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Effect of some vegetables (Carrots, Onion, Parsley, and Red radish) on Corrosion Behavior of Amalgam Dental Filling in Artificial Saliva

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ABSTRACT

This work involves study corrosion behavior of amalgam in presence of some vegetables including (Carrots, Onion, Parsley, and Red radish) which were chosen because they require mastication process by teeth and taking enough time that make them in a contact with amalgams filling in artificial saliva.

The corrosion parameters were interpreted in artificial saliva at pH (5.1) and (37±1^{o}C) by adding (50 ml/l) of vegetable juice to artificial saliva, which involve corrosion potential (E_{corr}), corrosion current density (i_{corr}), Cathodic and anodic Tafel slopes (b_c & b_a) and polarization resistance, the results of (E_{corr}) and (i_{corr}) indicate that the medium of saliva and (50 ml/l) onion is more corrosive than the other media. Cathodic and anodic tafel slopes were used to calculate the polarization resistance (R_p) to know which medium more effective on amalgam of dental filling, this study shows that the increasing in polarization resistance through the decreasing in corrosion rate values, the results of (R_p) take the sequence:

R_p:(saliva+ parsley) >(saliva+ red radish)> saliva>(saliva+ carrots) >(saliva+ onion).

While corrosion rates (C_R) take the sequence:

C_R: (Saliva+Parsley)<(Saliva+Red radish)<Saliva<(Saliva+Carrots)<(Saliva+ Onion)

Keyword: Amalgam, Corrosion in saliva, Potentiostatic measurements.

تأثير بعض الخضروات (الجزر , البصل , المعدنوس , الفجل الأحمر) على السلوك ألتآكلي لملغم حشوة الأسنان في اللعاب الصناعي

الخلاصة

يتضمن هذا العمل دراسة السلوك التاكلي للملغم بوجود بعض الخضروات والتي تتضمن (الجزر, البصل, المعدنوس, والفجل الأحمر) والتي تم اختيارها لأنها تتطلب عملية مضغ بالأسنان لفترة زمنية مما يجعلها أكثر اتصالا مع ملغم حشوات الأسنان في اللعاب الصناعي.

معاملات التآكل فسرت في اللعاب الصناعي عند دالة حامضية (5.1) و درجة حرارة (37±1) مئوية بإضافة (50مل /لتر) من عصير الخضروات إلى اللعاب الصناعي, والذي يتضمن جهد التآكل (E_{corr}), كثافة تيار التآكل (i_{corr}) , ميول تافل الكاثودية والانودية ومقاومة الاستقطاب , تشير نتائج جهد التآكل و كثافة تيار التآكل إلى إن وسط اللعاب و(50مل /لتر) بصل يعتبر وسط آكل أكثر من بقية الأوساط. تم استخدام ميول تافل

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الكاثودية والانودية لحساب مقاومة الاستقطاب (R_p) لمعرفة أي الأوساط أكثر تأثيرا على ملغم حشوه الأسنان, أظهرت هذه الدراسة زيادة في مقاومة الاستقطاب من خلال النقص في قيم سرعة التآكل , نتائج (R_p) تأخذ التسلسل التالي:

R_p : (لعاب + معدنوس) > (لعاب + فجل احمر) > لعاب > (لعاب + جزر) > (لعاب + بصل)

بينما سرعة التآكل (C_R) تأخذ التسلسل التالي:

C_R: (لعاب + معدنوس) < (لعاب + فجل احمر) < لعاب < (لعاب + جزر) < (لعاب + بصل)

INTRODUCTION :

Vegetables are vital to human body as they contain essential components needed by the human body such as carbohydrates, proteins, vitamins, minerals and also trace elements as shown in table (1)[1-3] .

All of the ingredients found in food and drink are capable of becoming incorporated into saliva .However; most of the foods are ingested before the breakdown into basic chemicals occurs. Some foods and beverages, though, contain chemicals that are reactive by themselves without any reductions and may become dissolved in saliva and affect the tarnish and corrosion of metallic materials [4]. Various studies have been conducted on Dental filling; Rivera P.C. and coworkers[5] studied the evaluation of the galvanic corrosion of three high copper dental amalgams by means of electrochemical techniques, the dental amalgams were: a national Nu Alloy(which is a dispersed-phase, high-copper-content dental alloy with no zinc content) (New Stetic) and two imported Contour (Kerr university , USA) and GS-80,(SDI, Australia) (SDI, is a specialist manufacturer and distributor of dental restorative materials), (alloy composition Ag 40%,Sn 31.3%, Cu 28.7%,Hg 47.9%). The dental metallic materials were: Titanium CP(Commercially Pure) , Ti-6Al-4V type COC (Ceramic-on-Ceramic) , International power system (IPS) design 15 (Ni-Cr-Mo) and IPS design 91 (Au-Pd). Under the test conditions, they concluded that the home amalgam has the same tendency to undergo galvanic corrosion as comparison to imported amalgams. Using statistical analysis of variance (ANOVA) method of a single via it was corroborated the same electrochemical behavior of dental amalgams . Alves and coworkers[6] studied electrochemical impedance applied to the corrosion behavior of dental amalgams in synthetic physiological fluids. This study was done with Duxalloy and Tytin Plus samples in four different electrolytes: Phosphate buffer saline, Hank solution, artificial saliva and NaCl 0.9%, they concluded that the passive film resistance is high at initial immersion times and decreases after 168h. Although this fact is systematic, the passive film continued to show its semiconductive and resistive properties even after a period of (168 h.) of immersion, in other words, it presented protective properties against corrosion and because of this, and the biomaterial does not produce potential risks to human health. Zhang and coworkers [7] studied the effect of silver on the corrosion behavior of Ti-Ag alloy in artificial saliva solutions, they concluded that, addition of Ag was effective in reducing the corrosion current density and increasing the open circuit potential of titanium in artificial saliva environment, and addition of fluoride ions in the solution severely reduced the corrosion resistance if Ti-Ag alloys. Zhang and coworkers [8] studied the corrosion behavior of Ti-5Ag alloy with and without thermal oxidation in artificial saliva solution, they concluded that, the corrosion resistance was enhanced by addition of Ag for titanium and could be further improved by thermal oxidation.

Experimental

Materials and Chemicals

The used alloy in this study was amalgam; the chemical composition of this alloy is shown in table (2) which prepared by triturating (0.7g) of powder alloy and the corresponding weight of mercury by amalgamator type(YDM-Pro) for (15sec.) at high speed. And then cold mounted using pyrax polymers to obtain only surface area of cylinder specimen, with (1.5cm) diameter.

The open side was polished mechanically to a mirror finish, rinsed in distilled water and stored in desiccators. First electrolyte was used as a reference by modified Fusayama artificial saliva [9], which closely resembles natural saliva, with composition of (0.4 g/L KCl, 0.4g/L NaCl, 0.906 g/L $CaCl_2.2H_2O$, 0.69 g/L $NaH_2PO_4.2H_2O$, 0.005g/L $Na_2S.9H_2O$ and 1g/L urea), all chemicals are from Thomas Baker (chemicals) PVT.Limited (India) with purity (98-99.5%) pH of this electrolyte was (5.1). The vegetables were washed with tap water followed by distilled water to eliminate attached soil particulates**,** and dried, then converting it to juice by juice maker.

50ml/L of each vegetable was added to artificial saliva to study of it on corrosion behavior of amalgam. The value of pH for artificial saliva after adding these vegetable was increased up to 5.6 or less depending on the type of vegetable as shown in table (3).

Corrosion Test

Polarization experiments were performed in WINKING M Lab 200 Potentiostat/Galvanostat from Bank-Elektronik with electrochemical standard cell with provision for working electrode (amalgam), auxiliary electrode (Pt electrode), and a Luggin capillary for connection with saturated calomel electrode SCE reference electrode. Electrochemical measurements were performed with a potentiostat by SCI electrochemical software at a scan rate of 3 $mV.sec^{-1}$.

The main results obtained were expressed in terms of the corrosion potentials (E_{corr}) and corrosion current density (i_{corr}) besides measurement of the tafel slops by tafel extrapolation method.

Results and Discussion

Corrosion Behavior

Figure (1) shows the variation of potential (OCP) with time for amalgam in saliva and mixture of saliva with some type of vegetable samples including (Carrots, Onion, Parsley, and Red radish), this behavior indicates that behavior of amalgam in (saliva & parsley) and (saliva& carrots)solutions more stable than (saliva& Red radish) and (saliva& Onion) solutions with time. This could be due to the mixed potential resulting from the ionic constitution of the solutions. The open circuit potential values take the following sequence for amalgam:

$\mathbf{E_{OCP}}$: saliva & parsley< saliva& carrots<saliva<saliva& Red radish<saliva& Onion**.**

The potentiodynamic polarization and cyclic polarization curves are shown in Fig. (2)and Fig. (3).These figures show the main two behavior of the anodic and cathodic regions; the lower section represents reduction reaction which includes evolution of hydrogen molecules because acidity of electrolyte (artificial saliva) as follows:

$$2H^{+} + 2e \rightarrow H_2 \quad …..(1)$$

In addition to reduction of oxygen to water molecules:

$$O_2 + 4H^{+} + 4e \rightarrow 2H_2O \quad ….(2)$$

While at anodic sites dissolution of metals in amalgam can occur such as Ag, Sn, and Cu. Mercury diffuses into the alloy particles and reacts with silver, tin and copper, forming various compounds. The exact compounds formed depend on the chemical composition of the powder and on particle shape (which can be spherical or irregular) but are mainly phases of the systems Sn–Hg, Ag–Hg, with Ag–Cu and Ag–Sn phases remaining from the reactants. For the currently used, high copper amalgams, the main reaction is [10]:

$$\gamma\text{-}Ag_3Sn + Ag\text{–}Cu + Hg \rightarrow \gamma_1\text{-}Ag_2Hg_3 + \gamma_2\text{-}Sn_7Hg + \gamma\text{-}Ag_3Sn + Ag\text{–}Cu \quad …..(3)$$

The Sn–Hg phase, which has a relatively low corrosion resistance, then undergoes further reaction, according to:

$$\gamma_2\text{-}Sn_7Hg + Ag\text{–}Cu \rightarrow \acute{\eta}\text{-}Cu_6Sn_5 + \gamma_1\text{-}Ag_2Hg_3 \quad …..(4)$$

The microstructure of the dental amalgam is complex, consisting of new microphases, as produced in the reactions above, and the remains of the powder alloy particles, within the γ_1-Ag_2Hg_3 matrix phase [10]. For this reason, and in order to understand better the role of the various phases, individual phases have electrochemical measurements can lead to an improved understanding of the processes that take place at the amalgam electrode surface as well as the influence of surface oxide. Hypothesis has also been proposed, that the released mercury may partly react with Ag_3Sn, to produce additional Sn_7Hg, so that the corrosion cycle can continue. The filling becomes porous and can lose most of its strength. Absorption of released mercury by Ag_3Sn requires the absorbing phase in close vicinity of the corroding Sn_7Hg-phase; otherwise there is no thermodynamical reason for mercury to diffuse into the filling with high mercury content. Otherwise, it will evaporate. The content of Ag_3Sn may vary depending on amalgam composition and working methods of the particular dentist. As the amount and distribution of Ag_3Sn cannot be controlled, the hypothesis about Ag_3Sn as a sink for all mercury released by corrosion is not substantiated. As reported by Brune [11] silver has been found in the solution already after a few days exposure to artificial saliva. Though ionized mercury also has been found among the dissolved corrosion products by radioactive tracer method [12] the main part is released as metallic mercury, which can be found as droplets on freshly corroded amalgam surfaces [13].

The corrosion parameters listed in Table (3) show that the sequence of corrosion potential of amalgam takes the following sequence:

-$E_{corr:}$ saliva& Onion> saliva& Red radish> saliva& carrots> saliva & parsley> saliva.

While the corrosion current densities values (i_{corr}) takes the following sequence:

i_{corr}: saliva& Onion> saliva& carrots> saliva> saliva& Red radish> saliva & parsley.

The rate of corrosion (C_R mm/y) for amalgam in saliva and mixture of saliva with some type of vegetable samples including (Carrots, Onion, Parsley, and Red radish) is directly proportional with its corrosion current density (i_{corr}) in accordance with the relation [14]:

$$C_R(mm/y) = 3.27\frac{e}{\rho}i_{corr.} \qquad .....(5)$$

Where $C_R(mm/y)$: corrosion rate in millimeter per year, e: equivalent weight of alloy (gm), and ρ: density of alloy (gm/cm^3).
The polarization resistance (Rp) can be determined from the Tafel slopes and according to Stern- Geary equation [15]and [16]:

$$R_p = \left(\frac{dE}{di}\right)_{i=0} = \frac{b_a b_c}{2.303(b_a + b_c)i_{corr}} \qquad ....(6)$$

The values of R_p which have been calculated from above equation are taken the following sequence:
Rp: saliva & parsley> saliva& Red radish>> saliva> saliva& carrots> saliva& Onion.

Cyclic polarization measurements were in a good agreement with potentiodynamic polarization as shown in Fig. (3).These curves show that forward scan and reverse scan shift to higher range of current densities for the presence of carrots and onion in artificial saliva, where these vegetables lead to increase corrosion rate of amalgam. This result of behavior of vegetables may be due to presence of various sulfides, sulfenic acids and acetic acid [17].

Cyclic polarization of amalgam in artificial saliva in the presence of parsley and red radish indicates that reverse scan shift to lower values of current density compared with forward scan, where these materials led to decrease corrosion rate of amalgam.

This result of behavior of vegetables may be due to presence of some contents which behave as inhibitors when it adsorbed on the amalgam surface such as Vitamin K, 4-methoxy-1*H*-indole-3-carboxaldehyde) ,and 1*H*-indole-3-carboxaldehyde, …etc. These contents may be acted as barrier between saliva and amalgam due to chain of hydrocarbons and other chemical functionally group work to isolate the metallic surface from corrosive electrolyte.

CONCLUSION:

Presence of carrots and onion in saliva increases corrosion rate of amalgam filling while presence of parsley and red radish in saliva decreases corrosion rate of amalgam filling.

Table (1): Some compounds in selected vegetable.

Compounds found in:-	
Carrots[a]	p-cymene, limonene, β-myrcene, sabinene, terpinolene, γ -terpinene, β -caryophylene, (E) - γ -bisabolene, β –bisabolene, α-pinene , 3-hydroxy- 2-butanone, ethanol, hexanal, acetic acid, and erythro- and threo-2,3-butanediol.
Onion[a]	Cysteine sulfoxides, Sulfenic acids, Propanethial-S-oxide, Thiosulfinates, Propanal, Polysulfides, Thiosulfonates
Parsley[b]	α-Pinene, β-Myrcene, α-Phellandrene, β-Phellandrene, cis-Ocimene, Isopropenyl-4-methylbenzene , α-Terpinolene, p-Mentha-1,3,8-triene, α-Copaene, Caryophyllene , β-Farnesene , β-Selinene , γ-Cadinene, Myristicin , β-Bisabolene, β-Sesquiphellandrene, Apiole .
Red radish[a,c]	4-methylthio-butyl isothiocyanate, 5-methylthio-pentyl isothiocyanate, dimethyl trisulfide, 2-phenylethyl isothiocyanate, acylated Anthocyanins, 4-methoxy-1*H*-indole-3-carboxaldehyde) , and 1*H*-indole-3-carboxaldehyde .

a: Ref.[1] , b: Ref.[2], c: Ref. [17,18].

Table (2): Chemical composition of amalgam.

Metal	***Ag***	***Sn***	***Cu***
Wt%	56.7	28.6	14.7

Table (3): Corrosion parameters of amalgam in artificial saliva and in presence saliva with (of Carrots; Onion; Parsley; and Red radish) at (37±1)°C.

Solution component	**pH of the solution**	**-E_{oc} mV**	**-E_{corr} mV**	**Corrosion current density i_{corr}/µA.cm^{-2}**	**Tafel slope (mV.dec-1)**		**Polarization resistance (Rp/Ω.cm^2)**	**C_R mm/y**
					-b_c mV.dec^{-1}	**b_a mV.dec^{-1}**		
Saliva	5.1	488	474.5	1.82	92.0	93.7	11.075	0.0611
Saliva+ 5%Carrots	5.63	485	491.5	2.06	112.5	87.9	10.401	0.0692
Saliva+ 5% Onion	5.05	509	545.1	2.08	94.9	94.9	9.905	0.0699
Saliva+ Parsley	5.23	466	478.8	1.65	110.5	106.0	14.237	0.0554
Saliva+ 5% Red	5.39	490	500.3	1.69	107.7	97.7	13.162	0.0568

radish								

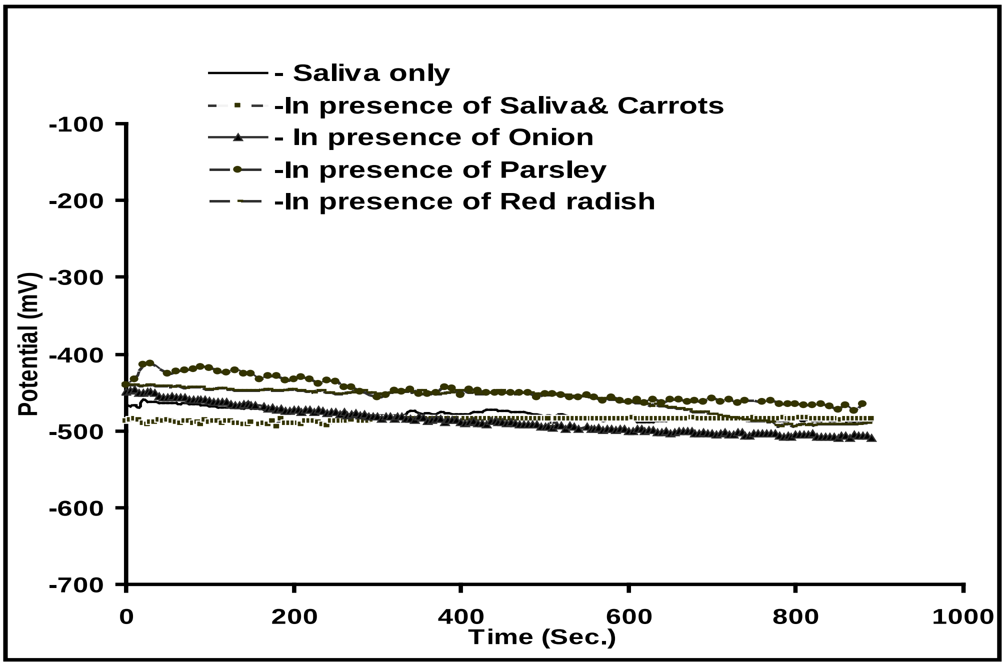


Figure (1): Variation of potential with time of amalgam in artificial saliva at (37±1)°C and in presence of Carrots, Onion, Parsley , and Red radish.

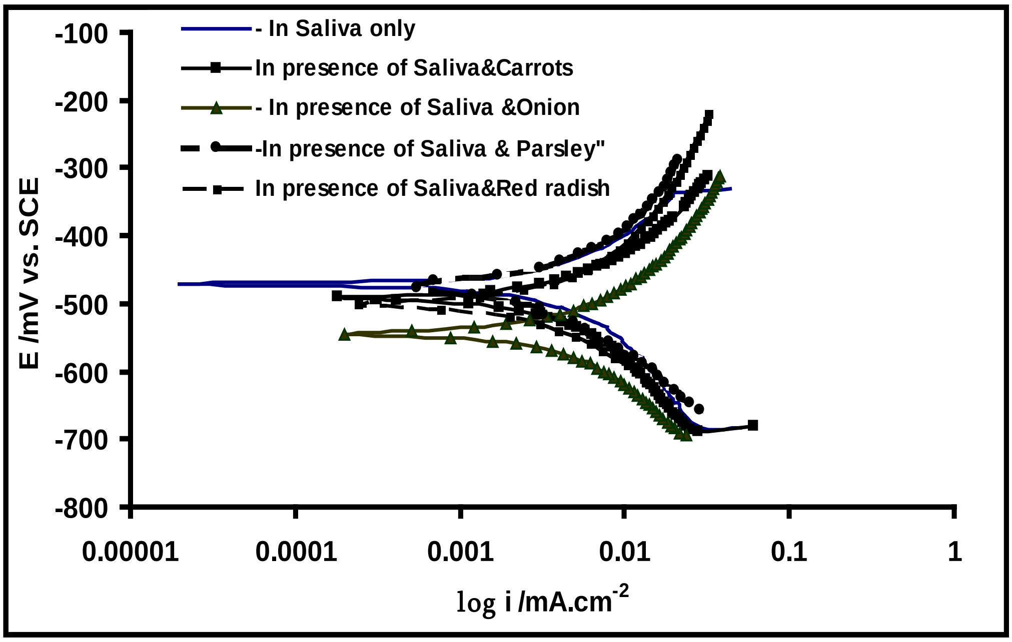
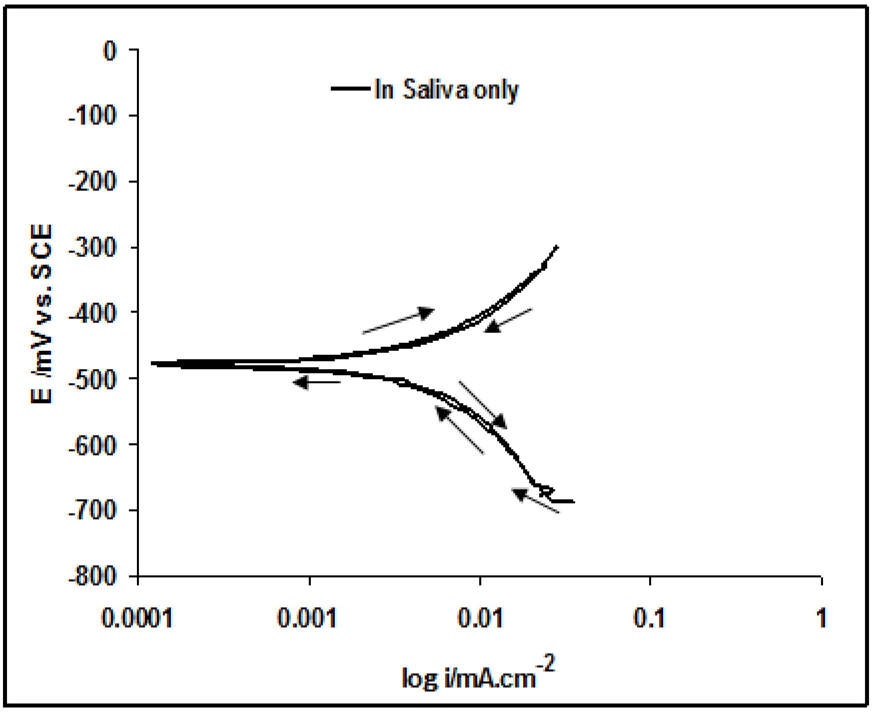


Figure (2): Linear polarization of amalgam in artificial saliva at (37±1)^{o}C and in presence of Carrots, Onion, Parsley, and Red radish .



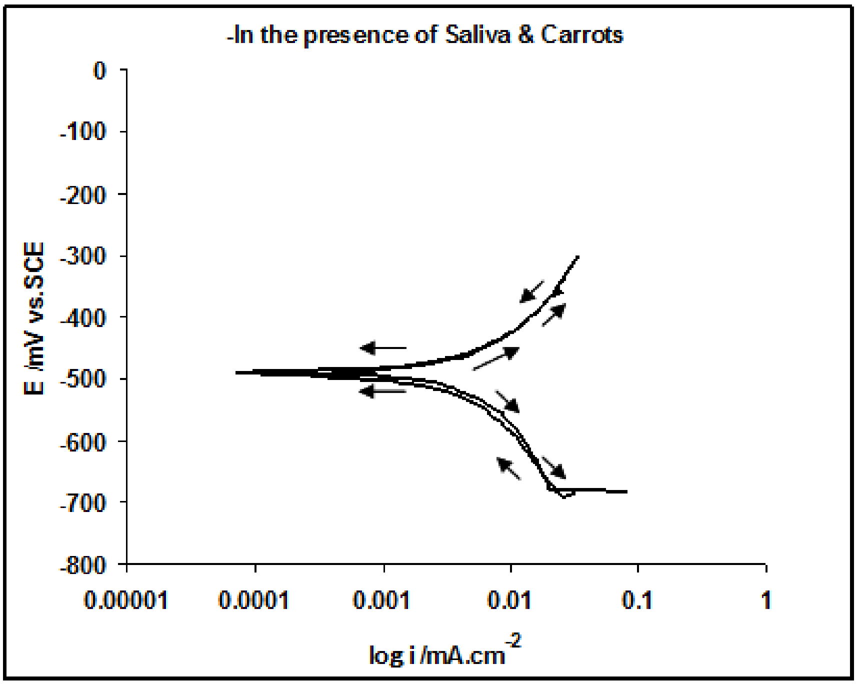
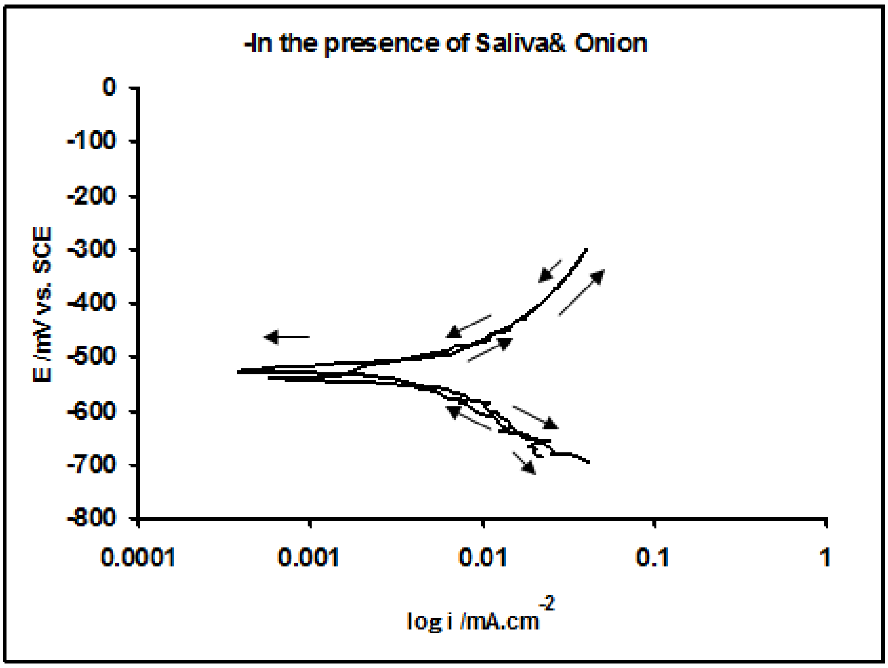
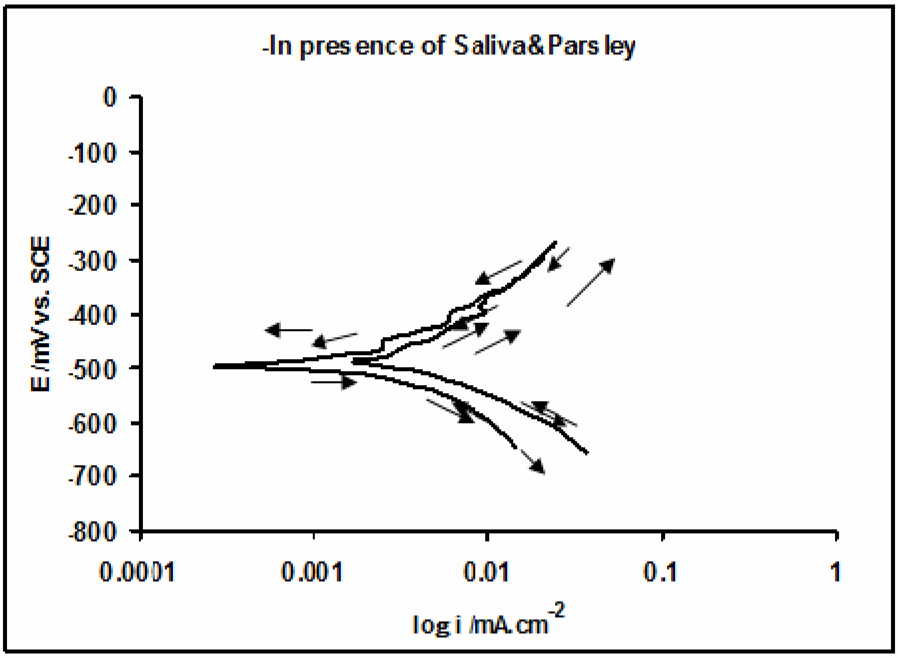


Figure (3) to be continued





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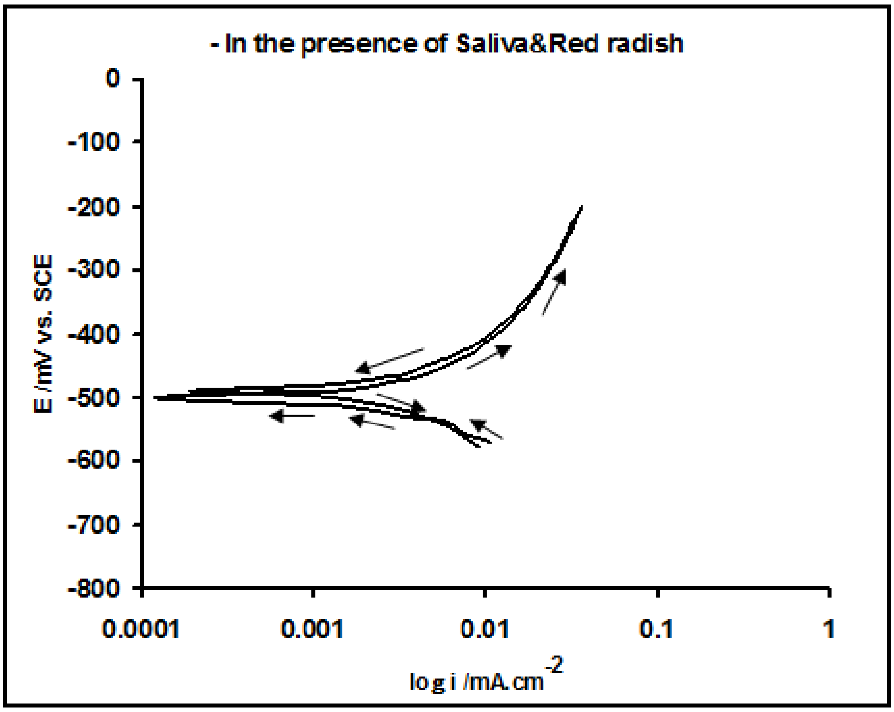

Figure (3): Cyclic polarization of amalgam in artificial saliva at (37±1)^{o}C and in the presence of Saliva with (Carrots, Onion, Parsley, and Red radish).

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