

Utilization of Green Tea as Environmentally Friendly Corrosion Inhibitor for Carbon Steel in acidic media

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Corrosion inhibitors from natural products have been considered preferential due to the environment friendly effect. Green tea extracts GTEs was tested as a corrosion inhibitor for carbon steel in both HCl and H₂SO₄ solutions using weight loss, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques. Maximum inhibition efficiency was found (81.47%) in 1M HCl, whereas, it was (71.65%) in 0.5M H₂SO₄ at concentration 500 ppm. The inhibition efficiencies obtained from all techniques employed are in good agreement with each other. The corrosion rate was found to decrease with the increases of concentrations while inhibition efficiency increases with increasing concentration of GTEs in both HCl and H₂SO₄ solutions. SEM studies confirmed the adsorption of the extract molecules on the carbon steel surface. Our study is also extended to calculate Some Quantum Parameters for Catechin Monomers.

Keywords: A. Carbon steel; B. SEM; C. Green tea; D. Adsorption

1. INTRODUCTION

Most corrosion inhibitors are either synthesized from cheap raw materials or are chosen from organic compounds containing electronegative functional groups and π -electrons in triple or conjugated double bonds. The presence of aromatic rings and heteroatoms are the major adsorption centers for these inhibitors.[1–6] Despite the broad spectrum of organic compounds available as corrosion inhibitors, the successful utilization of most corrosion inhibitors has been hindered by their toxic nature. [7] Green corrosion inhibitors have the advantages of, biodegradable, inexpensive, non-toxic and eco-friendly. These advantages have provoked numerous and intensive searches on the use of naturally occurring substances or their extracts for the inhibition of the corrosion of metals.[8–15] It has been reported that the inhibitory actions of plant extracts are due to the presence of some organic compound such as saponins, tannin, alkaloid, steroids, glycosides and amino acids.³⁷ Most of these

compounds have centers for π -electrons and functional groups (such as $-\text{C}=\text{C}-$, $-\text{OR}$, $-\text{OH}$, $-\text{COOH}$, $-\text{NR}_2$, $-\text{NH}_2$ and $-\text{SR}$), which provide electrons that facilitate the adsorption of the inhibitor on the metal surface. Also, the presence of hetero atoms such as P, O and S enhances the adsorption of the inhibitor on the metal surface. Amino acids in the plant extracts play an important role in the inhibition mechanism. [16–22] Tea leaves contain many compounds, such as polysaccharides, volatile oils, vitamins, minerals, purines, alkaloids (e.g. caffeine) and polyphenols (catechins and flavonoids). Monomeric flavanols, the major components in green tea, are precursors of condensed tannin. The flavanols are easily oxidized to the corresponding O – quinones. These flavanols and quinones can function as either hydrogen acceptors or hydrogen donors. In addition, tea polyphenols effectively interact with reactive oxygen species. In flavanol structure, the 5- and 7- dihydroxy groups and 1-oxygen make the carbons at positions six and eight strongly nucleophilic. Tea polyphenols also have a high complication affinity to metals, alkaloids, and biologic macromolecules such as lipids, carbohydrates, proteins, and nucleic acids. Green tea has very powerful antioxidant properties. In green tea, caffeine, theobromine, and theophylline, the principal alkaloids, account for about 4% of the dry weight. In addition, there are phenolic acids such as gallic acids and characteristic amino acids such as theanine. The complex nature of the tea's chemical composition and structure is expected to prove effective in corrosion inhibition of carbon steel. This work, therefore, reports the results obtained in the evaluation of the corrosion inhibitive effectiveness of the tea extract on the corrosion of carbon steel test specimens immersed in hydrochloric acid and dilute sulphuric acid at ambient temperature. The need for a possibility of using plant extracts as a natural source of inhibitor to mitigate against the corrosion of metals in corrosive environments necessitates this investigation. In addition, an effective inhibitor of a plant extract such as this will be very environmentally friendly. It is anticipated that the study will make a contribution to the present research interest in this area of studies. Economic and technological benefit is envisaged from a positive result in this work.

2. EXPERIMENTAL

2.1 Extract of *Camellia Sinensis*

The green tea extract was obtained directly from the tea bags of Lipton green tea. Stock solutions of the inhibitor extract were prepared by boiling 1.5 grams of dried tea bags in 250 ml of double distilled water for 30 min. The extract was left all night, then filtered and completed to 1000 ml with double distilled water. Both the freshly prepared extract and that aged in a refrigerator for one month gave almost the same results.

2.2. Test solutions

The corrosion tests were performed in 1M HCl and 0.5 M H_2SO_4 solutions in the absence and presence of various concentrations of the GTEs. All the test solutions were prepared from analytical grade chemical reagents in distilled water without further purification. For each experiment, a freshly

prepared solution was used. The test solutions were opened to the atmosphere and the temperature was controlled thermostatically at 303 K.

2.3. Weight loss measurements

The steel sheets of $7.0 \times 2.0 \times 0.3$ cm dimensions were abraded with different grades of emery papers, washed with distilled water, degreased with acetone, dried and kept in a desiccator. After weighing accurately by a digital balance with high sensitivity the specimens were immersed in a solution containing 1 M HCl and 0.5 M H₂SO₄ solutions with and without various concentrations of the investigated inhibitors. After 7 days exposure, the specimens were taken out, rinsed thoroughly with bi-distilled water, dried and weighted accurately again. Three parallel experiments were performed for each test. The average weight loss, ΔW (mg) was calculated using the following equation [23]:

$$\Delta W = W_1 - W_2 \quad (1)$$

Where W_1 and W_2 are the average weight of specimens before and after exposure, respectively.

2.4. Preparation of working electrodes

The working carbon steel electrode specimens were cut from a cylindrical rod to a length of 5 cm and covered by Teflon leaving only 0.5 cm² of the surface area exposed to the solution. The electrical conductivity was provided by a copper wire [24]. The chemical composition of working electrode (wt, %) was: 0.09% C, 0.29% Si, 1.66% Mn, 0.017% P, 0.005% S, 0.33% Cr, 0.19% Ni, 0.17% Mo, 0.01% Cu and the remainder Fe. Before measurements, the surface of working electrode was mechanically abraded using different grades of emery papers, which ended with the 1000 grade. The disc was cleaned by washing with bi-distilled water, thoroughly degreased with acetone, washed once more with bi-distilled water and finally dried with a filter paper. For each test, a newly abraded electrode was used.

2.5. Electrochemical measurements

The electrochemical measurements were carried out using Volta lab 40 (Tacussel-Radiometer PGZ301) potentiostat and controlled by Tacussel corrosion analysis software model (Voltmaster 4) under static condition. The corrosion cell used had three electrodes. The reference electrode was a saturated calomel electrode (SCE). A platinum electrode was used as auxiliary electrode. The working electrode was carbon steel pipelines. All potentials given in this study were referred to this reference electrode. The working electrode was immersed in test solutions for 30 minutes to establish steady state open circuit potential (E_{ocp}). After measuring the E_{ocp} , the electrochemical measurements were performed. The polarization curves were obtained in the potential range from -850 to -350mV(SCE) with 1 mV s⁻¹ scan rate.

2.6. Surface morphology studies

The surface morphology of the steel specimens was examined after exposure to 1M HCl in the absence and presence of 500 ppm of the selected inhibitor. JEOL 5410 scanning electron microscope SEM (Japan) was used for this investigation.

2.7. Molecular Modeling Studies

The energy levels viz., highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for various catechin monomers were calculated using the Restricted Hartree-Fock level PM3 method which are implemented in Hyperchem 8.0. The molecule 2D sketch was obtained by ISIS Draw 2.1.4.

3. RESULTS AND DISCUSSION

3.1. Chemical structure confirmation by FTIR

The green tea extracts were analyzed by FTIR spectroscopy for the identification of the functional groups. Figure 1 shows the IR absorption spectrum of the green tea extracts and the typical functional groups of catechin namely O-H, C=C (for aromatic rings), and C-O that were evidenced at 3400 to 3100, 1600, and 1150 to 1010 cm^{-1} , respectively.[25] These functional groups were identified already as potent anticorrosion groups in organic corrosion inhibitors as reported by many researchers.[26] It was assumed that a catechin monomer that has more numbers of hetero functionality and p-electronic clouds could serve as a better corrosion inhibitor. According to this consideration, an EGCG monomer was assumed to contribute more during the corrosion inhibition process because it has three aromatic rings along with eight OH groups, whereas ECG contains seven OH groups and EC. EGC has fewer aromatic rings and OH groups. Table 1. shows the Structures of Catechin Monomers and Caffeine.

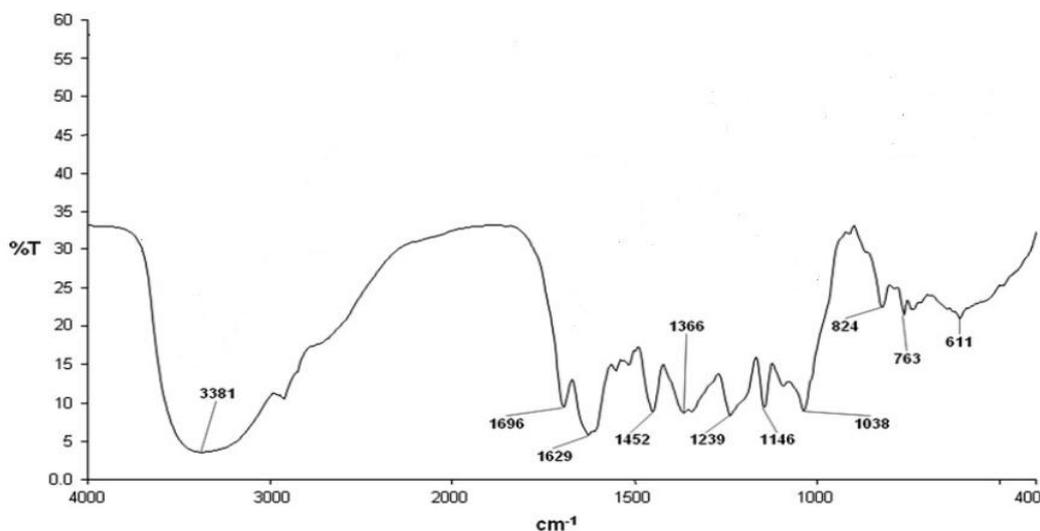
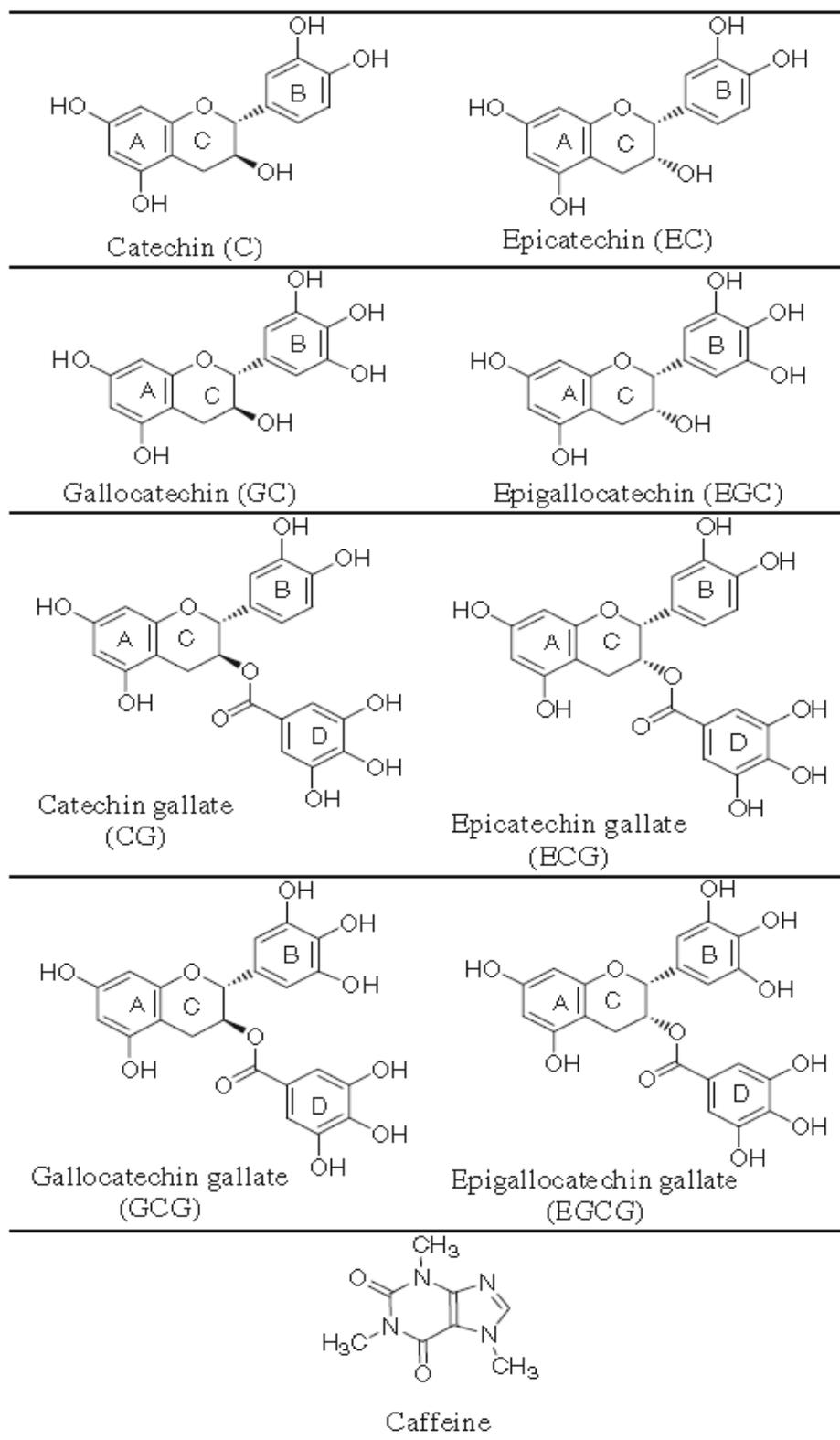


Figure 1. IR spectra of green tea extracts

Table 1. Structures of Catechin Monomers and Caffeine

3.2. Weight loss Method:

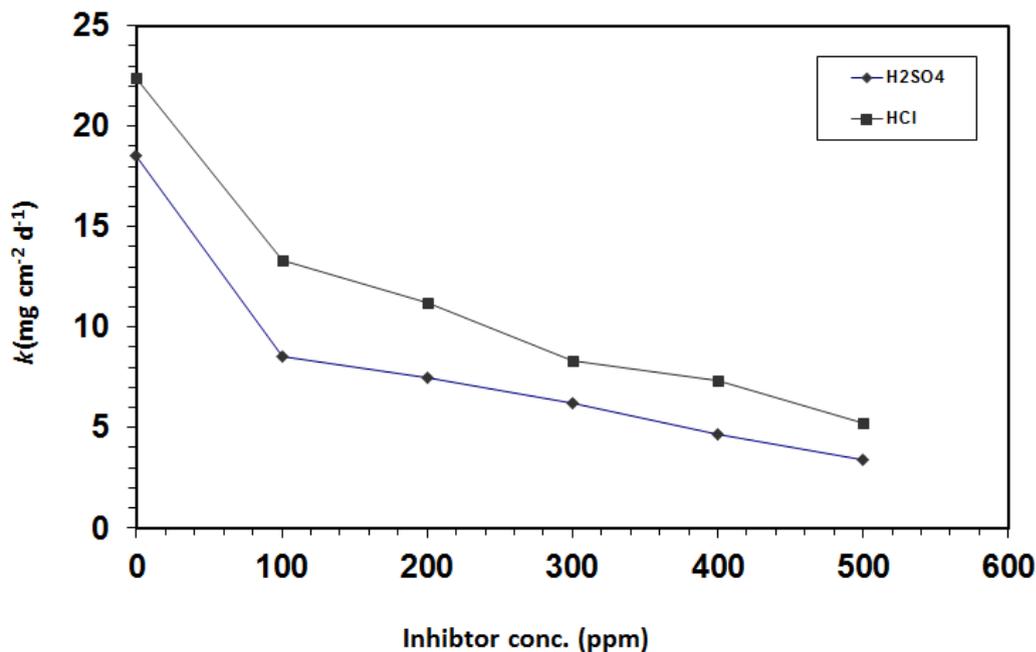


Figure 2. Relationship between the corrosion rate and inhibitor concentration for steel after 7days immersion in 1 M HCl and 0.5 H₂SO₄ at 303 K.

Table 2. Corrosion parameters of steel after 7days immersion in both 1M HCl and 0.5 M H₂SO₄ solution with and without various concentrations of GTEs at 303 K.

Inhibitor	Concentration (ppm)	1M HCl			0.5 M H ₂ SO ₄		
		k(mg cm ⁻² hr ⁻¹)	θ	η_w (%)	k(mg cm ⁻² hr ⁻¹)	θ	η_w (%)
Blank	0	18.52	---	---	22.43	---	---
GTEs	50	8.55	0.53	53.83	13.34	0.279	27.96
	200	7.45	0.59	59.77	11.23	0.39	39.36
	300	6.23	0.66	66.36	8.34	0.54	54.96
	400	4.65	0.74	74.89	7.32	0.60	60.47
	500	3.43	0.81	81.47	5.25	0.71	71.65

The corrosion rate (*k*) of steel specimens after 7 days exposure to 1M HCl and 0.5 M H₂SO₄ solutions with and without the addition of various concentrations of the investigated inhibitors was calculated and the obtained data are listed in Table 2. The variation of *k* with inhibitor concentrations is shown in Fig. 2. The corrosion rate; *k* (mg cm⁻² h⁻¹), surface coverage (θ) and inhibition efficiency η_w of each concentration were calculated using the following equations [27]:

$$k = \frac{\Delta W}{St}$$

$$\theta = \frac{k_{uninh} - k_{inh}}{k_{uninh}}$$

$$\eta_w = \left(\frac{k_{uninh} - k_{inh}}{k_{uninh}} \right) \times 100$$

where ΔW is the average weight loss (mg), S is the surface area of specimens (cm^2), and t is the immersion time (h), k_{uninh} and k_{inh} are corrosion rates in the absence and presence of inhibitor, respectively. It is clear From Table 2 that η_w increased with increasing inhibitor concentration, while corrosion rate decreased. This behavior can be attributed to the increase of the surface coverage due to the adsorption of extract components on the carbon steel surface. Maximum inhibition efficiency was found (81.47%) in 1M HCl acid, whereas it was (71.65%) in 0.5M H_2SO_4 acid with the same concentration. The results confirmed the very good effect of the GTEs extract on the corrosion inhibition of carbon steel in 1M HCl solution as corrosive media than the use of 0.5 H_2SO_4 at the same concentration. The optimum concentration required to achieve an efficiency of 81.47% was found to be 500 ppm. The variation of η_w and inhibitor concentrations in 1 M HCl and 0.5 M H_2SO_4 solutions at 303 K is shown in Fig. 3.

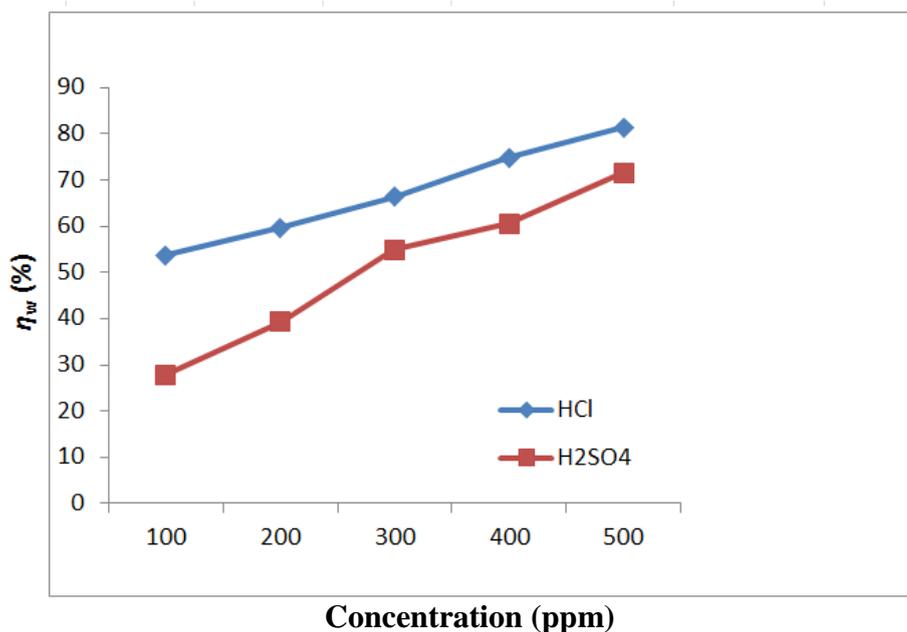


Figure 3. Relationship between the inhibition efficiency and inhibitor concentration for steel after 7 days immersion in 1 M HCl and 0.5 H_2SO_4 at 303 K.

When the concentration of GTEs is less than 500 ppm, the η_w increased sharply with an increase in concentration, while a further increase causes no appreciable change in performance.

3.3. Adsorption Isotherm

The efficiency of an organic compound as a successful inhibitor is mainly dependent on its ability to get adsorbed on the metal surface, which consists of the replacement of water molecules at the corroding interface. If it is assumed that the metals are corroding uniformly, then the corrosion rate in the absence of inhibitor is representative of the total number of corroding sites.

Values of surface coverage (θ) corresponding to different concentrations of GTEs, which calculated using the weight loss results at 303 K after 7 days of immersion were used to determine which isotherm best described the adsorption process. The results obtained for the investigated inhibitors in 1 M HCl solution were tested with several adsorption isotherms. However, the best agreement was obtained using the Langmuir adsorption isothermal equation as follows[41]:

$$\frac{C_i}{\theta} = \frac{1}{K_{ads}} + C_i$$

Where C_i is the concentration GTEs and K_{ads} the adsorptive equilibrium constant. Langmuir’s isotherm assumes that there is no interaction between the adsorbed molecules, the energy of adsorption is independent on the θ , the solid surface contains a fixed number of adsorption sites, and each site holds one adsorbed species. Plots of C_i / θ against C_i yield straight lines as shown in Fig. 4, and the linear regression parameters are listed in Table 3.

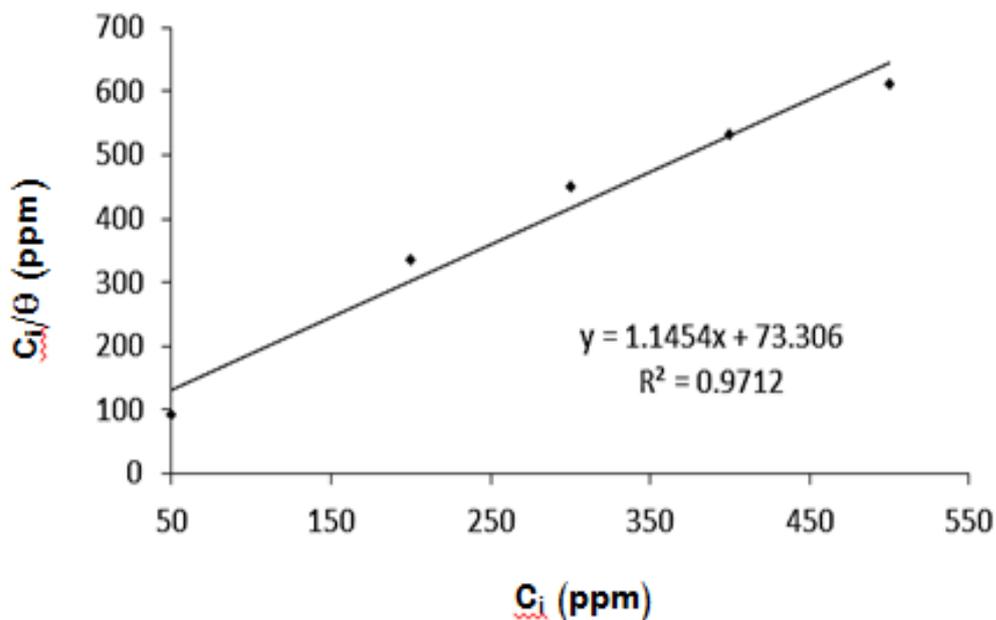


Figure 4. Langmuir adsorption plots of steel in 1 M HCl solution containing the investigated inhibitors at 303 K.

Table 3. Adsorption equilibrium constant (K_{ads}) and standard free energy of adsorption (ΔG°) of the GTEs for steel in 1 M HCl solution at 303 K.

Inhibitor	Linear correlation coefficient (r)	Slope	K_{ads} (M^{-1})	$-\Delta G^\circ_{\text{ads}}$ (kJ mol^{-1})
GTEs	0.971	1.14	757.1	-16.70

Both linear correlation coefficient (r) and slope are very close to 1, indicating the adsorption of the investigated inhibitors on steel surface obeys the Langmuir adsorption isotherm in 1 M HCl solution. The adsorptive equilibrium constant (K_{ads}) can be calculated from reciprocal of intercept of $C_i/\theta-C_i$ curve. K_{ads} is related to the standard free energy of adsorption ($\Delta G^\circ_{\text{ads}}$) as shown the following equation [40]:

$$K_{\text{ads}} = \frac{1}{55.5} \exp\left(\frac{-\Delta G^\circ_{\text{ads}}}{RT}\right) \quad (12)$$

where R is the gas constant ($8.314 \text{ J mol}^{-1} \text{ K}^{-1}$), T the absolute temperature (K), and the value 55.5 is the concentration of water in solution expressed in molar. Table 2 shows the calculated values of molecular interaction a , equilibrium constant of adsorption process, K_{ads} and free energy ($\Delta G^\circ_{\text{ads}}$) obtained from Langmuir plot. The value of a are positive shows that attraction exists in adsorption layer [28]. The relatively high and negative free energy values may indicate a relatively strong and spontaneous adsorption of the investigated compound on the metal surface, which explains its high corrosion inhibition efficiency. A value of -20 kJ mol^{-1} or less is usually adopted for physical adsorption [29]. The calculated values of $\Delta G^\circ_{\text{ads}}$, for the investigated extract with the metal surface is $-16.70 \text{ kJ mol}^{-1}$, which means that the inhibitor is physically adsorbed through electrostatic interaction [30].

3.4. Mechanism of corrosion inhibition

In acidic solutions, transition of the metal /solution interface is attributed to the adsorption of the inhibitor molecules at the metal /solution interface, forming a protective film. The rate of adsorption is usually rapid, and hence, the reactive metal surface is shielded from the acid solutions [31]. The adsorption of extract components depends on its chemical structure, its molecular structure, its molecular size, the nature and charged surface of the metal, and distribution of charge over the whole extract molecule. The exact nature of the interaction between a metal surface and an aromatic molecule depends on the relative coordinating strength towards the given metal of the particular groups present [32]. Tea component molecules contain many compounds such as, caffeine, alkaloids, phenolic substances, tannins, fats, flavonoids amino acids sterols and vitamin C, so green tea extract possess several heteroatoms containing active constituents, and therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies.

3.5. Potentiodynamic polarization measurements

The potentiodynamic polarization curves of carbon steel immersed in 1M HCl and 0.5 M H_2SO_4 in the absence and presence of green tea extract are shown in Fig. 5,6. It is clear from this

Figures that both anodic metal dissolution and cathodic H₂ reduction reactions were inhibited when the green tea extract was added to 1 M HCl and 0.5 M H₂SO₄. The corrosion parameters such as corrosion potential (E_{corr}), anodic and cathodic Tafel slopes β_a, and β_c, respectively, corrosion current (I_{corr}) and corrosion rate (R_{corr}) values were calculated and are given in the Table 4,5. Tafel lines are shifted to more negative and more positive potentials with respect to the blank curve by increasing the concentration of the investigated inhibitors.

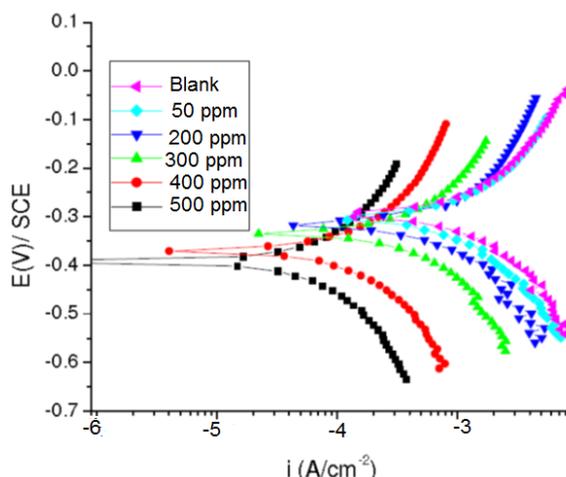


Figure 5. Polarization plots of steel electrode obtained in 1 M HCl solution and containing different conc. of GTEs at 303 K.

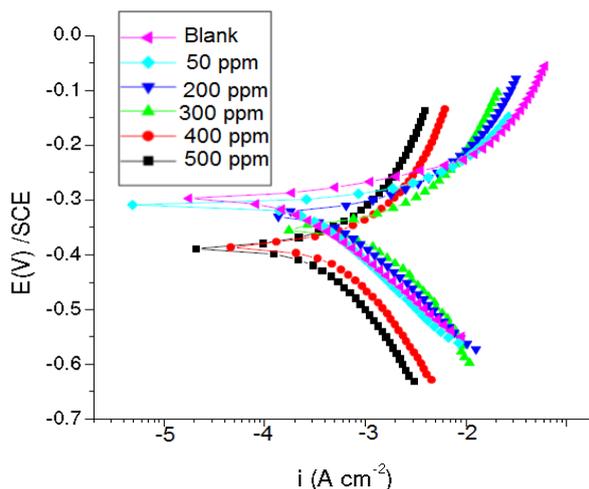


Figure 6. Polarization plots of steel electrode obtained in 0.5 H₂SO₄ solution and containing different conc. of GTEs at 303 K.

Table 4. Potentiodynamic electrochemical parameters for the corrosion of steel in 1 M HCl solution in the absence and presence of different concentration of GTEs at 303 K.

Conc.	$-E_{\text{corr}}$ mV(SCE)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	$-\beta_c$ (mV dec ⁻¹)	η_p (%)
Blank	337	0.41	213.7	-197.9	--
50	395	0.19	188.1	-213.4	52.5
200	401	0.17	188.1	-204.5	57.5

300	396	0.142	178.1	-243.4	64.5
400	387	0.11	200.8	-212.8	72.5
500	404	0.078	133.2	-206.2	80.5

These observations indicate that the green tea extract is a mixed-type inhibitor for the corrosion of carbon steel [33-36]. The results in Table 3 show that the increase in extract concentration leads to decrease in the corrosion current density (I_{corr}), but the Tafel slopes (β_a , β_c), are approximately constant indicating that the retardation of the two reactions (cathodic hydrogen reduction and anodic metal dissolution) was affected without changing the dissolution mechanism [37-39]. Also, it was found that the addition of 1M HCl is more effective than the use of 0.5 M H_2SO_4 where the inhibition efficiency was (80.5%) when using 1MHCl. This behavior is due to H_2SO_4 have H^+ ion twice as much as HCl and its effect in facilitating the corrosion process will be more than 1:1 ratio of H^+ ion conc. As in 1M HCl and 0.5 M H_2SO_4 together with competition for adsorption of inhibitor molecules, the inhibitor performance of GTEs in H_2SO_4 may be affected.

Table 5. Potentiodynamic electrochemical parameters for the corrosion of steel in 0.5 H_2SO_4 solution in the absence and presence of different concentration of GTEs at 303 K.

Conc.	$-E_{corr}$ mV(SCE)	i_{corr} (mA cm ⁻²)	β_a (mV dec ⁻¹)	$-\beta_c$ (mV dec ⁻¹)	η_p (%)
Blank	305	0.87	214	-120	--
50	337	0.66	145	-87	24.13
200	329	0.53	168	-113	39.08
300	310	0.41	176	-110	52.87
400	312	0.34	145	-119	60.91
500	311	0.26	152	-123	70.11

3.6. Electrochemical impedance spectroscopy (EIS) Measurements

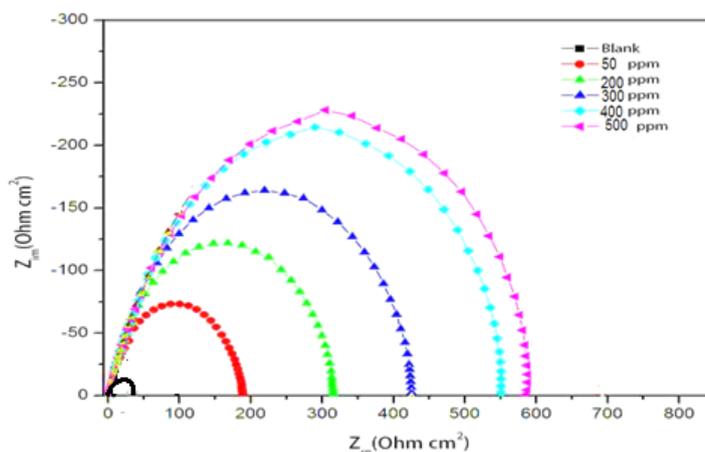


Figure 7. Nyquist plots for the carbon steel in 1 M HCl in absence and presence of different concentrations of GTEs.

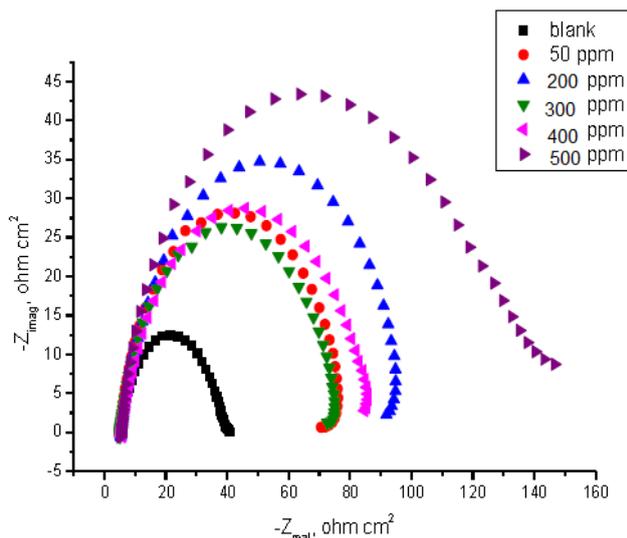


Figure 8. Nyquist plots for the carbon steel in 0.5 H₂SO₄ in absence and presence of different concentrations of GTEs.

EIS technique was applied to investigate the electrode /electrolyte interface and corrosion processes that occur on the carbon steel surface in the presence and absence of green tea extract. To ensure complete characterization of the interface and surface processes, EIS measurements were made at OCP in a wide frequency range at 303K. Fig.7, 8 shows Nyquist plots for carbon steel in 1M HCl and 0.5 M H₂SO₄ solutions at 303K in the absence and presence of different concentrations of green tea extract at the respective open circuit potential. According to act circuit theory, an impedance plot obtained for a given electrochemical system can be correlated to one or more equivalent circuit. The impedance data of the carbon steel electrode in the presence of different extract concentrations were analyzed using the equivalent circuit shown in Fig.9.

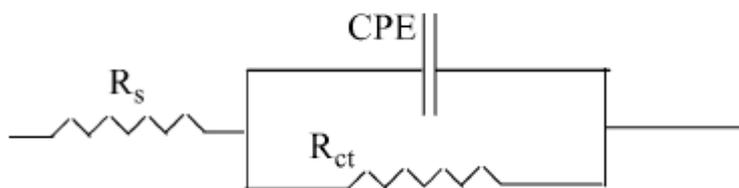


Figure 9. Suggested equivalent circuit model for the studied system

From these Nyquist plots, the difference in real impedance at lower and higher frequencies is generally considered as a charge-transfer resistance. The resistances between the metal and outer Helmholtz plane (OHP) must be equal to the R_{ct}. The adsorption of inhibitor molecules on the metal surface decreases its electrical capacity because they displace the water molecules and other ions originally adsorbed on the metal surface. This modification results in an increase of charge-transfer resistance. The R_{ct} values increased with inhibitor concentrations may suggest the formation of a protective layer on the carbon steel surface. This layer makes a barrier for mass and charge-transfer. The values of the charge-transfer resistance (R_{ct}) were obtained from the difference in real component

(Z) of impedance at lower frequencies. The double layer capacitances (Cdl) were calculated using Eq. [40].

$$C_{dl} = (2\pi f_{max} R_{ct})^{-1}$$

where f_{max} is the frequency value at which the imaginary component (Z'') of impedance is maximum. The data obtained from fitted spectra are listed in Table (6,7).

Table 6. EIS parameters for corrosion of carbon steel in 1 M HCl in absence and presence of different concentration of the GTEs.

Inhibitor	Conc.	R_{ct} (ohm cm^2)	C_{dl} ($\mu F cm^{-2}$)	η_I (%)
Absence	0.00	30	374.9	-
GTEs	50	190	358.0	47.36
	200	320	298.7	68.75
	300	430	355.8	76.74
	400	500	372.5	80.21
	500	555	326.4	81.98

Table 7. EIS parameters for corrosion of carbon steel in 0.5 M H_2SO_4 in absence and presence of different concentration of the GTEs.

Inhibitor	Conc	R_{ct} (ohm cm^2)	C_{dl} ($\mu F cm^{-2}$)	η_I (%)
Absence	0.00	40	131	-
GTEs	50	65	116	38.46
	200	70	111	42.85
	300	84	101	52.38
	400	90	81.4	55.55
	500	152	79.5	73.68

The degree of surface coverage (θ) and the inhibition efficiency (% η) was calculated from the EIS data using an equation:

$$\% \eta = \theta \times 100 = [1 - (R_{ct}^0 / R_{ct})] \times 100$$

where R_{ct} and R_{ct}^0 are the charge transfer resistances with and without the inhibitors, respectively, θ and % η are also listed in Table (6,7). By increasing the inhibitor concentration, the R_{ct} values increase and the calculated Cdl values decrease, as it can be seen from Table (6,7), the Cdl values tend to decrease with the increase of the concentration of green tea extract in 1 M HCl solution and 0.5 M H_2SO_4 . The decrease in the Cdl, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that green tea extract molecules function by adsorption at the metal/solution interface. The inhibition efficiencies calculated from impedance data are very close to those obtained from potentiodynamic polarization measurements. The results show better agreement between measurements obtained from both techniques.

3.7 Molecular Modeling Studies

Table 8: The Electron Density Distribution of Catechin Monomers (EC, EGC, ECG and EGCG)

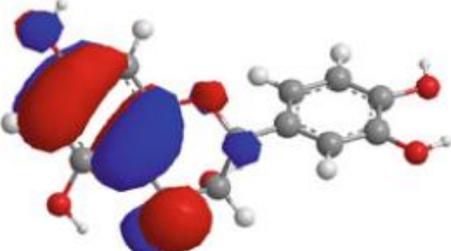
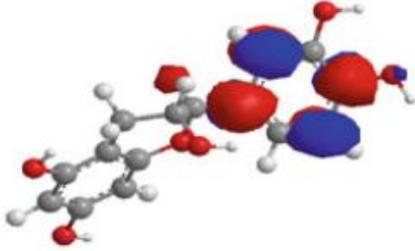
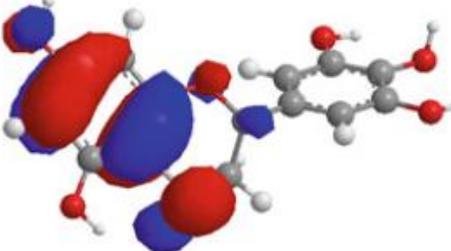
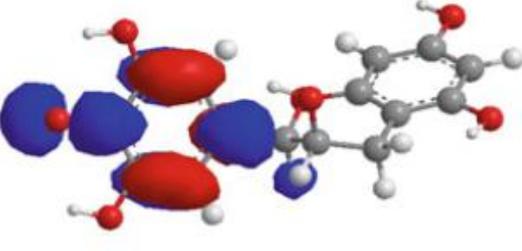
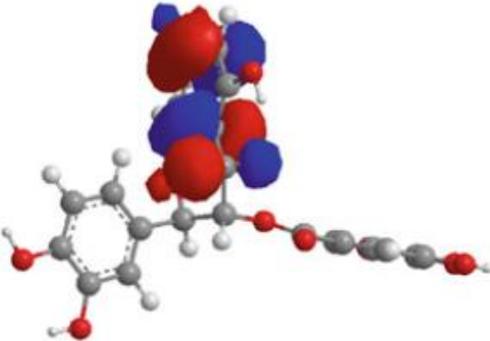
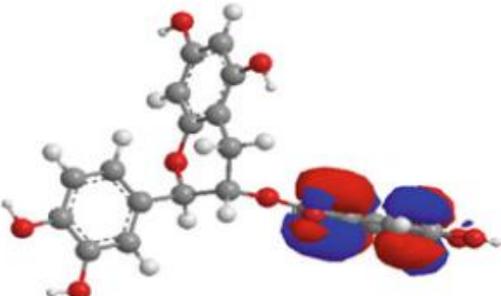
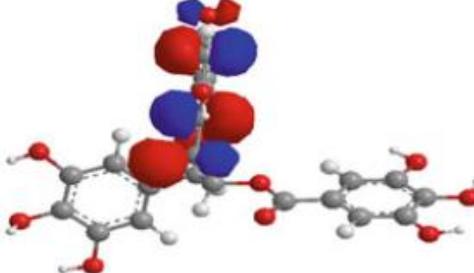
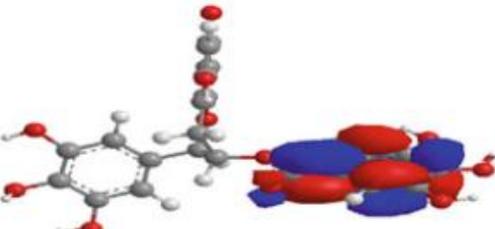
HOMO	LUMO
 <p data-bbox="443 734 528 779">(EC)</p>	 <p data-bbox="1027 719 1112 763">(EC)</p>
 <p data-bbox="432 1122 539 1167">(EGC)</p>	 <p data-bbox="1011 1115 1118 1160">(EGC)</p>
 <p data-bbox="432 1570 539 1615">(ECG)</p>	 <p data-bbox="1011 1541 1118 1585">(ECG)</p>
 <p data-bbox="416 1944 555 1989">(EGCG)</p>	 <p data-bbox="995 1951 1134 1995">(EGCG)</p>

Table 9. Quantum Parameters for Catechin Monomers

<i>Energy level</i>	<i>EC</i>	<i>EGC</i>	<i>ECG</i>	<i>EGCG</i>
<i>E HOMO (eV)</i>	-8.938	-8.941	-9.011	-9.053
<i>E LUMO (eV)</i>	-0.196	-0.185	-0.533	-0.497
ΔE (eV)	-8.742	-8.756	-8.478	-8.556

Electrochemical techniques coupled with surface analytical techniques can provide basic information on the mechanism of corrosion inhibition. A need exists for a systematic approach for the characterization of the interaction between the organic inhibitor molecule and the metal or alloy. Theoretical approaches provide useful means of analyzing these interactions. Furthermore, the quantum level calculation of molecules can explain also the mechanism of corrosion inhibition.[42] Table 8 shows the HOMO and LUMO surface images of catechin monomers viz., EC, EGC, ECG,

and EGCG. The orbitals are represented by colored lobes (red/ blue). Red represents more negative and blue represents less negative regions of electronegativity (electron density). The colored lobes also indicated the presence of p electron (electrons of p bonds) clouds over the phenyl rings. From the HOMO-LUMO images, it is obvious that the electron density was found to localize on either one of the aromatic rings and on hetero functional groups.

The HOMO-LUMO energy levels for various catechin monomers were calculated. The relevant quantum parameters are listed in Table 9. EHOMO values are often associated with the electron-donating ability of the molecule, and the high EHOMO values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low-energy molecular orbital. Increasing values of the EHOMO facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer. The ELUMO values represent the electron-acceptor ability of a molecule; lower values increases the electron accepting capacity. In addition, the energy gap (ΔE) implies high stability for the molecule in chemical reactions[42]; higher values prevent the interelectron transfer that may prefer the electron donation.[43] The green inhibitors probably are adsorbed physically over the carbon steel surface, and the interactions between the inhibitor and steel surface is probably ascribed to p-p orbital interaction.

3.7. Scanning electron spectroscopy (SEM) Measurements

The scanning electron microscope images were recorded in Fig.9 to establish the interaction of different components of the extract molecules with the metal surface after immersion for 24h in 1M HCl in the absence and presence of 500ppm of green tea extract. The images of SEM micrographs of a polished carbon steel surface Figure (9a) show the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. When the

specimen immersed in 1M HCl Figure (9b) has a rough surface covered with corrosion products and appeared like full of pits and cavities. Figure (9-c) indicates that in the presence of 500 ppm green tea extract the coverage of surface by extract components increases, which in turn results in the formation of insoluble complex on the metal surface. This indicated that the extract component molecules hinder the dissolution of iron by forming an adsorbed layer [39].

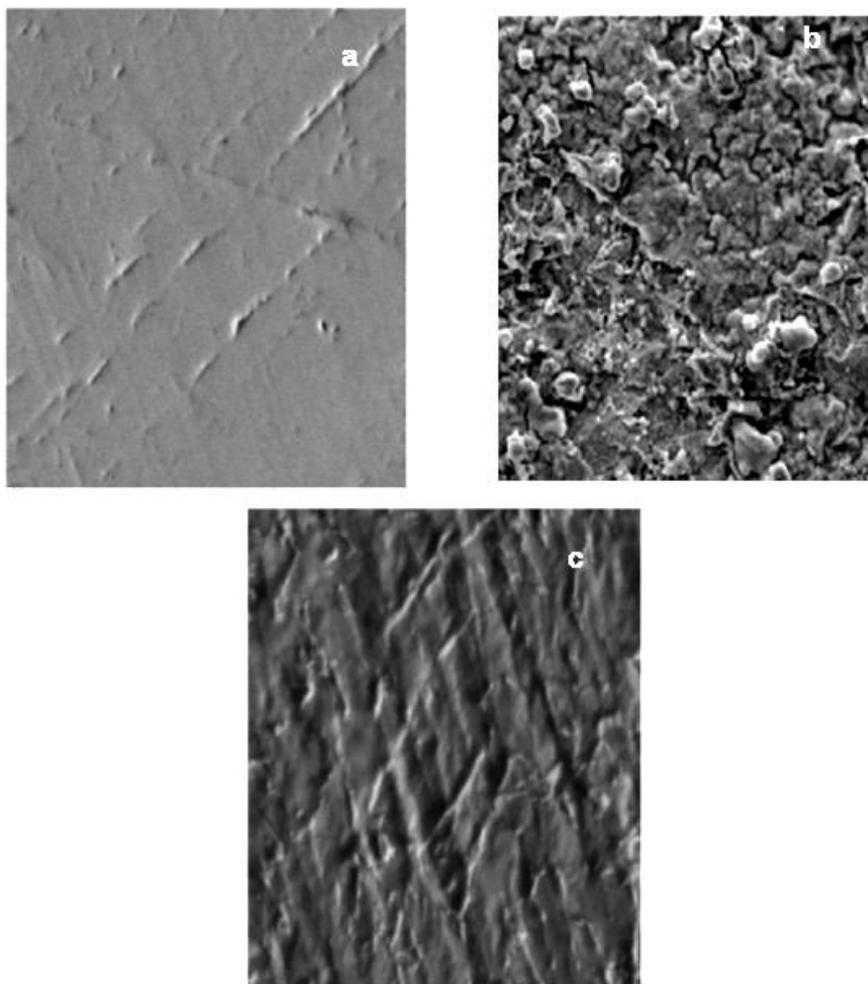


Figure 9. Scanning electron microgram of polished carbon steel (1500 X) (a)alone(b) after exposure to 1M HCl(c)after exposure to 1M HCl containing 500ppm of green tea extract.

4. CONCLUSIONS

- 1- The inhibition efficiency of green tea extracts on corrosion of carbon steel in 1MHCl solution increases by increasing the concentration of the extract. Potentiodynamic polarization measurement shows that, this extract acts as a mixed type inhibitor.
- 2- Adsorption of inhibitor molecules of the extract on carbon steel surface is found to obey Langmiur adsorption isotherm.
- 3- EIS measurement reveals that charge transfer resistance increases and the double layer capacitance decreases with increase in concentration of the extract

- 4- The SEM study confirms that the inhibition of corrosion of carbon steel is through adsorption of the components of the extract on the surface of metal and this study also confirms the results obtained from the electrochemical techniques.

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