Study the Effect of Punica Granatum as Oral Antifungal on the Corrosion Inhibition of Dental Amalgam Alloy in Saliva

Haider Abdulkareem Yousif AlMashhadani
Department of Dentistry, Al-Rasheed University College, Baghdad, Iraq

Abstract
The aim of this study is to investigate the corrosion inhibition of amalgam alloy in artificial saliva solution using Punica granatum extract (P.g.e) in concentration range (5-20) ppm at temperatures range (288-318)K using electrochemical measurement. The inhibition efficiency IE% was found to increase with increase in (P.g) concentration (from 5 to 15) ppm and decreasing with using 20ppm (P.g.e),and IE% decreased with temperature increase. The (P.g.e) acts as mixed inhibitor according to the corrosion potentials Ecorr shifted toward either noble or active direction in the presence of inhibitor. The adsorption of the extract molecules on the amalgam surface obeys Langmuir adsorption isotherm and occurs spontaneously. The activation energy as well as other thermodynamic parameters for the inhibition process was calculated.

1. Introduction
Dental amalgam, is widespread use for over 150 years, and it is one of the oldest materials used in oral health care [1]. Dental amalgam is a metallic alloy formed by adding mercury to a powder alloy containing silver (40–70%), tin (15–30%) and copper (10–30%), and sometimes also a small percentage of zinc [2-4]. Corrosion of dental amalgam is one such source of hazardous contamination with mercury in human body [5]. Until now, there is possible danger from the internal source of corrosion products of dental amalgam fillings, which has been mostly ignored. Currently, this problem is devoted special attention [6].
Where amalgam is still by far the most extensively used material for dental restorations [7]. Different reported types of amalgam degradation are available [8-14].
Dental amalgam fillings within the mouth interact continuously with physiological fluids. They are subjected to both chemical and physical stimulation, as well as the metabolism of large amount of bacteria [15]. Saliva is a hypotonic solution containing bioactive components, chloride, potassium, sodium, nitrogenous compounds and proteins [16]. The pH of saliva varies from 5.2 to 7.8. Corrosion is the graded degradation of dental amalgam fillings by electrochemical attack, which is of concern particularly when the orthodontic appliances are placed in the electrolytic environment of the human mouth [17-18]. Temperature, quantity and quality of the saliva, plaque, pH, proteins, food properties and oral conditions are the main factors, which influence the corrosion processes.
Plants containing phytochemicals such as alkaloids, tannins, essential oils and flavanoids have pronounced defensive and curative activity. There are many species of medicinal plants belonging to various families which are being used, traditionally, to control and cure a variety of dental problems by the population [41]. Pomegranate (Punica granatum L.) is used in several systems of medicine for a variety of ailments. In the past decade, numerous studies on the antioxidant, ant carcinogenic, and anti-inflammatory properties of pomegranate constituents have been published, focusing on treatment and prevention of cancer, cardiovascular disease, diabetes, dental conditions, erectile dysfunction, bacterial infections and antibiotic resistance, and ultraviolet radiation-induced skin damage [19].
In an interesting study, investigated the effect of (P.g.e) on the corrosion of amalgam filling in artificial saliva solution, in which an aqueous extraction of (P.g) was investigated for antifungal in denture stomatitis like Staphylococcus aureus, Staphylococcus, epidermis, Klebsiella pneumonia, Pseudomonas aeuruginosa and
Given the presence of national stocks of this tree in Iraq and the possibility of easy-to-prepare extracts and technologies for the cost of the cheapest, so this study included the use of aqueous extracts of (P.g.e).

This work includes investigation the effect of (P.g.e) on the corrosion of amalgam filling in artificial saliva with different concentration at temperature range (288-318) K.

2. Materials and Methods
The alloy used in this study was amalgam; with chemical composition show in table 1, which prepared by amalgamator, then mounted using pyrex-polymer for corrosion test to isolate all side except one and polished mechanically, rinsed by distilled water and then a hole made in mounted specimens for electrical connection.

Table 1. The chemical composition of amalgam.

<table>
<thead>
<tr>
<th></th>
<th>Ag</th>
<th>Sn</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt.%</td>
<td>56.7</td>
<td>28.6</td>
<td>14.7</td>
</tr>
</tbody>
</table>

The electrolyte reference used was modified Fusayama artificial saliva [22], which closely resembles natural saliva, the composition show in table 2, and pH of this electrolyte was 6.2.

Table 2. The composition of artificial saliva.

<table>
<thead>
<tr>
<th></th>
<th>KCl</th>
<th>NaCl</th>
<th>CaCl₂.H₂O</th>
<th>NaH₂PO₄.2H₂O</th>
<th>Na₂S.9H₂O</th>
<th>urea</th>
</tr>
</thead>
<tbody>
<tr>
<td>g/l</td>
<td>0.4</td>
<td>0.4</td>
<td>0.906</td>
<td>0.69</td>
<td>0.005</td>
<td>1</td>
</tr>
</tbody>
</table>

An aqueous extract by using Soxhlet extractor which was prepared by mixing (50)grams of dry grinded Pomegranate peel with 1000 ml of distilled hot water, continuous extraction during 24 hours, filtering and used freshly. Punica granatum extract (P.g.e) was used in concentration range (0, 5, 10, 15 and 20) ppm in artificial saliva solution.

The corrosion behaviors of amalgam filling investigated with Mlab (Germany, 2000) potentiostate and controlled by computer and MLabSci software, which were used for data acquisition and analysis under static condition. The corrosion cell used had three electrodes, amalgam filling used as a working electrode, the reference electrode was a silver-silver chloride and platinum electrode was used as auxiliary electrode. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in artificial saliva solution for 15 minutes to establish steady state open circuit potential (E_{ocp}), then electrochemical measurements were performed in potential range (±200) mV. All electrochemical tests have been performed in aerated solutions at (288-318) K.

The influence of temperature on the kinetic process of amalgam corrosion in free artificial saliva and in the presence of adsorbed inhibitor leads to get more information on the electrochemical behavior of metallic materials in aggressive media[24] more details in sec. 3.2.

FTIR analysis was carried out to determine the functional groups present in the Punica granatum extract (P.g.e) and that in the corrosion products from the surface of amalgam set ups containing the P.g.e extract which were carried out using Fourier Transform Infrared spectrophotometer. KBr was used in FTIR to analyse the samples.

3. Results and Discussion
3.1. Corrosion behavior
The polarization curves for the corrosion of amalgam immersed in artificial saliva without and with 15ppm (P.g.e) at different temperatures were respectively recorded and plotted in figure 1. The polarization curves in the presence of the other (P.g.e) concentrations show similar behavior with those in the presence of 15ppm (P.g.e). It can be seen from these figures that, in the absence of (P.g.e), show shifts in the anodic and cathodic branches are observed with the temperatures increased, and the anodic and cathodic current densities increase obviously with the increase in the temperatures. In the presence of 15ppm of (P.g.e), the anodic and cathodic current densities show slightly increased with temperature increase compared to that in the absence of (P.g.e), suggesting that (P.g.e) can inhibit the corrosion of amalgam.

Polarization parameters, including the corrosion potential (E_{corr}), cathodic Tafel slopes (βc), anodic Tafel slopes (βa) and corrosion current density (I_{corr}) obtained by extrapolation of the curves, are shown in table (3). The data listed in table (3) indicates that the corrosion potentials E_{corr} slightly shift toward more active direction in the presence of inhibitor, i.e., (P.g.e) acts as cathodic inhibitor.

The polarization curve of amalgam in artificial saliva a) without inhibitor and b) with 15ppm inhibitor.

**Table 3.** Corrosion kinetic parameters for amalgam in absence and presence of different *pinica granatum* concentration in artificial saliva at different temperature in the range (288-318)K.

<table>
<thead>
<tr>
<th>Temp./K</th>
<th>-OCP/mV</th>
<th>-E_{corr}/mV</th>
<th>i_{corr}/µA.cm(^{-2})</th>
<th>-bc/ mV .dec(^{-1})</th>
<th>ba/ mV .dec(^{-1})</th>
<th>IE%</th>
<th>θ</th>
<th>Rp/Ω.cm(^{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>471</td>
<td>389.1</td>
<td>3.68</td>
<td>149.9</td>
<td>194.1</td>
<td>-</td>
<td>-</td>
<td>9979.9</td>
</tr>
<tr>
<td>298</td>
<td>389</td>
<td>377.9</td>
<td>5.02</td>
<td>147.7</td>
<td>187.0</td>
<td>-</td>
<td>-</td>
<td>7137.8</td>
</tr>
<tr>
<td>308</td>
<td>370</td>
<td>378.7</td>
<td>5.55</td>
<td>149.6</td>
<td>217.2</td>
<td>-</td>
<td>-</td>
<td>6930.6</td>
</tr>
<tr>
<td>318</td>
<td>354</td>
<td>432.6</td>
<td>7.2</td>
<td>114.6</td>
<td>183.6</td>
<td>-</td>
<td>-</td>
<td>4255.2</td>
</tr>
<tr>
<td><strong>Without inhibitor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>391</td>
<td>425.5</td>
<td>1.31</td>
<td>61.8</td>
<td>70.8</td>
<td>64.4</td>
<td>0.644</td>
<td>10937.0</td>
</tr>
<tr>
<td>298</td>
<td>434</td>
<td>493.8</td>
<td>1.81</td>
<td>57.9</td>
<td>63.6</td>
<td>63.9</td>
<td>0.639</td>
<td>7270.8</td>
</tr>
<tr>
<td>308</td>
<td>444</td>
<td>562.4</td>
<td>3.13</td>
<td>33.4</td>
<td>57.6</td>
<td>43.6</td>
<td>0.436</td>
<td>2932.8</td>
</tr>
<tr>
<td>318</td>
<td>503</td>
<td>560.1</td>
<td>4.1</td>
<td>41.3</td>
<td>88.4</td>
<td>43.1</td>
<td>0.431</td>
<td>2981.2</td>
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<tr>
<td><strong>5ppm inhibitor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>448</td>
<td>475.9</td>
<td>0.916</td>
<td>76.6</td>
<td>102.3</td>
<td>75.1</td>
<td>0.751</td>
<td>20763.0</td>
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<tr>
<td>298</td>
<td>469</td>
<td>542.9</td>
<td>1.36</td>
<td>48.5</td>
<td>102.9</td>
<td>72.9</td>
<td>0.729</td>
<td>10524.0</td>
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<tr>
<td>308</td>
<td>424</td>
<td>442.3</td>
<td>1.56</td>
<td>74.7</td>
<td>80.6</td>
<td>71.9</td>
<td>0.719</td>
<td>10791.0</td>
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<tr>
<td>318</td>
<td>463</td>
<td>580.8</td>
<td>2.03</td>
<td>24.4</td>
<td>66.1</td>
<td>71.8</td>
<td>0.718</td>
<td>3811.9</td>
</tr>
<tr>
<td><strong>10ppm inhibitor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>466</td>
<td>494.3</td>
<td>0.514</td>
<td>40.7</td>
<td>66.6</td>
<td>86.0</td>
<td>0.860</td>
<td>21354.0</td>
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<tr>
<td>298</td>
<td>412</td>
<td>468.6</td>
<td>1.16</td>
<td>71.8</td>
<td>78.8</td>
<td>76.9</td>
<td>0.769</td>
<td>14062.0</td>
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<tr>
<td>308</td>
<td>467</td>
<td>453.0</td>
<td>1.55</td>
<td>94.5</td>
<td>111.7</td>
<td>72.1</td>
<td>0.721</td>
<td>14340.0</td>
</tr>
<tr>
<td>318</td>
<td>497</td>
<td>561.2</td>
<td>2.13</td>
<td>54.2</td>
<td>66.7</td>
<td>70.4</td>
<td>0.704</td>
<td>6095.0</td>
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<tr>
<td><strong>15ppm inhibitor</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>288</td>
<td>465</td>
<td>514.3</td>
<td>1.1</td>
<td>25.4</td>
<td>81.9</td>
<td>70.1</td>
<td>0.701</td>
<td>7652.0</td>
</tr>
<tr>
<td>298</td>
<td>452</td>
<td>510.4</td>
<td>1.53</td>
<td>30.6</td>
<td>77.7</td>
<td>69.5</td>
<td>0.695</td>
<td>6230.5</td>
</tr>
<tr>
<td>308</td>
<td>439</td>
<td>508.7</td>
<td>2.33</td>
<td>33.9</td>
<td>88.6</td>
<td>58.0</td>
<td>0.586</td>
<td>4569.2</td>
</tr>
<tr>
<td>318</td>
<td>466</td>
<td>537.6</td>
<td>3.12</td>
<td>34.4</td>
<td>58.8</td>
<td>56.7</td>
<td>0.567</td>
<td>3020.4</td>
</tr>
</tbody>
</table>

The data of the table shows that the corrosion current density, slightly increased with temperature increasing in absence and presence of different (P. g.e) extraction concentrations. It is clear from the results of electrochemical polarization measurements that the addition of inhibitor causes a decrease in the current density. The values \(i_{corr}\)
of amalgam in the inhibited artificial saliva are smaller than those for the free artificial saliva. Tafel plots confirm the presence of both anodic and cathodic sites on the surfaces of samples [22]. At cathodic sites, reduction of hydrogen can occur due to acidity of saliva according to the following reaction:

\[ 2H^+ + 2e \rightarrow H_2 \]  

(1)

In addition to reduction of oxygen to water molecules:

\[ O_2 + 4H^+ + 4e \rightarrow 2H_2O \]  

(2)

While at anodic sites dissolution of metals in amalgam can occur such as Ag, Sn and Cu. Mercury (50% to alloys) diffuses into the alloy particles and reacts with silver, tin and copper, forming various compounds. Products of amalgamation are the $\gamma$-phase of the silver–mercury system, designated $\gamma_1$-Ag$_2$Hg$_3$, the $\gamma$-phase of the tin-mercury system, designated $\gamma_2$-Sn$_7$–8Hg, and the intermetallic compounds of the tin–copper system, $\eta$-Cu$_3$Sn and $\epsilon$-Cu$_6$Sn$_5$ [40]. There are also particles of the original alloys which did not react during the amalgamation process such as, for example, $\gamma$-Ag$_3$Sn and the Ag–Cu eutectic.

The inhibition efficiency IE (%) can be calculated using the equation given below[23]:

\[
IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldOTS3.2. Kinetic parameters for the corrosion inhibition process

The influence of temperature on the kinetic process of amalgam corrosion in free artificial saliva and in the presence of adsorbed inhibitor leads to get more information on the electrochemical behavior of metallic materials in aggressive media [24]. The relationship between the corrosion current density ($i_{corr}$) of amalgam alloy in artificial saliva solution and temperature (T) is expressed by the modified Arrhenius equation [25-28]:

\[
\log i_{corr} = \frac{-E_a}{2.303RT} + \log A \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldOTS\]  

(5)

![Figure 2](image-url)
where \( E_a \) is the apparent effective activation energy, \( R \) molar gas constant and \( A \) the Arrhenius pre exponential factor.

The values of activation energy (\( E_a \)) and Arrhenius factor (\( A \)) can be determined from the relation between logarithm of corrosion rate versus \( 1/T \) which gave straight line with regression coefficient close to unity as shown in figure (3). The calculated activation energies (\( E_a \)) and pre-exponential factors (\( A \)) at different inhibitor concentrations are listed in table (4).

**Table 4.** Activation energy (\( E_a \)), pre exponential factor (\( A \)) and the thermodynamic parameters for the corrosion activation complex of amalgam in artificial saliva solution in the absence and presence of (P.g.e) concentration over the temperature range 288 - 318 K.

<table>
<thead>
<tr>
<th>( C_{inh} )</th>
<th>( \Delta G^*/kJ.mol^{-1} )</th>
<th>( \Delta H^*/kJ.mol^{-1} )</th>
<th>( -\Delta S^*/kJ.mol^{-1} )</th>
<th>( Ea/\text{kJ.mol}^{-1} )</th>
<th>( A/\text{Molecules.c m}^{-2}.\text{S}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>288</td>
<td>298</td>
<td>308</td>
<td>318</td>
<td></td>
</tr>
<tr>
<td>without</td>
<td>67.28</td>
<td>69.15</td>
<td>71.01</td>
<td>71.87</td>
<td>13.6</td>
</tr>
<tr>
<td>5ppm</td>
<td>69.87</td>
<td>71.33</td>
<td>72.8</td>
<td>74.26</td>
<td>27.73</td>
</tr>
<tr>
<td>10ppm</td>
<td>70.57</td>
<td>72.43</td>
<td>74.30</td>
<td>76.17</td>
<td>16.77</td>
</tr>
<tr>
<td>15ppm</td>
<td>71.74</td>
<td>73.10</td>
<td>74.47</td>
<td>75.83</td>
<td>32.42</td>
</tr>
<tr>
<td>20ppm</td>
<td>70.26</td>
<td>71.85</td>
<td>73.44</td>
<td>75.03</td>
<td>24.51</td>
</tr>
</tbody>
</table>

The calculated values of activation energies ranged from 16.12 to 34.93 \( \text{kJ mol}^{-1} \) in the presence and absence of inhibitor respectively. From the results it is apparent that the activation energies for the corrosion of amalgam in the presence 15ppm of (P.g.e) reach a maximum value, that indicate the resistance of the amalgam to corrosion is the highest. While \( A \) values were increased with adding inhibitors which indicate the rising of the corrosion sites number.

![Figure 3. Arrhenius Plot of \( \log i_{corr} \) Versus 1/T for the corrosion of amalgam in artificial saliva solution in absence and presence of various (P.g.e) concentrations.](image)

Other kinetic date (enthalpy and entropy of activation) are accessible using the alternative formulation of Arrhenius equation [29]:

\[
\log \frac{i_{corr}}{T} = \log \frac{R}{Nh} + \frac{\Delta S^*}{2.303R} - \frac{\Delta H^*}{2.303RT} \quad \ldots \quad (6)
\]

Where \( CR (i_{corr}) \) is the corrosion rate, \( h \) is the Plank’s constant \((6.626176 \times 10^{-34} \text{ J.s})\), \( N \) is the Avogadros number \((6.022 \times 10^{23} \text{ mol}^{-1})\), \( \Delta S^* \) is the entropy of activation and \( \Delta H^* \) is the enthalpy of activation. The plot of \( \log i_{corr}/T \) vs. \( 1/T \) obtained straight lines were obtained with the slope of \((-\Delta H^*/2.303 R)\) and an intercept of \([\log (R/Nh) + (\Delta S^*/2.303 R)]\) from which the values of \( \Delta H^* \) and \( \Delta S^* \), respectively were calculated figure (4), while the free energy \( \Delta G^* \) was calculated using the following equation [2]:

\[ \Delta G_a = \Delta H_a - T \Delta S_a \Delta G^* = \Delta H^* + T \Delta S^* \quad \ldots \ldots (7) \]

The negative values of \( \Delta S^* \) were slightly change with increase inhibitor in artificial saliva indicate that the forming of activated complex not the rate determining step and there is no change in disorder of transition state. The values of \( \Delta H^* \) were increased with increase the concentration of (P.g.e) that show the higher value with 15ppm of (P.g.e) which reach to 32.42 kJ.mol\(^{-1}\).

The positive values of \( \Delta G^* \) indicate that the activated complex forming in artificial saliva were nonspontaneous reaction and in table (5) the \( \Delta G^* \) values increased with increasing temperature and slightly increased with increasing concentration of inhibitors, which means that inhibitor cause to reduced the thermodynamic feasibility of activation complex forming.

3.3. Adsorption isotherm:

Adsorption isotherms are usually used to describe the adsorption behavior of the adsorbate on the amalgam surface. Adsorption of the inhibitor compounds depends upon the charge and the nature of the metal surface, electronic characteristics of the metal surface and adsorption of solvent and other ionic species, temperature of the corrosion reaction and the electrochemical potential at the metal solution interface [30-34]. The adsorption isotherms can describe the nature of the metal-inhibitor interaction.

The degree of surface coverage (\( \theta \)) by different concentrations of inhibitor was evaluated from potentiostatic polarization measurements data using the flowing equation [35]:

\[ \theta = \frac{\text{IE} \%}{100} \quad \ldots \ldots (8) \]

Where IE (\%) is the percentage inhibition efficiency as calculated using equation (3). The data was applied to various isotherms including Langmuir, Temkin and and Frumkin isotherms. Proving that the adsorption of the inhibitors from artificial saliva solution on the amalgam surface obeys the Langmuir adsorption isotherm [36]:

\[ \frac{\theta}{C_{\text{inh}}} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \quad \ldots \ldots (9) \]

Where \( K_{\text{ads}} \) is the adsorption/desorption equilibrium constant, \( C_{\text{inh}} \) is the inhibitor concentration in the artificial saliva, and \( \theta \) is the surface coverage. The plot of \( C_{\text{inh}}/\theta \) vs. \( C_{\text{inh}} \) gave a straight line with an intercept of \( 1/K_{\text{ads}} \). The results obtained isotherm is presented in table (5), it shows that the \( R^2 \) values are very close to unity, indicating the obey of Langmuir adsorption isotherm.

Table 5. Thermodynamic parameters for adsorption of the inhibitors on the surface of carbon steel in 3.5% NaCl solution.

<table>
<thead>
<tr>
<th>Temp.</th>
<th>( K_{\text{ads}} )</th>
<th>( \Delta G_{\text{ads}}/\text{kJ.mol}^{-1} )</th>
<th>( R^2 )</th>
<th>( -\Delta S_{\text{ads}}/\text{J.K}^{-1} \text{.mol}^{-1} )</th>
<th>( -\Delta H_{\text{ads}}/\text{kJ.mol}^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>288</td>
<td>6.361</td>
<td>-14.0498</td>
<td>0.9516</td>
<td>130.46</td>
<td></td>
</tr>
<tr>
<td>298</td>
<td>3.409</td>
<td>-12.9921</td>
<td>0.9855</td>
<td>129.63</td>
<td></td>
</tr>
<tr>
<td>308</td>
<td>0.843</td>
<td>-9.85018</td>
<td>0.9009</td>
<td>135.62</td>
<td></td>
</tr>
<tr>
<td>318</td>
<td>1.076</td>
<td>-10.8151</td>
<td>0.8999</td>
<td>128.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>51.6226</td>
</tr>
</tbody>
</table>

...
Figure 5 shows the Langmuir adsorption isotherms for the adsorption of (P.g.e) on the amalgam surface. Values of $K_{ads}$ denotes the adsorption strength between the adsorbate and adsorbent. Large values of $K_{ads}$ imply more efficient adsorption and hence better protection efficiency [37].

\[ y = 1.328x + 0.1572 \]
\[ R^2 = 0.95161 \]
\[ y = 1.3728x + 0.2933 \]
\[ R^2 = 0.9855 \]
\[ y = 1.5184x + 1.1858 \]
\[ R^2 = 0.90085 \]
\[ y = 1.5684x + 0.9291 \]
\[ R^2 = 0.89985 \]

**Figure 5.** Langmuir isotherm plot for the adsorption of Cactus on the surface of amalgam.

Thermodynamic function for the adsorption process ($\Delta H_{ads}$, $\Delta S_{ads}$, $\Delta G_{ads}$) can be calculated using the known formulas [25]:

\[ K_{ads} = \frac{1}{55.5} \exp \left( \frac{-\Delta G_{ads}}{RT} \right) \] 

\[ \Delta G_{ads} = -2.303RT \log(55.5K_{ads}) \]

Assuming the thermodynamic model, corrosion inhibition of amalgam in presence of (P.g) can be better explained using the enthalpy of adsorption $\Delta H_{ads}$ and entropy of adsorption $\Delta S_{ads}$ which can be calculated from the integrated vant Hoff equation:

\[ \log K_{ads} = -\frac{\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R} + \log \frac{1}{55.5} \]

To calculate the enthalpy of adsorption and entropy of adsorption, $\log K_{ads}$ was plotted against $1/T$ and straight line was obtained with slope equal to ($-\Delta H_{ads}/2.303R$) and intercept equal to ($\Delta S_{ads}/2.303R+\log1/55.5$). The calculated values of the heat of adsorption and entropy of adsorption are listed in table (5) also.

### 3.4. FTIR & Inhibition Mechanism analysis of the extract and corrosion product

From the experimental and theoretical results obtained, the inhibition effect of (P.g.e) in artificial saliva solution can be explained as follows:

\[ \text{Inh.} + xH^+ \rightleftharpoons \text{Hinh}_x^{x+} \]

In artificial saliva solutions, the inhibitor exists either as neutral molecules or in the form of cations (protonated inhibitor).

The dominant adsorption mode will be dependent on factors such as the extract composition, type of corrosive medium ions as well as chemical changes to the extract. The (P.g.e) including polyphenols compounds (Flavonoids, Tannins, phytosterols and saponines) [38] and the chemical structures which is shown in figure (6). P.g.e structures have compounds contain many O atoms in functional groups, π-electrons and O–heterocyclic rings which give the reasons of its inhibition effect. The (P.g.e) may be adsorbed on the metal surface via the chemisorption mechanism involving the displacement of water molecules on the metal surface and the sharing of electrons between oxygen atom and silver. The (P.g) molecules can be adsorbed also on the metal surface on the basis of donor–acceptor interactions between π-electrons of the heterocycle and vacant d-orbitals of silver.

FT-IR Spectra for free (P.g) and the corrosion inhibition product are represented as shown in figures (8 ,9) respectively. A strong stretching O-H band at 3406 cm$^{-1}$, C=O stretching at 1720 cm$^{-1}$, C=C stretching at 1610 cm$^{-1}$, C-H stretching at 3074 cm$^{-1}$ and C-O for alcohol stretching at 1058 cm$^{-1}$
Figure 6. Shows structures of most important phytochemicals found in punica granatum.[39]

Figure 7. FT-IR spectra of extracted punica granatum.

Figure 8. FT-IR spectra of punica granatum film adsorbed on amalgam surface after immersion and corrosion in saliva solution.
It is clear from comparison between FT-IR spectra for isolated (P.g.e) extract and it film on the amalgam surface, that the absorbance frequency of all functional groups have been shifted to less value due to the force of binding between the interface of amalgam surface and the inhibitor, table (6).

**Table 6.** Wave number of FT-IR adsorption for extracted (P.g.e) and adsorbed (P.g.e) as corrosion inhibitor

<table>
<thead>
<tr>
<th>Ext,Pure (P.g.e)</th>
<th>Corrosion product</th>
<th>Group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wave number (cm⁻¹)</td>
<td>Wave number (cm⁻¹)</td>
<td>Assignment</td>
</tr>
<tr>
<td>3406.05</td>
<td>3434.98</td>
<td>OH stretch</td>
</tr>
<tr>
<td>3074.32</td>
<td>3122.54</td>
<td>CH stretch</td>
</tr>
<tr>
<td>1058.85</td>
<td>1033.77</td>
<td>C-O stretch</td>
</tr>
<tr>
<td>1720.39</td>
<td>1739.67</td>
<td>C=O stretch</td>
</tr>
<tr>
<td>1610.45</td>
<td>1631.67</td>
<td>C=C stretch</td>
</tr>
</tbody>
</table>

**Conclusions**

1. The extract of Punica granatum might be used in the control of common oral pathogens responsible for caries, stomatitis and periodontal diseases.
2. The results of inhibition efficiency determined by potentiodynamic polarization measurements are in good agreement.
3. Inhibition efficiency value increases with the increasing of the extract concentration from 5 to 15 ppm, then decreasing with 20 ppm of extract while the efficiency decreased with increasing the temperature.
4. Polarization curves indicated that the extract acts as mixed type inhibitor in artificial saliva solutions.
5. The inhibition is accomplished by adsorption of the extract components on the amalgam surface, and the adsorption is spontaneous and obeys the Langmuir isotherm.
6. The increase in Ea is proportional to the inhibitor concentration, indicating that the energy barrier for the corrosion interaction is also increased.

**Acknowledgements** - I would like to acknowledge Prof. Dr. Khulood Abid Al-Saadie for her encouraging support and efforts in the completion of this study.

**References**
