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Characterization and Study the Inhibition Activity of Pomegranate Peel Extract for α-Brass corrosion in H_2SO_4 Solution

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ABSTRACT

The present research focuses on the inhibition acting of green corrosion inhibitor of aqueous extract of pomegranate peel on α-brass alloy corrosion in 2M H_2SO_4 at temperature range (293-313) K. The pomegranate peel extract was characterized using Fourier infrared Spectroscopy (FTIR), Gas Chromatography Mass Spectroscopy (GC-MS) and Electrochemical polarization. The Tafel Plots revealed that the pomegranate peel extract acts as mixed-type inhibitor in sulfuric acid solution. Inhibition Efficiency (IE%) was increased significantly with increase the inhibitor concentration reaching up to (91.86%) at 500 ppm and decrease with increasing temperature. The corrosion products were investigated using X-ray Diffraction (XRD) analysis which confirmed the aggressivity of sulfate ions and formation of zinc sulfide (ZnS). Scanning Electron Microscope (SEM) examined the α-brass surface corrosion was prevented due to adsorption of inhibitor molecules on its surface. The adsorption of inhibitor molecules on brass obeys langmiur adsorption isotherm.

KeyWords: Corrosion; α-brass; Pomegranate; Polarization; GC-MS; H_2SO_4

INTRODUCTION

Corrosion is defined as a destruction of a metal by chemical attack or reaction with its environment, causing a serious and continuous problem[1]. Copper and copper-based alloys are widely used in different industries. Brass has been used in industry applications and in heat exchange tubes for instance cooling water systems, power generations and heat exchangers[2]. These equipment should constantly be cleaned because of their heating transmission resulted of precipitating oxides and carbonates. Acid solutions such as (sulfuric acid) are widely used in industry in most important areas of applications being acid pickling, cleaning and descaling[3]. There are several ways to reduce the corrosion rates at which propagate with enhance the metallic and alloys lifetime using inhibitors for the corrosion control of the metal or alloy in contact with aggressive environments is among the acceptable practices to reduce corrosion rate. A corrosion inhibitor defined as a substance which when added in minimal concentration levels to an environment causes effectively reduces the corrosion rate of a metal or alloy to that environment[4]. Generally organic compounds with higher molecular weight and hetero atoms (N, S and O) are using as effective inhibitors for brass in H_2SO_4, most of organic and inorganic inhibitors are toxic, costly and non-biodegradable. As result of increasing awareness of health and environment nowadays more researchers work and study on using natural products fruits and plants parts as green corrosion inhibitors they are non-toxic, cheap and easily available. The fruits peel extracts are organic in nature and contain polycarboxylic acids, phenolic compounds, polysaccharides acids, alkaloids and pigments these derivatives have a potential to be used as corrosion inhibitors[5]. The aim of present work is to characterized the pomegranate peel extract and study its electrochemical behavior on α-brass in acidic medium.

EXPERIMENTAL

Specimen preparation

Commercially circular α-brass (70% Cu, 30% Zn) with dimensions (1.2mmX 2cm were polished with emery papers 320, 500, 2000 and 4000 degreased with ethanol and etched with acetone rinsed with distilled water and left to dry at room temperature.

Solution preparation

The aggressive solution, 2M H_2SO_4 was prepared by dilution of analytical grade with distilled water in 1L volumetric flask.

Inhibitor preparation

The aqueous extract of pomegranate peel was obtained by following steps:-

1 The peel were collected from local market in Baghdad cleaned and left 5 days to dry then grinded by electric mixer.

2 Weight about 20g and dissolved in an appropriate of deionized water the mixture was heated until boiling then cooled overnight at room temperature.

3 The mixture was filtered several times to extract the same output then heated to concentrate the extract.

4 The extract was collected and placed in 250 ml volumetric flask, (6) completed by deionized water then different concentrations (200, 300, 400, 500) ppm were prepared.

Electrochemical polarization measurement

The corrosion cell was constructed of three-electrode system in flat bottom Pyrex glass flask. The circular α-brass was used to construct the working electrode with surface area of 1 cm^2. The saturated calomel and platinum electrode was used as reference and axillary electrodes respectively. The polarization tests were carried out by potentiostat/galvanost at 200 Mlab (2007) Germany connected to a host computer and programmed by software throughout the experiment which contains all the necessary parameters for polarization process. Before the polarization process occurred, the working electrode left about 15 min to attain the steady state open circuit potential (OCP) after obtaining this potential the polarization was achieved by polarizing the working electrode about range (±200 mv) at scan rate 2 mV/s which permit to determine the electrochemical parameters.

Gas Chromatography Mass Spectrum Measurement

The methanolic extract of pomegranate peel was prepared by dissolve 3 g of the peel powder in 30 ml of methanol and left for 3 days so that all the biological components dissolve. Then the mixture was filtered using What man No.1 filter paper (7). GC-MS that used for analysis was made (QP 2010 Plus SHIMADZU, Japan) computerized control. The measurement began with inject of 2 µL using micro syringe at 70 eV using Helium as inert gas .The runtime of the entire experiment was 30 min. The unknown sample is compared to standards based on database library.

Fourier infrared Spectroscopy

The powder peel was subjected for FTIR spectroscopy (Shimadzu, IR Affinity 1, Japan) with scan range between 4000-500 1/cm.

X-ray Diffraction

The x-ray diffraction analysis was carried out using Diffractometer (Bruker, 2D Phaser, Germany). The specimen was measured 48 h after the polarization finished.

RESULTS AND DISCUSSION

Potentiodynamic polarization curves

Figure 1 shows the polarization curves for α-brass in 2M H_2SO_4 solution in absence and presence of different concentrations of pomegranate peel extract the curves show that the addition of the inhibitor with different concentration retard both metal dissolution and hydrogen processes[8] by shifting the corrosion potential toward the noble direction as cleared as at 200, 300, 400 ppm and toward active direction at 500 ppm which indicated that the peel extract acts as mixed-type inhibitor [9].

The corrosion parameters E_{corr}, i_{corr}, anodic and cathodictafel slopes and corrosion rate in absence and presence the inhibitor concentration were listed below in table 1. The corrosion potential values were found to be varied throughout the experiment[10]. The great extent values of current density in the blank solution attributed to the great oxidizing power that H_2SO_4 exhibits also due to dissolved oxygen at Air/solution interface. Addition of different concentration of the inhibitor significantly reduces current density that's attributed to formation of protective film via adsorption process[11]. The inhibition efficiency was increased with increasing the pomegranate peel extract and decreased with increasing temperature. The anodic and cathodictafel slopes (b_a, b_c) were found to be varied at all the inhibitor concentrations which indicate that the pomegranate peel acts as mix-type inhibitor[12].

Gas Chromatography Mass Spectrum

Fruits and plants contain numerous natural organic and inorganic compounds. Table 2 shows the main phytochemicals that presence in methanolic extract of pomegranate peel. GC-MS measurement of the peel extract confirmed presence of alcohols compounds, ketones, polycarboxylic and amines such of these compounds contain large number of hetero atoms (N, S, O ,P) these atoms contain electronic density (lone pair) which make it more versatile to adsorb on the metal surface and improve of protective film to prevent the interaction at metal/solution interface. The presence of hetero atoms in large number provides an evidence of high inhibition efficiency of pomegranate peel extract.

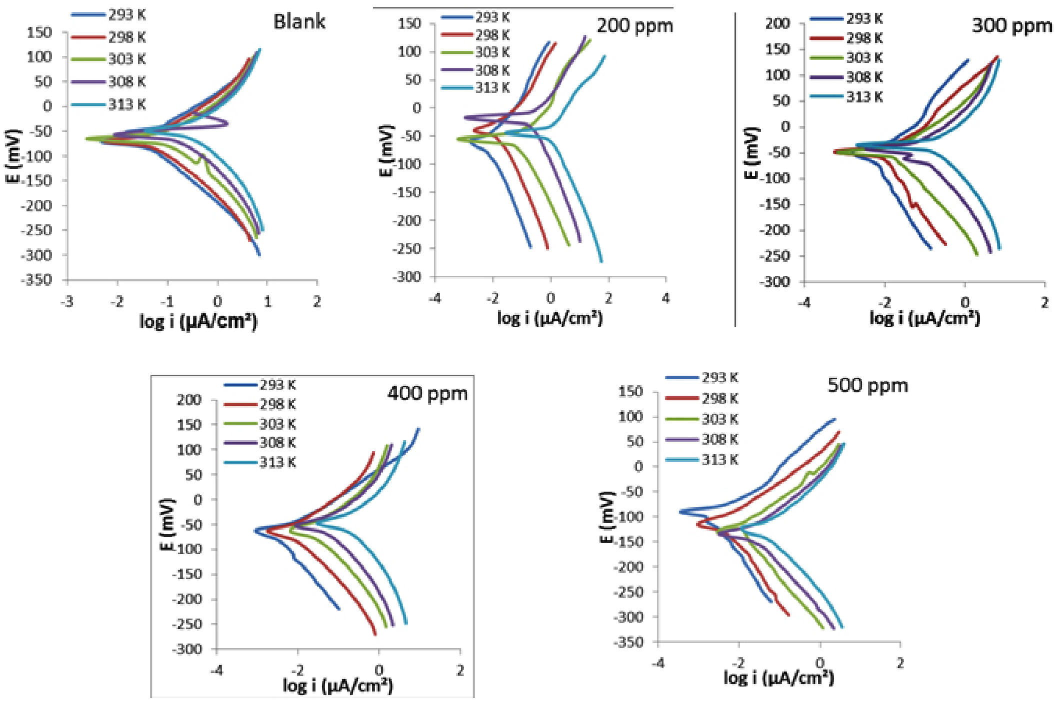


Fig. 1: Polarization curves for α-brass corrosion in 2M of the blank (H_2SO_4 solution) and in presence of different pomegrnate peel concentrations (a) 200 ppm, (b) 300 ppm, (c) 400 ppm and (d) 500 ppm at temperature range (293-313)K.

Table 1: Corrosion parameters of α-brass in 2M H_2SO_4 and in presence of different concentrations of pomegranate peel extract at temperature range (293-313)K

Inh.(ppm)	T(K)	$-E_{corr}$(mV)	i_{corr}(μA/cm²)	Tafel slope (mV/dec)		CR(g/m²d)	PR(mm/Y)
				$-b_c$	$+b_a$		
0	293	68.1	29.34	77.9	63.1	8.35	0.342
	298	69.3	57.03	75.8	66.2	15.02	0.664
	303	67.3	141.61	89.2	82.1	33.2	1.65
	308	56.7	148.99	83.9	75.9	41.08	1.93
	313	47.1	239.77	85	74.2	47.9	2.79
200	293	51	11.34	140.1	84.7	2.96	0.13
	298	39.9	22.4	128.6	93.4	6.27	0.257
	303	67	57.3	122.6	96.7	15.9	0.649
	308	17.3	62.28	89.1	74.3	17.1	0.702
	313	44	108.18	103	87.1	30.8	1.26
300	293	47.3	5.8	151.3	70.2	1.66	0.0643
	298	48.6	12.3	142.7	86	3.42	0.14
	303	49.2	31.4	93.4	78.5	9.21	0.375
	308	43	47.82	107.5	90.6	13.6	0.557
	313	34.8	79.92	97.1	84.4	22.1	0.903
400	293	60.2	3.1	94	48.7	0.866	0.0354
	298	61.7	9.1	126	79.9	2.55	0.107
	303	64.8	23.15	121	96.3	6.6	0.27
	308	53.2	27.25	82	68.3	7.91	0.324
	313	48.8	51.14	102	84.7	14.5	0.592
500	293	89.8	2.4	151.9	81.7	0.682	0.0279
	298	115.5	4.81	118	62.8	1.37	0.0559
	303	120.4	13.25	101.4	78.3	1.68	0.0639
	308	133	20.97	106.5	81.3	3.27	0.201
	313	123	39.24	124.8	98.5	10.2	0.418

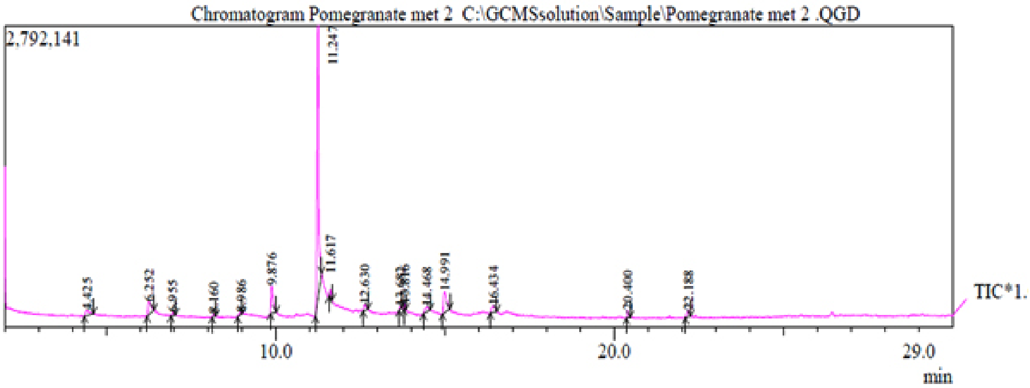
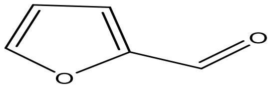
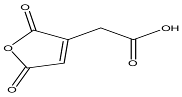
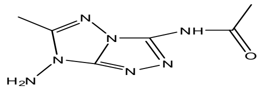
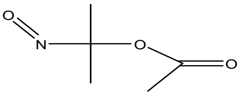
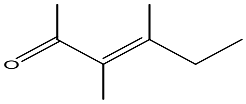
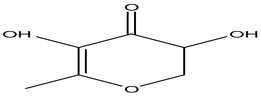
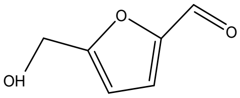
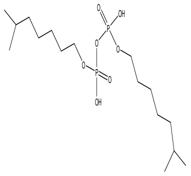
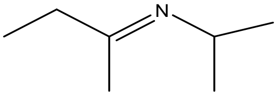
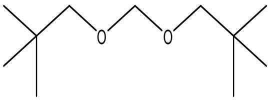
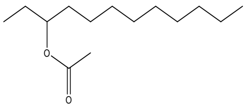
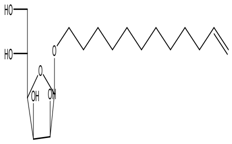
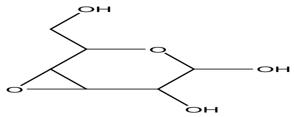
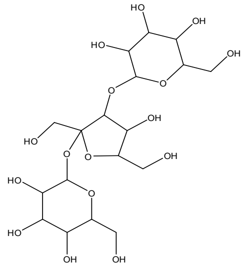
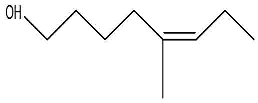


Fig. 2: Chromatogram of methanolic extract of pomegranate peel.

Table 2: The major identified compounds in methanolic extract of poemgranate peel

NO.	Name of Compound	RT (min)	Chemical formula	M.Wt (g/mole)	structure
1	2Furancarboxaldehyde	4.425	C5H4O2	96	
2	(Z)-Aconitic anhydride	6.252	C6H4O5	156	
3	3-Acetamido-6-methyl-7H -s-triazolo[5,1-c]-s-triazole	6.955	C6H9N7O	195	
4	1-Methyl-1-nitrosoethyl Acetate	8.16	C5H9NO3	131	
5	(3E)-3,4-Dimethyl-3-hexen-2-one	8.986	C8H14O	126	
6	3,5-Dihydroxy-6-mthyl-2, 3-dihydro-4H-pyran-4one	9.876	C6H8O4	144	
7	5Hydroxymethylfurfural	11.247	C6H6O3	126	
8	Bis(6-methylheptyl dihydrogendiphosphate	11.617	C16H36O7P2	402	
9	2-Propanamine, N-(1-methylpropylidene) 2-proanamine,N-(1-methylpropylidene)	12.63	C7H15N	113	
10	2,2Dimethyl-1-[(neopenty loxy)methoxy]propane	13.682	C11H24O2	188	
11	3-Acetoxydodecane	13.816	C14H28O2	228	
12	beta.-D-Mannofuranoside	14.468	C17H32O6	332	

13	3,4-Altrosan	14.991	C6H10O5	162	
14	Methyl14-(2-octylcyclo propropyl) tetradecanoate	16.434	C26H50O2	394	
15	6,6-((4-hydroxy-2,5bis (hydroxymethyl) tetrahydroxydrofuran-2,3diyl)bis(oxy)bis (2hydroxymethyl) tetrahydro-2H-pyran-3.4.5-tiol)	20.4	C18H32O16	504	
16	5-methyl-5-octen-1-ol	22.188	C9H18O	142	

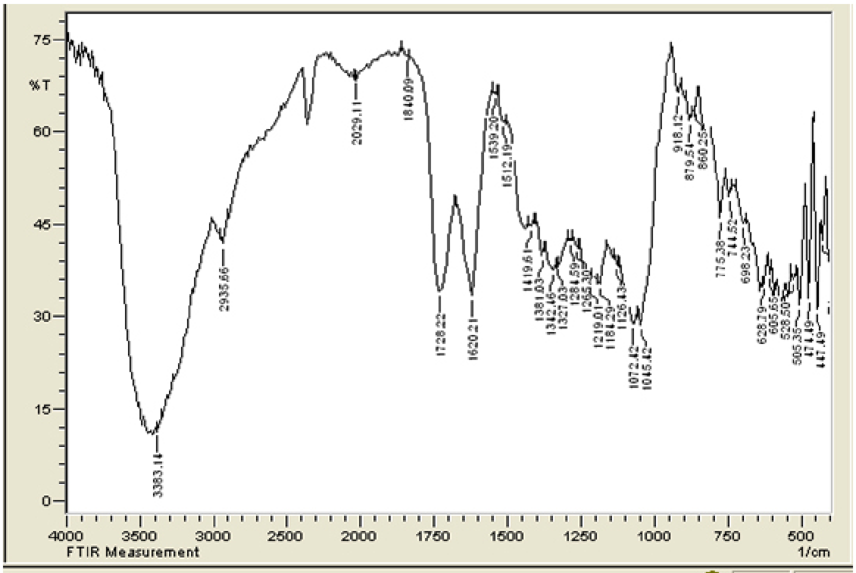


Fig. 3: FTIR spectrum of powder pomegranate peel.

Table. 3: The main bands in pomegranate peel powder

NO.	Peak number (cm-1)	Bond	Group assignment	NO.	Peak number (cm-1)	Bond	Group assignment
1	3384.14	O-H	Alcohols	6	1219	C-O	Ethers
2	2935.66	C-H	Alkanes	7	1072	C-N	Amides
3	1728.22	C=O	Carbonyl compounds	8	698.23	C-H	Alkenes
4	1620.00	C=C	Alkenes	9	918.12	C-H	Alkenes
5	3460.16	N-H	Amines				

Fourier infrared Spectroscopy

Figure 3 shows the spectrum of pomegranate peel powder. The spectrum proved the presence of Alcohols compounds, Alkenes, Carboxlic acids, Esters, Amines, Ethers, Aldehydes and Ketones. The major bands of functional groups were listed below in table 3.

X-ray Diffraction investigation Analysis

X-ray Diffraction provides a convenient method for corrosion products investigation. The measurement begins when a beam of X-ray interact with crystalline materials which resulted scattered beam and diffracted others. The diffractometer compares the data form the specimen under the investigation and standards based on values of 2 theta. Figure 4 shows the diffractogram of α-brass in absence of pomegranate peel inhibitor.

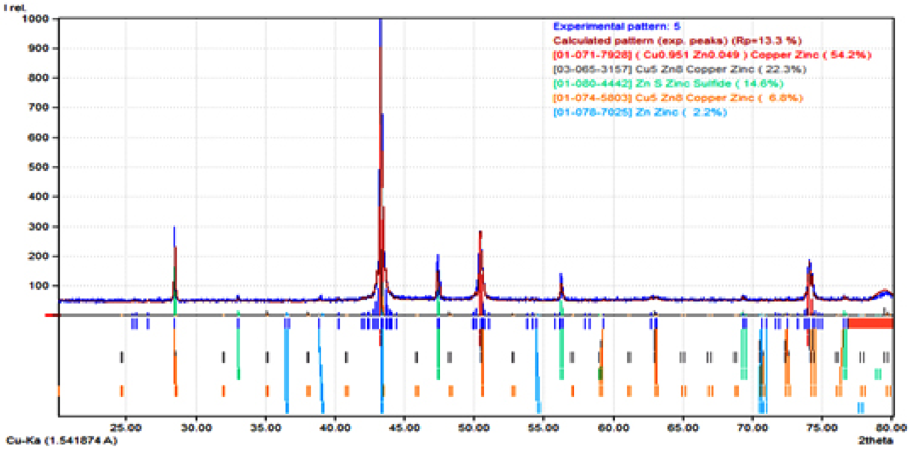


Fig. 4: The interpreted diffractogram of α-brass in 2M H_2SO_4

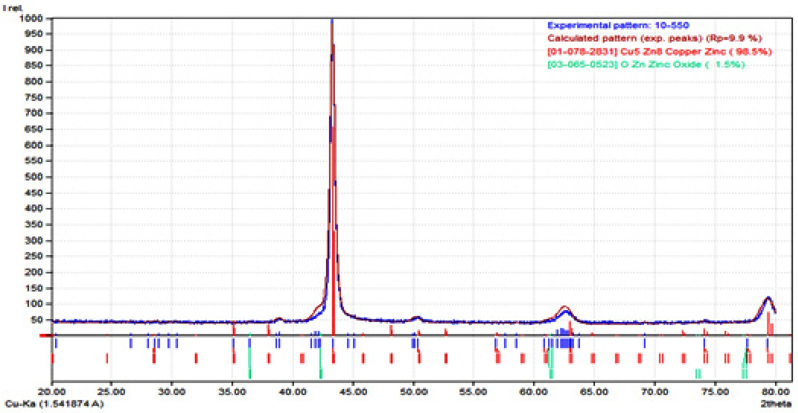


Fig. 5: The interpreted diffractogram of α-brass in 2M H_2SO_4 and in presence of 500 ppm of pomegranate peel extract

X-ray patterns of α-brass in the blank confirms the most accepted mechanism about corrosion of brasses alloys which stated that the first step is dissolution of zinc from alloy surface[13]. The diffractogram also confirmed the aggressivity of sulfate ions and formation of zinc sulfide. When the inhibitor added a significant decrease in zinc dissolution is occurred and prevented ZnS formation which provides another evidence of formation a protective film that's prevent the interaction between metal and electrolyte at metal/electrolyte interface.

Effect of Temperature

The effects of temperature on corrosion of α-brass have been discussed using Arrhenius equation. The Kinetic parameters in absence and presence of the inhibitor have been calculated using a logarithmic form of the equation:

$$log\, i_{corr} = \frac{-E_a}{2.303\, RT} + log A$$

Where A is pre-exponential factor in (molecules.cm^{-2}.s^{-1}), E_a is activation energy in (kJ/mol), T is absolute temperature in (kelvin) and R is gas constant in (J/mol.K). The calculated values of E_a in absence and presence of the pomegranate peel inhibitor were listed in table 4. E_a values in presence of the inhibitor were found to be higher

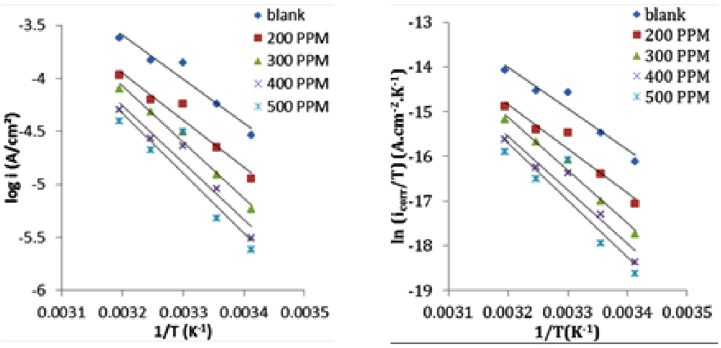


Fig. 6: Arrhenius plots of log i_{corr} versus 1/T and ln (i_{corr}/T) vs 1/T of α-brass in 2M of acidic solution and in presence of pomegranate peel at different concentration with various temperature range (293-313)K

Table 4: Arrhenius parameters for corrosion of α-brass in 2M acidic solution and in presence of different cocentrations of poemgranate peel at temperature range (293-313)K

Inh.	Conc.(ppm)	E_a(kJ.mol ^{1})	A× 10^{33} (molecules.cm^{-2}.s^{-1})	ΔH_a (kJ.mol^{-1})	ΔS_a (J.K^{-1}.mol^{-1})
Blank	-	79.02	2.47	76.48	-69.33
Pomegranate	200	84.73	9.77	82.20	-57.69
Peel Extract	300	100.94	3710	98.42	-8.39
	400	102.63	4670	100.10	-6.56
	500	108.26	34700	105.73	10.14

than those for the blank solution which indicated adsorption of inhibitor molecules and accomplished the inhibiting action by increasing the energy barrier from reactants to activated complex which hindered the corrosion process. In order to evaluate the other parameters Enthalpy of activation ΔH_a and Entropy of activation ΔS_a an alternative form of Arrhenius equation is used[14].

$$i_{corr} = \left(\frac{RT}{Nh}\right) exp\left(\frac{\Delta S_a}{R}\right) exp\left(\frac{-\Delta H_a}{RT}\right)$$

Where N is Avogadro's number, h is plank's constant and i_{corr} is current density in (Amper.m^{-2}). The equation above can be rewritten as:

$$ln\left(\frac{i_{corr}}{T}\right) = ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right) - \left(\frac{\Delta H_a}{RT}\right)$$

Plots log i_{corr} vs. 1/T and ln (i_{corr}/T) vs. 1/T are given below where the enthalpy of activation and entropy of activation determined from slopes and intercepts respectively. The positive sign of the enthalpy represents the endothermic nature of α-brass corrosion. The large values of entropy activation represent the increase in randomness as the concentration of the inhibitor increase this can be explained that a decrease in disorder occurred when the reactants transform to the activated complex. The activated complex represents association rather than dissociation in the rate determining step.

Inhibition Efficiency and Thermodynamic

The inhibition efficiencies and surface coverage values of pomegranate peels extract inhibitor where obtained from the relations:-

IE% = 100 [1- $(i_{corr})2$ / ($i_{corr})1$] and

θ = [1- $(i_{corr})2$ / ($i_{corr})1$]

Where (icorr)1 and (icorr)2 are the corrosion current densities in the absence and presence of various concentrations of inhibitor. Data obtained are presented in table 5. IE% values are increased with increasing inhibitor concentration and decreased with increasing temperatures.

Parameters of Adsorption

The adsorption mechanism of the inhibitor molecules on the metal surface can be explained using Langmuir adsorption isotherm. Where the surface coverage (θ) depends on the concentration of the inhibitor (C). This isotherm models is used because the corrosion of α-brass met the conditions of the isotherm since its homogenous monolayer and the collected data fit the regression line with value of determination coefficient R^2 is 0.99.

The expression of Langmuir equation is:

$$\left(\frac{c_{inh}}{\theta}\right) = \frac{1}{K_{ads}} + c_{inh}$$

Where K_{ads} is adsorption equilibrium constant, C is the concentration of the inhibitor in (g/L).

The calculated values of K_{ads} were used to evaluate the standard Gibbs energy of adsorption $\Delta G°_{ads}$ using the equation:

$$\Delta G°_{ads} = -RTln(1000K_{ads})$$

Where 1000 is the molar concentration of water in (g/L)[15], T is the absolute temperature and R is gas constant. The other thermodynamic of adsorption ΔH_{ads} and ΔS_{ads} where calculated using well known equation:

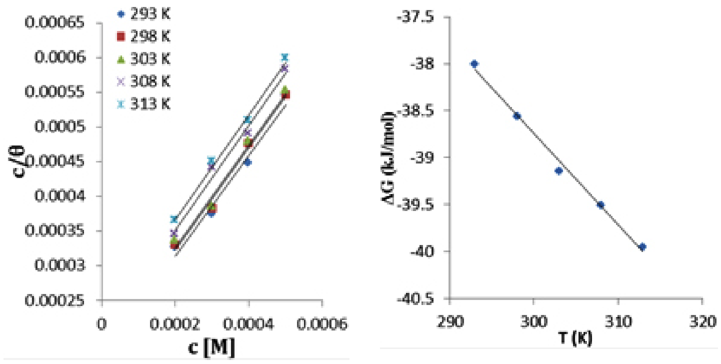


Fig. 6:Langmuir isotherm plots for adsorption of pomegranate peel on α-brass surface in 2M H_2SO_4 solution.

Table 5: Inhibition efficiencies and surface coverages of Pomegranate Peel extract at various concentration with temperature range (293-313)K in H_2SO_4 medium

Inh	T(K)	200ppm IE%	θ	300ppm IE%	θ	400ppm IE%	θ	500ppm IE%	θ
Pomegranate Peel Extract	293	61.35	0.6135	80.23	0.8023	89.34	0.8934	91.86	0.9186
	298	60.65	0.6065	78.43	0.7843	85.79	0.8579	91.58	0.9158
	303	59.53	0.5953	77.82	0.7782	83.65	0.8365	90.64	0.9064
	308	57.93	0.5793	67.9	0.679	81.7	0.817	85.92	0.8592
	313	54.82	0.5482	66.66	0.6666	79.5	0.795	83.63	0.8363

Table 6: Thermodynamic parameters for adsorption of pomegranate peel extract on α-brass surface in 2M H_2SO_4 solution

Inh.	T(K)	K_{ads}(g^{-1}.L)	-ΔG_{ads}(kJ.mol^{-1})	-ΔH_{ads}(kJ.mol^{-1})	ΔS_{ads}(J.K^{-1}.mol^{-1})
Pomegranate	293	5952.381	37.999		
	298	5747.126	38.561		
Peel Extract	303	5586.592	39.137	9.619	97.1
	308	5025.126	39.511		
	313	4651.163	39.951		

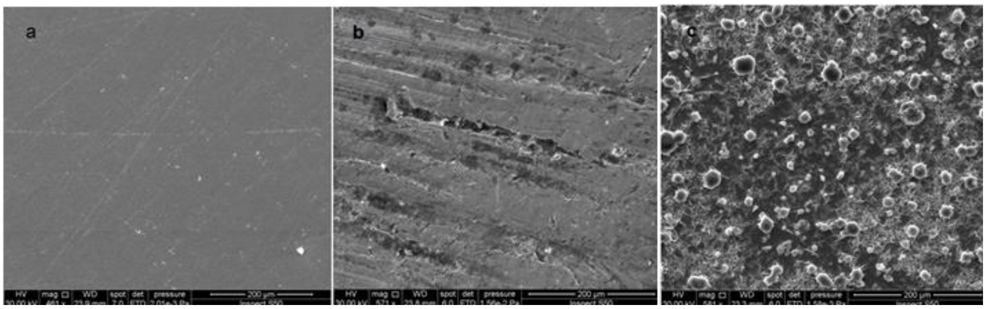


Fig. 7: Scanning electron micrographs of α-brass (a): bare polished alloy (b): after immersion 24h in 2M H_2SO_4 (c): after immersion 24h in 2M H_2SO_4 and in presence of 500 ppm of pomegranate peel extract.

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads}$$

The negative sign of ΔG_{ads} indicates the spontaneous process of formation of protective film on the metal surface. It's known that values of ΔG_{ads} Lower than -20 kJ/mol (in minus) indicate the adsorption process occurred via physisorption an electrostatic interaction occurred by adsorbed of polarizable species and it's decreased with increasing temperature. And if ΔG_{ads} values are -40 kJ/mol (in minus) or higher suggest the adsorption process occurred via chemisorption mechanism that involves strong interaction via the electron density found on the hetero atom and resulted of formation of coordinate bond. Chemisorption is increased with increasing temperature. The calculate values of ΔG_{ads} were found to be in minus at the range of (39.95-37.99) kJ/mol which indicate the adsorption of pomegranate peel occurred via both (Chemisorption & physisorption)[17]. The negative sign of the enthalpy indicates the exothermic process of the adsorption of the inhibitor molecules. The positive sign of the entropy gives the indication of the increase the randomness of the adsorption process this may be attributed to the Inhibitor molecules replace the water molecules at the surface which leads to increase the randomness of the solution[16].

Scanning Electron Microscope

The surface morphology of α-brass were examined using SEM. Fig 5 shows the optical micrographs of α-brass shows the alloy attacked by the aggressive solution after immersion 24h the surface appeared to be rough due to the aggresivity of the environment. The inhibited system shows the adsorbed molecules and confirms of formation of protective film.

CONCLUSIONS

1. The inhibition efficiency of pomegranate peels extract increases with increasing inhibitor concentration with maximum inhibition efficiency of 91.86% at 500 ppm concentration of inhibitor.

2. Potentiostatic studies indicates that pomegranate peels extract behaves as mixed type inhibitor.
3. The mechanism of corrosion inhibition of α-brass using of pomegranate peels extract is chemior physi- sorption as indicating by thermodynamic data obtained.

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