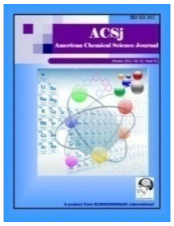

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Corrosion Inhibition by Pumpkin Peels Extract in Petroleum Environment

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

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ABSTRACT

The corrosion inhibition of carbon steel in petroleum environment by ethanolic extract of pumpkin peels has been studied in relation to three concentrations of the inhibitor include 3, 5 and 7mL/L at four temperatures over the range 50–80°C using electrochemical measurements (open circuit potential measurements and galvanostatic polarization). The results were supplemented with optical microscopy and FTIR spectroscopy. All the methods employed are in reasonable agreement. Inhibition efficiencies were calculated and the results show that 5mL/L of pumpkin peels extract gave the best inhibition which ranged from 72.4 to 75.7%. Thermodynamics of adsorption (enthalpy of adsorption, the entropy of adsorption and Gibbs free energy) were calculated and discussed. Thermodynamic functions of adsorption processes were calculated from experimental polarization data and the interpretation of the results reveals that this pumpkin peels extract obey Langmuir adsorption isotherm. Polarization curves indicate that green inhibitor is a mixed type inhibitor, which decreases both Tafel slopes.

Keywords: Green inhibitors; natural products; petroleum medium.

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1. INTRODUCTION

The use of inhibitors for the control of corrosion of metals and alloys which are in contact with aggressive environment is an accepted practice. Large number of organic compounds were studied and are being studied to investigate their corrosion inhibition potential. All these studies reveal that organic compounds especially those with N, S and O showed significant inhibition efficiency. But, unfortunately most of these compounds are not only expensive but also toxic to living beings. It is needless to point out the importance of cheap, safe inhibitors of corrosion. Plant extracts have become important as an environmentally acceptable, readily available and renewable source for wide range of inhibitors. They are the rich sources of ingredients which have very high inhibition efficiency. This article gives a vivid account of natural products which are used as corrosion inhibitors for various metal and alloys in aggressive media.

Many authors focused on development of naturally occurring substances as corrosion inhibitors. The available literature on corrosion inhibitors obtained from naturally occurring substances has been reviewed. The characteristic features of the investigations have been highlighted [1-15].

The aim of present work is attempt to inhibit the corrosion in petroleum medium by ethanolic extract of pumpkin peels PP at four temperatures over range 50–80ºC using galvanostat. FTIR spectra and optical microscopy were supplemented the corrosion test.

2. EXPERIMENTAL PART

2.1 Materials and Solutions

Carbon steel was used in this work (chemical composition wt%: 0.121 C, 0.22 Si, 0.44 Mn, 0.014 P, 0.016 S, 0.041 Cr, 0.002 Mo, 0.022 Ni, 0.02 Al, 0.002 Co, 0.055 Cu and Fe remain) obtained by Spectro MAX. Cubic carbon steel (10x10x3mm) with a square surface area ($1cm^2$) was used in all experiments. The specimen was mounted by hot mounting using formaldehyde (Bakelite) at 138ºC for 8 minutes to insulate all but one side and made a hole on one side of electrical connection and then the mounted specimens has been polished with SiC emery papers in sequence of 220, 400, 600, 800, and 1200 grit to get flat and scratch-free surface and polished to mirror finish using polish cloth and alpha alumina 0.5μm and 1μm, and then washed with distilled water, degreased with acetone and rinsed with distilled water.

The base electrolyte was petroleum medium obtained from Iraqi oil refinery at light naphtha unit which is works in temperature range of 50-80ºC. Analysis of medium is listed in (Table 1) obtained by many techniques.

Table 1. Analysis of petroleum medium

Analysis	Amount
Total carbon	48.67%
Total hydrogen	8.73%
Total nitrogen	0.13%
Total sulfur	0.71%
pH	5.25
Elect. conductivity	300μS/cm
TDS	296mg/L
H_2O content	40%

Extraction of pumpkin peels PP was achieved by washing the peels by distilled water and then dried and grounded. Ethanolic extract carried out by dissolving 5gm of ground peels in 200mL ethanol and then refluxed at 45ºC. The obtained extract was filtered by using Whatmann filter paper and concentrated to 100mL, which is soluble in aqueous and non aqueous solution. Three volumes of ethanolic extract were used as inhibitor includes 3, 5 and 7mL/L at four different temperatures.

3. METHODS

3.1 Electrochemical Measurements

Electrochemical cell was composed of platinum counter electrode, prepared carbon steel specimen as working electrode and saturated calomel electrode (SCE) as a reference electrode according to ASTM standard cell G5-94 was used. The electrochemical behavior of carbon steel in inhibited and uninhibited solution was studied by WINKING M Lab Galvanostat by recording anodic and cathodic galvano dynamic polarization curves. Measurements were carried out by changing the electrode current automatically from -15 to +15mA at scan rate $1mA.sec^{-1}$, while open circuit potential recorded after immersion in test electrolyte for 600sec. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion parameters.

3.2 FTIR Measurements

The film formed on the metal surface (after immersing in the oil sour medium for 20 days till drying) was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in Bruker Tensor 27 Fourier Transform Infrared Spectrophotometer.

3.3 Optical Microscopy

The carbon steel specimens were corroded in various test solutions containing four different concentrations of inhibitor; the specimens were taken out and dried. The nature of the film formed on the surface of the metal specimen was analyzed by NIKON, ECLIPSE-ME600 Optical Microscope. All micrographs are taken at a magnification of 20X after immersion for 15 days.

4. RESULTS AND DISCUSSION

4.1 Galvanostatic Measurements

(Fig. 1) shows the Tafel plots for carbon steel in petroleum environment in absence and presence of pumpkin peels extract. These plots reveal the cathodic and anodic behavior, where at cathodic sites, the reduction of hydrogen can occur; while at anodic sites, the dissolution of metal takes place as follow:

$$2H^+ + 2e \rightarrow H_2 \quad \text{At Cathode}$$
$$Fe \rightarrow Fe^{2+} + 2e \quad \text{At Anode}$$

(Table 2) gives the values of corrosion parameters as the corrosion potential E_{corr}, corrosion current density i_{corr}, and Tafel slopes (b_c and b_a) for the corrosion of carbon steel with different concentrations of pumpkin peels PP extract. The corrosion current densities were estimated by Tafel extrapolation of the cathodic and anodic curves to the open circuit corrosion potential. From this table, it can be concluded that:

- The i_{corr} values decrease in presence of PP extract.
- The cathodic Tafel slopes were decreased. This result indicates the influence of the inhibitor on the kinetics of the hydrogen evolution reaction.
- The anodic Tafel slopes were decreased. This result indicates the influence of the inhibitor on the kinetics of the dissolution of the carbon steel.
- The values of inhibition efficiency (IE %) gave acceptable inhibition especially at 5mL/L of inhibitor concentration reaching a maximum value (75.7%) at 333K.
- The PP extract is a mixed inhibitor through the decreasing in Tafel slopes.

The inhibition efficiency IE (%) can be calculated using the equation given below [16]:

$$IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100 \qquad (1)$$

Where $(i_{corr})_a$ and $(i_{corr})_p$ are the corrosion current density ($\mu A.cm^{-2}$) in the absence and the presence of the inhibitor, respectively. The efficiencies varied with increasing temperature due to variation in cathodic and anodic sites on steel surface.

The performance of an organic inhibitor is related to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, p-orbital character, and the electronic structure of the molecule. The inhibition could be due to (i) Adsorption of the molecules or its ions on anodic and/or cathodic sites, (ii) increase in cathodic and/or anodic over voltage, and (iii) the formation of a protective barrier film.

4.2 FTIR Spectra

(Figs. 2 and 3) show the FTIR spectra for pumpkin peels and film formed on carbon steel in petroleum medium in the presence of three concentrations of PP extract after immersion for 20 days in test medium respectively. FTIR spectrum of pumpkin peels indicates the presence of some chemical functionality groups. Wave number at 3407.46cm^{-1} can be attribute to ≡C–H stretch for alcohol and H–bonded, C–H aliphatic and –CHO aldehyde appear at 2923.4 and 2852.13cm^{-1}. Disubstituted or symmetrically substituted C≡C stretch give either no absorption or weak absorption at 2362.07cm^{-1}. C–O stretch occurs at 1109.38 cm^{-1}, while vinyl and aromatic C=C stretch appears at 1654.88 and 1430.73cm^{-1}. These peaks indicate that pumpkin peels may be containing alcohols and phenols. The spectra of film formed on metallic surface indicate that the stretching frequency of many peaks was decreased. This suggests the coordination with Fe^{2+} on the anodic sites of the metal surface, also resulting in the formation of Fe^{2+}—PP—complex.

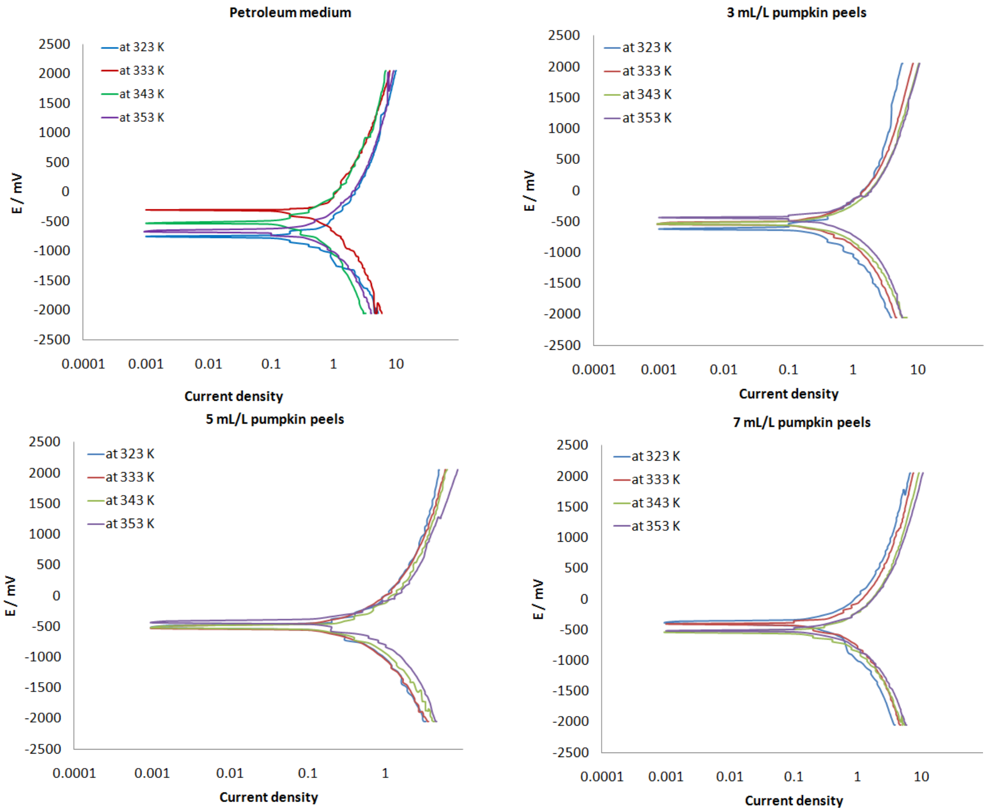


Fig. 1. Tafel plots for carbon steel in petroleum environment in the absence and presence of PP extract at four temperatures

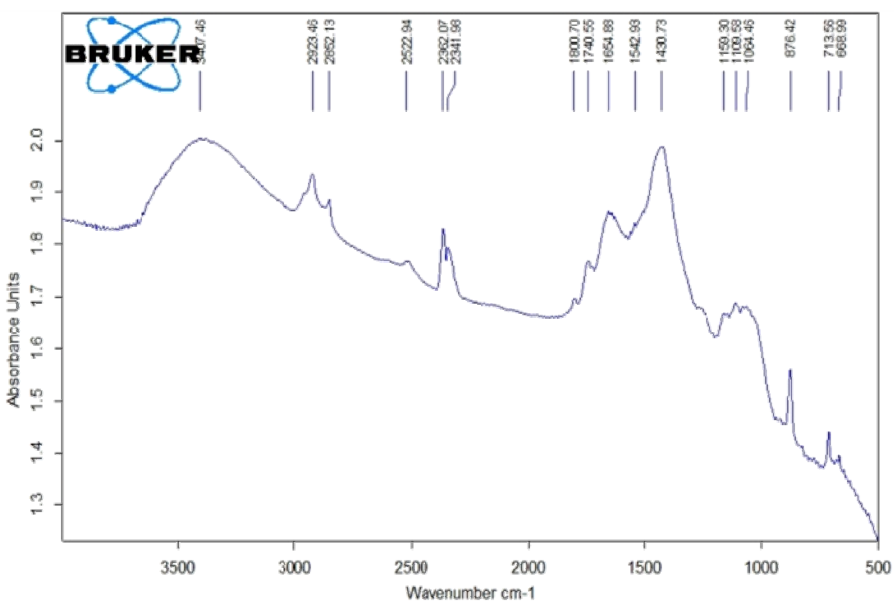


Fig. 2. FTIR spectrum for pumpkin peels

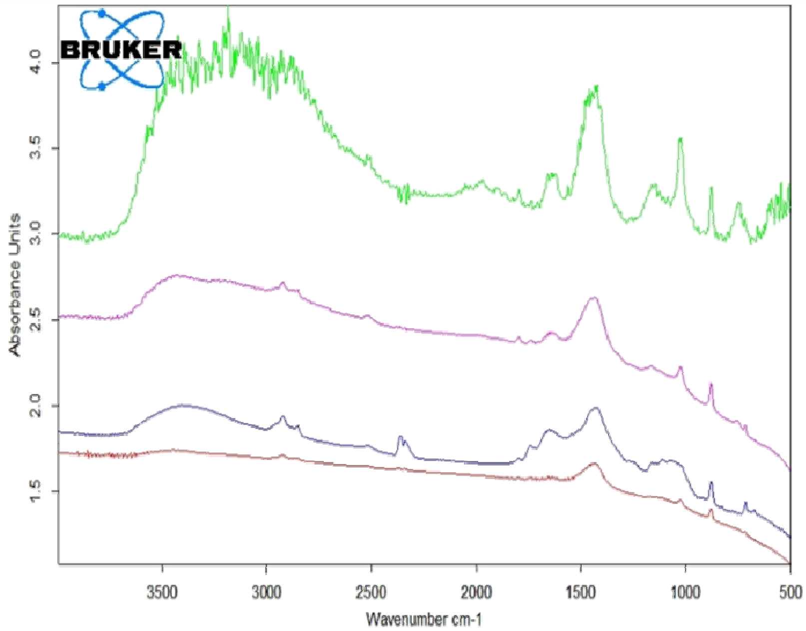


Fig. 3. FTIR spectra for pumpkin peels and film formed on corroded surface in petroleum medium in presence of PP extract; Pumpkin peels (blue line), 3mL/L of PPE (red line), 5mL/L of PPE (pink line), and 7mL/L of PPE (green line)

4.3 Adsorption Isotherm

The interaction between the inhibitors and steel surface can be provided by the adsorption isotherm. During corrosion inhibition of carbon steel, the nature of inhibitor on the corroding surface has been deduced in terms of adsorption behavior of inhibitors. Langmuir adsorption isotherm was used for PP extracts on carbon steel. According to this isotherm, θ is related to the C and adsorption equilibrium constant K_{ads}, via:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C, \qquad where\ \theta = 1 - \frac{(i_{corr})_p}{(i_{corr})_a} \tag{2}$$

The plot of C/θ versus C gave a straight line (Fig. 4) with a slope of about unity confirming that the adsorption of PP extracts on carbon steel surface obeys the Langmuir adsorption isotherm and R^2 values were in the range $0.991 \geq R^2 \geq 0.919$ as listed in (Table 3). K_{ads} is connected to the standard Gibb's free energy of adsorption ΔG_{ads}, according to the equation given below:

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G_{ads}}{RT}\right) \tag{3}$$

and

$$\ln K_{ads} = ln\left(\frac{1}{55.5}\right) - \frac{\Delta G_{ads}}{RT} \tag{4}$$

Where R is the universal gas constant, T is the absolute temperature and 55.5 is the concentration of water in solution ($mol.L^{-1}$). This isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. The values of K_{ads} are relatively small indicating that the interaction between the adsorbed extract molecules and steel surface is physically adsorbed. This is also supported by lower negative (ΔG^o_{ads}) values for PP extract. Generally, values of (ΔG^o_{ads}) up to –20 kJ/mol are consistent with electrostatic interactions between the charged molecules and the charged metal surface, which indicates physical adsorption [17]. The negative values of ΔG_{ads} suggest that the adsorption of inhibitor onto steel surface is a spontaneous process [18]. More negative values of ΔG_{ads} also indicate the strong interaction of the inhibitor molecules onto the metal surface [19]. The values of ΔH_{ads} and ΔS_{ads} can be calculated by using following equation:

$$\Delta G_{ads} = \Delta H_{ads} - T\Delta S_{ads} \tag{5}$$

Using Eq. (5), the plot of ΔG_{ads} versus T gives a straight line with a slope of **-** ΔS_{ads} and intercept of ΔH_{ads}. The values obtained are correlated with those obtained from Eq. (5). The negative values of ΔH_{ads} indicate that the adsorption process is an exothermic phenomenon [20]. The exothermic process is attributed to either physical or chemical adsorption or mixture of [21] whereas endothermic process corresponds to chemisorption [21-23]. The negative values of ΔS_{ads} in both the acids implies that the activated complex in the rate determining step denotes an association rather than a dissociation step, meaning that a reduction in disordering takes place on going from reactants to the activated complex.

The inhibitive characteristics of such compounds derive from the adsorption ability of their molecules, with the polar group acting as the reaction center for the adsorption process. The resulting adsorbed film acts as a barrier that separates the metal from the corrodent, and efficiency of inhibition depends on the mechanical, structural, and chemical characteristics of the adsorption layers formed under particular conditions.

4.4 Optical Microscopy

Optical microscope test shows the surface of carbon steel before and after adding PP extract with three concentrations. (Fig. 5) shows that corrosion has added some undesirable features to the material samples. These images show a noticeable reduction in corrosion sites and corrosion products on the corroded surface after adding the inhibitors as compared with the case of corrosion in the petroleum medium without inhibitor especially in the presence of the best concentration of inhibitor 5mL/L.

Table 2. Corrosion parameters for polarization of carbon steel in petroleum medium in the absence and presence of alcoholic extract of pumpkin peel at four temperatures

Conc. of extracted	Temp. K	E_{corr} mV	i_{corr} $\mu A.cm^{-2}$	$-b_c$ $mV.dec^{-1}$	$+b_a$ $mV.dec^{-1}$	P%
0	323	-759.8	497.68	1095.3	1087.7	-
	333	-322.0	682.72	1632.2	1647.9	-
	343	-496.2	694.09	2321.5	1957.9	-
	353	-665.1	719.78	1606.6	1597.8	-
3mL/L	323	-599.8	166.51	512.0	527.1	66.54276
	333	-519.5	166.75	442.9	425.0	75.57564
	343	-525.4	214.32	416.9	433.2	69.12216
	353	-438.8	271.24	495.7	465.7	62.31626
5mL/L	323	-506.9	137.15	510.9	475.2	72.44213
	333	-506.8	165.82	590.1	573.9	75.71186
	343	-524.7	176.10	481.0	455.8	74.62865
	353	-445.7	177.69	467.6	459.0	75.31329
7mL/L	323	-378.4	157.08	468.6	403.4	68.43755
	333	-407.0	272.16	627.8	607.7	60.13593
	343	-530.3	297.49	623.7	599.9	57.13956
	353	-487.3	311.08	632.9	547.2	56.78124

Table 3. Thermodynamic parameters for adsorption of PP extract on carbon steel in petroleum medium at different temperature

Temp. K	R^2	K_{ads} $L.mL^{-1}$	ΔG_{ads} $kJ.mol^{-1}$	ΔH_{ads} $kJ.mol^{-1}$	ΔS_{ads} $J.mol^{-1}K^{-1}$	ΔG_{ads}(eq.4) $kJ.mol^{-1}$
323	0.991	3.597	-13.9086	-26.68	-40.06	-13.741
333	0.968	2.320	-13.1521			-13.340
343	0.948	1.812	-12.8570			-12.939
353	0.919	1.490	-12.6716			-12.539

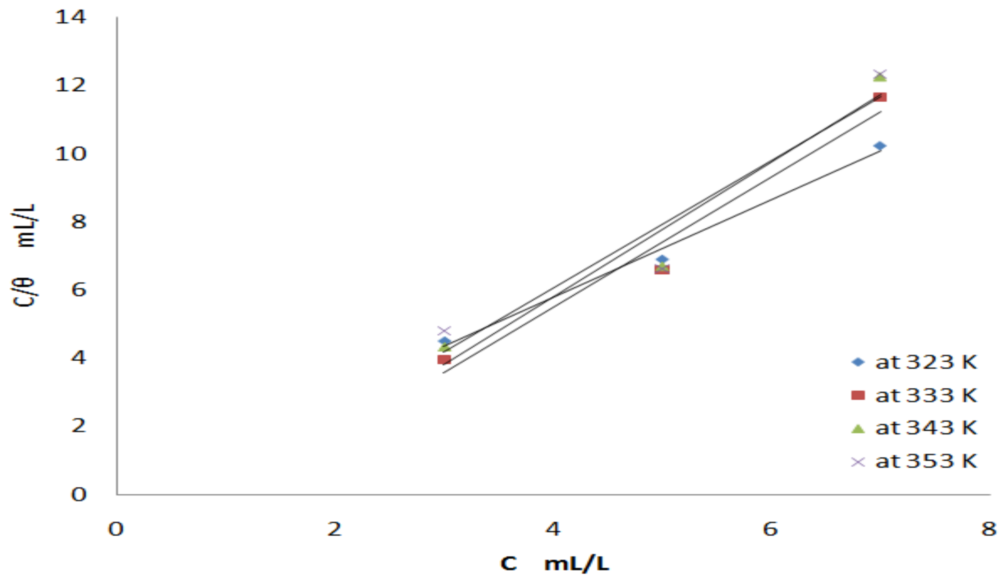
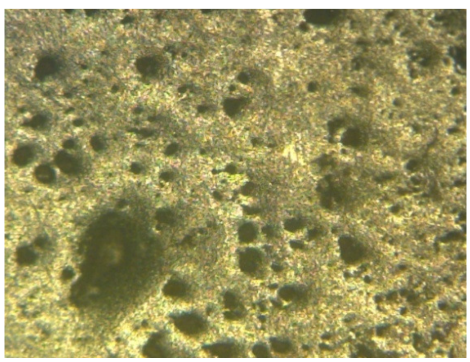
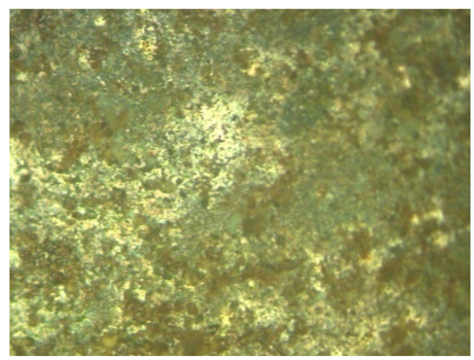


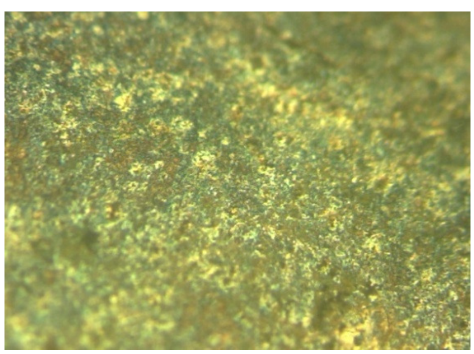
Fig. 4. Langmuir adsorption isotherm of PP extracts on steel in petroleum medium at various temperatures



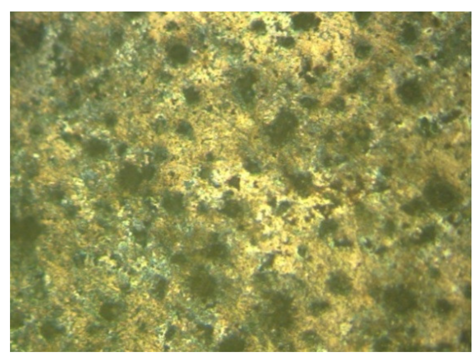
In petroleum medium



Petroleum+3mL/L PP



Petroleum+5mL/L PP



Petroleum+7mL/L PP

Fig. 5. Optical microscopies for corroded surface in petroleum medium in absence and presence PP extract

The optical microscopy of surface of corroded specimen in petroleum medium without inhibitor shows flakes with dark color which refers to corrosion products due to expose to aggressive corrosion results from direct exposure to petroleum medium, but in the presence of the inhibitors there is a much smaller damage on the surface and rather clear color. This is attributed to the formation of a good protective film on the carbon steel surface prevents direct contact between metal and petroleum medium.

5. CONCLUSION

Ethanolic extract of pumpkin peels has been studied as corrosion inhibitor for carbon steel in petroleum medium with three concentrations 3, 5 and 7mL/L at four temperatures over the range 50–80ºC using electrochemical measurements and FTIR spectra supplemented with optical microscopy. Pumpkin peels extract gave the best inhibition which ranged from 72.4 to 75.7%.Thermodynamic functions of adsorption processes were calculated from experimental polarization data and the interpretation of the results reveals that this pumpkin peels extract obey Langmuir adsorption isotherm. Polarization curves indicate that green inhibitor is a mixed type inhibitor.

COMPETING INTERESTS

Author has declared that no competing interests exist.

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