

Quantum Chemical and Electrochemical Studies of Water and Ethanol Extracts of *Salvadora Persica* (Miswak) as a New Green Inhibitor for Dental Amalgam in Artificial Saliva

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Abstract

The corrosion-inhibitive properties of *Salvadora Persica* water and ethanol extracts as a novel green inhibitor for dental amalgam in artificial saliva were studied by using potentiodynamic polarization measurements and electrochemical impedance spectroscopy measurements (EIS). The electrochemical results revealed that the *Salvadora Persica* extracts demonstrated strong inhibitory effects at 0.66 g/L and implied that the water extract was more effective than the ethanol extract. The inhibition efficiency (IE%) increases with increasing concentrations of both *Salvadora Persica* extracts and decreases with increasing temperature. The results of this work indicated that *Salvadora Persica* extracts act as mixed-type inhibitors, inhibiting the corrosion of dental amalgam by the adsorption process, which followed the Langmuir adsorption isotherm model. The thermodynamic results revealed that the adsorption process is endothermic with electrostatic interaction (physisorption). Various DFT parameters, like HOMO and LUMO energy, gap energy (ΔE), electronegativity (χ), softness (σ), and global hardness (η) were derived for all major molecules of *Salvadora Persica* extract molecules and correlated with experimental results.

Keywords: Dental amalgam; Corrosion; Green inhibitor; Electrochemical study; Artificial saliva; *Salvadora Persica*, Extraction, Quantum chemical, DFT Calculation.

المخلص: تعد المركبات الطبيعية أحد أهم مصادر مثبطات التآكل الصديقة للبيئة (Eco-friendly corrosion inhibitors). في هذا البحث تمت دراسة الخصائص المثبطة لتآكل ملاغم الاسنان (Dental amalgams) باستخدام المستخلص المائي والايثانولي لجذور نبات الاراك (*Salvadora Persica*) كنوع جديد من المثبطات الصديقة للبيئة المستخدمة لمنع تآكل ملاغم الأسنان. تمت الدراسة في وسط من اللعاب الاصطناعي، وذلك باستخدام (Potentiodynamic polarization measurements and electrochemical impedance spectroscopy measurements (EIS)). أظهرت النتائج الكهروكيميائية أن مستخلصي جذور نبات الاراك لها تأثير قوي في تثبيط تآكل ملاغم الأسنان، كما ان هذه القدرة التثبيطة تزداد بزيادة التركيز حيث وصلت إلى 78 % عند تركيز مقداره 0.66 جم/لتر بالنسبة للمستخلص المائي، في حين وصلت إلى 66 % بالنسبة للمستخلص الایثانولي، كما تتناقص فعالية تثبيط كلا المستخلصين بزيادة درجة الحرارة. تشير الدراسة إلى أن المستخلصين يتصرفا كمثبطات مختلطة، (Mixed type inhibitors)، كما تتبع (Langmuir adsorption isotherm model) في الامتزاز على سطح المعدن. أظهرت الحسابات الترموديناميكية (Thermodynamic) أن عملية الامتزاز ماصة للحرارة كما يشكل المستخلص مع سطح المعدن روابط كهروستاتيكية، أي ان الامتزاز من النوع الفيزيائي (Physisorption). استكمل هذا البحث من خلال تدعيم الجانب العملي بدراسة نظرية فاستخدام نظرية المدارات (Density Functional Theory; DFT) تم حساب مختلف المعاملات النظرية مثل طاقة أعلى مدار رابط (HOMO)، طاقة أقل مدار غير رابط (LUMO)، وفرق الطاقة بينهما (ΔE) السالبة الكهربائية (χ)، النعومة الكيميائية (σ) (Softness) والعسر الكيميائي (global hardness; η) وغيرها من المعاملات وقد وافقت النتائج النظرية تلك النتائج المحصل عليها عمليا.

1. Introduction

Dental amalgam is the most widely used material for the restoration of teeth. Their composition varies according to the types of amalgam. It has been widely used as a direct filling material because of its properties such as favorable mechanical properties and also its low cost and quick installation [1-2].

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A further concern results from the possible release of mercury and mercury vapour as well as the effect that mercury can have on antioxidant activity and neurotoxic logical effects [3-8].

The metallic composition is a primary parameter that dictates the properties of alloys. The dental amalgam is formed by the rapid reaction between mercury (nearly 50% wt.) and a powder alloy containing silver (40–70%), tin (15–30%) and copper (10–30%) and sometimes also a small percentage of zinc [9-13]. Dental silver amalgam is a poly-phase material, and the electrode potential differences between the various phases are substantial. In dentistry, galvanic corrosion is one of the problems associated with the use of amalgams. Many authors have demonstrated that the corrosion of dental amalgams, the less corrosion resistance phase is γ_2 -Sn₇Hg, is characterized by an anodic attack on the γ_2 -phase of the amalgam, [14-19].

The *Salvadora Persica* (Arak tree) is the most common source of chewing sticks which is used in Africa, South America, Asia, and the Middle East. It has different names in different societies as Arak and Miswak in the Arab world [20-22]. The Miswak is the root of the Arak tree, that used traditionally for the treatment of oral infections and the young roots, stems and branches are used as toothbrushes [23-25]. All parts of this plant (roots, leaves, and seeds) have been subjected to medical activities in different domains (22, 26-29). The inhibitor is a substance that is usually added in small amounts to slow down the corrosion rate. The best inhibitors are usually enhanced by the presence of hetero atoms in aromatic compounds and/or have a center π electron [30-34]. These substances can be synthesized (they are called also organic inhibitors) or natural products, and due to the toxicity of many of these organic inhibitors, the search for non-toxic corrosion inhibitors (natural products) was increased. On the other hand, plant extracts are also inexpensive and considered a great source of eco-friendly corrosion inhibitors [35, 36].

This study investigated the corrosion behavior of the dental amalgam alloy in artificial saliva, with and without the addition of the *Salvadora Persica* aqueous and ethanol extracts using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. The thermodynamic parameters, the process of adsorption, and the effect of inhibitor concentration variation were also studied.

2. Material and Methods

2.1. Extracts Preparation

The roots of the Arak tree (*Salvadora Persica*) were collected from the Sa'adah governorate in the north of Yemen. They were air-dried at room temperature for 15 days and then were powdered to use for extract preparation; i) water extract was obtained by the haut maceration technique. Before being maceration processed, the plant was washed and separated from foreign material, then 30 g of roots powder was immersed in a haut distilled water (about 500 ml) inside an airtight container for three hours, after that the decoction was filtered, ii) Ethanol extract was obtained by using classic Soxhlet extractor, which was then placed onto a flask containing 700 ml of ethanol, as extracted solvent, after the roots powder (100 g) had been placed inside a cellulose thimble, which was loaded in the Soxhlet reservoir, then the Soxhlet associated with a condenser. Both extracts were concentrated to dryness and kept in a refrigerator at 4°C [37-40], to use as eco-friendly corrosion inhibitors of the dental amalgam.

2.2. Specimen Preparation

Dental amalgams (Septalloy NG, France) in two-part plastic capsules separated by a membrane were mixed in a mechanical vibrator (amalgamator). The composition of powder alloy (600 mg) is 46.0 % Silver, 31.3% Tin, and 22.7 % Copper with mercury (720 mg). It was immediately cast into cylinder-shaped pieces of a diameter of 1.5 cm and a height of 3 mm. The dental amalgam surface was polished with SiC paper down to 2000 grit. The specimen surface is polished as necessary between experiments.

2.3. Synthetic Saliva Preparation

The synthetic saliva medium was prepared by dissolving both analytical salts; 1.24g of NaHCO₃ and 1.2 g of KCl in distilled water to get one litre of saliva. The concentration range of *Salvadora Persica* root extracts employed varied from 0.2g/l to 0.6g/l. In all electrochemical measurements, 100 ml of electrolyte was used.

2.4. Electrochemical Impedance Spectroscopy (EIS) Measurements

Electrochemical impedance spectroscopy (EIS) was conducted using a Potentiostat Voltalab 300 PGZ monitored by a PC and Voltmaster 4.0 as software for calculating the polarization resistance (R_p) and double layer capacitance (Cdl). The electrode was held in the electrolyte for 30 minutes to obtain the potential steady state in the open circuit potential (OCP). All experiments were made at corrosion potential (E_{corr}) with a frequency ranging from 10 kHz to 100 Hz. The inhibition efficiency (EI %) is calculated using the following equation:

$$(EI\%) = \frac{R_o - R}{R_o} \times 100 \tag{1}$$

R_o and R are the polarization resistance of dental amalgam in the presence and the absence of an inhibitor respectively.

2.4. Potentiodynamic Polarization Measurements

Electrochemical measurements were made in a three electrodes cylindrical glass cell with 100 ml electrolyte capacity, containing dental amalgam as the working electrode (WE), a saturated calomel electrode (SCE) as a reference electrode, and platinum as a counter electrode (CE). The polarization curves $E = f(I)$ were recorded by changing the potential in a range from -1000 to 1000 mV with a scanning rate of 1mV/Sec. Before drawing these curves, the working electrode is maintained at its corrosion potential (drop potential) for 30 minutes. The inhibition efficiency (EI%) is calculated using the following equation:

$$(EI\%) = \frac{I_o - I}{I_o} \times 100 \tag{2}$$

I_o and I are, respectively, the corrosion current densities in the absence and the presence of an inhibitor.

3. Results and Discussion

3.1. Open Circuit Potential Measurements

Open circuit potential (OCP) measurements have been carried out after immersion of the electrode in artificial saliva with or without inhibitor to demonstrate the differences in corrosion behaviour under ventilated conditions and differences in the phase structure of dental amalgams. The OCP curves are represented in Figures 1 and 2.

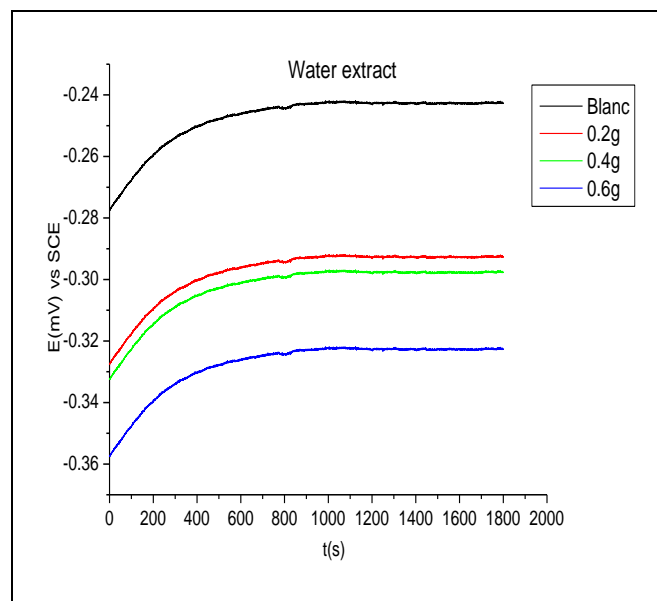


Figure 1: the open circuit potential curves of dental amalgam in artificial saliva without and with various concentrations of the *Salvadora Persica* ethanol extract.

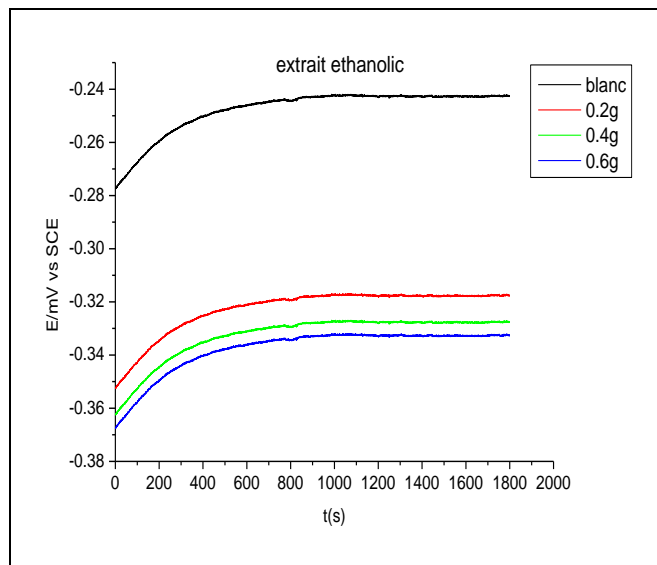


Figure 2: the open circuit potential curves of dental amalgam in artificial saliva without and with various concentrations of the *Salvadora Persica* water extract.

The variations of the OCP curves, as shown in Figures 1 and 2, toward to more positive direction at the first minutes of immersion can be explained by the formation of corrosion film. According to the less corrosion resistance phase (γ_2 -Sn₇Hg) in amalgam alloy, the formed film probably is tin oxide [14,15], which may accelerate the adoption of extract molecules on the specimens' surface. On the other hand, the variations of the OCP curves generally in the presence of both extracts toward to more negative direction indicated to protect the amalgam surface against the corrosion phenomena.

3.2. Electrochemical Impedance Spectroscopy (EIS)

After the amalgam electrode had been immersed in the free potential for 30 minutes, the impedance curves of the amalgam specimens in artificial saliva with or without aqueous and ethanol *Salvadora Persica* extract were recorded and presented in Figures 3 and 4 respectively. The electrochemical data extracted from these curves are reported in Table 1.

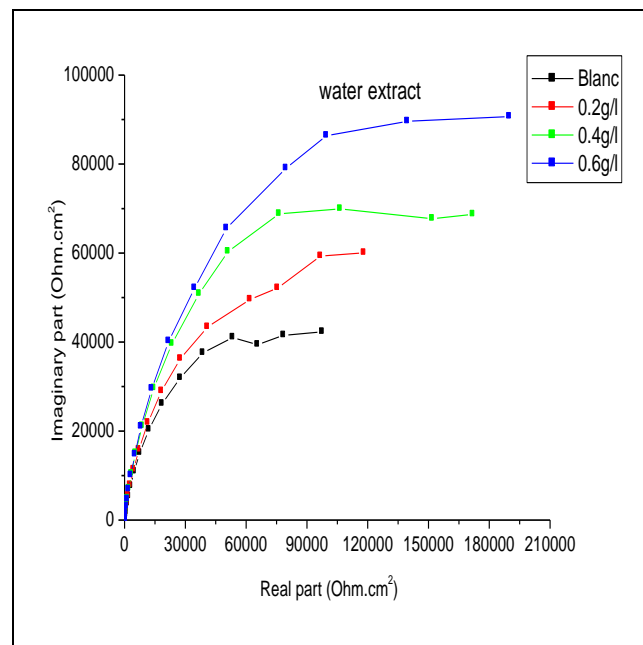


Figure 3: Impedance curve of dental amalgam in artificial saliva with and without different concentrations of water extract.

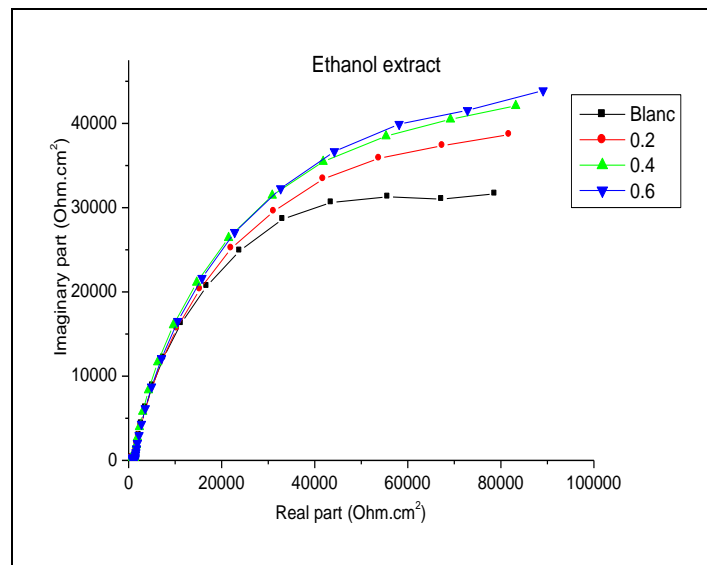


Figure 4: Impedance curve of dental amalgam in artificial saliva with and without different concentrations of ethanol extract.

As shown in Figures 3 and 4, the diameter of the depressed semicircles increased with increasing the concentration of both water and ethanol *Salvadora Persica* extracts, this means that the inhibition efficiency increased with increasing the inhibitor concentration. The capacitive loop observed is generally described as being representative of the charge transfer resistance on the bare metal or in the pores of a layer of corrosion products deposited on the metal surface.

Table 1: Results of the fitting for the impedance measurements in water and ethanol extract

Conc g/l	R ₁ (KΩcm ²)	C ₁ (μF.cm ⁻²)	α ₁	R ₂ (KΩcm ²)	C ₂ (μf cm ⁻²)	α ₂	E (%)
Blank	1.42	0.028	0.774	120.87	29.38	0.815	--
Water extract							
0.2	1.28	0.031	0.85	368.32	2.16	0.81	67
0.4	1.36	0.029	0.88	388.10	1.02	0.80	69
0.6	1.45	0.027	0.80	478.79	0.55	0.90	75
Ethanol extract							
0.2	1.39	0.057	0.830	244.36	3.25	0.779	50
0.4	1.53	0.026	0.811	264.36	1.50	0.851	54
0.6	1.65	0.016	0.792	330.54	0.80	0.824	63

The results listed in the previous Table 1 indicated that the values of double-layer capacitance decreased, while the charge transfer resistance increased, with increasing the concentration of both extracts. These results can be explained that the extracts increased the specimen resistance by adsorbing their molecules on the specimen surface, which increased the surface coverage, thus increasing the electrical double-layer thickness which was responsible for double-layer capacitance values decreasing. This may indicate that both extract molecules adsorbed at the interface of metal/solution by the water molecules piecemeal replacement to form a physical protective film, which isolated the corrosive medium from the metal surface [23, 41-43].

3.4. Potentiodynamic Polarization

After the amalgam electrodes had been immersed in the free potential for 30 minutes, the polarization curves of the amalgam specimens in artificial saliva with or without aqueous and ethanol *Salvadora Persica* extracts were recorded and presented in Figures 5 and 6 respectively. The electrochemical polarization corrosion parameters extracted from these curves are reported in Table 2.

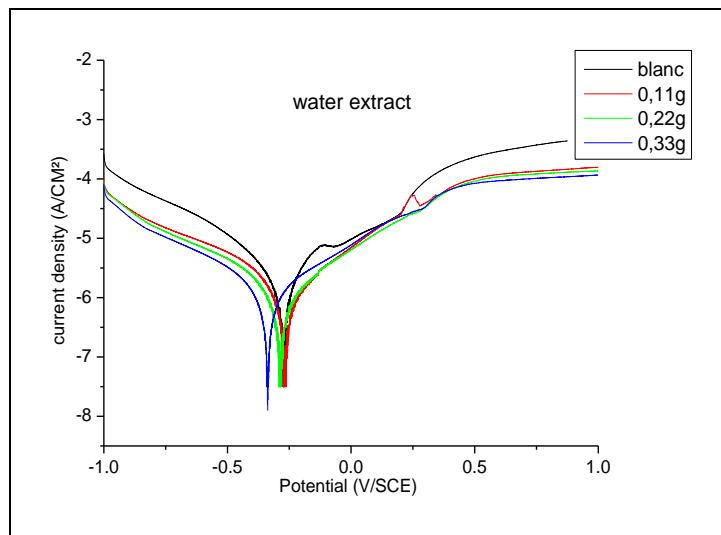


Figure 5: Polarization curves of dental amalgam in artificial saliva with and without various concentrations of water *Salvadora Persica* extract.

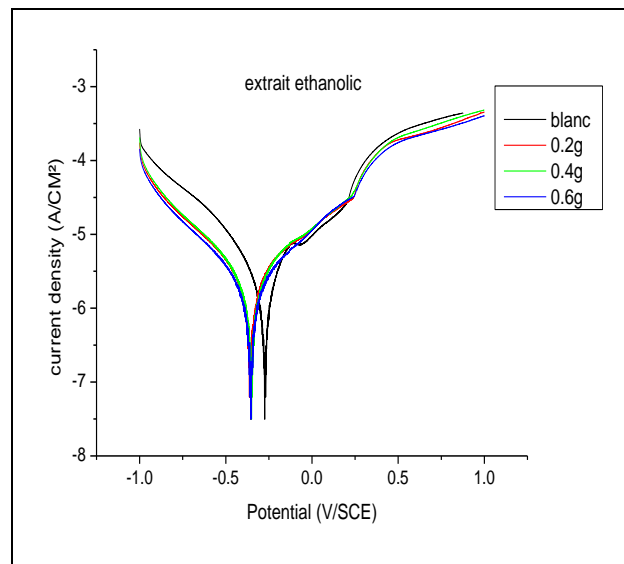


Figure 6: Polarization curves of dental amalgam in artificial saliva with and without various concentrations of ethanol *Salvadora Persica* extract

The listed results in Table 2 show that the evolution of the H^+ ion (cathodic reaction) was inhibited and the inhibition efficiency increased as the increasing of both the ethanol and water *Salvadora* extracts concentration. The addition of both extracts shifted the corrosion potential (E_{corr}) values toward more negative. As in Table 2, the largest change was 65 mV for ethanol extract at 0.6 g/l. Generally, the inhibitor can be classified as a mixed-type inhibitor when the corrosion potential change is non-existent or less than 85 mV [44-47], as well as in this work. Both ethanol and water *Salvadora* extracts act as a mixt-type and good eco-friendly inhibitor for the dental amalgam in artificial saliva. The inhibition efficiency is up to 65% with the ethanol extract at 0.6 g/l and to 78% with the aqueous extract at the same concentration.

Table 2: Corrosion electrochemical parameters of dental amalgam in artificial saliva with and without various concentrations of water and ethanol extracts.

C. (g/l)	E_{corr} mV (SCE)	I_{corr} (mA cm ⁻²)	Θ	E (%)
Blank	-292	4.92	-	-
Water extract				
0.2	-326	1.36	0.724	72.4
0.4	-296	1.28	0.74	74
0.6	-354	1.10	0.78	78

Ethanol extract				
0.2	-356	2.51	0.49	49
0.4	-351	2.32	0.53	53
0.6	-357	1.75	0.65	65

The organic extraction technique is less safe than those used for water extract. On the other hand, many authors reported that the ethanol extract has more corrosion inhibition efficiency than water extract [35, 36]. But in this study, as shown in Tables 1 &2, the water extract has more corrosion inhibition efficiency, which makes the *Salvadora Persica* extracts easily applied, especially in the field of human use.

3.5. Adsorption Isotherm

The interaction information between the water and ethanol extract of the *Salvadora Persica* and the dental amalgam surface can be provided by adsorption isotherm. The following adsorption isotherms are the most common models to study the mechanism of corrosion inhibition [48–50]:

$$\frac{C_{inh}}{\theta} = f(C_{inh}) \tag{3}$$

Its linear equation:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{4}$$

Temkin adsorption isotherm:

$$\theta = f(\ln C_{inh}) \tag{5}$$

Frumkin adsorption isotherm:

$$\ln\left(C_{inh}\left(\frac{1-\theta}{\theta}\right)\right) = f(\theta) \tag{6}$$

Freundlich adsorption isotherm:

$$\ln(\theta) = f(\ln C_{inh}) \tag{7}$$

The correlation coefficient (R^2), as shown in Table 2, was used to choose the best isotherm, which was the best-fitted straight line obtained from the plot of C_{inh}/θ versus C_{inh} its slopes around 1.2 for both extracts. This suggests that the adsorption of both extracts on the surface of amalgam followed Langmuir adsorption isotherm.

Table 3: The correlation coefficient (R^2) for Langmuir, Temkin, Frumkin, and Freundlich isotherm.

Isotherm types	Langmuir	Temkin	Frumkin	Freundlich
Water extract (R^2)	0.9983	0.8536	0.1743	0.8595
Ethanol extract (R^2)	0.9616	0.8254	0.6138	0.8474

According to the adsorption isotherm of Langmuir, as shown in Figure 7, the $k_{id/s}$ values were calculated and then used to calculate the free energy of adsorption (ΔG_{ads}^0) by using the following equation.

$$K_{ads} = \frac{1}{55.5} e^{\left(\frac{-\Delta G_{ads}^0}{RT}\right)} \tag{8}$$

$$\Delta G_{ads}^0 = -(\ln K + \ln 55.5) \times RT \tag{9}$$

$$\Delta G_{ads}^0 = -(\ln K + \ln 1000) \times RT \tag{10}$$

Where K is a constant, R is the constant of perfect gases (8,314 J/Kmol) T is the experimental temperature in Kelvin, and the numerical values (55.5 M and 1000 g/l) in the equations indicate the concentration of water [35]. Many authors use natural products as green inhibitors, they reported the inhibitor concentration in grams per litre (g/l). and use of the value (55.5 M; as in equation 9) of the molar concentration of water, this is conceptually wrong [51,52]. Therefore, some researchers use equation 10 with a water concentration of 1000 g/l, to homogenize the units in the equation [53].

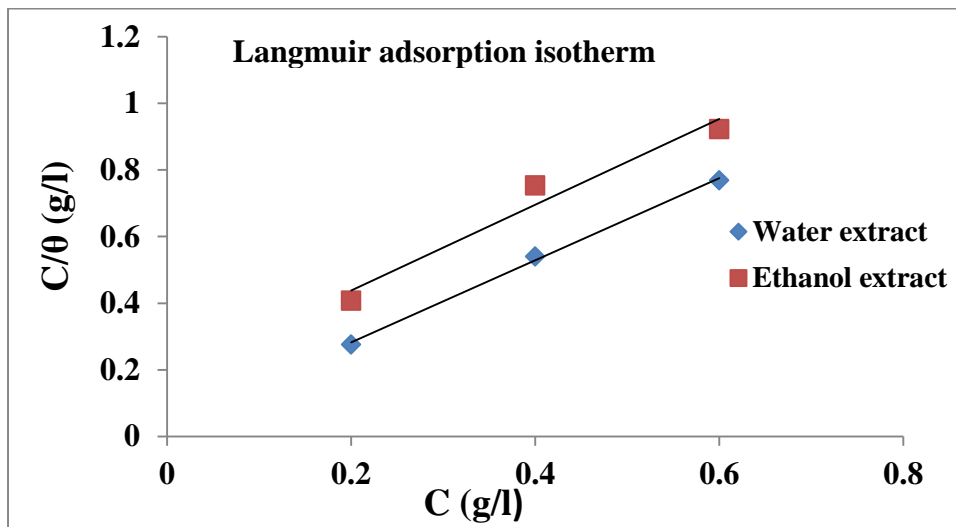


Figure 7: Plots of Langmuir adsorption isotherm of *Salvadora Persica* extracts on the amalgam surface at room temperature.

The calculated value of free energy of adsorption (ΔG_{ads}^0), as shown in Table 4, was found to be -25.38 and -21.37 KJ/mol for water and ethanol extract respectively. the negative sign of ΔG_{ads} indicates that the extracts adsorb spontaneously onto the amalgam surface [54, 30]. Generally, the magnitude of ΔG_{ads} around -20 kJ/mol or less negative is assumed for electrostatic interactions exist between the inhibitor and the charged metal surface (physisorption), and beside those around -40 kJ/mol or more negative indicate charge sharing or transferring from organic specie with the metal surface to form a coordinate type bond (chemisorption) [36]. The value of free energy suggested that the adsorption mechanism of both extracts onto the amalgam surface accomplishes electrostatic force (physisorption), which was stronger in the presence of the water extract.

Table 4: Thermodynamic and adsorption parameters of water and ethanol onto dental amalgam surface in artificial saliva solutions.

Inhibitor	K_{ads}	ΔG_{ads}^0 (kJ/mol)	E_a (kJ/mol)	ΔH_{ads}^0 (kJ/mol)	ΔS_{ads}^0 (J/mol)
Blank	—	—	- 9.36	-11.83	-387.5
Water extract	28.01	-18.2	13.46	10.99	-323.7
Ethanolic extract	5.54	-14.2			

The Temperature Effect.

According to inhibitory efficiency, the *Salvadora Persica* water extract was chosen for the temperature effect tests. The activation energy of the adsorption (E_a), the entropy of adsorption (ΔS_{ads}^0), and the heat of adsorption (ΔH_{ads}^0) were the most important thermodynamic adsorption parameters, which were given by the following relations [54].

$$\ln I_{corr} = \ln k - \left(\frac{E_a}{RT} \right) \tag{11}$$

$$\ln \frac{I_{corr}}{T} = \left(\ln \frac{R}{Nh} + \frac{\Delta S_a^0}{R} \right) - \frac{\Delta H_a^0}{RT} \tag{12}$$

Where K is the Arrhenius pre-exponential constant, R is the gas constant, T is the experimental temperature in Kelvin, N is the Avogadro's number and h is the Planck's constant.

Figure.8 and 9. show the Arrhenius plots for the corrosion rate, the first one, the plot of $\ln I_{corr}$ versus $1/T$ plots, was used to calculate the values of activation energy for amalgam specimen in artificial saliva with or without aqueous and ethanol *Salvadora Persica* extract. On the other hand, the second (figure 9) plot of $\ln I_{corr}/ T$ versus $1/T$ plots, is used to calculate the values of enthalpies and entropy. The extracted thermodynamic parameters of adsorption are given in Table 4.

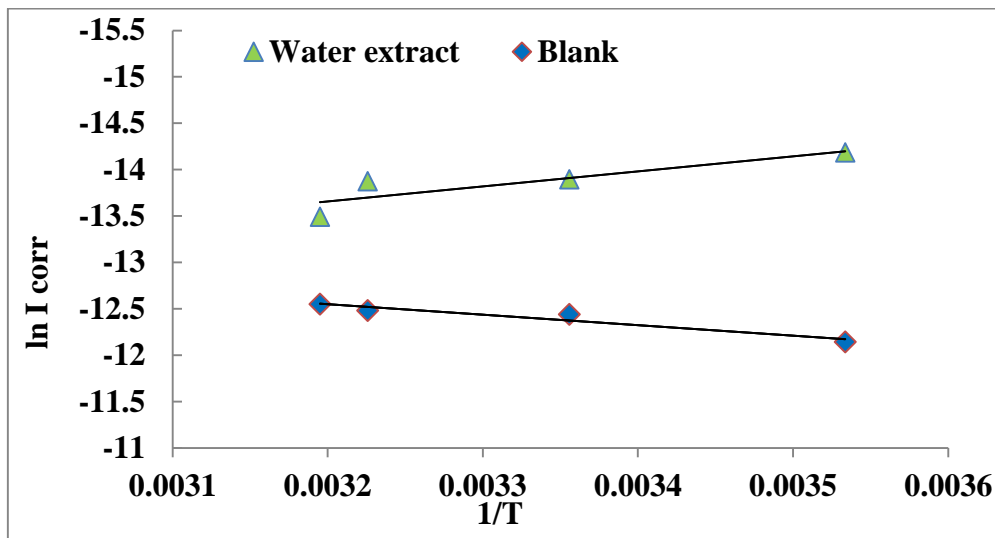


Figure 8: The plots of $\ln I_{corr}$ versus $1/T$ for dental amalgam in artificial saliva with and without optimal concentration (0.6 g/l) of water *Salvadora Persica* extract

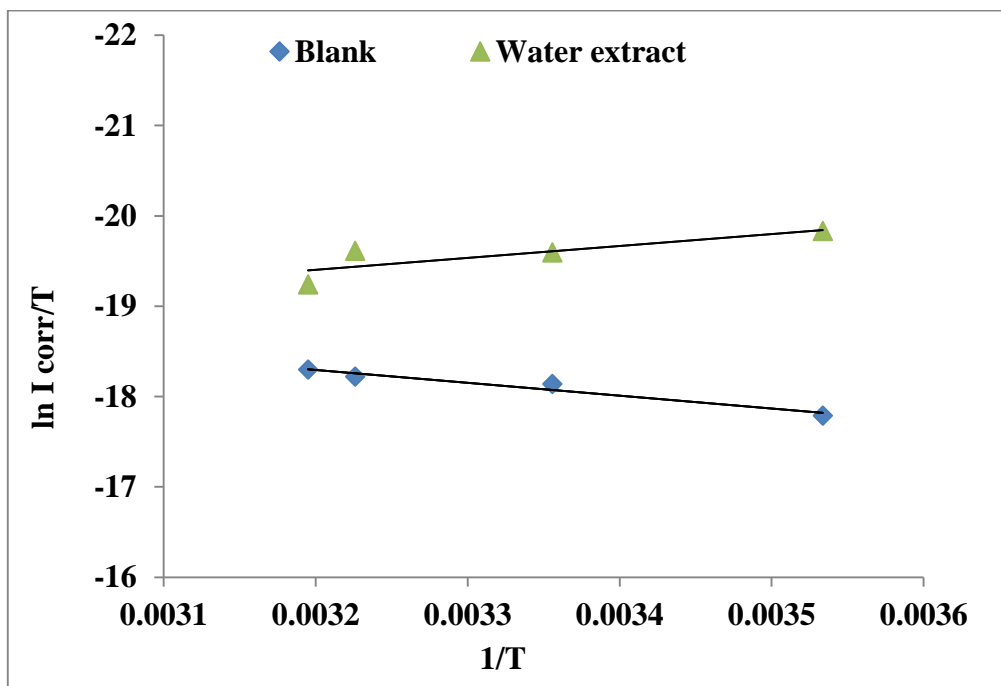


Figure 9: The plots of $\ln I_{corr} / T$ versus $1/T$ for dental amalgam in artificial saliva with and without optimal concentration (0.6 g/l) of water *Salvadora Persica* extract

As shown in Table 4, the value of activation energy (E_a) in the presence of water extract is larger than in blank solution ($E_{a(inh)} > E_a$). This result suggested that the adsorption mechanism of the extract onto the amalgam surface accomplishes electrostatic force (physisorption) [46, 54], which confirmed the results of the free energy.

The negative sign of enthalpy in the blank solution indicates that the process of amalgam dissolving is exothermic. Besides, its positive sign in the blank solution indicates that the process of amalgam dissolving is endothermic. Moreover, the large value of enthalpies in the presence of the water extract compared with a blank solution means more energy barrier is needed for the amalgam dissolution (the extract increases the corrosion resistance of amalgam).

The negative sign and large value of entropy indicated that the formation of the activating complex in the rate of determining step represents an association rather than dissociation. This means there is a decrease in disorder when the reactant is transformed into the activated complex [36].

3.6. ESP and DFT Calculations:

The chemical constituents of the *Salvadora Persica* (Miswak) were reported in many studies earlier, which demonstrated a high ratio of alkaloids such as; trimethylamine, salvadorine, and vitamin C;

and small quantities of tannins, saponins, flavonoids, and sterols. The previous chemical composition of the *Salvadora Persica* indicated also the presence of chlorides, fluorides, and moderate concentrations of silica and sulfur [55-57]. The Mulliken charge and the optimized structure of these molecules are shown in Figure 10.

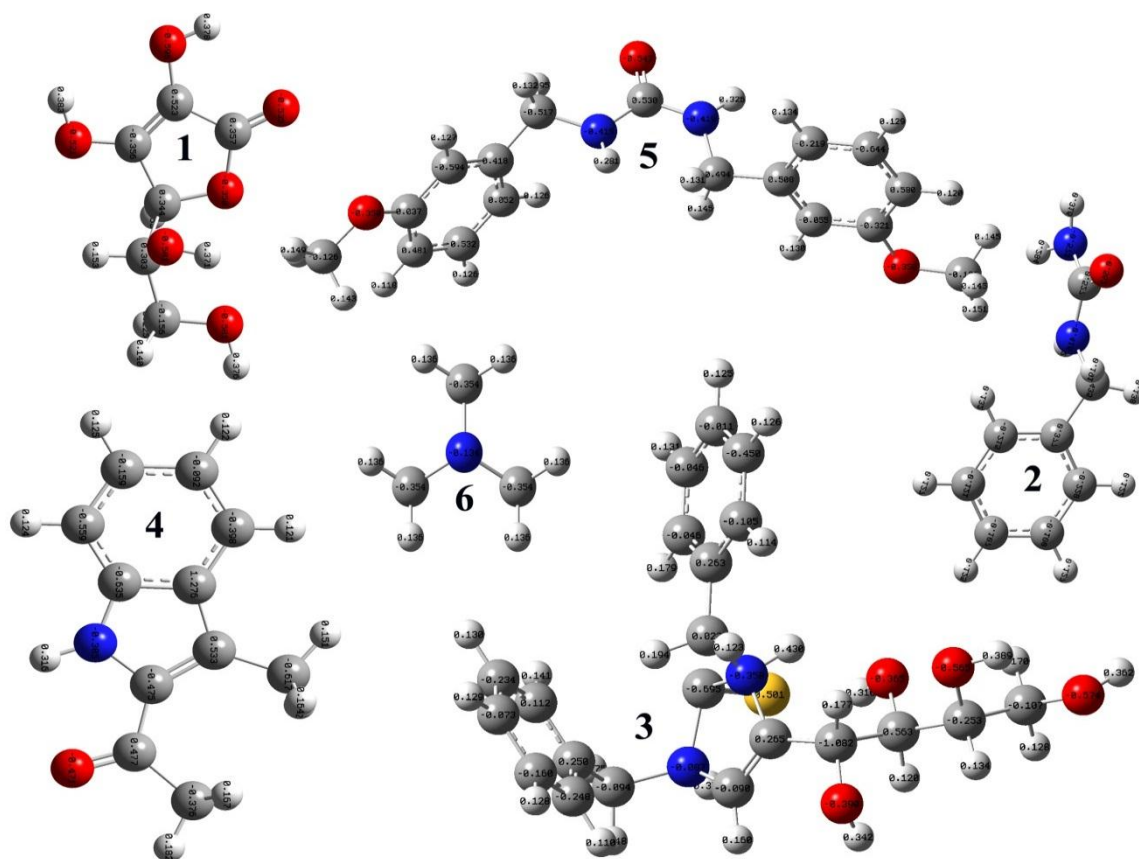


Figure 10: The Mulliken charge and optimized structure of the major molecules of *Salvadora Persica* extract; Ascorbic Acid (1); Benzylurea (2); Persicaline (3); Salvadouricine (4); SalvadOurea (5) and Trimethylamine (6).

The quantum chemical calculations were performed using DFT (density functional theory) with Beck's three parameter exchange functional along with the Lee–Yang–Parr nonlocal correlation functional (B3LYP) complemented with basis set with 6-31G +(d,p) that was carried out on Gaussian 09 [22]. Frontier molecular orbitals (FMO) distribution density of the energy of the highest occupied molecular orbital (E_{HOMO}) and the low unoccupied molecular orbital (E_{LUMO}) suggests that the selectivity site of the molecular systems and chemical reactivity depends on the energy of gap (ΔE), electronegativity (χ), ionization potential (I), chemical potential (μ), electron affinity (A), global softness (σ), global hardness (η), global electrophilicity index (ω), electro-accepting power (ω^+), electro-donating power (ω^-), net electrophilicity ($\Delta\omega^\pm$) and back-donation energy ($\Delta E_{\text{B,D}}$) and electronegativity (global electronic chemical potential; χ) which explain the eventual charge-transfer interaction within the molecule, they are caudated using the following equations [58-61].

$$I = -E_{\text{HOMO}} \quad (13)$$

$$A = -E_{\text{LUMO}} \quad (14)$$

$$\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}} \quad (15)$$

$$\eta = \frac{1}{2}(E_{\text{LUMO}} - E_{\text{HOMO}}) \quad (16)$$

$$\sigma = \frac{1}{\eta} \quad (17)$$

$$\chi = \frac{1}{2}(-E_{\text{HOMO}} - E_{\text{LUMO}}) \quad (18)$$

$$\mu = -\chi = \frac{1}{2}(E_{\text{HOMO}} + E_{\text{LUMO}}) \quad (19)$$

$$\omega = \frac{\mu^2}{2\eta} \quad (20)$$

$$\omega^+ = \frac{(-3E_{\text{LUMO}} - E_{\text{HOMO}})^2}{16 \times (E_{\text{LUMO}} - E_{\text{HOMO}})} \quad (21)$$

$$\omega^- = \frac{(-E_{\text{LUMO}} - 3E_{\text{HOMO}})^2}{16 \times (E_{\text{LUMO}} - E_{\text{HOMO}})} \quad (22)$$

$$\Delta\omega^{\pm} = \omega^+ + \omega^- \quad (23)$$

$$\Delta E_{B,D} = -\frac{\eta}{4} \quad (24)$$

The calculated quantum chemical parameters of the major molecules of *Salvadora Persica* extract related to the most stable conformation of molecule electronic structure are shown in Table 5.

Table 5: Quantum chemical parameters of major molecules of *Salvadora Persica* extract.

Extract's molecules	Trimethyl Amine	Salvad-Ourea	Salvadou-ricine	Persica-line	Benzyl-urea	Ascorbic Acid
LUMO (eV)	2.85	-0.09	-1.43	-0.69	0.14	-0.49(5)
HOMO (eV)	-5.23	-5.66	-5.70	-3.79	-6.18	-5.82
ΔE (eV)	8.08	5.57	4.27	3.10	6.31	5.33
I (eV)	5.23	5.66	5.70	3.79	6.18	5.82
A (eV)	-2.85	0.09	1.43	0.69	-0.14	0.49(5)
χ (eV)	1.19	2.88	3.57	2.24	3.02	3.16
σ (eV ⁻¹)	0.33	0.36	0.48	0.45	0.33	0.36
η (eV)	4.04	2.78	2.13	1.55	3.16	2.66
ω (eV)	0.18	1.49	2.98	1.62	1.44	1.87
μ (eV)	-1.19	-2.88	-3.57	-2.24	-3.02	-3.16
ω^+ (eV)	0.29	0.78	2.02	2.03	0.80	1.06
ω^- (eV)	3.16	4.21	5.94	6.15	4.55	4.88
ω^{\pm} (eV)	3.45	4.99	7.96	8.18	5.36	5.94
$\Delta E_{B,D}$	-0.76	-0.69	-0.52	-0.56	-0.76	-0.69

A high LUMO energy value indicates that a molecule's electron-accepting ability is weaker. On the other hand, a low LUMO energy shows that a molecule is a good electron acceptor. HOMO energy represents the molecule donating electron [58, 59]. Low-value LUMO energy and high-value HOMO are associated thereby high protection ability and strong bending between metal and inhibitor [58]. As shown in Table 5, Persicaline has a higher value HOMO and Benzylurea has the lowest which indicates that Persicaline has better corrosion inhibition properties and it is the best electron donor.

The higher value (ΔE) implies that Trimethylamine is a poor corrosion inhibitor and less reactive compared with other extract molecules. The higher value of electronegativity (χ) also shows that the inhibitor acts as a poor corrosion inhibitor [59,60]. Global softness (σ) and global hardness (η) were also calculated for all extract's molecules, the low value of η is related to high reactivity; electron donating ability, adsorption tendency and inhibition efficiency and the converse is true for σ [61-63]. The results imply that Persicaline has a high value of σ and a low value of η , which means it is more reactive and consequence more effective corrosion inhibitor. And besides, Trimethylamine is the less effective corrosion inhibitor, because it has a high value of η and a low value of σ . The frontier orbital distribution HOMO, LUMO, and ESP of major molecules of *Salvadora Persica* extracts are presented in Figure 11. Generally, the compound electron-donating capacity if the back-donation energy is less than zero ($\Delta E_{B,D} < 0$) [64]. According to the results of Table 5, the back-donation energy ($\Delta E_{B,D}$) of all *Salvadora Persica* extract molecules was less than zero ($\Delta E_{B,D} < 0$), which indicated that the charge transfer from the metal surface to the inhibitor, followed by a back-donation from the inhibitor, was the preferable energetical procedure.

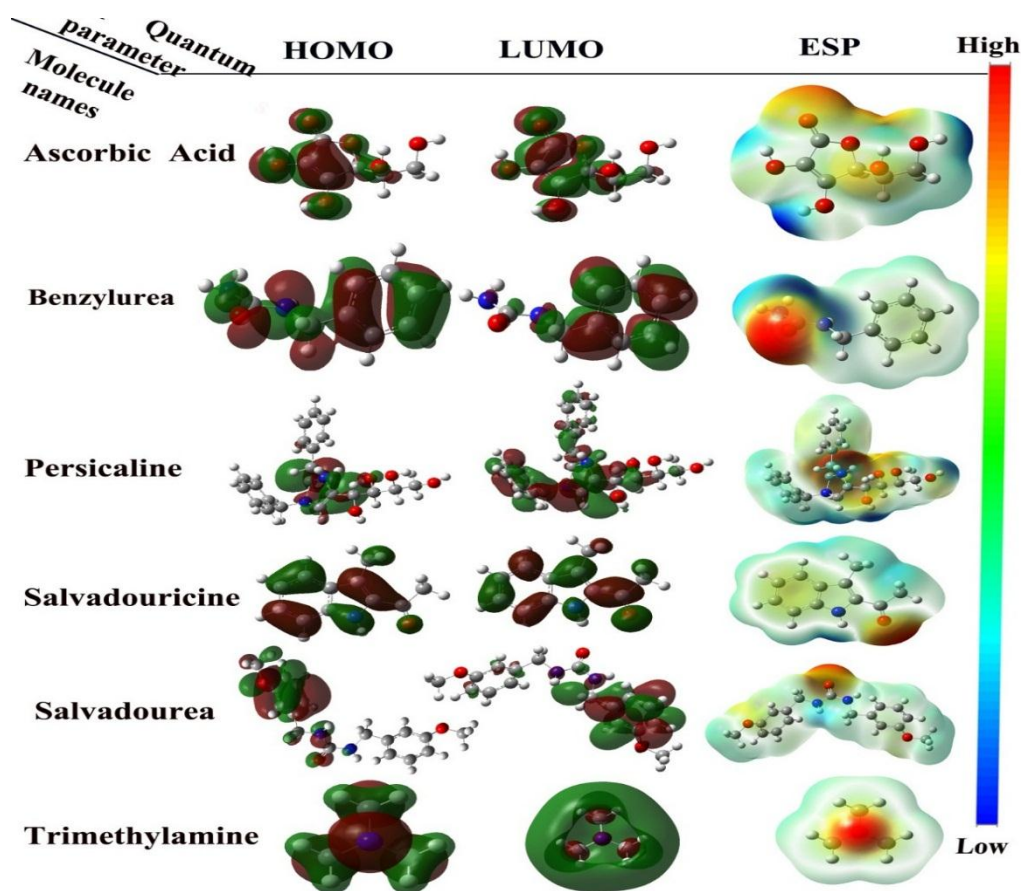


Figure 11. The frontier orbital distribution HOMO, LUMO, and ESP of major molecules of *Salvadora Persica* extract.

CONCLUSION

In this study, we can conclude that the ethanol and water extracts of the *Salvadora Persica* (Miswak) act as a good green inhibitor of dental amalgam corrosion in artificial saliva. A good agreement was obtained for the inhibition efficiency determined by electrochemical methods. The inhibition efficiency increased with the increasing immersion time and the concentration of both ethanol and water *Salvadora Persica* extracts. The inhibition efficiency was better with the water extract than with the ethanol extract. DFT studies carried out major molecules of *Salvadora Persica* extracts provide good support for the experimental results and it established that Persicaline interacts more strongly with the amalgam surface compared to other extract molecules.

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