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RESEARCH ARTICLE

Black Tea as Green Corrosion Inhibitor for Carbon Steel in 1 M Hydrochloric Acid Solutions

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Abstract

Corrosion inhibitors from natural products have been considered preferential due to the environment friendly effect. Black tea was tested as corrosion inhibitor for carbon steel in 1 M HCl solution using electrochemical frequency modulation (EFM), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) techniques. The inhibition efficiencies obtained from all techniques employed are in good agreement with each other. Potentiodynamic polarization measurement indicates that black tea acts as a mixed type inhibitors. The adsorption of the extract on carbon steel is found to obey Temkin adsorption isotherm. SEM study confirmed the adsorption of the extract molecules on the carbon steel surface.

Introduction

Acid solutions are widely used in various industries for the pickling of ferrous alloys and steel. They are also used in oil and gas production to stimulate and increase the oil and gas flow and to disqualify encrustations in production wells. Among various acids, hydrochloric acid is widely used for this purpose. Due to the extremely aggressive nature of the acidic medium the practice of inhibition is commonly used to reduce acid attack on the substrate metal. An important method of protecting metallic materials against deterioration due to corrosion is by the use of inhibitors. Organic compounds have become widely accepted as effective corrosion inhibitors in various media. Most of the organic inhibitors containing nitrogen, oxygen, sulfur atoms, and multiple bonds in their molecules facilitate adsorption on the metal surface[1-4].Although many synthetic compounds showed good anticorrosive properties, most of them are highly toxic to both human being and environment [5].The known hazardous effect of most synthetic organic inhibitors and restrictive environmental regulations have now made researchers to focus on the need to develop cheap, non-toxic and environmental friendly inhibitors likes natural products as corrosion inhibitors [6]. The natural product extracts are viewed as an incredibly rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost and biodegradable in nature. This area of research is of much importance because in addition to being environmentally friendly and ecologically acceptable. Plant products are inexpensive, readily available and renewable source of materials [7].The use of these natural products such as extracted compounds from the leaves, flowers, seeds and roots as corrosion inhibitors have been widely reported by several authors [8-16].
The aim of the present work is to find a naturally occurring, cheap and environmentally safe substance that could be used as corrosion inhibitors for carbon steel in acidic medium. In this present work, the black tea extracts were tested as green corrosion inhibitors using various electrochemical techniques. Also, surface examination was tested using scanning electron microscopy (SEM).

Experimental

Materials and solution

Carbon steel electrodes

The working electrodes were machined to have a fixed exposed surface area of 1 cm^2 from carbon steel sample with composition (weight %): 0.200 C, 0.350 Mn, 0.024 P, 0.003 Si and the balance Fe. The electrodes used were fixed with epoxy resin at one end into a Pyrex glass tubing of appropriate diameter leaving the exposed length, 1cm, to contact the solution.

Hydrochloric acid solution

The corrosive medium (1 M HCl) was prepared from a stock 8 M HCl solution by dilution with doubly distilled water from the concentrated acid solution (37 % Merck). The concentration was checked by standard solution of Na_2CO_3. 1 M HCl solutions were prepared by dilution from 8 M acid with doubly distilled water. This solution was used as a blank.

Black tea solution extract

The black tea extract was obtained directly from the tea of Lipton black tea. Black tea were soaked in methanol and left standing for 5 days. The solution was filtered and further distilled at 40°C to remove the methanol from the tea solution extracts and then concentrated to dryness. The experiment was performed in 1M HCl.

Chemical composition of black tea

The chemistry of tea is extremely complicated. Black tea contains caffeine (1–5%), with small amounts of other xanthine alkaloids (theobromine, theophylline, dirnethylxanthine, xanthine, adenine, etc.) also present. Part of the caffeine is present. They also contain large amounts of tannins or phenolic substances(5–27%).Other components present in tea include 4–16.5% fats; flavonoids (quercetin, quercitrin, rutin, etc.); anthocyanins; amino acids; triterpenoid saponin glycosides (theasaponin, isotheasaponins, and assamsaponins); sterols; vitamin C; flavour and aroma chemicals including theaflavin, thearubigin, *l*-epicatechin gallate, theogallin, theaspirone, dihydroactinidiolide, dimethyl sulfide, ionones (α- and β-), damascones (α- and β-), jasmone, furfuryl alcohol, geranial, *trans*-hexen-2-al, and others, totaling over 300 compounds; proteins; polysaccharides; pigments (carotenoids); and others. Theaflavin, thearubigin, and l-epicatechin gallate are reported to be important taste components of black tea.

Potentiodynamic polarization measurements

The electrochemical measurements were performed as follows: carbon steel rod as working electrode exposing a 1 cm^2, it was abraded with different grades of emery papers up to 1200 grit size. After that, the electrode was washed with acetone, rinsed different times with distilled water and dried.The potentiodynamic current – potential curves were recorded by changing the electrode potential automatically from -1.2 V to 0.5 V at a scan rate of 1 mVs^{-1}. The degree of surface coverage (θ) and inhibition efficiency (η) were calculated using eq. (1):

$$\% \eta = \theta \times 100 = [1-(I/ I^\circ)] \times 100 \quad (1)$$

Where I° and I are the current densities in the absence and presence of the extract, respectively.

Electrochemical frequency modulation (EFM)

EFM as a novel technique for online corrosion monitoring was proposed by Bogaerts et al [17, 18]. In this technique, current responses due to a potential perturbation by one or more sine waves are measured at more frequencies than the frequency of the applied signal, for example at zero harmonic and Intermodulation frequencies. EFM can be used successfully for corrosion rate measurements under various corrosion conditions. EFM experiments were performed with applying potential perturbation signal with amplitude 10 mV with two sine waves of 2 and 5 Hz. The choice for the frequencies of 2 and 5 Hz was based on three arguments [17].The larger peaks were used to calculate the corrosion current density (I_{corr}), the Tafel slopes (β_c and β_a) and the causality factors CF-2 and CF-3 [19, 20].

Electrochemical impedance spectroscopy (EIS)

Electrochemical impedance spectroscopy was performed at corrosion potentials, E_{corr}, over a frequency range of 10^5Hz to 0.2 Hz with a signal amplitude perturbation of 5 mV. Experiments were always repeated at least three times.

All the electrochemical measurements were carried out in a conventional three-electrode glass cell with a platinum counter electrode and a saturated calomel electrode (SCE) as a reference electrode. The cell was kept at a constant temperature (25± 1^oC).

All electrochemical measurements (potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM)) were carried out using Gamry Potentiostat/Galvanostat/ZRA (model PCI4/300) with a Gamry framework system based on ESA400. Gamry applications include software DC105 for potentiodynamic polarization, EIS300 for EIS measurements and EFM140 for EFM measurements; computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data.

Scanning electron microscopy

The carbon steel specimen immersed in different test solutions for one day, then taken out, rinsed with double distilled water and dried then subjected to the surface examination. The surface morphology measurements of the carbon steel surface were carried out using scanning electron microscopy (SEM) Model HITACHI S-3000H.

Results and discussion

Potentiodynamic polarization measurements

The potentiodynamic polarization curves of carbon steel immersed in 1M HCl in the absence and presence of black tea extract are shown in Figure (1). It is clear from this Figure that both anodic metal dissolution and cathodic H_2 reduction reactions were inhibited when the black tea extract was added to 1 M HCl. The corrosion parameters such as corrosion potential ($E_{corr.}$), anodic and cathodic Tafel slopes βa, and β_c, respectively, corrosion current (I_{corr}) and corrosion rate ($R_{corr.}$) values were calculated and are given in the Table (1). The corrosion potential is almost unchanged. 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. These observations indicate that the black tea extract is a mixed-type inhibitor for the corrosion of carbon steel in 1 M HCl [21-24]. The results in Table (1) 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) were affected without changing the dissolution mechanism [25-27]

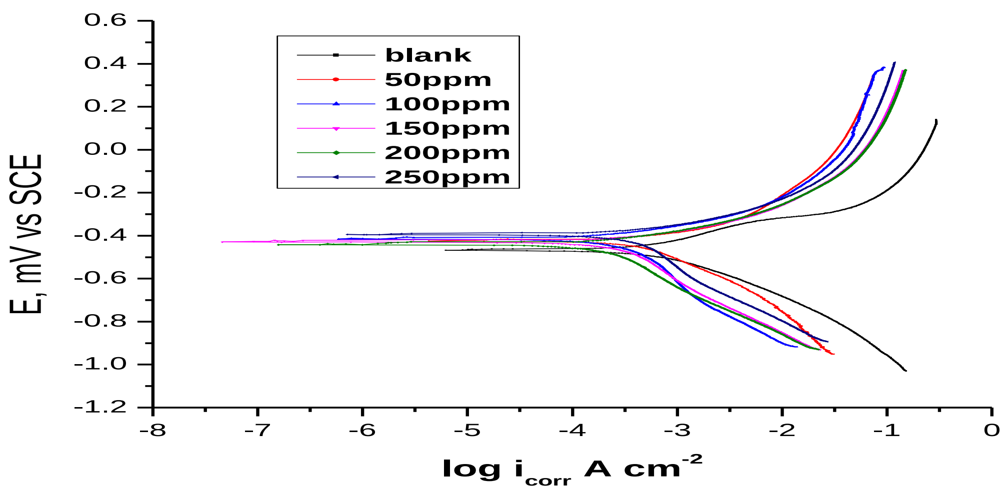

Figure 1.Potentiodynamic polarization curves for carbon steel in 1 M HCl solution in the absence and presence of different concentrations of black tea extract at 298 K

Table1.Electrochemical parameters of carbon steel corrosion in 1 M HCl solution in the absence and presence of different concentrations of black tea extract at 298 K

Conc., ppm	$-E_{Corr}$ mVvs.SCE	$I_{orr.}$ $mAcm^{-2}$	β_c, mV dec^{-1}	β_a, mV dec^{-1}	R_P	% η	θ	$R_{corr.}$ mmy^{-1}
blank	440	0.565	347.3	301.7	60.20			6.55
50	424	0.449	330	288	74.47	20.5	0.205	5.2
100	420	0.350	347.8	316	634	38.1	0.381	4.06
150	419	0.189	300.4	308	1225	66.5	0.665	2.19
200	430	0.165	354.3	306.7	1944	70.8	0.708	1.91
250	395	0.158	204	255.3	2370	72.0	0.720	1.83

Electrochemical impedance spectroscopy (EIS) Measurements

EIS technique was applied to investigate the electrode /electrolyte interface and corrosion processes that occur on carbon steel surface in the presence and absence of black tea extract. To ensure complete characterization of the interface and surface processes, EIS measurements were made at OCP in a wide frequency range at 298K. Figure (2) shows Nyquist plots for carbon steel in 1M HCl solution at 298K in the absence and presence of different concentrations of black tea extract at the respective open circuit potential. It is clear from the Figure (2) that the diameter of the semicircle increases with the increase in extract concentration in the electrolyte, indicating an increase in corrosion resistance of the material [28].The Bode plot, Figure (3) shows resistive region at high frequencies and capacitive region at intermediate frequencies but do not show a clear resistive region (horizontal line and a phase angle =0) at low frequencies. These plots show two overlapped phase maxima at intermediate and low frequencies. According to act circuit theory, an impedance plot obtained for a given electrochemical system can be correlated to one or more equivalent circuits. The impedance data of the carbon steel electrode in the presence of different extract concentrations were analysed using the equivalent circuit shown in Figure (4). From these Nyquist plots, the difference in real impedance at lower and higher frequencies is generally considered as 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 inhibitors 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 ($Z^{\backslash}$) of impedance at lower frequencies. The double layer capacitances (C_{dl}) were calculated using Eq. (2) [29].

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

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 (2).The degree of surface coverage (θ) and the inhibition efficiency (% η) was calculated from the EIS data using equation (3):

$$\% \eta = \theta \times 100 = [1-(R^{\circ}_{ct}/ R_{ct})] \times 100 \quad (3)$$

where R_{ct} and R°_{ct} are the charge transfer resistances with and without the inhibitors, respectively, θ and % η are also listed in Table (2). By increasing the inhibitor concentration, the R_{ct} values increase and the calculated C_{dl} values decrease, as it can be seen from Table (2), the C_{dl} values tend to decrease with the increase of the concentration of black tea extract in1 M HCl solution. The decrease in the C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that black 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 the good agreement between measurements obtained from both techniques.

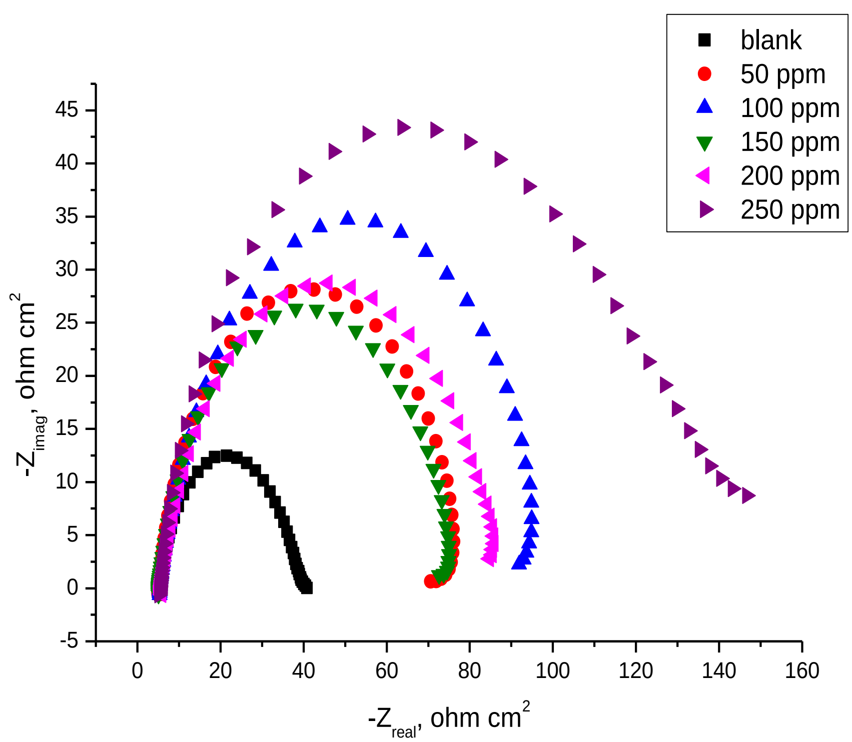

Figure 2.Nyquist plots for carbon steel in 1 M HCl in absence and presence of different concentrations of black tea extract

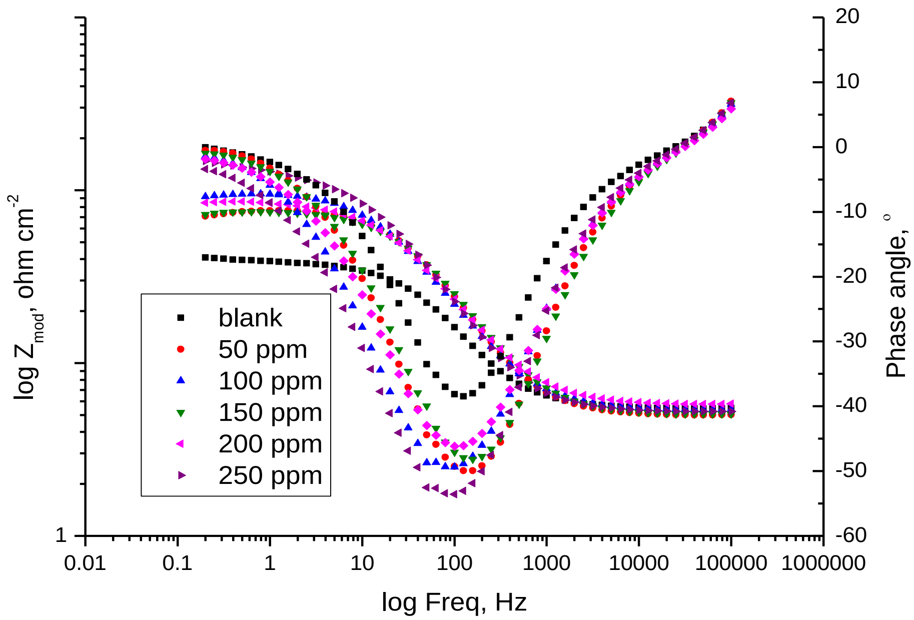

Figure 3.Bode plots for carbon steel in 1 M HCl in absence and presence of different concentrations of black tea extract

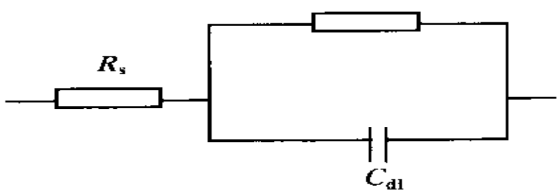

Figure 4.Equivalent circuit proposed to fit the EIS experimental data

Electrochemical frequency modulation (EFM) measurements

Electrochemical frequency modulation (EFM) technique has many features [30-32]. It is a non-destructive corrosion measurement technique that can directly give values of the corrosion current without prior knowledge of Tafel constants. Like EIS, it is a small signal ac technique. Unlike EIS, however, two sine waves (at different frequencies) are applied to the cell simultaneously. Because current is a non- linear function of potential excitation. The current response contains not only the input frequencies, but also contains frequency components which are the sum, difference, and multiples of the two input frequencies. The two frequencies may not choose at random. They must both be small, integer multiples of a base frequency that determines the length of the experiment.

Table2.Impedance parameters for the corrosion of carbon steel in 1MHCl containing different concentrations of black tea

Conc., ppm	R^*_{ct}, Ω cm^{-2}	R_{ct}, Ω cm^{-2}	Y° x 10^4 μ$Ω^{-1}s^n$	C_{dl}, μF cm^{-2}	θ	% η
blank	5.459	33.67	3.32	131	--------	--------
50	5.028	70.49	1.98	116.0	0.522	52.2
100	4.988	71.35	1.79	111.0	0.528	52.8
150	5.741	80.7	2.70	101.0	0.583	58.3
200	5.35	92.23	2.66	81.4	0.635	63.5
250	5.167	128.4	2.53	79.0	0.738	73.8

extract

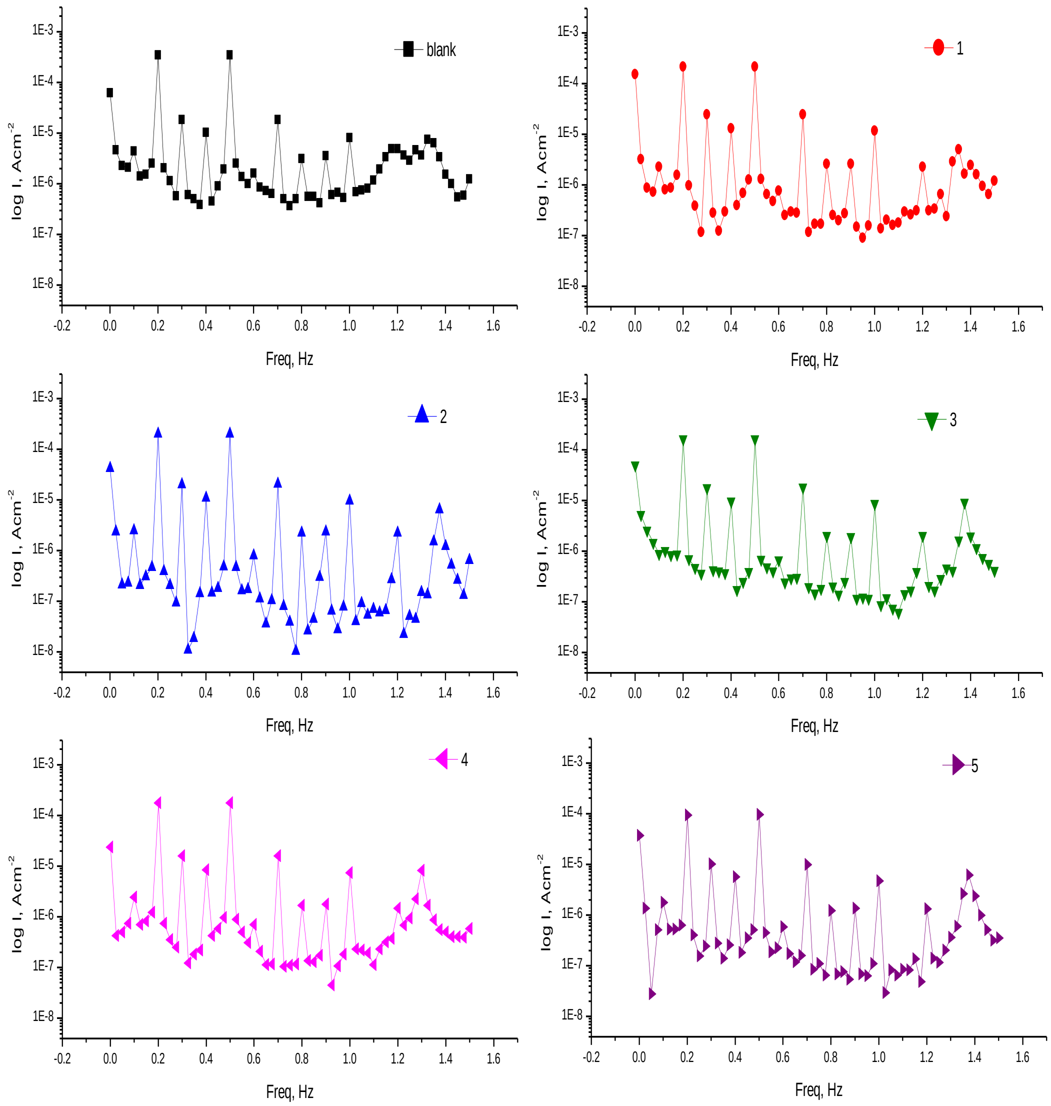

Figure 5.Intermodulation spectra recorded for carbon steel electrode in 1MHCl solutions in the absence and presence various concentrations of black tea extract [(1) 50 ppm, (2) 100 ppm, (3) 150 ppm, (4) 200 ppm, (5) 250 ppm]

The calculated electrochemical parameters at different concentrations of extract at 25°C (I_{corr}, β_a, β_c, CF-2, CF-3and % η_{EFM}) are given in Table (3).Figure(5) represents the EFM Intermodulation spectra(spectra of current response as a function of frequency) of carbon steel in 1 M HCl devoid of and containing different concentrations of black tea extract. The inhibition efficiency, % η_{EFM} and the degree of surface coverage (θ) of black tea extract was calculated using equation (4):

$$\% \eta = \theta \times 100 = [1 - (I_{corr}/I^{\circ}_{corr})] \times 100 \quad (4)$$

Where I°_{corr} and I_{corr} are corrosion current density in the absence and presence of black tea extract. The causality factors are calculated from the frequency spectrum of the current response. If the causality factors differ significantly from the theoretical values of 2.0 and 3.0, then it can be deduced that the measurements are influenced by noise. If the causality factors are approximately the predicted values of 2.0 and 3.0, there is a causal relationship between the perturbation signal and the response signal. Then the data are assumed to be reliable [33].The obtained causality factors in Table (3) indicate that the measured data are of good quality. From the results of Table (3), it can be seen that by increasing the concentration of extract to the medium the corrosion current density (I_{corr}) decreases, indicating that the extract inhibits the 1 M HCl corrosion of carbon steel through adsorption. The calculated inhibition efficiency η_{EFM}% enhances with increasing black tea extract concentration.

Table 3.Electrochemical kinetic parameters obtained by EFM technique for carbon steel in 1 M HCl in the absence and presence of different concentrations of black tea extract

Conc., ppm	I_{corr} , μA cm^{-2}	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	θ	% η	$R_{corr.}$ mmy^{-1}
Blank	585.5	94	137	1.993	2.791	-------	-------	6.79
50	465.5	95	292	2.000	2.440	0.205	20.5	5.4
100	403.3	93	221	1.971	3.224	0.311	31.1	4.68
150	372.3	99	295	1.962	3.198	0.364	36.4	4.32
200	368.3	98	214	2.018	2.808	0.371	37.1	4.27
250	163.2	82	171	1.924	3.021	0.721	72.1	1.89

Scanning electron spectroscopy (SEM) Measurements

The scanning electron microscope images were recorded in Figure (6) to establish the interaction of different components of the extract molecules with the metal surface after immersion for 24h in 1M HCl in absence and presence of 250ppm of black tea extract. The images of SEM micrographs of a polished carbon steel surface Figure (6a) shows the smooth surface of the metal. This shows the absence of any corrosion products or inhibitor complex formed on the metal surface. The specimen when immersed in 1M HCl Figure (6b) has rough surface covered with corrosion products and appeared like full of pits and cavities. Figure (6-c) indicates that in the presence of 250 ppm black 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 components molecules hinder the dissolution of iron by forming adsorbed layer [34].

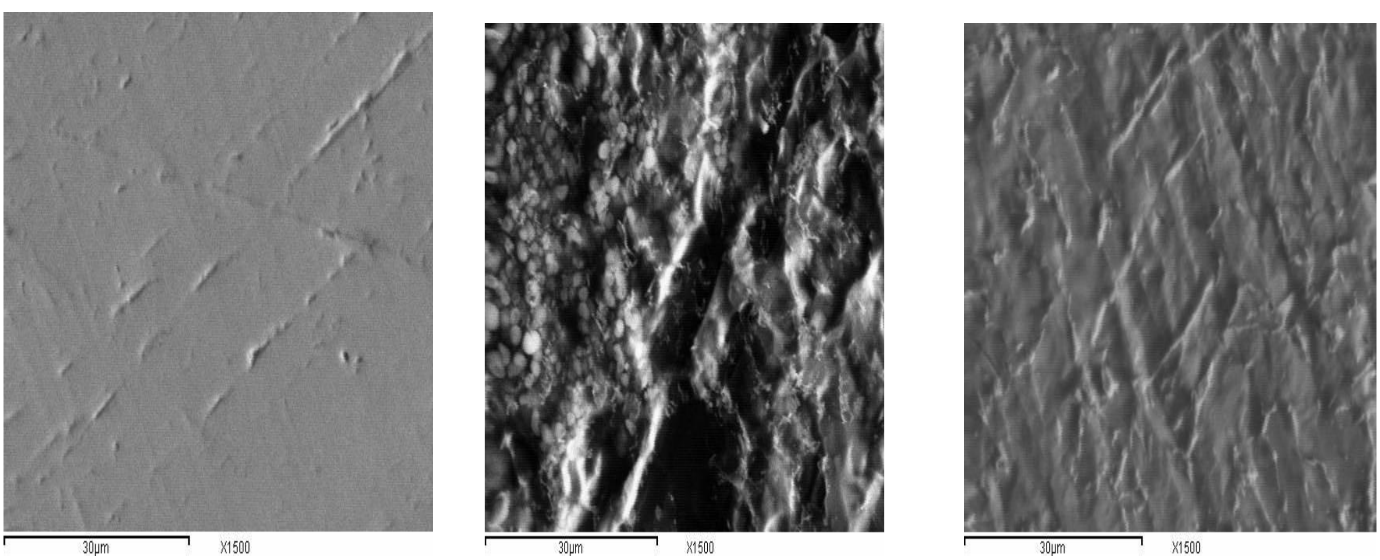

Figure 6.Scanning electron microgram of polished carbon steel (1500x) (a)alone(b) after exposure to 1M HCl(c)after exposure to 1M HCl containing 250ppm of black tea extract

Adsorption isotherms

To understand the mechanism of corrosion inhibition, the adsorption behavior of the adsorbate on the metal surface must be known [34].Figure (7) demonstrates the variation of the degree of the surface coverage with bulk concentration of the additives by the potentiodynamic technique. The obtained line in θ-log C of coordinates Temkin's approach was considered [33].The Temkin isotherm has the formula given in Eq (5):

$$K_{ads}C=\exp(-2a\theta) \quad (5)$$

where a is a molecular interaction parameter depending upon molecular interactions in the adsorption layer and the degree of heterogeneity of the surface, C is the concentration of adsorbed substance in the bulk or the solution and K_{ads} is the modified equilibrium constant of the adsorption process. It is well known that the equilibrium constant of adsorption (K_{ads}) is related to the standard adsorption free energy (ΔG^o_{ads}) and can be calculated by the following equation [34]:

$$K_{ads} = 1/55.5 \exp [-\Delta G^o_{ads}/RT] \quad (6)$$

A plot of θ against log C for all concentrations of extract is shown in Fig. 7 gives a straight line relationship in all cases which suggests that the adsorption of the studied extract on the carbon steel surface follow Temkin adsorption isotherm. The strong correlation (R^2=0.996) for the Temkin adsorption isotherm plot confirmed the validity of this approach.

Table (4) shows the calculated values of molecular interaction a, equilibrium constant of adsorption process, K_{ads} and free energy (ΔG^o_{ads}) obtained from Temkin plot. The value of a are positive shows that attraction exists in adsorption layer [35].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 [36].The calculated values of ΔG^o_{ads}, for the investigated extract with the metal surface is −18.8 kJ mol^{-1}, which means that the inhibitor is physically adsorbed through electrostatic interaction [37].

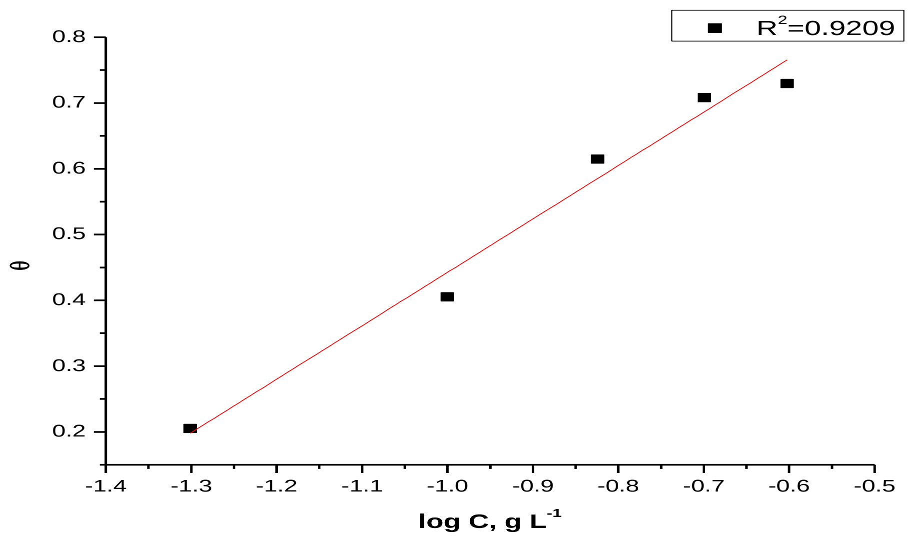

Figure 7.Effect of black tea concentration on the degree of surface coverage for carbon steel in 1 M HCl from different techniques

Table 4.Equilibrium constant and adsorption free energy of the investigated extract adsorbed on C-steel surface

	Temkin adsorption isotherm		
Black tea extract	a	$K_{ads} \times 10^{-3}$, g^{-1} L	$-\Delta G^\circ_{ads}$, kJ mol^{-1}
	2.8	35.1	18.8

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 [38]. 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. In fact, adsorption process can occur through the replacement of solvent molecules from the metal surface by ions and molecules accumulated near the metal /solution interface. Ions can accumulate at the metal /solution interface in excess of those required to balance the charge on the metal at the operating potential. 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 [39].Generally, two modes of adsorption were considered. In one mode, the neutral component molecules of black tea extract can be adsorbed on the surface of carbon steel through the chemisorption mechanism, involving the displacement of water molecules from the carbon steel surface and the sharing electrons between the heteroatoms and iron. The inhibitor molecules can also adsorb on the carbon steel surface based on donor –acceptor interactions between π –electrons of the aromatic/heterocyclic ring and vacant d-orbitals of surface iron. In another mode since it is well known that the steel surface bears the positive charge in acidic solutions [39], so it is difficult for the protonated component molecules extract to approach the positively charged carbon steel surface (H_3O/metal interface) due to electrostatic repulsion. Since chloride ions have smaller degree of hydration, thus they could bring excess negative charges in the vicinity of the interface and favor more adsorption of the positively charged inhibitor molecules and the negatively charged metal surface. Tea component molecules contain many compounds such as, caffeine, alkaloids, phenolic substances, tannins, fats, flavonoids amino acids sterols and vitamin C, so black tea extract possess several heteroatoms containing active constituents, and therefore there may be a synergism between the molecules accounting for the good inhibition efficiencies.

Conclusions

1- The inhibition efficiency of black tea extract on corrosion of carbon steel in 1MHCl solution increases by increasing the concentration of extract. Potentiodynamic polarization measurement show that , this extract acts as mixed type inhibitor

2- Adsorption of inhibitor molecules of extract on carbon steel surface is found to obey Frumkin adsorption isotherm.

3- EFM appears capable of monitoring the corrosion inhibition of carbon steel in 1M HCl solution in the presence of black tea extract. Corrosion current densities (I_{corr}) obtained using this technique was in good agreement with those obtained from Tafel extrapolation technique. In addition the Causality factors were good internal check for verifying the validity of data obtained by this technique

4- EIS measurement reveals that charge transfer resistance increases and the double layer capacitance decreases with increase in concentration of the extract

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

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