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Corrosion Inhibition of Steel (St 44-2) by Pomegranate Shells in Acidic Medium

Abstract- *Pomegranate shells were investigated as green inhibitors for steel 44-2 in 0.1M HCl at various temperatures (30, 40, 50, and 60) °C using electrochemical technique. Five concentrations of inhibitor were added 4, 8, 12, and 16 ppm. Corrosion tests were performed by Potentiostat at 5 mV.sec-1 scan rate and the data measured by Tafel extrapolation method such as Tafel slopes, corrosion current density and corrosion potential. Inhibition efficiencies were calculated and indicated that 8 ppm was the best concentration for inhibition especially at 60oC, where was 96.47%. Pomegranate Shells behaves as anodic inhibitor type and obeys Langmuir adsorption isotherm. The equilibrium constant of the adsorption-desorption process and the apparent free energy of adsorption confirm the physicsorption of Pomegranate shells. FTIR spectroscopy was used to test film formed on steel surface compared with FTIR spectrum of Pomegranate Shells. These spectra confirm the formation of* Fe^{2+}*—Pomegranate shells complex*.

Keywords- *Pomegranate Shells, green inhibitor, carbon steel.*

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1. Introduction

Various natural and engineered mixes demonstrate a good anticorrosive action, the majority of which are profoundly dangerous to environment and human. This toxic effect has led to use natural anti-corrosion products that are safe and Environment friendly. Green inhibitors extracted as dried stems, seeds and leaves other parts of plant [1-4]. Commonly found in many plants, ellagic acid exhibits antioxidant properties and powerful anticarcinogenic, propelling it to the forefront of pomegranate research. Many commercially available pomegranate extracts are being standardized to contain 40-percent (or more) ellagic acid; however, Lansky, a prominent researcher on the medicinal properties of pomegranate, cautions against focusing on ellagic acid standardization to the exclusion of other therapeutically important pomegranate constituents[3]. Many authors interested in inhibition of steel using natural product such as Hibiscus Sabdariffa Extract [5], Aloe vera extract [6], Shahjan (Moringaoleifera), Orange (Citrus aurantium) and Pipali (Piper longum) [7], Aningeria robusta extract [8], Artemisia pallens(Asteraceae) [9], Musa acuminata bract [10], Mentha Pulegium Extract (MPE) [11], and Hyoscyamus Muticus Extract (HME) [12]. Most of these studies used FTIR to confirm the inhibition action of green inhibitors. The aim of this work is to investigate the inhibition action of Pomegranate shells as green inhibitor for steel in 0.1M HCl at four different temperatures.

2. Experimental Work

I. Methods and Material

Steel (St 44-2) was used in this work (chemical composition wt%: 0.115 C, 0.228 Si, 0.54 Mn, 0.012 P, 0.008 S, 0.017 Cr, 0.011 Mo, 0.018 Ni, 0.067 Al, 0.004 Co, 0.022 Cu, 0.008 V and Fe remain) obtained by Spectro MAX. The specimens were cut into a cubic shape of dimension (10 x 10 x 3 mm) with a square surface area ($1cm^2$) was utilized in all experiments and then grinded with SiC emery papers in sequence of 320, 600, 800, and 1200 grit to get free of scratch and flat surface and polished to mirror finish using both alpha alumina 0.5µm and 1µ m and polish cloth, then the specimen surface is cleaned using distilled water and acetone. The base electrolyte for corrosion test was 0.1 M HCl solution.

II. Preparation of pomegranate shells extract

Pomegranate shells were dried and grounded to fine powder to use it as corrosion inhibitor. Four concentrations of inhibitor were added 4, 8, 12 and 16 ppm at various temperatures (30, 40, 50 and 60) °C.

3. Electrochemical Measurements

WINKING M Lab 200 potentiostat/Galvanostat with SCI software was used for electrochemical measurements at a scan rate 5 $mV.sec^{-1}$ to obtain corrosion data by changing the potential (E_{oc}) ±200mV. The basic results were obtained and expressed in terms of the corrosion current

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density (i_{corr}) and corrosion potentials (E_{corr}) by Tafel extrapolation method.

4. FTIR Measurements

The FTIR test was conducted by Bruker Tensor 27 Fourier Transform Infrared Spectrophotometer. After immersing the specimens in an inhibited media for 15 days until drying, the film formed on the metal surface was carefully removed and mixed with KBr.

5. Results and Discussion

Tafel plots of steel in uninhibited and inhibited media are shown in Figure 1, these plots show the cathodic regions where the reduction of hydrogen can occurs and anodic regions since the dissolution of metals can take place. Corrosion data for curves are shown in Table (1). Which shows Tafel slopes, corrosion current density (i_{corr}) and corrosion potential (E_{corr}), while corrosion rates C_R was calculated using the following formula [13, 14]:

$$C_R = 0.13 \times i_{corr} \times \left(\frac{e}{\rho}\right) \quad (1)$$

Where e and ρ are equivalent weight and density of carbon steel respectively. These data show generally that corrosion potentials little shifted to noble direction, this means that *Pomegranate* shells behave as anodic inhibitor. The corrosion current densities were decreased in presence of *Pomegranate* shells; this can confirm that *Pomegranate* shells act as inhibitor. The current density increases with increasing temperature due to increasing the kinetic energy of particulate entity (atoms or ions) to surmount barrier energy. Tafel slopes also influenced due to variation in cathodic and anodic sites. The current densities can be used to calculate inhibition efficiency according to equation (2) [13]:

$$IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \quad (2)$$

Where $(i_{corr})_a$ and $(i_{corr})_p$ are the corrosion current density ($\mu A.cm^{-2}$) in absence and presence of the inhibitor, respectively. The data of IE% (in Table 1) indicate that 8 ppm is the best concentration for inhibition. The role of *Pomegranate* shells to inhibition is due to the constituents of this plant. *Pomegranate* contains a wide range of polyphenolic compounds including anthocyanidins, ellagic acid, flavonoids, tannins, anthocyanidins, gallic acid as well as vitamin C. The structure of some these compounds are shown in Figure 2. Figure 3 shows the FTIR of *Pomegranate* shells. This figure shows the main important peaks such as C-H aliphatic, aromatic and vinyl stretching, CH_2 and CH_3 in the range of 3130.57 to 3454.62 cm^{-1}. Stretching of C=C aromatic and vinyl appears two bands at 1444.73 and 1600.97 cm^{-1}. Also stretching of C≡C occurs at 2362.88 cm^{-1}. Symmetric and asymmetric absorption of C—O bond occur at 1024.24 and 1016.52 cm^{-1}. The FTIR spectra of film formed on steel surface in presence *Pomegranate* shells in corrosive medium are shown in Figure 4, these spectra show the decreasing in intensities due to adsorption of green inhibitor on the metallic surface and form Fe^{2+}—*Pomegranate* shells complex [15]. The adsorption of inhibitor on steel surface led to highly decreasing in C—O stretching in addition to increasing the intensity of C=C due to the bonding between inhibitor molecules and ferrous ions. The H-bonded appears after inhibition due to formation of solvated metal ions.

Langmuir isotherm was tested for its fit to the experimental data. The plots of *C/θ* against *C* for the *Pomegranate* shells at four temperatures in the range 303–333 K were straight lines (Figure 5) indicating that the *Pomegranate* shells obey Langmuir adsorption isotherm which given by the following equation [16]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (3)$$

Where K_{ads} is the equilibrium, constant of the adsorption - desorption process, *C* is concentration of inhibitor in the bulk solution and θ *is* the degree of surface coverage.
Adsorption of inhibitor followed Langmuir adsorption isotherm according to the linear regression coefficient which is close to the unity. R^2 values were 0.840, 0.903, 0.920 and 0.964 at 303, 313, 323 and 333K respectively. The Langmuir Isotherms depend on the metal surface will carry the adsorbed molecules. Therefore, the steel surface will be covered by the inhibitor-adsorbed molecules instead of adsorbed H_2O molecule. The apparent free energy of adsorption (ΔG^o_{ads}) is calculated from the following equation [16]:

$$\Delta G^o_{ads} = -2.303RT\ log 55.5\ K_{ads},$$
$$where\ K_{ads} = \frac{\theta}{C(1-\theta)} \quad (4)$$

The values of Kads and ΔG^o_{ads} are shown in Table 2. Spontaneous adsorption to *Pomegranate* shells according to negative values of ΔG^o_{ads}. The small values of K_{ads} and ΔG^{o}_{ads} refer to the physically adsorption of pomegranate shells on steel surface.

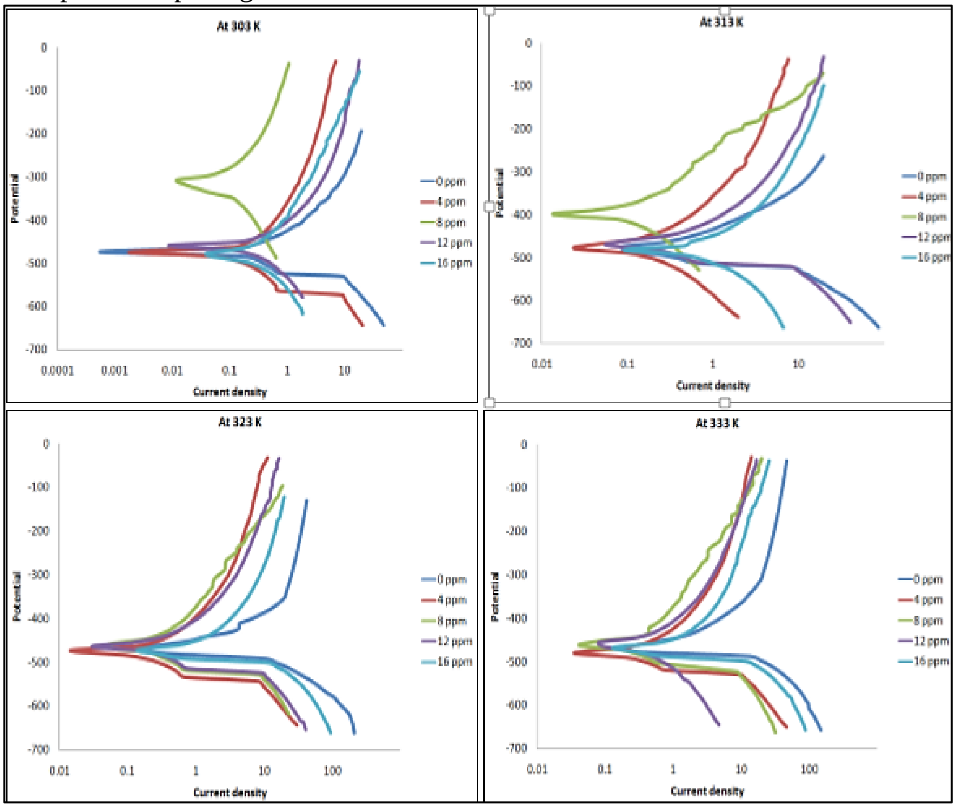

Figure 1: Tafel plots of uninhibited and inhibited 0.1 M HCl media at different temperatures, a. 303 k, b. 313k, c. 323k, d. 333k.

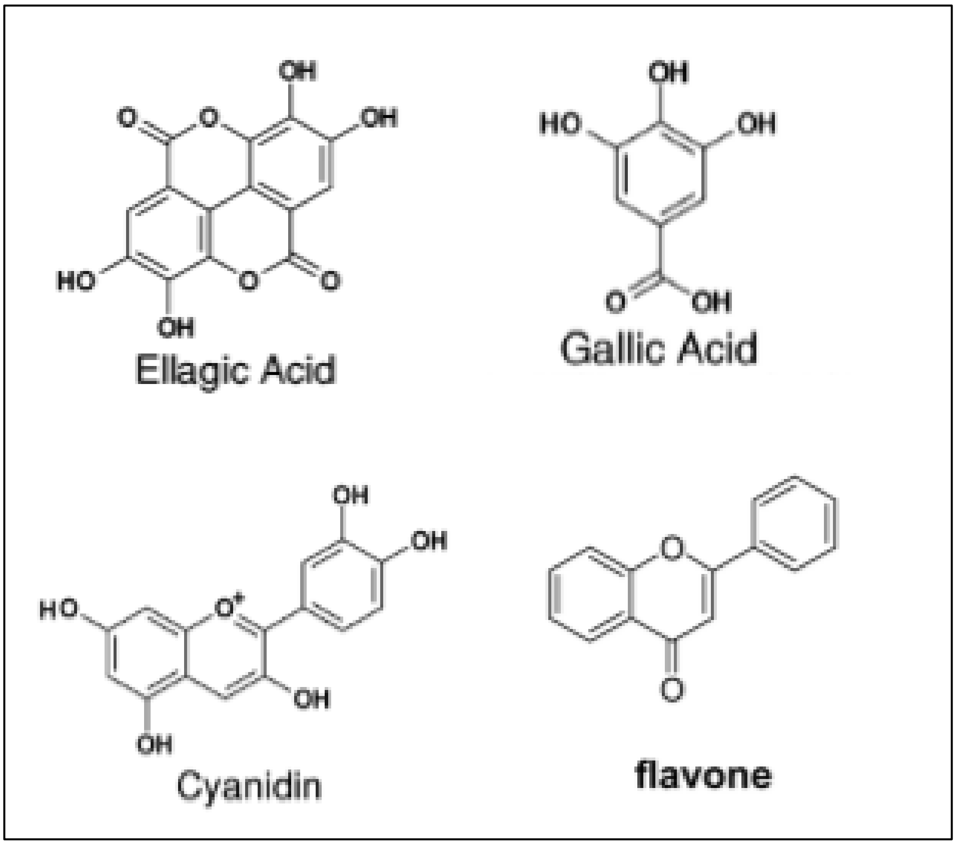

Figure 2: Structure of some compounds in Pomegranate Shells.

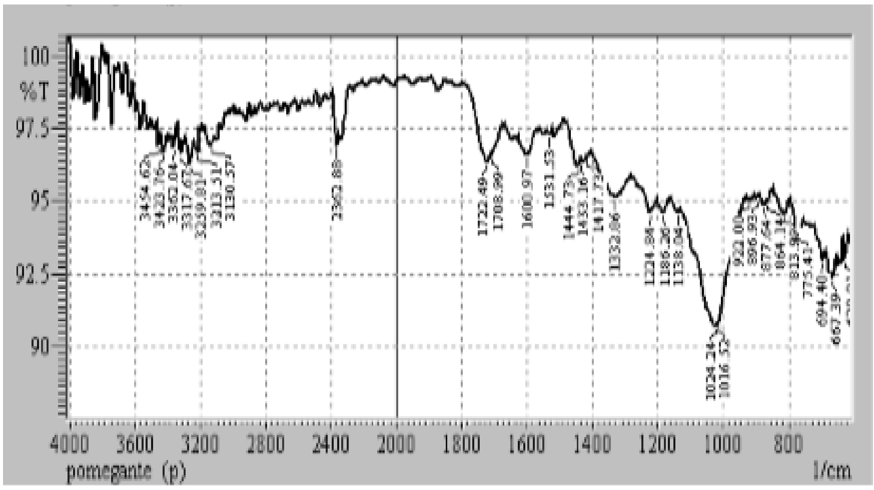

Figure 3: FTIR of *Pomegranate* shells.

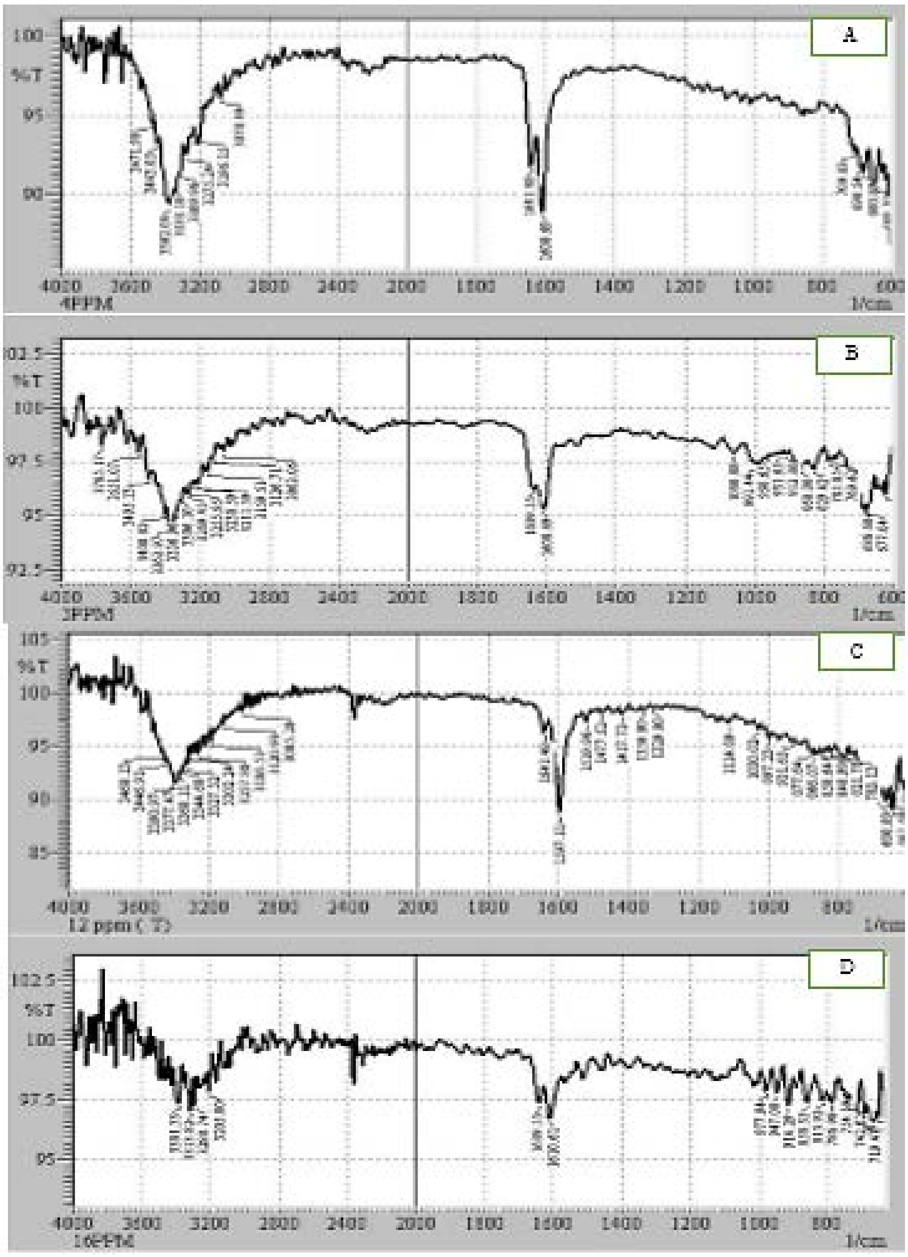

Figure 4: FTIR of film formed on steel surface after immersion in inhibited medium, A. 4ppm, B. 8ppm, C. 12ppm, D. 16ppm.

Table 1: Corrosion parameters for inhibition steel using *Pomegranate* shells with four concentrations at four temperatures in 0.1M HCl solution

Conc. (ppm)	*Temp. (^oC)*	*$-E_{corr}$ (mV)*	*i_{corr} ($\mu A.cm^{-2}$)*	*$-b_c$* (mV.dec^{-1})	*$+b_a$*	*C_R (mpy)*	*IE (%)*
0	30	473	169.62	78.7	64.2	79.16	-
	40	478	388.12	41.5	83.1	181.1	-
	50	470	2130.0	67.2	90.0	994.0	-
	60	470	3350.0	78.0	162.0	1563.3	-
4	30	473	75.83	62.9	65.1	35.39	55.29
	40	476	93.53	79.8	93.3	43.65	75.90
	50	472	132.44	77.6	77.1	61.81	93.78
	60	480	134.14	50.8	71.4	62.60	95.99
8	30	307	49.31	115.9	95.1	23.01	70.93
	40	397	51.32	70.4	72.8	23.95	86.78
	50	463	111.41	77.9	89.8	51.99	94.77
	60	460	118.22	64.4	84.4	55.17	96.47
12	30	456	121.53	70.9	49.5	56.71	28.35
	40	470	141.44	59.9	65.3	66.01	63.56
	50	462	177.69	80.5	79.1	82.92	91.66
	60	460	251.83	92.7	87.3	117.5	92.48
16	30	478	105.14	62.8	62.8	49.07	38.01
	40	481	328.5	85.6	91.9	153.3	15.36
	50	472	804.6	38.5	115.9	375.5	62.23
	60	468	884.64	37.3	142.2	412.8	73.59

Table 2: Thermodynamic function for adsorption of *Pomegranate* shell sin 0.1M HCl medium at four temperatures

Conc. Ppm	*Temp. K*	*K_{ads}*	*ΔG^o_{ads}/kJ.mol^{-1}*
4	303	0.309	-3.059
	313	0.787	-8.048
	323	3.769	-39.762
	333	5.984	-65.083
8	303	0.305	-3.018
	313	0.821	-8.388
	323	2.265	-23.894
	333	3.416	-37.151
12	303	0.033	-0.326
	313	0.145	-1.486
	323	0.916	-9.661
	333	1.025	-11.145
16	303	0.038	-0.379
	313	0.044	-0.446
	323	0.103	-1.086
	333	0.174	-1.894

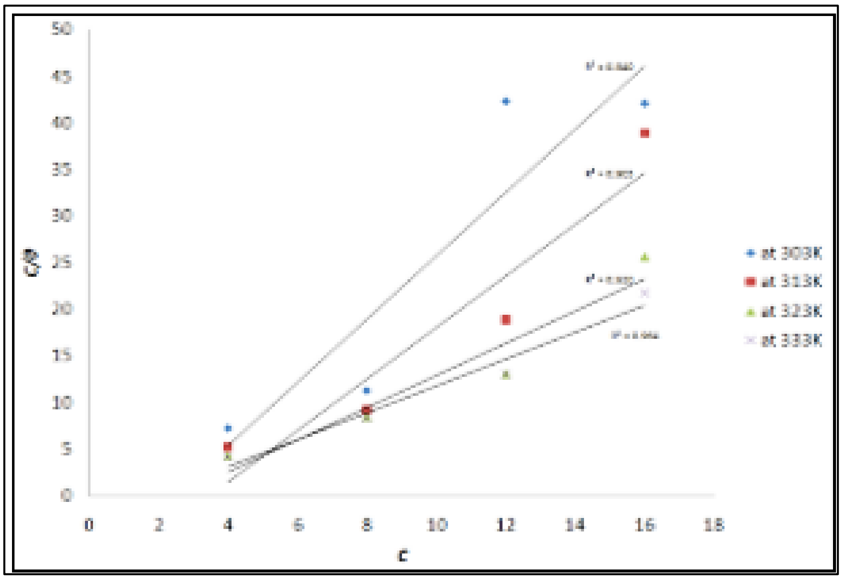

Figure 5: Langmuir adsorption plots for steel in 0.1M HCl at four temperatures

6. Conclusions

Pomegranate shells have been investigated as green inhibitor for steel in 0.1M HCl at 30, 40, 50 and 60^{o}C. These shells behaved as good inhibitor with acceptable inhibition efficiencies. *Pomegranate* shells act as anodic inhibitor through the shifting corrosion potentials toward noble direction. *Pomegranate* shells obey Langmuir adsorption isotherm with linear regression coefficient close to unity. K_{ads} and ΔG^o_{ads} values indicated that *Pomegranate* shells were physically adsorbed on steel surface.

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