. Potentiodynamic polarisation curves for cp-Ti in Fusayama-Meyer with different concentrations of F$^-$ ions at 37 °C.

Table 2. Corrosion parameters of cp-Ti in Fusayama-Meyer with different concentrations of Fluoride.

	E$_{corr}$ (mV/SCE)	**I$_{corr}$ * 10^{-6} (A.cm^{-2})**	**V$_{corr}$*10^{-3} (mm.yr^{-1})**	**R$_p$*10^6 (Ω.cm^2)**
100 ppm	400.6	0.33	2.84	488
1000 ppm	-375.40	0.92	7.92	44
12300 ppm	-459.70	7.69	66.26	21

b. Electrochemical impedance spectroscopy measurements

The spectra (EIS) are plotted on Nyquist diagram **(Fig. 4)**. The all diagrams shows more of a semicircle, but the impedances values calculated in Fusayama-Meyer (at pH 6 and 12300 ppm F$^-$ ions) are much lower than those obtained in saliva (at pH 6 and 100 ppm F$^-$ ions) or (at pH 6 and 1000 ppm F$^-$ ions).

In artificial saliva containing 100 and 1000 ppm F$^-$, the Equivalent Electrical Circuit, which gives the good fitting and the best experimental EIS data, is characterized by a constant phase element (CPE) that represents the capacitance of the titanium oxide film (CPE$_f$) and the resistance of that passive film (R$_f$) lying in parallel with CPE, as shown in Fig. 5a.

This equivalent electrical circuit, also known as Randle's circuit, is applicable in the presence of a compact passive layer on titanium. In our study, such equivalent electrical circuit indicated thus the presence of a compact film at a passive state. Fitting data are listed in Table 3.

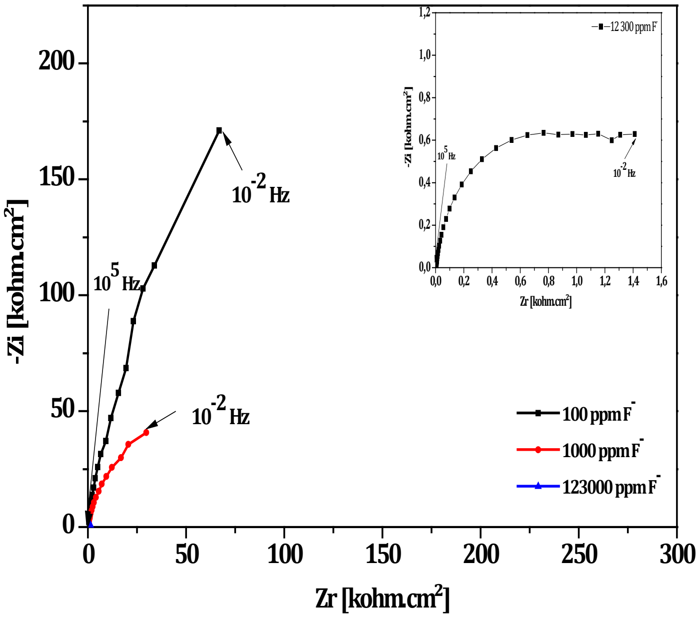


Fig. 4. Nyquist plots from EIS recorded for cp-Ti in Fusayama-Meyer with different concentrations of F⁻ ions at 37 °C

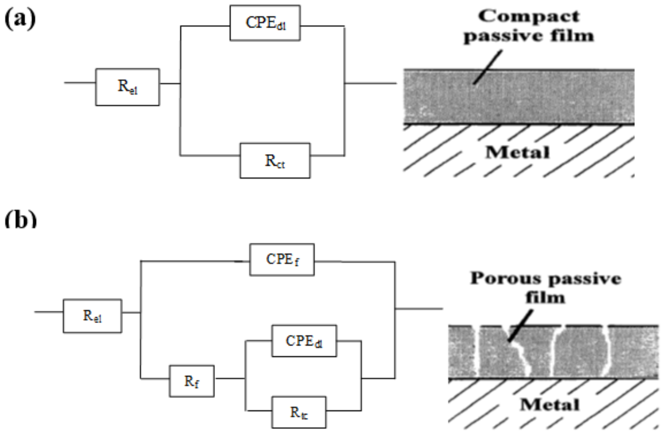


Fig. 5. Equivalents Electricals Circuits used for fitting the experimental data

Table 3. Fitting parameters determined from Nyquist diagrams based on the equivalent circuit presented in Fig. 4

	R_{el} ($\Omega.cm^2$)	CPE_f*10^{-6} ($\Omega^{-1}.cm^{-2}.s^n$)	n_1	R_f ($\Omega.cm^2$)	$CPE_{dl}*10^{-6}$ ($\Omega^{-1}.cm^{-2}.s^n$)	n_2	$R_{ct}*10^6$ ($\Omega.cm^2$)
100ppm	183	-	-	-	59	0.91	0.53
1000ppm	71	-	-	-	89	0.91	0.05
12300ppm	42	159	0.94	711	0.53	0.50	0.2

Nyquist diagrams of the same shape and same order of impedance values were obtained for cp-Ti by Sousa et al. [19] in saliva of pH 5.5 containing 20 to 227 ppm F^-.The EIS spectra recorded cp-Ti immersed in a solution containing 12300 ppm F^- (Fig. 4) were best fitted with an equivalent circuit containing two CPEs that represent the capacitance of the titanium oxide surface film (CPE_f) and a double layer capacitance (CPE_{dl}) in the circuit (Fig. 5b). This circuit suggests the presence of defects in the oxide surface film that this has to be considered as a porous oxide film (Fig. 5b).

3.2.2. Effect of inhibitor concentrations

a. Linear polarization curves

The influence of propolis extract on the behavior of titanium in fluoride artificial saliva solution was evaluated based on the polarization curves. The titanium samples were left in the corrosive solution for either 24-hours, then the polarization curves were plotted starting from the cathodic to the anodic potentials. Polarization curves recorded in solution contains the propolis extract concentration present in artificial saliva with 12300 ppm of F^- ions are shown in Fig. 6, and corrosion parameters are listed in Table 4.

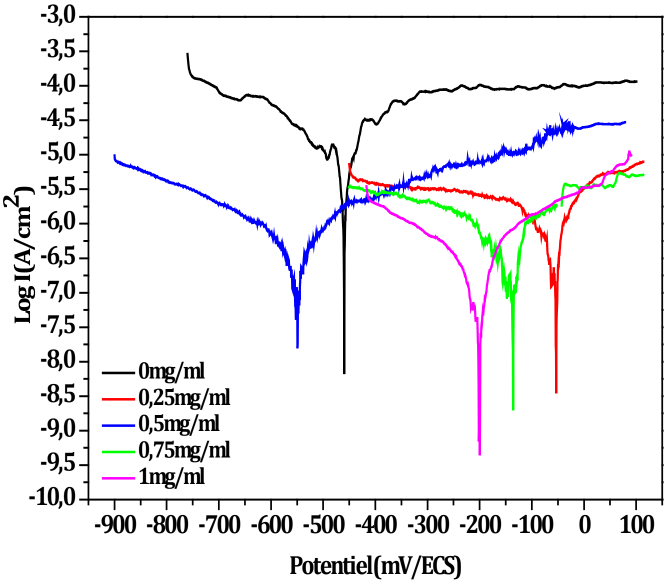


Fig. 6. Potentiodynamic polarisation curves for cp-Ti in floured artificial saliva with different concentrations of propolis extract at 37 °C

Corrosion parameters, counting the corrosion potential (E_{corr}), the cathodic (β_c) and anodic (β_a) Tafel slopes, and the corrosion current density (I_{corr}) were calculated by Tafel extrapolation and the results obtained at different concentrations of inhibitor are shown in Table 4 which contains the inhibiting efficiency (IE) values calculated according to the following equation [2]:

$$\mathrm{IE}\ \% = \frac{\mathrm{I^0_{corr}} - \mathrm{I_{corr}}}{\mathrm{I^0_{corr}}} \times 100 \qquad (2)$$

where I^0_{corr} and I_{corr} are the values of the corrosion current densities in the absence and presence of the propolis extract, respectively.

Electrochemical results show that there is an optimization condition at pH 6.0, meaning that the most value of the current and the least value of the potential were obtained at this pH level. Fig. 2 shows the pH optimization selected at pH=6 in this work to investigate other electrochemical parameters.

Table 4. Electrochemical parameters obtained from Tafel plot for cp-Ti in fluored artificial saliva with different concentrations of propolis extract

	C_{inh} (mg/ml)	**I_{corr} * 10^{-6} (A.cm^{-2})**	**V_{corr}*10^{-3} (mm.yr^{-1})**	**R_P* 10^6 (Ω.cm^2)**	**IE (%)**	**θ**
Blank	**0**	7.69	66.26	20.76	-	-
Propolis extract	**0.25**	1.08	9.30	98.16	85.95	0.85
	0.5	0.58	5.00	411.84	92.45	0.92
	0.75	0.79	6.80	404.09	89.72	0.89
	1	0.48	4.13	4264.53	93.75	0.93

As it can be observed in Table 4, the addition of propolis extract at different concentrations reduced the corrosion current density values. In the experiment conditions, the lowest I_{corr} values were recorded in the presence of 1 mg/ml propolis extract. Less of this threshold concentration, the I_{corr} values slightly increased, but they remained considerably lower as compared to the blank sample. On the other hand, the inhibition efficiency reaches its maximum (93.75 %) at the same concentration.

These results confirmed the capacity of propolis extract to minimize the corrosion phenomenon, probably due to the adsorption of propolis extract components on the titanium surface, through the oxygen atoms within their functional groups and the aromatic rings.

b. EIS measurement

The impedance spectra for titanium in artificial saliva solution at 37 °C with different concentrations of propolis extract are presented in Fig. 7. The EIS parameters derived from these investigations are regrouped in Table 4. The inhibition efficiency is calculated using the following relationship [2]:

$$\mathrm{IE\%} = \frac{\mathrm{R_{ct}} - \mathrm{R^0_{ct}}}{\mathrm{R_{ct}}} \times 100 \qquad (3)$$

where R_{ct} and R^0_{ct} are the charge transfer resistances in inhibited and uninhibited solutions, respectively.

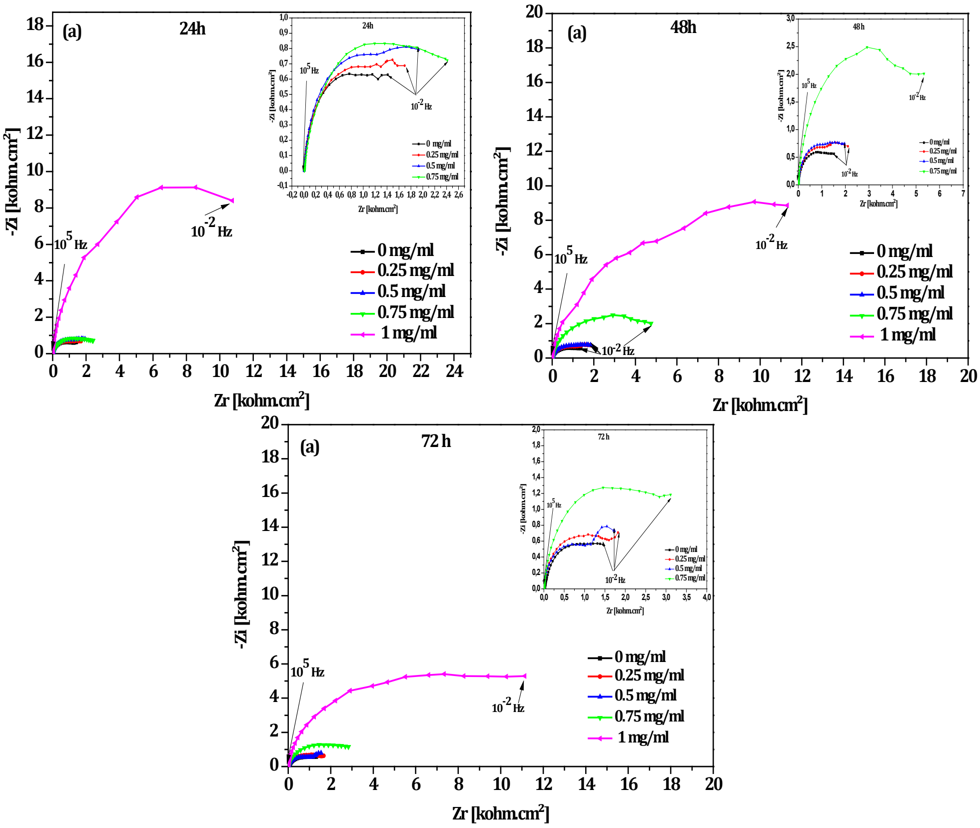


Fig.7. Nyquist plots from EIS recorded for titanium in fluoride artificial saliva solution with different concentrations of propolis at different time of immersion: (a) 24 h,(b) 48 h and (c) 72 h.

Fitting of the experimental results from EIS to equivalent circuit gave all parameters impedance listed in Table 5. All spectra of Figs. 7a, 7b and 7c show a semi-circular form, representing a charge transfer process mainly controls the corrosion of titanium, the diameter of capacitive circle with inhibitor is larger than that without inhibitor, where the biggest diameter was obtained at high concentration of inhibitor (1mg/ml). In the other hand, the diameter of the capacitive circle which increased at 1mg/ml of inhibitor indicated that propolis extract increased the charge transfer resistance and gave an inhibition effect on the titanium corrosion in fluoride artificial saliva.

The results found were fitted with the equivalent circuit appear in Fig. 8 in which the resistance of the electrolyte (R_{el}) is linked serially with two time constants. The high frequency time constant (CPE_1 (R_1)) is the result of the fast charge transfer process during the Ti dissolution in artificial saliva solution: R_1 represents the charge transfer resistance, while CPE_1 replaces the capacitance of the electrochemical double layer. The time constant in the low frequency region (CPE_2 (R_2)) results from mass transfer (mainly Ti ions) through the surface film of corrosion products: R_2 is the surface film resistance; CPE_2 replaces the capacitance of the surface film. The fitting parameters are presented in a Table 5.

Table 5. Fitting parameters determined from Nyquist diagrams based on the equivalent circuit appear in Fig. 7

		Element circuit							
C_{inh}, (mg/ml)		**R_{el} * 10^{-3} ($\Omega.cm^2$)**	**CPE_f ($\Omega^{1}\cdot cm^{2}.s^{\alpha}$)**	**α_1**	**R_f ($\Omega.cm^2$)**	**CPE_{dl} ($\Omega^{-1}.cm^{-2}.s^{\alpha}$)**	**α_2**	**R_{ct} ($\Omega.cm^2$)**	**IE (%)**
24 -hours immersion									
Blank	**0**	4	0.24	0.88	1.55	4.18	1	1.40	-
Propolis extract	**0.25**	9	0.08	0.94	1.05	1.15	0.75	2.41	41.90
	0.5	9	0.13	1	0.98	0.80	0.72	2.74	48.90
	0.75	13	0.09	0.97	3.35	0.48	0.80	4.07	65.60
	1	19	34.09	0.35	0.01	0.05	0.95	21.25	93.41
48 -hours immersion									
Blank	**0**	10	0.24	1	0.69	1.10	0.73	1.59	-
Propolis extract	**0.25**	9	0.09	0.95	1.04	0.86	0.75	2.26	29.64
	0.5	7	0.11	1	0.95	0.81	0.69	2.53	37.15
	0.75	13	0.09	0.97	3.35	0.48	0.80	4.07	60.93
	1	12	0.22	0.86	132.20	0.06	1	8.43	81.13
72 -hours immersion									
Blank	**0**	0.14	0.31	0.81	1.61	0.20	0.40	0.02	-
Propolis extract	**0.25**	7	1.49	0.76	2.32	0.08	0.93	1.27	98.42
	0.5	7	0.09	0.97	0.86	1.05	0.74	2.55	99.21
	0.75	12	0.13	0.99	1.63	0.59	0.79	2.63	99.23
	1	17	0.16	0.87	10.71	0.07	1	4.84	99.58

Referring to the impedance data (Table 5), we observe an increase in R_{ct} value demonstrate the quantity of inhibition from the propolis extract addition after 24, 48 and 72 hours of immersion. In the other hand, increasing of the R_{ct} value with inhibitor addition of 1mg/ml gave a better performance to retard corrosion due to the oxide layer formation and decrease of the double layer capacitance with increasing inhibitor concentration indicates that the propolis extract inhibits the corrosion rate of titanium by an adsorption mechanism [10].

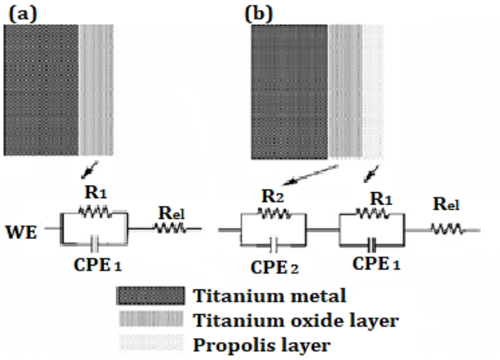


Fig. 8. Equivalents circuits used for fitting

For that reason, the decrease in the C_{dl} value can be attributed to a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, signifying that the inhibitor molecules function by adsorption at the metal/solution interface as a result of the substitute of water molecules by the inhibitor molecules [10].

The optimum IE% was 93.75% after 24-hours of immersion which was gained on the addition of 1mg/ml (Table 4). These results indicated that the corrosion rate of titanium can be inhibited effectively with the increase of concentration that reached 1mg/ml. Increasing of IE% value is proportional to the decreasing of current density. Data obtained from polarization are used to analyze the adsorption mechanism [2,20]. At the concentration of 1mg/ml, the smallest current density was produced due to the uniform adsorption of inhibitor molecules on metal surfaces.

3.3. Mechanism of adsorption

The adsorption phenomenon behavior of inhibitor molecule on metal surface can be evaluated by several adsorption isotherms, among which the most usually used ones include Temkin isotherm, Langmuir isotherm, Frumkin isotherm. To get the isotherm, surface coverage degree (θ) as a function of inhibitor concentration, was calculated by charge transfer resistance values using the following equation [10,21,22]:

$$\theta = \frac{R_{ct} - R_{ct}^{0}}{R_{ct}} \qquad (4)$$

R_{ct} charge transfer resistance with inhibitor ($\Omega.cm^2$), R^0_{ct} charge transfer resistance without inhibitor ($\Omega.cm^2$). Langmuir isotherm has been tested for its suitability to the experimental data. Langmuir isotherm is given by the expression [10,23]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \qquad (5)$$

where θ is the degree of surface coverage, C is the concentration of inhibitor in mg/ml, K_{ads} is the equilibrium constant of adsorption phenomenon, which can be obtained from the intercept of the straight line on the C/θ versus C plot (Fig. 9) and the related standard free energy of adsorption ΔG_{ads} can be estimated by the following equation [10, 24-26]:

$$\Delta G^0_{ads} = -RT \ln(55.5\ K_{ads}) \qquad (6)$$

The equilibrium constant K of the adsorption reaction was also determined K_{ads}= 5.58, which lead to ΔG^0_{ads}= − 14.78 kJ/mol. The plot of C/ θ versus C give a straight line with a slope close to 1 and a correlation coefficient of 0.9994, which confirms that the propolis extract adsorption on the cp-Ti surface in fluoride artificial saliva solution obeys the Langmuir adsorption isotherm.

Generally, the values of ΔG_{ads} less negative or equal to -20 Kj/mol (as obtained in this study) signify physical adsorption, which is consistent with electrostatic interaction between charged molecules and a charged metal [10] while values more negative than -40 KJ/mol signify chemical adsorption [27-29].

As expected, the inhibition effectiveness of propolis extract strongly depended on its concentration and exposure time to corrosive electrolyte. From Table 5 is clear that propolis extract exhibited a reasonable anticorrosive effect on titanium at 24-hour immersion. Therefore, the calculated IE value was low (41.90 %) in the solution containing 0.25 mg/ml propolis extract at 24-hours, but it progressively increased with the inhibitor concentration and reached the maximum value of 93.41% in presence of 1mg/ml propolis extract. By delaying the titanium exposure to inhibitor containing electrolytes up to 72-hours, an important increase of propolis inhibitive effect was observed for all studding concentrations (Table 5).

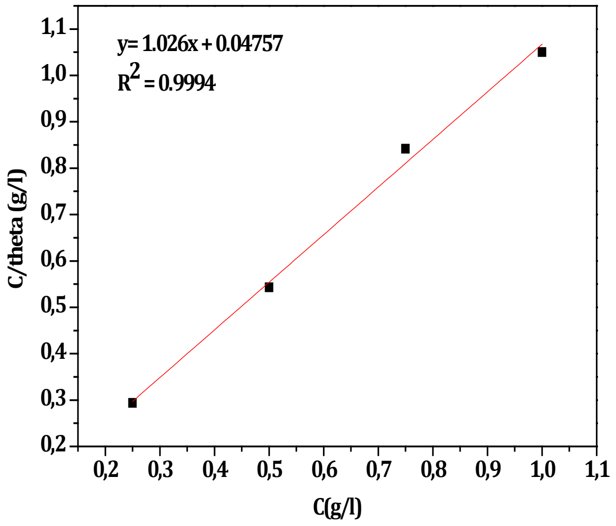


Fig. 9. Langmuir adsorption plot for titanium in fluoride artificial saliva containing different concentrations propolis extract from Charge transfer resistance

The highest IE value of 99.58% was reached after 72-hours of titanium immersion in 1mg/ml propolis-containing electrolyte. Over this concentration, the anticorrosive proprieties of propolis extract a little decreased for both short and long exposure times.

4. CONCLUSION

Titanium behavior in a floured artificial saliva solution with and without propolis extract as corrosion inhibitors have been performed using EIS method. Polarization resistance values for Ti in floured artificial saliva solution are considerably higher in the existence of propolis extract, and the values of corrosion current densities are significantly reduced demonstrating propolis corrosion inhibiting activity. Results of EIS measurement reveals that charge transfer resistance increases with increase in concentration of propolis extract, signifying that the inhibition increases with increase in concentration. Charge transfer resistance from EIS measurement decreases with increase of the inhibitor concentration, which confirms that the adsorption of propolis extract on the titanium surface in Fusayama-Meyer solution obeys the Langmuir adsorption isotherm. Morphological surface of Ti surfaces after immersion in artificial saliva containing 12 300ppm F^- have revealed that general corrosion occurs on the surface of the electrode causing the rough surface. After adding 1mg/ml of inhibitor extract, propolis coating still fully cover the surface of the Ti electrodes, indicating good adhesion of propolis extract to the Ti electrode.

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