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Green corrosion inhibitor: inhibitive action of aqueous extract of *Punica Granatum* for the corrosion of mild steel in 0.5 M H_2SO_4 and 1 M HCl solutions.

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ABSTRACT

The inhibition of the corrosion of mild steel by *punica granatum* (PG) extract in 0.5M sulfuric acid medium and with a combination of potassium iodide in 1M hydrochloric acid medium by the weight loss method, potentiodynamic polarization technique and electrochemical impedance spectroscopy (EIS). The result Indicate that PG extract is a good inhibitor of mild steel in 0.5 M H2SO4 in 1M HCl ,but slightly better in H2SO4 solution than in HCl. The effect of temperature on corrosion behaviour with the addition of an optimal concentration of 3 g .l-1of PG extract was studied in a temperature range of 298-318 K. The addition of Potassium iodide with PG extract in 1M HCl medium has a positive effect on inhibition efficacy. The effectiveness of the protection increases with the increase of the concentration of the inhibitor in the both medium 0.5 M H2SO4 and 1 M HCl and but not with the effect of the temperature. Adsorption of PG extract on the surface metal obeyed the Langmuir adsorption isotherm. Thermodynamic parameters were calculated to understand the mechanism of inhibition.
Keywords: Mild steel, corrosion, *punica granatum*, adsorption, synergistic effect

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INTRODUCTION

Steel and their alloys are widely used in the industrial sector. Corrosion protection is a topic that has been studied in previous years. The use of a strong acid in industrial cleaning and in acid pickling and other fields [1] caused damage to the surface of equipments. It is stated that if organic molecules have double or triple bonds or if unpaired electrons have proved to be very good inhibitors for the corrosion of metals in acid solution [2-7].The presence of halide ion in acidic media increases the adsorption capacity of certain organic compounds and most often in the presence of iodide ions. The pronounced synergistic action is due to the larger atomic rays, hydrophobicity and low electronegativity of iodide ions compared to other halide ions [8-11].The use of plant extracts as corrosion inhibitors has been developed in recent years because of their availability; biodegradability and their costs [12,13]. The latter possess several families of natural organic compounds such as (flavonoids, tanains, phenolic compounds ....) which contain heterocycles and antioxidants. The fruit of grenadine (leaf, bark and seed) is rich in phenolic compounds [14, 15].Preliminary research indicates that the pomegranate would possibly have anti-inflammatory properties [16], antibacterial [17] and antiviral [18, 19].Other confirms that pomegranate is at the top of the list of antioxidant [20].The corrosion of mild steel of aqueous extract of *punica granatum* (PG) plant in 0.5M H_2SO_4 and a synergistic effect with potassium iodide (KI) in 1M HCl have been studied by weight loss method, potentiodynamics polarisation technique and electrochemical impedance spectroscopy (EIS).

MATERIALS AND METHODS

Preparation of extract of *punica granatum*

The barks of *Punica granatum* are collected and washed with water to remove mud or dust, if any; and were completely dried in the shade. The dried bark was crushed and extracted using a Soxhlet extractor and distilled. The viscous extract was used to study the corrosion inhibition properties. 0.5M H_2SO_4 and 1M HCl solutions were prepared by diluting 98% H_2SO_4 and 37% HCl using distilled water. The concentration range of the peel extract PG used varies from 1 to 3 g .l^{-1}.

Mild steel used

Mild steel samples having the following composition: 0.38% (C), 0.23% (Si), 0.68% (Mn), 0.01% (P), 0.02% (S) and the rest of the iron were used studies. The specimens were polished with emery papers of grade 180 to 1000, washed with distilled water, cleaned with acetone and dried in a desiccator.

Weight loss method

Rectangular specimens with a size of (1 x 4 x 0.5) cm were used in weight loss experiments. The weight loss of the mild steel coupons immersed in 100 ml of the electrolyte with and without plant extract (PG) was determined after 24 hours at 298 K at 318 K. The inhibition efficiency (IE %) was calculated from the following equation:

$$\%IE = \frac{w_{corr}^0 - w_{corr}^{inb}}{w_{corr}^0} \times 100$$

Where w_{corr}^0 and w_{corr}^{inb} are weight losses of mild steel in absence and presence of the extract.

Electrochemical measurements

A set of electrochemical cells with three electrodes was used for potentiometric bias and electrochemical impedance measurements in which the working electrode was made of mild steel; a saturated calomel electrode (SCE) is the reference electrode and the counter-electrode in platinum (CE). The working electrode was entirely coated with epoxy resin, which made it possible to preserve a surface of 1 cm2 for the study. The surfaces were then decreased with the abrasive paper and washed with distilled water and dried with acetone and before the experiment. The equipment used is: EC-Lab SP 200 Research Grad potentiostat model / galvanostat / FRA. The data was analyzed using EC-Lab V10.40 software. The polarization curves were recorded using a three-electrode system. Potentiodynamic polarization curves were recorded automatically by

changing the electrode potential from 10 to 10 mVSCE relative to an open potential at a scanning rate of 1 mV / s. EIS measurement experiments were performed on a potential open circuit whose frequency varies from 100 kHz to 10 mHz, with a signal amplitude perturbation of 10 mV. Electrochemical measurements were initiated about 30 minutes after the working electrode was immersed in the solution to stabilize the open circuit potential in steady state (E_{ocp}). Inhibition efficiency (% IE) is defined as:

$$\%IE = \frac{i^0_{corr} - i^{inh}_{corr}}{i^0_{corr}} \times 100$$

Where i^0_{corr} and i^{inh}_{corr} represent corrosion current density values without and with inhibitor, respectively.

$$\%IE = \frac{R^{inh}_{ct} - R^0_{ct}}{R^{inh}_{ct}} \times 100$$

Where R^0_{ct} and R^{inh}_{ct} are charge transfer resistance in the absence and presence of the inhibitor, respectively.

RESULTS AND DISCUSSIONS

Weight loss method

weight loss method with and without plant extract (PG) in 0.5 M H_2SO_4 and its synergistic effect with potassium iodide in 1 M HCl medium and over 24 hours in a temperature range of 298 K to 318 K are summarized in Tables(1and 2).

Table 1: Inhibition efficiency obtained by weight loss of mild steel in 0.5 M H2SO4with and without various concentrations of PG extract at 298 K to 318 K

C(g/L)	25°C		35°C		45°C	
	C_R(mg/ cm².h)	%IE	C_R(mg/ cm².h)	%IE	CR(mg/ cm².h)	%IE
0	4,9357		5,6807		7,8679	
1	1,0338	79,05	2,0624	63,69	3,6981	53
1,5	0,8026	83,74	1,5587	72,56	3,2462	58,74
2	0,4431	91,02	1,2592	77,83	3,0266	61,53
2,5	0,2736	94,46	0,8541	84,96	2,8069	64,32
3	0,1819	96,31	0,8055	85,82	2,3722	69,85

Table 2: The inhibition efficiency obtained by the weight loss of mild steel in 1 M HCl with and without various concentrations of PG extract and 10.10⁻³ M KI at 298 K at 318 K

C(g/L)	25°C		35°C		45°C	
	C_R(mg/ cm².h)	%IE	C_R(mg/ cm².h)	%IE	C_R(mg/ cm².h)	%IE
0	0,2201		1,5396		2,7815	
1	0,1106	49,75	0,6189	59,80	1,1258	59.53
1,5	0,1014	53,93	0,567	63,17	1,1159	59.88
2	0,0998	54,66	0,4695	69,51	0,753	72.93
2,5	0,094	57,29	0.4288	72,10	0,721	74.08
3	0,0731	66,79	0,3699	75,97	0,632	77,28

1+10.10-3 KI	0,0605	72,51	0,44	71,42	1,0386	62,66
1,5+10.10-3KI	0,0499	77,33	0,3882	74,79	1,0223	63,25
2+10.10-3KI	0,0438	80,10	0,2804	81,79	0,819	70,56
2,5+10.10-3 KI	0,0417	81,05	0,2672	82,64	0,4766	82,87
3+10.10-3 KI	0,0406	81,55	0,255	83,44	0,4413	84,13

Figure 1: Variation of % IE versus T in the presence of different concentration of PG extractin0.5 M H_2SO_4
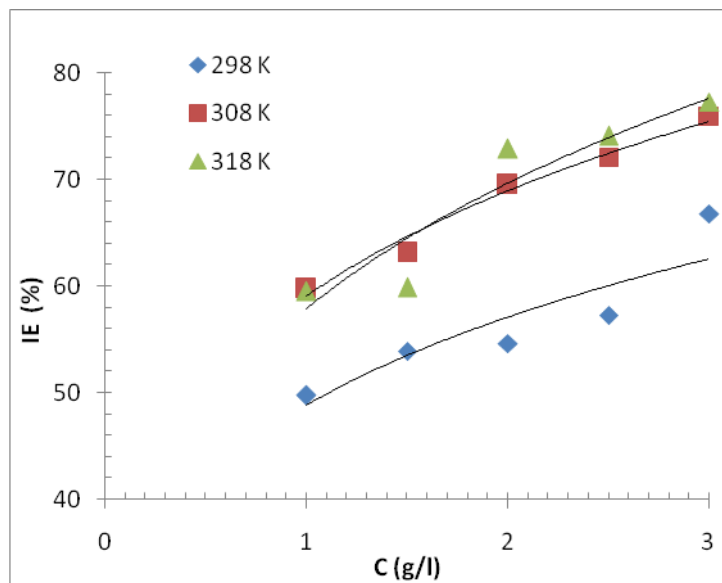

Figure 2:Variation of % IE versus T in the presence of different concentration of PG extractin1 M HCl
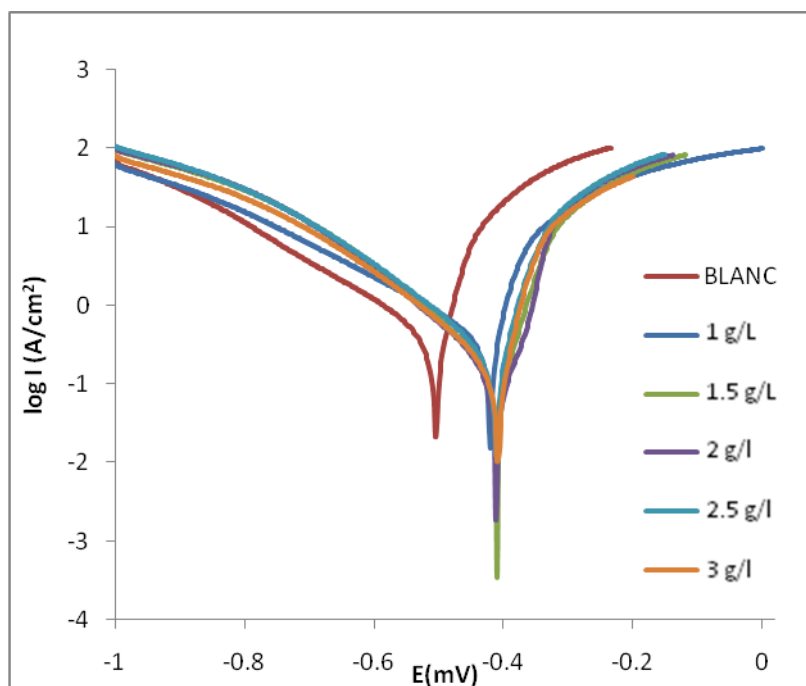
Figure 3: Tafel polarization curves for mild steel immersed in 0.5 M H_2SO_4 with various concentrations of PG extract at 298 K

From the above results it can be seen that the inhibitory efficiency increases with the addition of the concentrations of the plant PG extract; Inhibitory efficiency was 96.31% in 0.5M H_2SO_4 and 66.79% in 1M HCl at 298K. It can be said that the increase in inhibitory efficiency by the presence of OH group in the phenolic compounds exist in the aqueous extract that has formed a barrier between the metal and the electrolyte may be justified [21-26]. The same results were found in the tests of natural extracts as corrosion inhibitors for steel in acidic medium, leaves of thyme (Ibrahim &al., 2012), extracts of bark of fruit: banana peels (Eddy & Ebenso, 2008, Ji & al., 2015. The synergistic effect of mild steel in the presence of 10 .10 [-3] M KI with different concentrations of PG is significantly increasing the inhibitory efficiency is about 81.55% to 298 K. This increase may be explained by the fact that there is a synergy between the halide ion I[-] and the organic cations present in the extract, which allowed I[-]to form a bridge between the surface of the metal and these organic cations [27] . In other words, all the metal sites have been satisfied. The effect at the temperature of 298 K at 318 K decreased the effectiveness of 69.85% in the medium 0.5 M H_2SO_4 this decrease can be attributed to the desorption of the inhibitor. The Inhibition efficiency of about 84 13% of the PG extract with KI in can be said that the part of the metal surface covered by the inhibitory molecules increases.

Potentiodynamic polarization measurements

The representative potentiodynamic polarization curves of the mild steel electrode, obtained in0.5 M $H_2SO_4$and 1M HCl for various concentrations of PG extract in the absence and in the presence of KI, are summarized in Tables (3 and 4). Numerical values of corrosion variation current density (icorr), corrosion potential (Ecorr), Tafel anode slope (βa), Tafel cathode slope (βc) and percent efficiency. This shows that the addition of PG extract reduces the anodic dissolution and also delays the evolution reaction of the hydrogen, which indicates that PG extract is a mixed type inhibitor and controls both. Anodic and cathodic reactions. The addition of 10.10[-3]M KI for two concentrations of PG extracts reduced (icorr) from 12.84% to 30.58% for g .l[-1]and from 68.09% to 72.09% for g .l[-1]. The anodic and cathodic Tafel slopes (βc and βa) are approximately constant.

Table 3: Potentiodynamic polarization parameters for mild steel in 0.5 M H₂SO₄with and without PG extract at 298K

C (g/L)	-E$_{coor}$(mV/ESC)	I$_{coor}$(μA/cm²)	β$_c$(mV)	β$_a$(mV)	%IE
0	505,274	358,365	190,8	49	
1	412,314	192,812	144,1	52	0,46
1,5	408,706	139,163	136,4	55,8	0,61
2	409,472	101,001	102,6	45	0,72
2,5	406,848	65,845	82,1	30,1	0,82
3	410,051	29,195	33,2	34,4	0,92

Table 4: Potentiodynamic polarization parameters for mild steel in 1M HClwith and without PG extract and in combination with 10.10 -3 M KI for two concentration of this latter at 298K

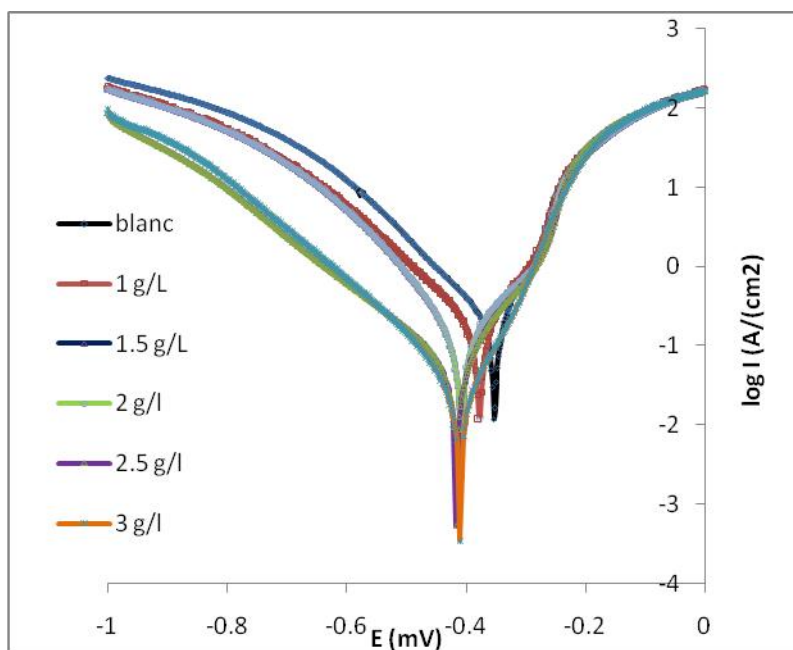| C (g/L)	- E$_{coor}$(mV/ESC)	I$_{coor}$(μA/cm²)	β$_c$(mV)	β$_a$(mV)	%IE
0	352,321	197,15	135,7	73,6	
1	407,894	171,838	130,5	161,3	12,84
1,5	344,387	116,179	152	54,4	41,07
2	416,147	62,916	180,6	107,8	68,09
2,5	446,7	57,427	147	167,4	70,87
3	410,145	27,892	122,2	101,3	85,85
1+KI	396,739	136,864	140	153,1	30,58
2+KI	446,701	55,029	143,5	160,5	72,09

Figure 4: Tafel polarization curves for mildsteelimmersedin1 M HCl with various concentrations of PG extract at 298 K
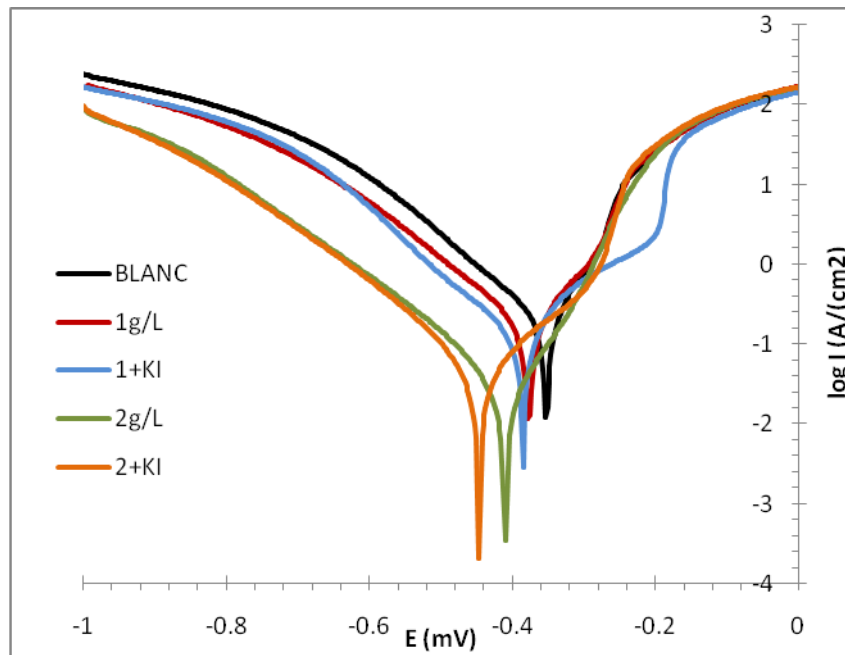
Figure 5: Tafel polarization curves for mild steel immersed in1 M HCl for two concentration of PG extract with combination 10.10 $^{-3}$M KI at 298K
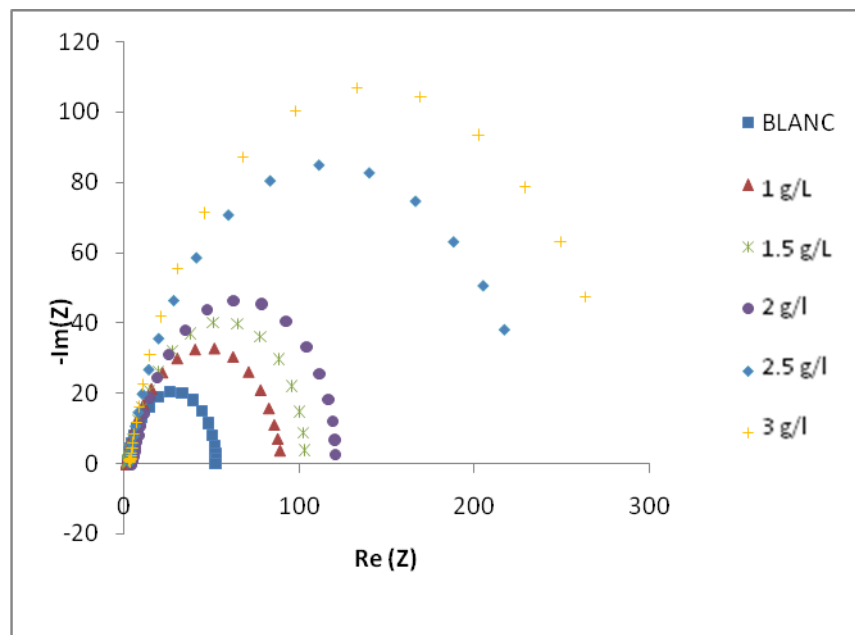

Figure 6: Nyquist plots for the mildsteelspecimenin0.5 M H_2SO_4acidcontainingdifferent concentrations of PG extract at 298K

These results indicate that this combination of PG extract with KI slightly increases inhibition efficiencies reveals that the inhibition action is due to adsorption on the surface of the steel and the adsorption is known to depend on the structure extract chemical.

By the comparison of polarization curves (figs 3,4 and 5), we see that they change from one medium to another which may be due to the structure of the constituents of the PG extract. Inhibition efficiency increases in following order: PG in 0.5 M H_2SO_4> PG with KI in1M HCl> PG alone in 1M HCl this gives a good argument with that obtained by the weight loss measurements.

Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy was used to determine the behavior of the metal/solution interface in the absence and in the presence of inhibitors. The representative Nyquist plots of the mild steel electrode, which was obtained in 0.5 M H_2SO_4 and 1M HCl solutions in the absence and presence of various concentrations of PG extract, with the synergistic effect of 10.10^{-3} KI for two concentrations of the extract in 1M HCl medium are shown in figures (6, 8 and 9).
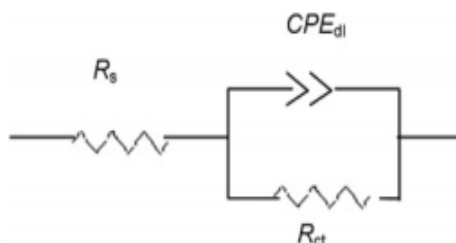

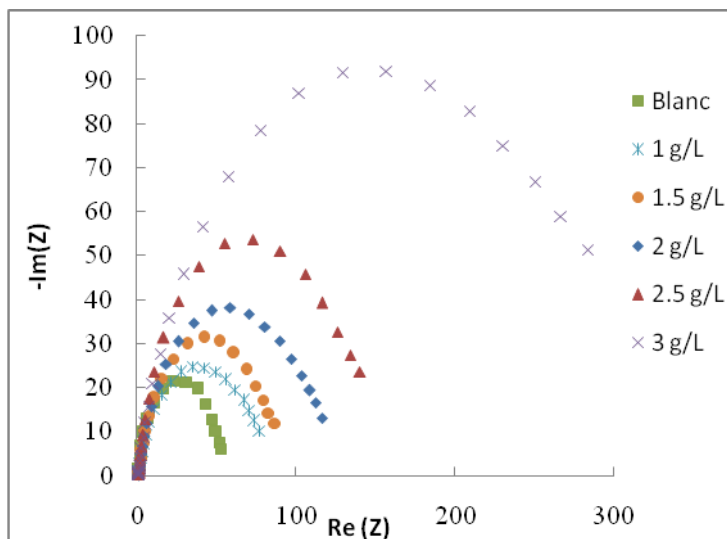**Figure 7:The equivalent circuit model**

Figure 8: Nyquist plots for the mild steel specimen in1 M HCl acid containing different concentrations of PG extract at 298K
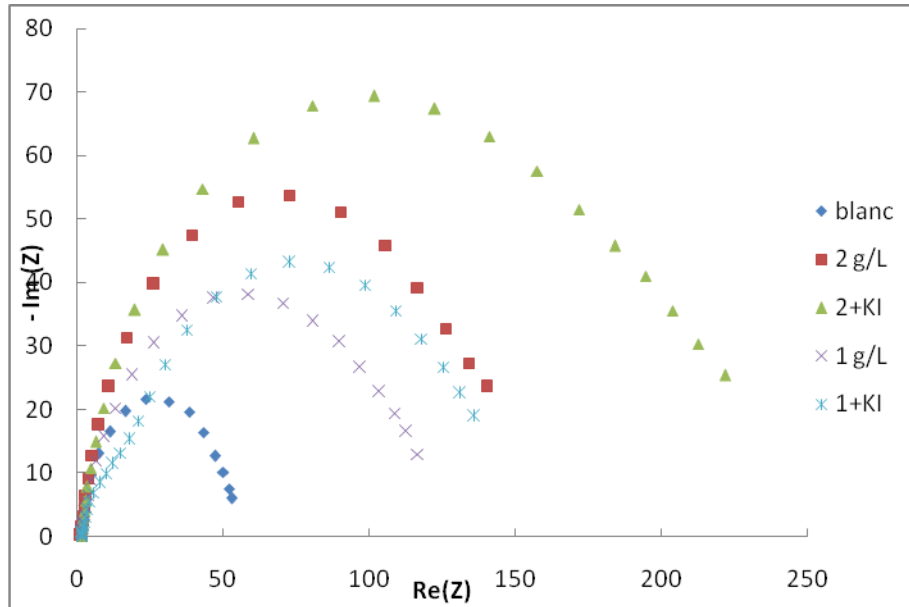
Figure 9: Nyquist plots for the mild steel specimenin 1 M HCl for two concentration of PG extract with combination 5.10^{-3}MKI at 298K

It is clear that the diameter of the semi circle increases with increasing concentration of the extract, at a maximum value 81,81% in 0.5 M H_2SO_4 and 82,85% in 1M HCl that indicating an increase in the corrosion resistance of the metal. In addition, the highest concentration of PG inhibitor (3 g .l^{-1}) results in a much larger half-circle diameter than the other four lower concentrations of PG. These diagrams have a similar shape in all tested concentrations, indicating that almost a change in the corrosion mechanism occurs due to the addition of inhibitors [28].The circuit consists of a constant phase element (CPE) Q, in parallel with a resistor R_{ct}. The use of a CPE type impedance has been widely described [29-31]:

$$ZCPE = [Q(jw)^n]^{-1}$$

The equation above provides information on the degree of non-ideality in capacitive behavior. Its value makes it possible to differentiate the behavior of an ideal capacitor (n = 1) and a CPE (n <1)[32].The capacitance value C_{dl} can therefore be calculated for a parallel circuit composed of a CPE (Q) and a resistor (R_{ct}), according to the following formula [33-34]:

$$Q = \frac{(Cdl\ Rt)n}{Rt}$$

Impedance data of mild steel in 0.5 M H_2SO_4 and1 M HCl medium without and with different concentrations of the PG extract and with the synergistic effect of 10.10^{-3} KI for two concentrations of extracted in 1M HCl medium were recorded and shown in Tables 5 and 6.Respectively;it can be seen that the presence of PG improves the values of R_{ct} and reduces the C_{d1} values. The decrease in C_{d1} is due to the adsorption of PG on the metal surface to form an adherent film and suggests that the coverage of the metal surface with this film decreases the local dielectric constant and / or increase in the thickness of the double layer mentioned in the work done [35-36-37]. The addition of 10 .10 $^{-3}$ M KI further enhances the R_{ct} values and reduces the C_{d1} values. This can be attributed to enhanced adsorption of the PG in the presence of 10.10^{-3} M KI due to the synergistic effect of iodide ions.

Table 5: Electrochemical parameters of impedance for carbon steel in 0.5 M H₂SO₄with and without PG extract at 298K.

C (g/L)	$R_{ct}(\Omega/cm^2)$	$C_{dl}(F/cm^2)$	Q e-3	n	%IE
0	51,66	0,453 *10^-3	0,638	0,848	
1	89,27	0,122*10^-3	0,284	0,813	42,13
1,5	109,3	0,1*10^-3	0,251	0,797	52,74
2	127,6	0,0572*10^-3	0,161	0,789	59,51
2,5	227,8	0,140*10^-3	0,253	0,829	77,32
3	284	0,122*10^-3	0,213	0,835	81,81

Table 6: Electrochemical parameters of impedance for carbon steel in 1 M HCl with and without PG extract and its combination with5.10 $^{-3}$ M KI for two concentration of this latter at 298K.

C (g/L)	$R_{ct}(\Omega/cm^2)$	$C_{dl}(F/cm^2)$	Q e-3	n	%IE
0	50,77	0,453*10^-3	0,638	0,909	
1	74,2	0,309*10-3	0,717	0,775	31,58
1,5	85,77	0,283*10^-3	0,508	0,817	40,81
2	113,9	0,0773*10^-3	0,217	0,781	55,43
2,5	206,2	0,0676*10^-3	0,167	0,787	75,38
3	296,1	0,0855*10-3	0,216	0,747	82,85
1 +KI	108,1	0,0917*10-3	2,374	0,588	53,03
2+KI	164,2	0,0859*10-3	1,931	0,586	69,08

Adsorption isotherms

The mechanism of the interaction between the inhibitor and the electrode surface can be explained using adsorption isotherms. [38]. This adsorption process is influenced by the chemical structures of organic compounds, the charge distribution in the molecule, the nature and surface charge of the metal and the type of aggressive medium[39].The most frequently used isotherms are Langmuir [40], Frumkin [41] and Temkin [42]. The Langmuir isotherm (C / θ vs. C) assumes that there is no interaction between the adsorbed molecules on the surface. The Frumkin adsorption isotherm (θ vs. C) assumes that there is some interaction between the adsorbents, and the Temkin adsorption isotherm (θ vs. log C) represents the effect of the cover multilayer [43]. In this study, the best fit was determined using the Langmuir adsorption isotherm (Figures 10&11). It is represented by the following equation [44]:

$$\frac{C}{\theta} = c + \frac{1}{K_{ads}}$$

Where θ is the fraction of surface coverage, C is the inhibitor concentration, K is the equilibrium constant for the adsorption/desorption process.

The constant of adsorption, k_{ads}, is related to the standard free energy of adsorption, $\Delta G°_{ads}$, with the following equation:

$$k_{ads} = \frac{1}{55,5} \exp\left(\frac{-\Delta G_{ads}}{RT}\right)$$

The value 55.5 in the above equation is the concentration of water in solution in mol. l^{-1} [45]. The standard free energy of adsorption ($\Delta G°_{ads}$) can be calculated. The negative values of $\Delta G°_{ads}$ ensure the spontaneity of the adsorption process and stability of the adsorbed layer on the steel surface. Generally, values of ($\Delta G°_{ads}$) up to 20 Kj. mol^{-1} are consistent with the electrostatic interactions between the charged molecules and the charged metal (physisorption) while those around 40 Kj. mol^{-1} or higher are associated with

chemisorption as a result of sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate type of bond (chemisorption) [46, 47].The average values of ΔG°_{ads} calculated in the case of PG alone and mixture (PG + KI) that recorded in Tables 7 and 8 are respectively equal to -17, 56 and -16, 91 kJ / mole signifying spontaneous adsorption and confirming the physisorption mechanism. The ΔH_{ads} value is positive, suggests that the adsorption of inhibitor's molecules onto metal surface is an endothermic process, the latter decreased for (PG + KI) due in the presence of ions I- simultaneous adsorption of anions and cations occurs. This phenomena accompanied by the appearance of attractive forces that give rise to the formation of a compact adsorption layer having a value of ΔH°_{ads} weak.
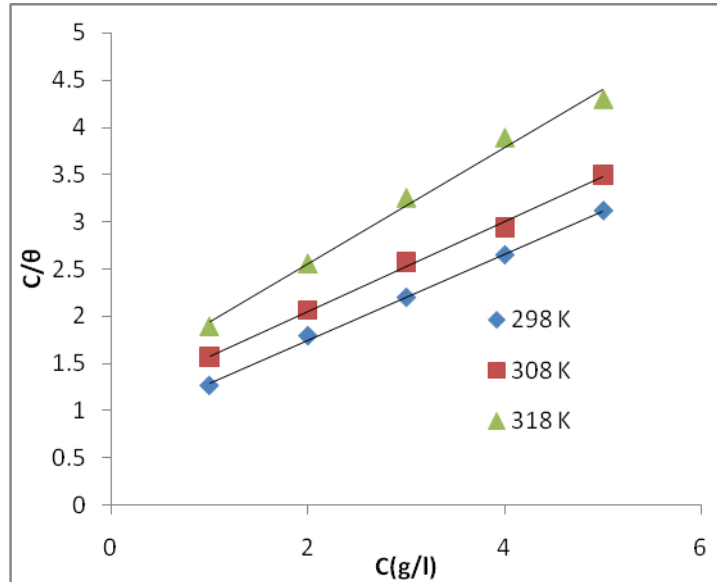

Figure 10: Langmuir adsorption isotherm for adsorption of PG extractin0.5M H_2SO_4on surface of mild steel
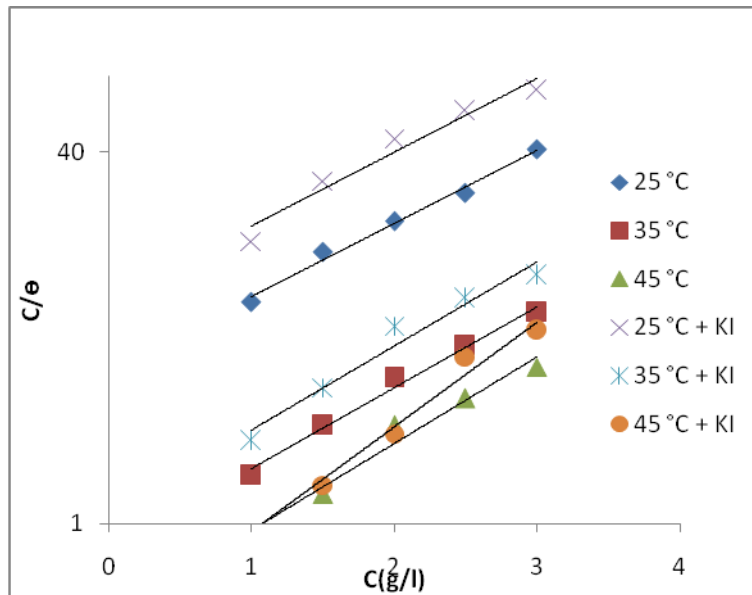

Figure 11: Langmuir adsorption isotherm for adsorption of PG extract and (PG + KI) in 1 M HCl on surface of mild steel

Table 7: Adsorption parameters for mild steel corrosion in the presence of PG extract in 0.5M H₂SO₄

T (K)	Slope	intercept	R^2	ΔG°_{ads} (kJ.mol^{-1})	ΔH°_{ads} (kJ.mol^{-1})	ΔS°_{ads} (kJ.mol^{-1}.K^{-1})
298	0,836	0,455	0,998	-17,56	18,22	0,002
308	1,111	0,472	0,997	-17,42	18,22	0,002
318	1,329	0,614	0,992	-17,51	18,22	0,002

Table 8: Adsorption parameters for mild steel corrosion in the presence of PG extract alone and with KI in 1M HCl

T (K)		ΔG°_{ads} (kJ.mol^{-1})	ΔH°_{ads} (kJ.mol^{-1})	ΔS°_{ads} (kJ.mol^{-1}.K^{-1})
	PG	-16,85	10,24	0,022
298	PG+KI	-16,91	3,87	0,043
	PG	-17,13	10,24	0,022
308	PG+KI	-17,22	3,87	0,043
	PG	-17,30	10,24	0,022
318	PG+KI	-17,78	3,87	0,043

Fourier Transform Infrared Spectroscopy (FTIR)

In the present study, FTIR spectra were used to support the fact that corrosion inhibition of mild steel in 1M HCl medium is due in part to the adsorption of inhibitory molecules on the surface of the material [48]. , 49]. The spectrum of the aqueous extract of PG as an inhibitory layer since the extract contained organic compounds that were adsorbed on the metal surface providing protection against corrosion. Thus, FTIR metal surface assays may be useful in predicting whether organic inhibitors are adsorbed or non-adsorbed on the metal surface (Figs. 12 and 13). The presence of an OH group is confirmed by the presence of an intense band between 3000 and 3500cm^{-1} (Fig 12) but after inhibition there is disappearance of this band and appearance of two bands between 1000 and 1500cm^{-1} (Fig. 13). We conclude that the FTIR spectra support a good inhibition performance of the PG extract for a good corrosion of the steel in a hydrochloric acid solution .
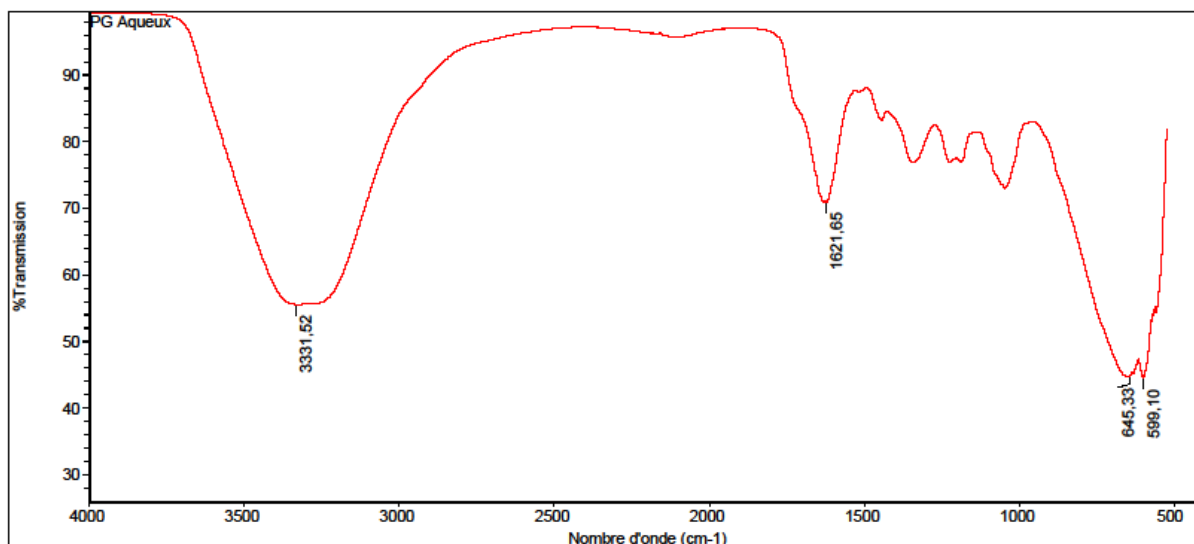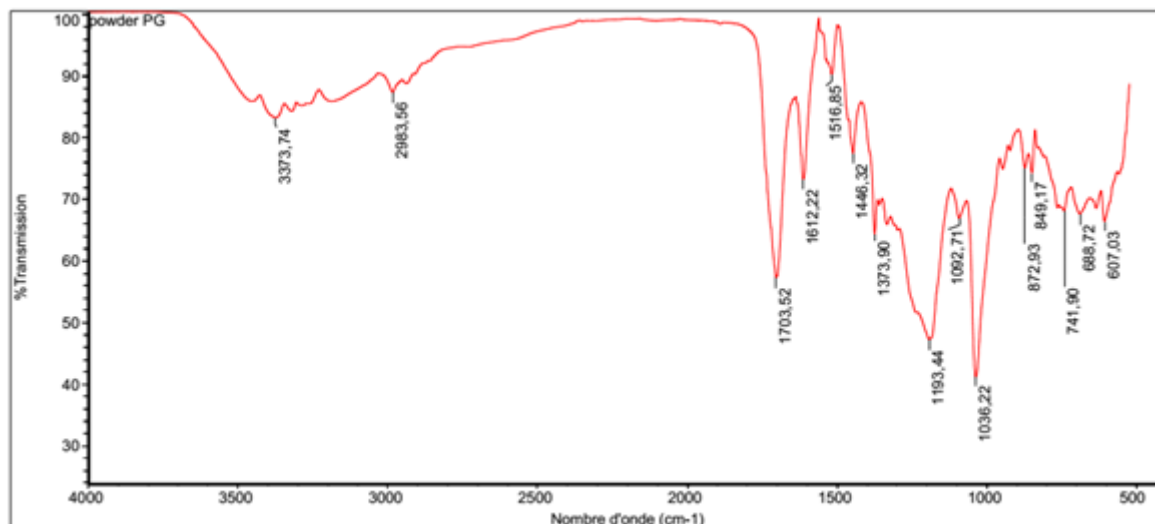

Figure 12: IR spectra of PG extract

Figure 13: IR spectra of the product between PG extract and MS powder specimen

CONCLUSION

➢ The PG peel aqueous extract is a good inhibitor of the corrosion of mild steel in both medium but better in H_2SO_4 than HCl.

➢ Polarization curves indicated that the PG peel aqueous extract act as mixed type.

➢ The adsorption of PG peel aqueous extract is well described by Langmuir isotherm model under all of the studied temperatures.

➢ The value of ΔG_{ads} in our measurement suggests that the adsorption of PG extract involves physisorption.

ACKNOWLEDGEMENTS

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