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Pomegranate Peel Extract as Green Corrosion Inhibitor for α-Brass in 2M HCl Solution

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ABSTRACT
The present work throws the light on the inhibitive action of green corrosion inhibitor of aqueous pomegranate peel extracton α-brass alloy corrosion in 2M HCl at temperature range (293-313)K. Pomegranate peel extract was characterized using Fourier infrared Spectroscopy(FTIR). The inhibition performance of the aqueous extract was investigated using electrochemical polarization measurement which revealed that the aqueous peel extract acts as mixed-type inhibitor. Inhibition Efficiency (IE%) was increased with increasing the inhibitor concentration giving an acceptable inhibition(67.42%)at 0.5 g/L and decrease with increasing temperature. The isotherm plots of the adsorption of the inhibitor molecules showed that the adsorption of the peel extract obeys Langmuir isotherm. Scanning Electron Microscope (SEM) micrographs examined the alloy surface corrosion was prevented due to adsorption of inhibitor molecules on its surface.

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Introduction

Brasses alloys are widely used in many outdoor applications as well as in industrial fields they are particularly used as heat exchangers, condensers due to its good thermal and electrical properties (1). The brasses-based equipments are regularly cleaned in order to remove the accumulated precipitates and oxides that resulted from continuous heat transmission. Acids like (Hydrochloric acid) are widely used as pickling, cleaning and descaling for brasses (2), however such of these acids are considered very destructive and corrosive. Dezincification of brass defined as leaching out of zinc from the alloy leaving a porous copper layer in either uniform or plug type corrosion (3). There are several ways to reduce that undesired phenomenon and corrosion rate of brasses it's the use of corrosion inhibitors which approved to be effective against different corrosive media a corrosion inhibitor defined as a substance that can be added in small quantity to a certain environment to reduce corrosion of certain metallic martial in that environment (4). In general many organic inhibitors with higher hetero atoms content (O, N, S, P) are considered effective inhibitors for brasses alloys (5-6), however these types of inhibiters are toxic and difficult to prepare. In recent years many researchers focus on eco-friendly, cheap and effective natural inhibitors. Pomegranate peel reported to have many polycarboxylic acids, phenols and unsaturated alkenes (7). These types of compounds possess many hetero atoms that have free lone pairs could coordinated onto metal surface and inhibit its corrosion.
The aim of present work is to investigate the performance of pomegranate peel extract for α-brass alloys in 2M HCl.

Experimental

Solution preparation

The corrosive solution, 2M HCl was prepared by dilution of analytical grade with double distilled water in 1L volumetric flask as the final volume.

Inhibitor preparation

The fresh peel was collected and cleaned with distilled water and left 4 days to get dry and grinded with electric grinder. 20 g of the POM powder was dissolved of deionized water and heated until boiling and left 24 h at room temperature. The cooled mixture was filtered several time and then concentrate the final solution by gentle heating (8) from the stock solution different concentrations was prepared 0.2, 0.3, 0.4 and 0.5 g/L.

Specimen preparation

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

Potentiodynamic polarization Measurement

Electrochemical measurement was performed construing the corrosion cell with three electrodes working electrode (WE) which contains the specimen under the study, reference electrode (RE) and (Saturated Calomel Electrode) (SCE) to maintain the voltage across (WE) and platinum electrode (RE) as an axillary electrode to complete the cell. All three electrodes are connected to a device called potentiostat/galvanostat M lab which connected to a host computer to run the entire process by a computerized software.

Fourier infrared Spectroscopy

The pomegranate peel powder was characterized by using for FTIR spectroscopy (Shimadzu, IR Affinity 1, Japan).

Results and Discussion

Potentiodynamic polarization Measurement

The polarization curves of α-brass in 2M HCl was shown in Fig. 1 in absence and presence of the aqueous peel extract. The curves show that the addition of the inhibitor with

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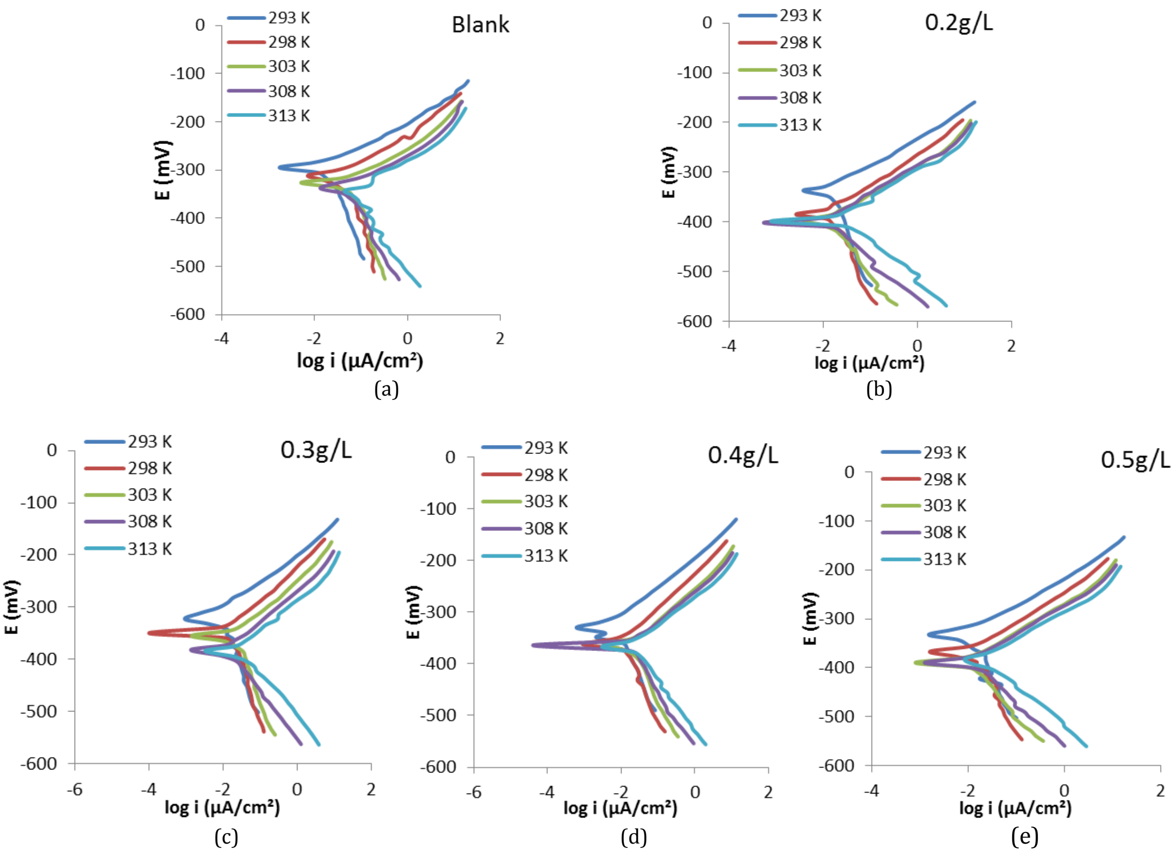


Figure 1: Polarization curves for α-brass corrosion in 2M HCl and in presence of different pomegrnate peel concentrations (a) blank solution (b) 0.2 g/L, (c) 0.3 g/L, (d) 0.4 g/L and (e) 0.5 g/L at temperature range (293-313)K

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

Inh. (g/L)	T (K)	$-E_{corr}$ (mV)	i_{corr} ($\mu A/cm^2$)	Tafel slope (mV/dec) $-b_c$	$+b_a$	CR (g/m^2d)	PR (mm/Y)
0	293	292.5	24.62	89.6	75.7	4.17	0.117
	298	305.5	36.21	77.3	68.4	10.3	0.422
	303	327.7	62.20	91.6	82.9	17.7	0.724
	308	338.2	71.31	76.0	69.6	20.3	0.830
	313	343.0	83.28	90.9	81.6	23.7	0.970
0.2	293	341.8	13.32	87.8	69.1	2.49	0.102
	298	385.1	20.41	91.2	73.8	5.71	0.234
	303	397.0	38.10	81.7	72.9	10.9	0.448
	308	398.9	44.50	75.8	67.5	13.0	0.520
	313	400.5	53.80	90.4	78.6	16.3	0.655
0.3	293	318.4	10.83	103.4	77.5	2.02	0.0825
	298	344.6	18.75	83	69.4	4.70	0.209
	303	352.6	33.09	105.6	90.5	9.62	0.039
	308	380.5	39.50	78.5	69.6	10.8	0.444
	313	384.6	48.10	82.9	72.2	13.6	0.556
0.4	293	326.8	9.94	122.8	91.3	1.95	0.0796
	298	351.3	17.10	101.1	80.9	4.21	0.130
	303	361.2	31.40	107.3	92.4	7.11	0.220
	308	362.1	37.20	90.2	78.6	7.90	0.291
	313	363.3	44.60	102.9	88.2	8.40	0.410
0.5	293	331.4	8.02	110.2	84.2	1.46	0.0599
	298	371.0	13.46	98.1	77.3	3.83	0.157
	303	389.3	25.43	116.4	98.1	4.30	0.310
	308	389.8	29.50	79.8	69.8	5.70	0.507
	313	383.0	37.22	82.1	71.7	6.30	0.710

different concentration disturbs both anodic dissolution metal and cathodic evolution of hydrogen gas. The calculated corrosion parameters E_{corr}, i_{corr}, corrosion rate (CR), penetration rate (PR), cathodic and anodic tafel slopes (b_a, b_c) were listed in table 1 in absence and presence different concentrations of the extract peel over temperature range (293-313) K. The obtained corrosion parameters values of E_{corr}, i_{corr}, CR and PR in presence and absence of the extract peel were decreased with increasing the inhibitor concentration and increase with increasing temperature (9).

The corrosion parameters for blank solution show that the alloys suffers a great corrosion extent in 2M of HCl with maximum corrosion current density 83.23 $\mu A/cm^2$ which is attributed to presence of aggressive chloride ions when the inhibitor added the remarkable reduce in corrosion current is observed reaching up to 37.22 $\mu A/cm^2$ which attributed that the inhibitor molecules imporve a protictive film that reduce the contact between alloys surface and the aggressive solution. The corrosion potential (E_{corr}) values where shifted in both directions (active and noble) that bring evidence that the pomegranate peel extract acts as mix-type inhibitor (10).

Table 2: Surface coverages and Inhibition efficiencies of Pomegranate Peel extract at various concentration with temperature range (293-313)K in HCl medium

Inh.	T (K)	0.2 g/L IE%	θ	0.3 g/L IE%	θ	0.4 g/L IE%	θ	0.5 g/L IE%	θ
POM	293	45.90	0.4590	56.01	0.5601	59.63	0.5963	67.42	0.6742
	298	43.64	0.4364	48.21	0.4821	52.77	0.5277	62.82	0.6282
	303	38.74	0.3874	46.80	0.4680	49.51	0.4951	59.11	0.5911
	308	37.59	0.3759	44.60	0.4460	47.83	0.4783	58.63	0.5863
	313	35.39	0.3539	42.24	0.4224	46.83	0.4683	55.30	0.5530

The inhibition efficiency (IE%) were calculated using the equation:-

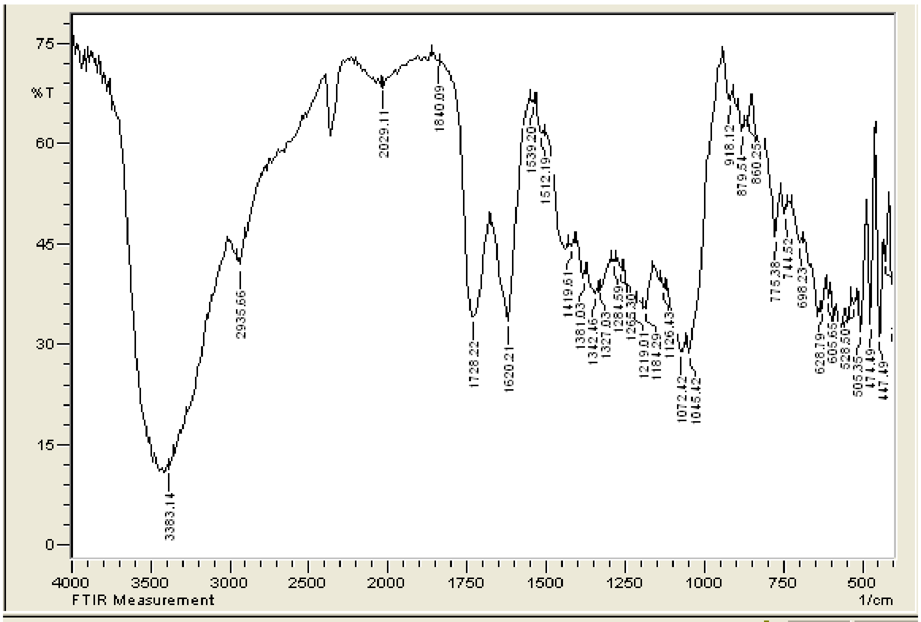


Figure 2: FTIR spectrum for pomegranate peel powder

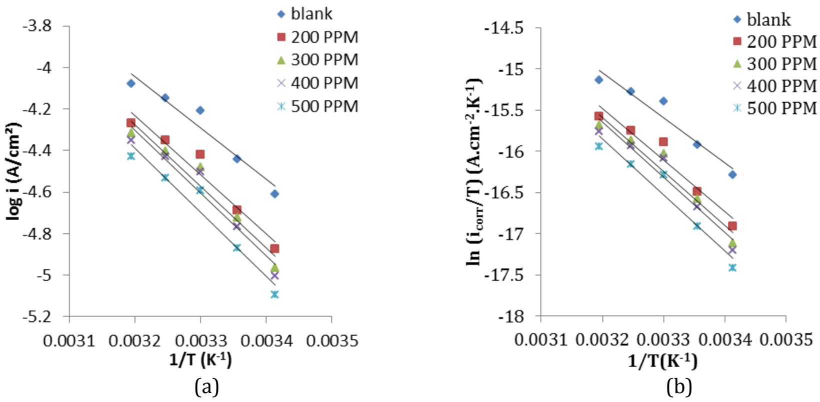


Figure 3: Arrhenius plots of (a) log i_{corr} versus 1/T,(b) ln (i_{corr}/T) vs 1/T of α-brass in 2M HCl in presence of pomegranatepeel at different concentration with various temperature range (293-313)K

$$IE\% = \frac{I^{o}_{corr} - I_{corr}}{I^{0}_{corr}} \qquad (1)$$

Where I^{o}_{corr} and I_{corr} represent the uninhibited and inhibited corrosion current density listed in Table 2. The maximum (IE %) obtained is 67.42 % which being acceptable due to the aggressive given acidic medium.

Fourier infrared Spectroscopy

The Fig. 2 shows the FTIR spectrum of the pomegranate peel powder. The spectrum confirms that the peel contain numerous compounds such as phenolic, carboxylic acids, alkenes, ethers and others. These compounds contain hetero atoms (N, O, P, S) these atoms have electronic density and can adsorbs on the alloy surface via coordinated bond.

Activation Parameters of Corrosion

The activation parameters of corrosion were calculated using Arrhenius equation:-

$$log i_{corr} = \frac{-E_a}{2.303\ R\ T} + log A \qquad (2)$$

Where i_{corr} is corrosion current density, E_a is the activation energy in kJ/mol, A is pre-exponential factor in (molecules.cm^{-2}.s^{-1}), R is gas constant (J/mol.K) and T is absolute temperature. The values of the activation energy (E_a) and the pre-exponential factor (A) are calculated from the slopes and intercepts respectively of plot of log i vs. 1/T. An alternative form of Arrhenius equation was used to calculate other remaining parameters the enthalpy of activation ΔH_a and entropy of activation ΔS_a. The plot ofln(i/T) vs. 1/T in Fig. 3 where the enthalpy of activation and entropy of activation calculated from slopes and intercepts respectively.

$$ln i_{corr\ /T} = ln\left(\frac{R}{Nh}\right) + \left(\frac{\Delta S_a}{R}\right) - \left(\frac{\Delta H_a}{RT}\right) \qquad (3)$$

Where h is plank constant, N is Avogadro constant. Table 3 shows the values of the activation parameters Ea values were higher in presence of the inhibitor than those for blank solution which indicated an increase in energy barrier as reactants go to products and hindrance the corrosion process. The positive sign of the enthalpy of activation indicate the endothermic nature of brass corrosion. The large negative values of entropy of activation represent that increase in randomness of solution as reactants go to products.

Table 3: Activation parameters for corrosion of α-brass in 2M of HCl in presence of different cocentrations of poemgranate peel at temperature range (293-313)K.

Inh.	Conc. (g/L)	E_a (kJ.mol^{-1})	A (molecules.cm^{-2}.s^{-1})	ΔH* (kJ.mol^{-1})	Δs* (J.K^{-1}.mol^{-1})
Blank	-	47.72	5.16×10^{27}	45.20	-178.06
POM	0.2	54.70	4.92×10^{28}	52.17	-159.32
	0.3	57.03	1.09×10^{29}	54.50	-152.71
	0.4	57.93	1.44×10^{29}	55.40	-150.37
	0.5	59.04	1.81×10^{29}	56.51	-148.47

Adsorption Isotherm

The surface coverage (θ) which represents the area in which the inhibitor molecules cover the alloy surface which related to the concentration of the inhibiter (C) through Langmuir equation as shown in Fig. 4.

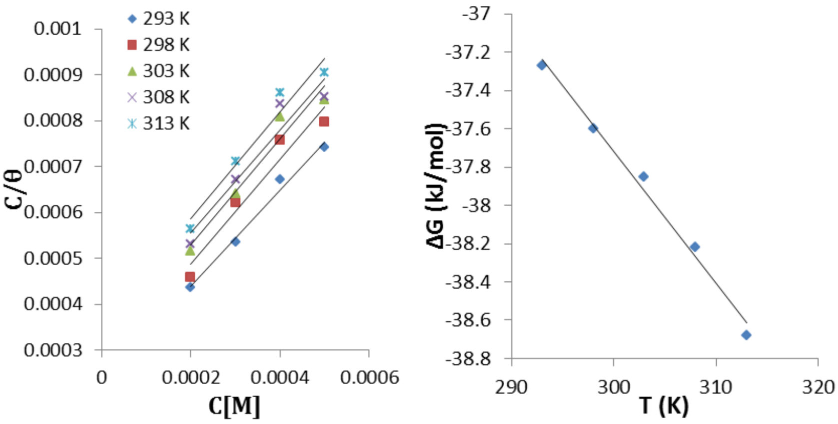
$$\left(\frac{C_{inh}}{\theta}\right) = \frac{1}{K_{ads}} + C_{inh} \quad (4)$$

Where K_{ads} represents adsorption equilibrium constant in (L/g) from values of equilibrium constant the free Gibbs energy were determined. The calculated thermodynamics parameters of adsorption were listed in Table 4.

$$\Delta G^\circ_{ads} = -RTln(1000K_{ads}) \quad (5)$$

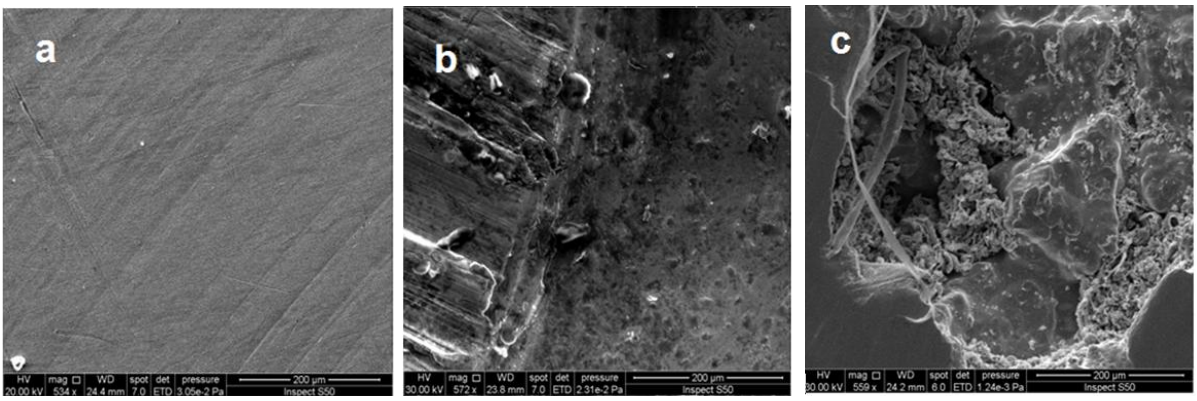
Where 1000 is the molar concentration of water (11). From values of free Gibbs energy the other thermodynamic parameters of adsorption were calculated by the equation:-

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \quad (6)$$



(a) (b)

Figure 4: (a) Langmuir isotherm plots for adsorption of pomegranate peel in 2M HCl solution, (b)The variation of Gibbs free energies (ΔG_{ads}) with temperature



(a) (b) (c)

Figure 5: Scanning electron micrographs of α-brass (a) polished alloy; (b) after immersion 24h in 2M HCl, (c) after immersion 24h in 2M HCl and in presence of 0.5g/L of the peel extract

Table 4: Thermodynamic parameters for adsorption of pomegranate peel extract on α-brass surface in 2M HCl solution

Inh.	T (K)	K_{ads} (g.L^{-1})	$-\Delta G_{ads}$ (kJ.mol^{-1})	$-\Delta H_{ads}$ (kJ.mol^{-1})	ΔS_{ads} (J.K^{-1}.mol^{-1})
POM	293	4405.286	37.27	17.08	68.8
	298	3891.051	37.60		
	303	3355.705	37.85		
	308	3039.514	38.22		
	313	2849.003	38.68		

The negative value of the enthalpy of adsorption indicates the exothermic nature of the adsorption of inhibitor molecules on the alloy surface. The large positive value of the entropy of adsorption indicates the increase in randomness as the inhibitor molecules replace water molecules at metal/electrolyte interface (12). The large and negative values of Gibbs free energy indicate the spontaneous process of adsorption of inhibitor molecules its values were around -40kJ.mol^{-1} which indicated that adsorption occurred via chemisorption mechanism that involve strong coordinate bond formed via hetero atoms with vacancy orbitals of the metal (13).

Scanning Electron Microscope

The surface of α-brass alloy was investigated using SEM as shown in Fig. 5 the observed micrograph in blank solution shows the roughness of the surface due to the aggressive chloride ions when the inhibitor is added the adsorbed inhibitor molecules were clearly observed that confirms the formation of protective layer via adsorption of inhibitor molecules.

Conclusions

The aqueous extract of pomegranate peel showed good inhibition efficiency for α-brass corrosion against the aggressive chloride ions with maximum inhibition efficiency 67.42%. The corrosion parameters showed that the pomegranate peel extract acts as mixed-type inhibitor by retard both cathodic and anodic reactions. The micrographs showed clear indications of the accomplishment of adsorption process of the inhibitor molecules onto the alloy surface.

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