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Thyme Extract as Corrosion Inhibitor for Teeth Filler Alloy in Saliva Media

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Abstract
In this work the study mainly investigated the inhibition behavior, and the adsorption properties of different concentrations of an aqueous extraction of thyme plant range (5-20) ppm at the temperature range (288-318) K for corrosion of dental amalgam in artificial saliva, by applying electrochemical method. The result showed good inhibitive action for all thyme extract concentration with slight decreases by increasing temperature. The physisorption for thyme extract compound on the surface of dental amalgam obeys Langmuir isotherm. The kinetic parameter for corrosion process and thermodynamic data for adsorption process has been calculated.

Keywords: Dental amalgam, Saliva, Thyme plant, Corrosion, Adsorption

مستخلص الزعتر كمثبط لتأكل سبيكة حشوة الاسنان في وسط اللعاب

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الخلاصة
في هذا العمل :تحقق دراسة السلوك التثبيطي وصفات الامتزاز للمستخلص المائى لنبات الزعتر بمدى تراكيز (5–20) جزء بالمليون ومدى درجات حرارة (288–318) كلفن . بتطبيق الطريقة الكهروكيميائية . واظهرت النتائج فعل تثبيطي جيد لكل تراكيز مستخلص الزعتر مع انخفاض طفيف عند زيادة درجة الحرارة .الامتزاز فيزياوى لمركبات مستخلص الزعتر على سطح ملغم الاسنان مع اطاعة لمتساوى درجة الحرارة للنكماير .المعاملات الحركية لعملية التأكل والمعاملات الحرارية لعملية الامتزاز تم حسابها.

Introduction
There is a various and available method for metals and alloys protection from corrosion. Using inhibitor is very popular methods. Inhibitors are chemical compounds when added in a little amount to corrosive environment prevent or decrease corrosion [1], but these compounds, unfortunately, are expensive and toxic for human living and environment [2]. New substances extracted from plants are utilized as corrosion inhibitors for metals and alloys. This substance provides cheap sources, isolated with simple method and environment safe [3] Plants extract have a various organic compounds with the heteroatoms such as N, O, S, and P. these atoms form protective layer by coordination with metal on surface ions [4].

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(Thymus vulgaris L) is the scientific name of Thyme [5].In the Greek; the word means courage or strength [6]. Thyme is used everywhere in the world for medicinal and spice purpose, [7]. The active substance isolated from thyme plant is saponins, volatile oil, and tannins with the percentage (59.2%), (21.1%) and (9.7%) respectively [8].

Saliva is a complex, dilute, colorless and opalescent, aqueous solution with 1003 specific gravity [9] contains inorganic and organic compounds [10]. Artificial saliva prepared for several tests with similar chemical conditions pertaining in the mouth [11].

Dental amalgam is a mercury alloy with metallurgical complex structure. One part of liquid mercury is mixed with one part of alloy powder contains copper (10-30%), tin (15-30%), silver (40-70%) [12], to form stable phase such as “Ag-Hg, Sn-Hg, Ag-Cu and Ag-Sn” [13]. Dental amalgam is used more than 165 years ago [14].

This work investigated the inhibitive action of aqueous extract of thyme plant on dental amalgam alloy in artificial saliva media.

Materials and Methods

The chemical compounds of dental amalgam that are used in this study are shown in Table-1, [15].

Table 1-The percentage of one part of alloy powder.

	Ag	Sn	Cu
Wt.%	56.7	28.6	14.7

The alloy of amalgam mounted and polished mechanically, and washes with distilled water then isolated by using Pyrex –polymer except the polished side to prepare the working electrode that connected electrically in corrosion cell. Table-2 showed the composition of artificial saliva [16] with PH equal 6.2.

Table 2-Artificial saliva components.

	KCl	NaCl	$CaCl_2H_2O$	$NaH_2PO_4.2H_2O$	$Na_2S.9H_2O$	Urea
g/l	0.4	0.4	0.906	0.69	0.005	1

Thyme plant was collected from a local market in Baghdad. Grinding by using an electrical grinder, then an aqueous solution was prepared by using 8 grams of grinding plant with 500 mL of distilled water in the soxhlet extractor for 24 hours. The aqueous solution was dried in air, then collected the solid to prepare different concentrations range (0, 5, 10, 15, 20) ppm in artificial saliva to use as an electrolyte for corrosion cell. Reference silver –silver chloride electrode, auxiliary platinum electrode and dental amalgam as working electrode are the three electrodes for corrosion cell that are used to obtain the corrosion parameter using Mlab potentiostat (Germany 2000,provide with Mlabsci –software). The working electrode was immersed for 15 minutes in artificial saliva (with and without inhibitor)to obtain the open circuit potential (E_{ocp}) then measuring the polarization curve range of -200 mV to +200mV with respect to open circuit potential at temperature range (288-318) K in areated solution ,to calculated the impact of temperature on the kinetic of dental amalgam corrosion in presence and absence of inhibitor (thyme extract)in artificial saliva(electrolyte solution) and the electrochemical behavior of dental amalgam corrosion in aggressive media . The FT-IR analysis for pure thyme and its absorption layer on the dental amalgam surface have been carried out by using Fourier transform infrared spectrophotometer (Shimadzu Japan).

Result and discussion

Dental amalgam corrosion is a very complex process because there are different phases formed during amalgamation process with various corrosion potential [17].

Equation for Phase formation

$$\gamma\text{-}Ag_3Sn + Ag\text{–}Cu + Hg \rightarrow \gamma_1\text{-}Ag_2Hg_3 + \gamma_2\text{- }Sn_7Hg + \gamma\text{-}Ag_3Sn + Ag\text{–}Cu$$

$$\gamma_2\text{-}Sn_7Hg + Ag\text{–}Cu = \eta\text{-}Cu_6Sn_5 + \gamma 1\text{-}Ag_2Hg_3$$

Due to acidity of saliva reduction of hydrogen or oxygen can occur at cathodic sites, according to the following reactions:

$$2H^+ + 2e \rightarrow H_2$$

$$O_2 + 4H^+ + 4e \rightarrow 2H_2O$$

Dissolution of material in amalgam can occur at anodic sites by the tin-mercury phase (γ_2- Sn_7Hg), has the lost corrosion potential, taken after by Ag_2Hg_3, Ag_3Sn, Ag_3Cu_2, Cu_3Sn, Cu_6Sn_5, so that the most corroded phase is γ_2- Sn_7Hg. forming tin oxide or tin oxychloride and pure mercury [18],and this caused low strength and porosity in tooth filler.

Polarization curve of the corrosion of dental amalgam in the presence of 5 ppm thyme extract concentration was shown in Figure-1; the same result was appeared for other concentrations.

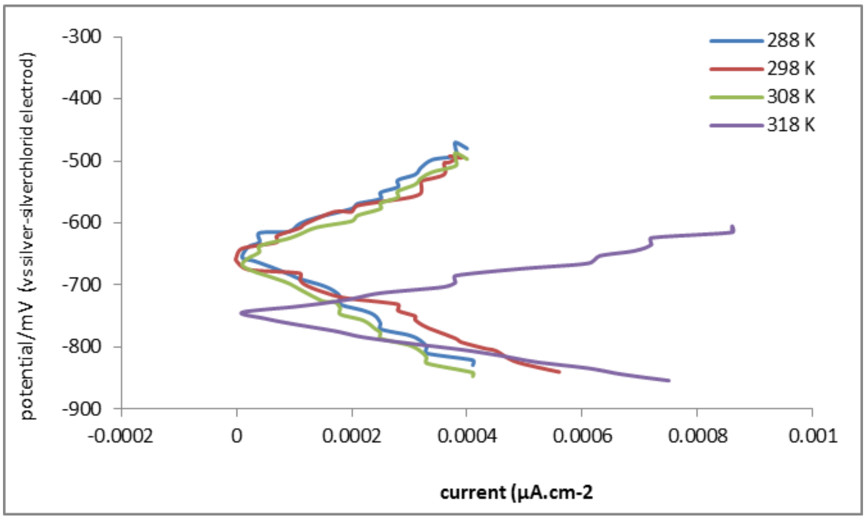


Figure 1- The polarization curve of dental amalgam in 5 ppm concentration of thyme extract in artificial saliva.

Equation 1 was used to calculate the inhibition efficiency % IE for corrosion process [19], where i_{corr}. and i^o_{corr}. are the current density of corrosion with and without inhibitor, sequences

$$\% IE = \theta \times 100 = 1-(i_{corr} / i^o_{corr}) \times 100 \ldots \qquad \ldots\ldots\ldots(1)$$

Potential corrosion E_{corr} vibrated with concentration and temperature due to phase variation. The current density i_{corr} of corrosion process increased with increasing temperature and the inhibitor concentration. The data of corrosion was represented in Table-3.

Table 3- Corrosion kinetic parameters for amalgam in absence and presence of different concentration of thyme extracts (5-20) Ppm at a different temperature range (288-318) K.

		-OCP /mV	$-E_{corr}$ mV	i_{corr}/μA.cm^{-2}	-bc/ mV .Dec^{-1}	ba/ mV. Dec^{-1}	IE %	Θ
Without inhibitor	288	471	386.1	4.85	228.4	424.5	-	-
	298	389	376.3	5.27	170.6	260.5	-	-
	308	370	379.1	5.78	160.9	241.4	-	-
	318	354	380	6.74	124.8	197.8	-	-
5ppm inhibitor	288	654	652.3	0.146	445.5	402.1	96.9	0.9698
	298	664	651.5	0.161	368.0	352.5	96.9	0.9694
	308	670	684.4	0.212	325.4	342.3	96.3	0.963
	318	787	746.8	0.340	327.1	342.1	94.9	0.949
10ppm inhibitor	288	201	146.6	0.722	125.8	195.5	85.1	0.851
	298	323	294.3	0.816	64.0	76.2	84.4	0.844
	308	340	344.7	1.01	51.4	86.8	82.2	0.822
	318	395	402.2	1.26	67.7	99.2	81.3	0.813
15ppm inhibitor	288	729	761.6	0.346	35.1	310.6	92.8	0.928
	298	773	845.1	0.425	214.2	248.6	91.9	0.919
	308	806	809.4	0.479	310.5	354.7	91.7	0.917
	318	856	842.1	0.639	272.6	360.1	90.5	0.905
20ppm inhibitor	288	382	487.6	0.892	47.7	33.4	81.6	0.816
	298	500	489.1	1.20	40.7	68.6	77.2	0.772
	308	449	495.2	1.70	54.2	51.4	70.5	0.705
	318	497	514.4	2.29	55.5	47.3	66.0	0.66

Kinetic of Corrosion

Arrhenius equation 2, [20] was used to study the impact of temperature on the kinetic of corrosion of dental amalgam with and without thyme extract as an inhibitor in free artificial saliva to clear the information of electrochemical reaction of amalgam in corrosive media.

$$\text{Log } i_{corr} = \text{Log } A - E_a / 2.303RT \qquad \ldots(2)$$

The straight line determined from a plot between 1/T and logarithm of i_{corr} (i_{corr} proportional with corrosion rate (CR)) to get the activation energy (E_a) from the slop of the straight line and pre exponential factor (A) from the intercept, Figure-2. The result showed that the activation energy increments with increasing of thyme extract concentration resulting increasing in active site on the surface of dental amalgam, as shown in Table- 4.

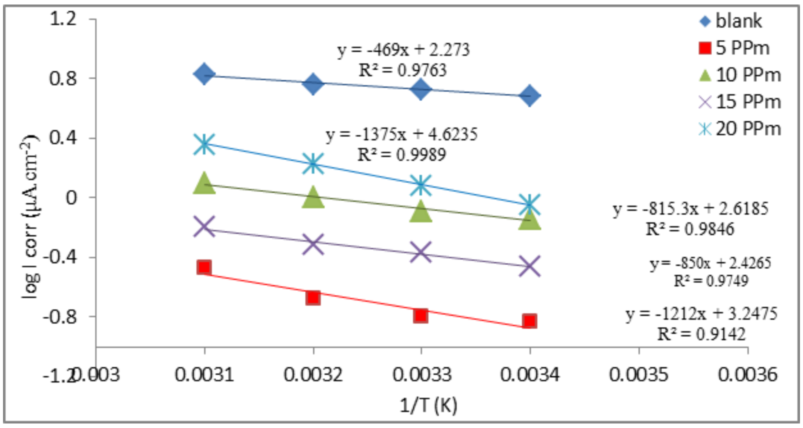


Figure 2- Arrhenius Plot of logI_{corr} versus 1/T for the corrosion of dental amalgam in artificial saliva when different concentrations of thyme extract absence or presence.

Table 4- The activation energy (E_a.), pre-exponential factor (A) and the thermodynamic parameters for the corrosion activation complex of amalgam in artificial saliva in a state of using inhibitor concentration or not, over the temperature range 288 -318 K.

C_{inh}	ΔG_a /kJ.mol^{-1}				ΔH_a/kJ .mol^{-1}	-ΔS_a/ J.mol^{-1} .K^{-1}	E_a/kJ. mol^{-1}	A Molecules. cm^{-2} .S^{-1}
	288	298	308	318				
without	66.72	68.82	70.92	73.02	6.24	210	8.980	13.6E+23
5ppm	75.68	77.58	79.50	81.41	20.67	191	23.20	19.5E+23
10ppm	71.33	73.36	75.39	77.42	12.86	203	15.61	15.7E+23
15ppm	73.19	75.26	77.33	79.40	13.57	207	16.27	14.6E+23
20ppm	71.22	72.87	74.52	76.17	23.70	165	26.32	27.8E+23

Enthalpies of activation ΔHa, the entropy of activation ΔSa, value (Table-4) are calculated by utilizing the option plan of Arrhenius condition 3 [21].

Log i_{corr} /T = log R/ Nh+ ΔS_a / 2.303R - ΔH_a / 2.303 TR … …(3)

The plot of log CR /T vs. 1/T to get strength line with slope = $-\Delta H_a$ /2.303 R and intercept equal log(R/Nh) +ΔS_a/2.303R as shown in Figure-3. Where R: gas constant, h: Planck's constant and N: Avogadro's number.

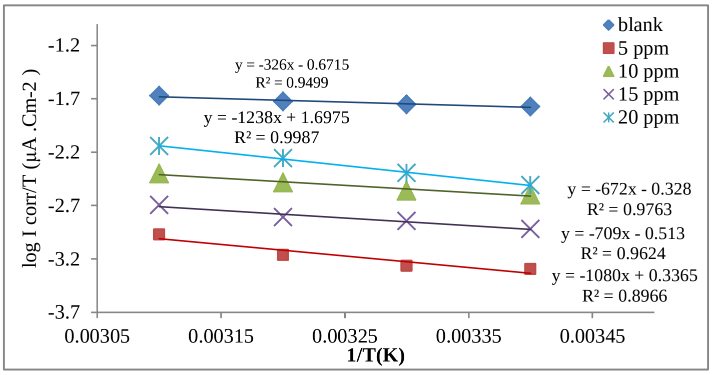


Figure 3- curve of log i_{corr} /T vs. 1/T for the corrosion of dental amalgam in artificial saliva solution in the state of using inhibitor concentration or not.

A negative value of ΔSa shows that the development of activated complex decreases and ordering took place, while the positive values of ΔHa indicate that the formation of activation complex is an endothermic process [22]. Free energy of activation (ΔG*) can be computed using thermodynamic equation 4 [23]. The positive value of activation free energy (ΔG*) meaning non-spontaneous corrosion reaction and its value increases with increasing the concentration of thyme extract.

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad \ldots(4)$$

Adsorption Isotherm

The general operation of inhibitors is forming and maintenance the layer on the metal surface [24]. The behavior of inhibitor adsorption process on the dental amalgam surface can be describing by different kinds of isotherm Langmuir, Freundlich, Temkin, and Frumkin.In electrochemical system physical counties (number of adsorbed molecules θ) relating potential of electrode or concentration of inhibitor to define the adsorbed state [25] surface coverage θ obtained from polarization measurement using equation 1. In Langmuir isotherm plot C_{inh}/θ versus concentration C_{inh} as given in equation five which can also be represented as equation six[26]. K_{ads} is the equilibrium constant of adsorption process calculated from the intercept of Langmuir plot Figure-4.

$$C_{inh}/\theta = K_{ads}^{-1} + C_{inh} \qquad \ldots(5)$$

$$\text{Log } C_{inh}/\theta = \text{Log } K_{ads}^{-1} + \text{Log } C_{inh} \qquad \ldots(6)$$

The value of regression coefficient R^2 as it appears in Table-5 is near to unity meaning that the adsorption isotherm obey Langmuir isotherm. The K_{ads} values are positive indicate that the adsorption process is favorable [27].

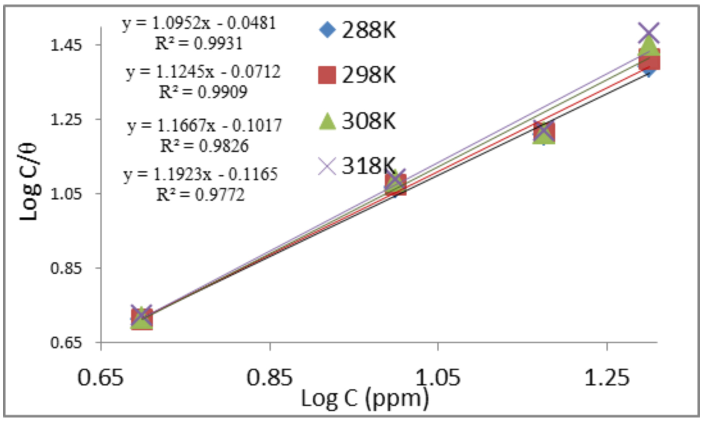


Figure 4-Curve of adsorption process (Langmuir isotherm) of thyme extract in artificial saliva on dental amalgam surface.

The free energy of adsorption (ΔG^o_{ads}) can be calculated by application of equation 7 [28]

$$\text{Log } K_{ads} = \text{Log } 1/55.5 - \Delta G^o_{ads} / 2.303RT \qquad \ldots(7)$$

The value 55.5mol/L represents the concentration of water; ΔG_{ads} is adsorption free energy, and T is absolute temperature. A negative value of ΔG^o_{ads} indicate that adsorption process is spontaneous and strong attract between dental amalgam surface and thyme extracted compound, consisting physisorption due to magnitude value of ΔG^o_{ads} which are less than -20 $kJ.mol^{-1}$ [29], Table- 5.

Table 5-Thermodynamic adsorption parameters.

Temp.	K_{ads}	ΔG^o_{ads}/ kJ/mol	$-\Delta S^o_{ads}$/ J/K.mol	ΔH^o_{ads}/ kJ/mol	R^2
288	0.895	-9.35	17.9	1.4938	0.9931
298	0.848	-9.54	27.0		0.9909
308	0.791	-9.68	26.5		0.9826
318	0.764	-9.90	26.4		0.9772

The enthalpy ΔH^o_{ads} and entropy ΔS^o_{ads} of adsorption process can be calculated by using equation four for adsorption process. Plot of ΔG^o_{ads} vs. T to get a strength line with slope equal $-\Delta S^o_{ads}$ and intercept equal ΔH^o_{ads} as shown in Figure-5

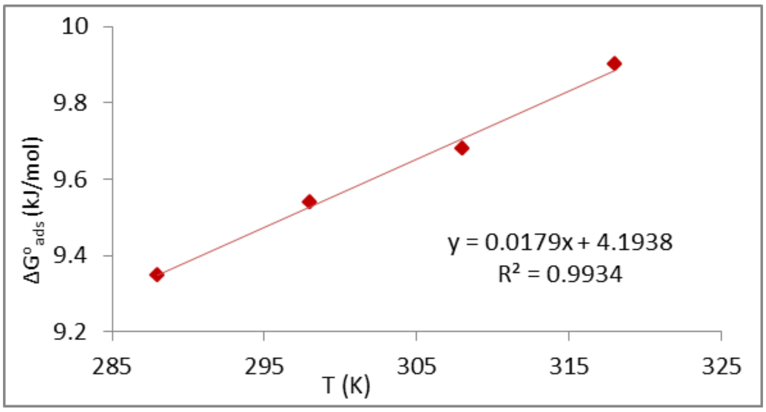
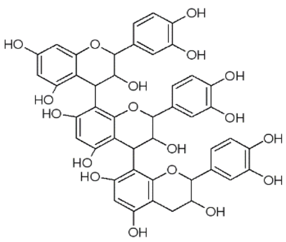


Figure 5-Curve of free energy versus absolute temperature.

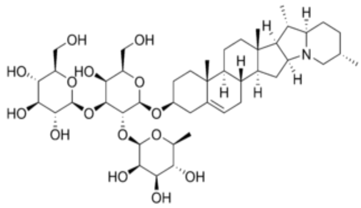
The positive values of enthalpy change ΔH^o_{ads} confirmed the endothermic adsorption process for organic inhibitor molecules from the aqueous solution on the metal surface, while negative values for entropy change ΔS^o_{ads} accompanied the adsorption process [30].

FT-IR analysis

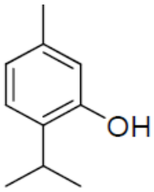
The main compound isolated from thyme plant is saponins, tannins and volatile oil with the percentage (59.2%), (9.7%) and (21.1%). The main constituent of volatile oil is thymol and carvacrol [31]. Figure- 6 represents the structures of these compounds which have different active groups such as O-H, C=O, C=C, Π electrons and heterocyclic ring [32, 33].



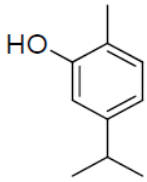
Tannins



Saponins



Thymol



Cravacrol

Figure 6- Structures of the main compounds isolated from thyme plant.

Table 6- represented the frequency of functional group for FT-IR spectra of pure thyme extract and its film formed on the surface of dental amalgam. The results showed shifting of frequency for O-H bond, and C-O bond to new value and less intensity due to the binding force result from adsorption process between dental amalgam surface and the organic molecules isolated from thyme plant as it appears in Figure-7(a) and (b),while C=C bond did not affect.

Table 6- FT-IR spectral data for pure thyme and its film formed on dental amalgam surface.

pure thyme extract	corrosion product	group
Wave number (cm^{-1})	Wave number (cm^{-1})	
3446	3404	O-H stretch
1390	1356	O-H bending
1056	1033	C-O stretch
1647	1647	C=C stretch

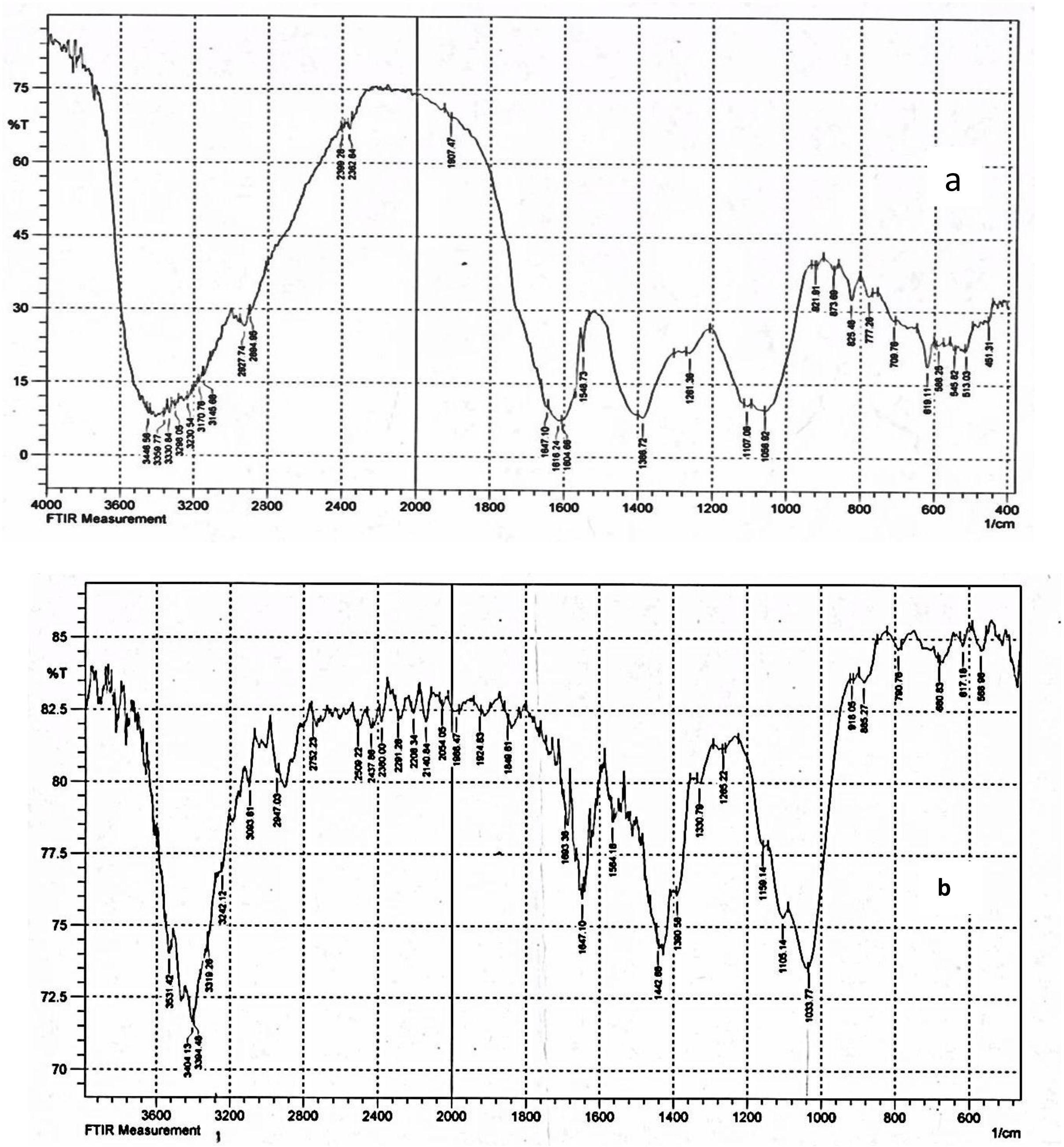


Figure 7- FT-IR spectra of pure thyme extract (a) and its film formed on the surface of dental amalgam (b).

Conclusions

The inhibition efficiency increased with increasing thyme extracts which mean that thyme extract is a good inhibitor for teeth filler.

Inhibition of efficiency was decreased with increasing the temperature and increased with increasing concentration of extract of thyme plant.

The value of activation energy increased with increasing the concentration of thyme extracts, meaning that the energy barrier for corrosion process is increased.

The physisorption process is spontaneous and accompanied Langmuir adsorption isotherm.

References

1. khan1, G., Newaz1, K. S., Basirun, W. J., Mohd Ali, H.B., Faraj, F. M. and Khan, L. G.**2015**. Application of natural product extracts as green corrosion inhibitors for metals and alloys in acid pickling processes- a review. *International Journal of Electrochemical Science*, 10, pp: 6120-6134.
2. Singh, A., Ebenso, E. E. and Quraishi, A. **2011**. Corrosion inhibition of carbon steel in HCl solution by some plant extracts. *International Journal of Corrosion*, 2012, pp: 1-20.
3. Fouda, A.S., Shalabi, K. and Idress, A. A. **2014**. Thymus vulgarise extract as nontoxic corrosion inhibitor for copper and a-brass in 1 M HNO_3 solutions. *International Journal of Electrochemical Science*, 9, pp: 5126- 5154.
4. Sangeetha, M.,Rajendran, S. ,Muthumegala, T. S. and Krishnaveni, A. **2011**. Green Corrosion Inhibitors-An Overview. *Zaštita Materijala,* 52, (1), pp: 3-19.
5. Swayeh, N. H., Abu-Raghif, A. R., Qasim, B. J. and Sahib H. B .**2014**. The protective effects of thymus vulgaris aqueous extract against methotrexate- induced hepatic toxicity in rabbits. *International Journal of Pharmaceutical Sciences Review and Research,* 29(2), 32, pp: 187-193.
6. Charles, D. J. **2013**.*Antioxidant Properties of Spices, Herbs And Other Sources*. First Edition, Springer Verlag, New York.
7. Imelouane, B., Amhamd, H., Wathelet, J.P., Ankit, M., Khedid, K. and El Bachiri, A. **2009**. Chemical composition and antimicrobial activity of essential oil of thyme (thymus vulgaris) from eastern morocco. *International Journal of Agriculture & Biology,* 11 (2), pp: 205-208.
8. Fayad, N.K., AL- Obaidi, O. H. S. and Al-Noor, T. H. **2013**. Water and alcohol extraction of thyme plant (thymus vulgaris) and activity study against bacteria, tumors and used as anti-oxidant in margarine manufacture. *Innovative systems Journal of Design and Engineering*,4 (1), pp: 41-51.
9. Amal,A.S.S., Hussain,S. and Jalaluddin, M. A.**2015**. Preparation of artificial saliva formulation. International Conference ICB Pharma II. Universitas Muhammadiyah Surakarta, Indonesia, 31 October.
10. Preetha, A. and Banerjee, R. **2005**. Comparison of artificial saliva substitutes. *International journal of Trends in Biomaterials and Artificial Organs,* 18 (2), pp: 178-186.
11. Darvell,B.W. **1978**. The development of an artificial saliva for in viro amalgam corrosion studies. *Journal of Oral Rehabilitation*, 5, pp: 41-49.
12. Acciari, H.A., Guastaldi, A. C. and Brett, C.M.A.**2001**. Corrosion of dental amalgams: electrochemical study of Hg–Hg, Ag–Sn and Sn–Hg phases*. Electrochemical Acta*, 46, pp: 3887-3893.
13. Majed, R.A., Abdul kathem Ali, K., Al-Atrakchy, H. B. and Al-Deen, H. D.**2013**. Experimental study and mathematical modeling for corrosion of amalgam at different periods. *Journal for Dental Sciences,* 1, pp: 30-37.
14. Bharti, R., Wadhwani, K.K., Rakash Tikku, A. P., and Chandra, A. **2010**. Dental amalgam: an update. *Journal of Conservative Dentistry,* 13(4), pp: 204-208.
15. Anaee, R.A., Al-Zubaidi, A. A. and Al-Tabbakh, A. A. **2014**. Corrosion behavior of amalgam /cockles shells composites in artificial saliva. *International Journal of Engineering Sciences & Research Technology*, 3(12), pp 68-71.
16. Anaee,R.A. **2016**. Behavior of Ti/HA in saliva at different temperatures as restorative materials, *Journal of Bio- and Tribo-Corrosion*, 2(5), pp: 1-9.
17. Acciari, H.A., Guastaldi, A. C. and Brett, C. M.A. **2005**. Corrosion of the component phases presents in high copper dental amalgams. Application of electrochemical impedance spectroscopy and electrochemical noise analysis. *Corrosion Science*, 47, pp: 635- 647.
18. Fathi, M. and Mortazavi, V. **2004**. A review on dental amalgam corrosion and its consequences. *Journal of Research in Medical Sciences*, 1, pp: 42-51.
19. Sudheer, M. A., Ebenso, Eno.E. and Natesan, M. **2012**. Inhibition of atmospheric corrosion of mild steel by new green inhibitors under vapour phase condition. *International Journal of Electrochemical Science,* 7, pp: 7463-7475.
20. Singh, A., Singh, V.K. and Quraihi, M.A. **2010**.Aqueous extract of kalmegh (andrographis paniculata) leaves as green inhibitor for mild steel in hydrochloric acid solution. *International Journal of Corrosion*, 2010, pp: 1-10.

21. Abdul Nabi, A. S. and Hussain, A.A. A.**2012**. Synthesis, identification and study of some new azo dyes as corrosion inhibitors for carbon-steel in acidic media. *Journal of Basrah Researches (Sciences)*, 38(1), pp: 125-146.
22. Adejo,S. O.,Yiase,S. G.,Ahile, U. J. ,Tyohemba,T. G. and Gbertyo,J. A.**2013**. Inhibitory effect and adsorption parameters of extract of leaves of portulaca oleracea of corrosion of aluminum in H_2SO_4 solution. *Scholars Research Library Archives of Applied Science Research*,5 (1) ,pp: 25-32.
23. Khouri, S. J. **2015**. Titrimetric study of the solubility and dissociation of benzoic acid in water: effect of ionic strength and temperature. *American Journal of Analytical Chemistry,* 6(5), pp: 429-436.
24. Mehanna, N. Sh., Effat, B. A. M., Tawfik, N. F., Sadek, Z. I., Dabiza, N. M. A. , El-Shafie, K. and Abd-El-Khalek , A. B.**2013**. Evaluation of antibacterial activity of aqueous extracts of thyme and black pepper against pathogens and probiotics. *Journal of Applied Sciences Research,* 9(2) pp: 1181-1185.
25. Bockris, J. O. M., Reddy,A. K. N. and Gamboa-Aldeco, M. **2000**. *Modern Electrochemistry Fundamentals of Electrodes*. Second Edition. Volume 2a, Kluwer Academic/Plenum Publishers New York.
26. Abd El Rehim, S. S., Sayyah, S.M., El-Deeb, M. M., Kamal, S. M. and Azooz, R. E. **2016**. Adsorption and corrosion inhibitive properties of (2-aminobenzothiazole) on mild steel in hydrochloric acid media. *International Journal Industrial Chemistry,* 7, pp: 39-52.
27. Zarrouk, A., Dafali, A., Hammouti, B., Zarrok,H. ,Boukhris, S. and Zertoubi,M.**2010**. Synthesis, characterization and comparative study of functionalized quinoxaline derivatives towards corrosion of copper in nitric acid medium. *International Journal of Electrochemical Science*, 5, pp: 46- 55.
28. Dahmani, M., Et-Touhami, A., *Al*-Deyab, *S. S*., Hammouti , B. and Bouyanzer , A. **2010**. Corrosion inhibition of C38 steel in 1 M HCl: a comparative study of black pepper extract and its isolated piperine. *International Journal of Electrochemical Science*, 5, pp: 1060- 1069.
29. Manimegalai, S. and Manjula, P. **2015.** Thermodynamic and adsorption studies for corrosion inhibition of mild steel in aqueous media by sargasam swartzii (Brown algae). *Journal of Material and Environmental Science*, 6 (6), pp: 1629-1637.
30. Leelavathi, S. and Rajalakshmi, R. **2013**. Dodonaea viscosa (L.) Leaves extract as acid corrosion inhibitor for mild steel – a green approach. *Journal of Materials and Environmental Science*, 4(5), pp: 625-638.
31. Porte, A. and Godoy, R. L. O. **2008**.Chemical composition of thyme vulgaris l. (thyme) essential oil from the Rio de Janeiro (Brazil).*Journal of Serbian Chemical Society* ,73(3) , pp:307-310.
32. Işıl,Y. and Türkan, K. 2015 .Anticancer agents: saponin and tannin. *International Journal of biological chemistry*, 9 (6),pp: 332-334.
33. Abdel Wareth, A. A. M. **2011**. Effect of thym, organo and their major active compound on performance and intestinal microbial population of broilers .Ph.D. Thesis. Institute of Animal Science. Rheinische Friedrich-Wilhelms- Bonn, Germany.