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RESEARCH ARTICLE

Tobacco Plant Extracts as Save Corrosion Inhibitor for Carbon Steel in Hydrochloric Acid Solutions

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Abstract

The inhibitive action of the aqueous extract of tobacco towards the corrosion of C-steel in HCl solution was investigated. The inhibition efficiency was measured using weight loss, potentiodynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. The surface morphology of carbon steel was also studied. It was found that the addition of the extract reduces the corrosion rate of C-steel and hence increases the inhibition efficiency. The inhibitive effect of the tested extract was discussed in view of adsorption of its components on the steel surface. The adsorption of the extract components on the C-steel surface follows Langmuir adsorption isotherm. The thermodynamic functions of dissolution and adsorption processes were calculated and discussed. The inhibition efficiency increases as the temperature is increased. The presence of extract decreases the activation energy of the corrosion process.

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Introduction

Iron and its alloys which are widely used in a lot of industrial processes could corrode during these acidic applications particularly with the use of hydrochloric and sulphuric acid. Acid solutions are widely used in industry [1-4]. The steel corrosion in acidic solutions receives considerable concern. Corrosion inhibitors are widely used in industry to reduce the corrosion rate of metals and alloys which is present in contact with aggressive environments. Corrosion inhibitors are used to reduce the corrosion rates of metallic materials in acidic media [5]. Inhibitors are compounds that control, reduce or prevent reactions between a metal and its surroundings when added to the medium in small quantities [6]. The development of corrosion inhibitors is based on organic compounds containing nitrogen, oxygen, sulfur atoms, and multiple bonds in the molecules that facilitate adsorption on the metal surface [7,8].The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface, on the type of corrosive medium and on the chemical structure of the inhibitor [9, 10] in the recent years, there is an increasing awareness of environment and green chemistry. Therefore, many works were conducted to use the environment friendly substances, as corrosion inhibitors, instead of the harmful synthetic chemicals [11-15]. It has been reported [16-18] that plants of natural origin has organic compounds such as amino acids, tannins and alkaloid which have inhibitive effect.

There are numerous advantages of using tobacco extract as a metallic corrosion inhibitor. Initially, tobacco is a natural, renewable, environmentally benign, and relatively inexpensive source. In addition to leaves, tobacco waste (stems, twigs, etc.) can be used for corrosion inhibitor extraction. The active constituents in tobacco can be readily, inexpensively, and commercially extracted in a simple operation using only water as an extraction medium. In addition, the corrosion inhibitors in tobacco constituents can be extracted in a variety of additional or alternative media, as in steam, organic solvents, acids, etc.

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, tobacco plant extracts were

tested as green corrosion inhibitor using chemical technique and electrochemical techniques. Also, surface examination using scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) were tested.

Material and Methods

Tobacco plant extracts

The tobacco plant extract was obtained directly from the tobacco leaves. The dried plant sample was grounded to give 250 grams which was extracted by using dichloromethane as solvent three times. Then filtered and evaporated to give dichloromethane extract and then concentrated to dryness which yield nearly about 5 gm.

Chemical composition of tobacco

The chemistry of tobacco is extremely complicated. Tobacco plants produce ~4,000 chemical compounds—including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen-containing compounds, and alkaloids—that may exhibit electrochemical activity, such as corrosion inhibition. Compounds leached from tobacco with water have the ability to inhibit metallic corrosion [19].

Materials and solutions

Carbon steel coupons (1x1x0.2) cm size were used for weight loss measurements. Electrodes for electrochemical studies were embedded in araldite with an exposed surface area of $1cm^2$. The electrodes were abraded with different grades of emery papers (up to 1200 grit size), degreased with acetone and rinsed with bidistilled water. 1 M HCl solution was used as a test (corrosive) electrolyte, and was prepared by diluting concentrated HCl (37%) to a required concentration using bidistilled water.

Weight loss tests

Weight loss measurements were carried out in glass beakers containing 100 mL solution without and with different concentrations of tobacco plant extract in 1 M HCl solution. The weight loss tests were performed on coupons made of carbon steel. The weight loss tests were performed by triplicate at temperatures of 25, 30, 35, 40 and 45°C for 3 hrs, metallic coupons were then removed, washed, dried and weighed before and after immersion.

Electrochemical measurements

Potentiodynamic, EIS and EFM studies, a cylindrical rod embedded in araldite with exposed surface area of 1 cm^2, was used. The electrodes were treated as before. The experiments were carried out in 100 ml of solution containing various tobacco extract concentrations in1 M HCl at 25^0C with the exposure time of 30 min (or until a steady-state open circuit potential was obtained). The electrochemical cell was assembled in a 250 ml round-bottomed flask consisting of carbon steel working electrode; the platinum electrode of approximately 1 cm^2 diameter worked as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Tafel polarization curves were determined by polarizing to ±250 mV with respect to the free corrosion potential (E vs. SCE) at a scan rate of 0.5 mV/s. A 5 mV peak to-peak sine wave over ac frequency range extending from 100 kHz to 10 mHz was used for the impedance measurements.

The electrochemical measurements were carried out using Gamry Potentiostat/Galvanostat /ZRA (model PCI4-G750) with a Gamry framework system based on ESA400. Gamry applications include software 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. Each experiment was repeated at least three times to check the reproducibility. All tests have been performed in dearated solutions under unstirred conditions at 25°C.

Surface examination

The surface films were formed on the c-steel specimens by immersing them in inhibitor solutions for a period of 5 h. After the immersion period, the specimens were taken out, dried and the nature of the film formed on the surface of the metal specimen was analyzed by EDX and SEM techniques. Examination of C-steel surface after 5 h exposure to the 1 M HCl solution without and with inhibitor was carried out by (JOEL 840, Japan) scanning electron microscope. Rough elemental analyses for the exposed surface were conducted by EDX technique.

Result and Discussion

Weight loss measurements

Fig.1. shows the weight loss-time curves for different concentrations of tobacco extract in 1 M HCl. The corrosion rate and inhibition efficiency for carbon steel in 1 M HCl solution at 25, 30, 35,40and 45^{0}C in the absence and presence of tobacco extract are given in Table1. It is observed that corrosion rate of carbon steel decreased on increasing tobacco extract concentration (till 300 ppm). This behavior could be attributed to the increase in adsorption of tobacco extract at the metal/solution interface on increasing its concentration. It is indicated that inhibition efficiency of carbon steel increases with the increase of tobacco extract concentration up to 94.2% at 25^{0}C. The inhibition efficiency (IE) and the surface coverage (θ were calculated using Eq. (1):

$$\% IE = \theta \times 100 = [1- (W_1/W_2)] \times 100 \quad (1)$$

Where W_1 and W_2 are the weight losses in the presence and absence of tobacco plant extract, respectively

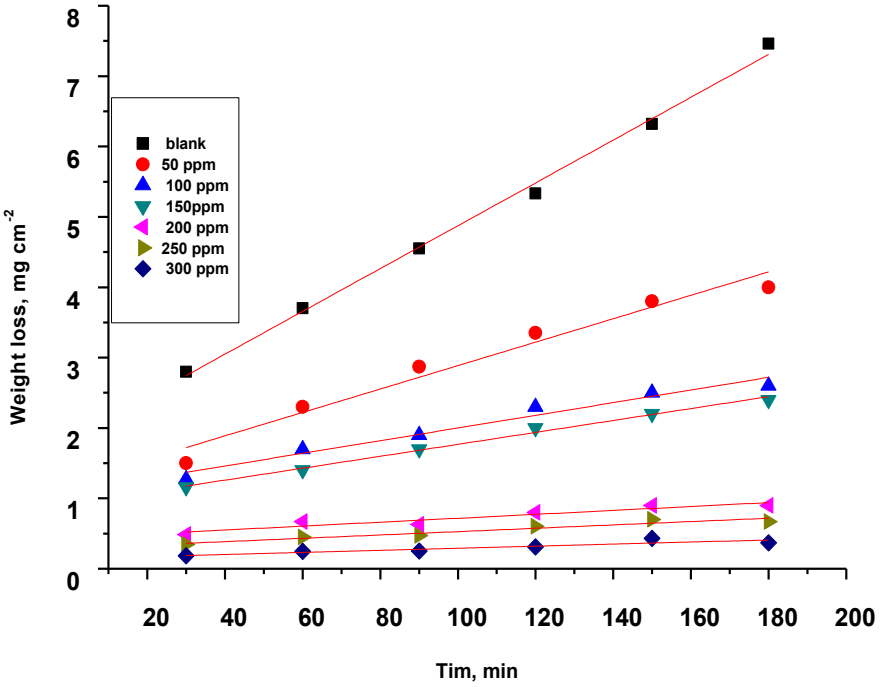


Figure 1: Weight loss-time curves of carbon steel in 1M HCl in the absence and presence of different concentrations of tobacco extract at 25°C

Table1: Data of weight loss measurements for carbon steel in 1M HCl solution in the absence and presence of different concentrations of tobacco extract 25°C

Conc., ppm	C.R., (mg cm^{-2}min^{-1})	θ	% IE
0.00	0.0444	-------	-------
50	0.0275	0.437	43.7
100	0.0179	0.597	59.7
150	0.01667	0.625	62.5
200	0.0067	0.849	84.9
250	0.0050	0.887	88.7
300	0.0026	0.942	94.2

3.2.

Potentiodynamic polarization curves

Figure 2 presents the anodic and cathodic polarization curves of C-steel in 1 M HCl solution in the absence and presence of tobacco extract. It can be seen that the corrosion potential remains almost constant in the presence of tobacco extract (data shown in Table 2). These polarization curves demonstrate, as a first sight, that in presence of tobacco extract the cathodic and anodic branches of the polarization curves are shifted towards lower currents to very similar extent, probably as a consequence of the blocking effect of the adsorbed tobacco extract

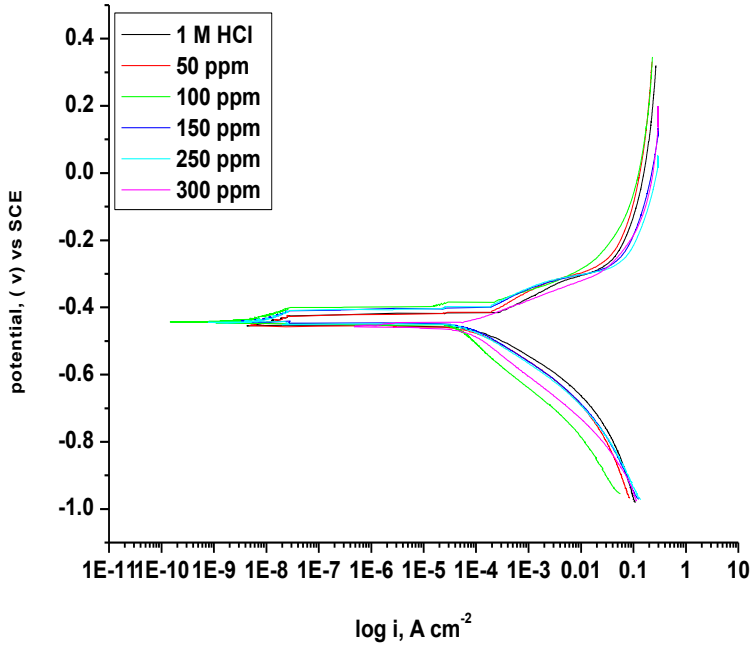


Figure 2: Potentiodynamic polarization for corrosion of carbon steel in 1 M HCl in the absence and presence of different concentrations of tobacco extract t at 25°C

The % IE and degree of surface coverage (θ) were calculated from Equation 2:

$$\% IE = \theta \times 100 = [1 - (i_{corr}/ i_{corr})] \times 100 \quad (2)$$

Where i_{corr} and i_{corr} are the corrosion current densities uninhibited and inhibited solution, respectively.

It is observed that the current density decreased when the tobacco extract concentration is increased. The slopes do not display an order with tobacco extract concentration; this feature indicates that corrosion inhibitors have no effect on both hydrogen evolution and iron dissolution, it appears that inhibition occurred by a blocking mechanism on the available metal spaces [20,21]. These results indicated that the presence of tobacco extract inhibited iron oxidation and in a lower extent hydrogen evolution, consequently these compounds can be classified as mixed corrosion inhibitors, as electrode potential displacement is lower than 85 mV in any direction [22].

Table 2: Potentiodynamic data of carbon steel in 1 M HCl in the presence and absence of different concentrations of tobacco extract at 25 ^{0}C

Conc., ppm	$-E_{corr}$, mVvs. SCE,	i_{corr} µA cm^{-2}	$-\beta_c$, $mVdec^{-1}$	β_a, $mVdec^{-1}$	θ	% IE	R, mmy^{-1}
Blank	456	1.260	28.0	16.6	---	---	576.1
50	455	0.430	30.9	23.3	0.659	65.9	71.0
100	456	0.360	48.4	48.4	0.714	71.4	38.9
150	456	0.042	28.4	22.1	0.966	96.6	20.8
200	446	0.029	51.5	38.7	0.976	97.6	15.3
250	448	0.021	33.5	47.6	0.983	98.3	12.2

300	441	0.015	36.7	33.4	0.988	98.8	11.0

Electrochemical impedance spectroscopy measurements

Figure 3 shows Nyquist plots of steel obtained in 1 M HCl solution in the absence and presence (0-300 ppm) of tobacco extract. It is apparent from Fig. 3, that the Nyquist plots of carbon steel in uninhibited and inhibited solutions show a semicircular shape. Although the appearance of Nyquist plots remained the same, their diameter increased after the addition of tobacco extract to the corrosive solution [23]. The Nyquist plots were not perfect semicircles as expected from the theory of EIS. The Nyquist plots obtained in the real system represent a general behavior where the double layer on the interface of metal/solution does not behave as a real capacitor. As for the depressed semicircle at high frequencies, Mansfield et al. [24, 25] have suggested an exponent n in the impedance function as a deviation parameter from the ideal behavior. By this suggestion, the capacitor in the equivalent circuit can be replaced by a so-called constant phase element (CPE) that is a frequency dependent element and related to surface roughness. The Nyquist plots are analyzed in terms of the equivalent circuit composed with classic parallel capacitor and resistor (shown in Figure 4) [26] the impedance of a CPE is described by the equation (3):

$$Z_{CPE} = Y_0^{-1} (j\omega)^{-n} \quad (3)$$

Where Y_0 is the magnitude of the CPE, j is an imaginary number, ω is the angular frequency at which the imaginary component of the impedance reaches its maximum values and n is the deviation parameter of the CPE: $-1 \leq n \leq 1$. The values of the interfacial capacitance C_{dl} can be calculated from CPE parameter values Y_0 and n using equation 4:

$$C_{dl} = Y (\omega_{max})^{n-1} \quad (4)$$

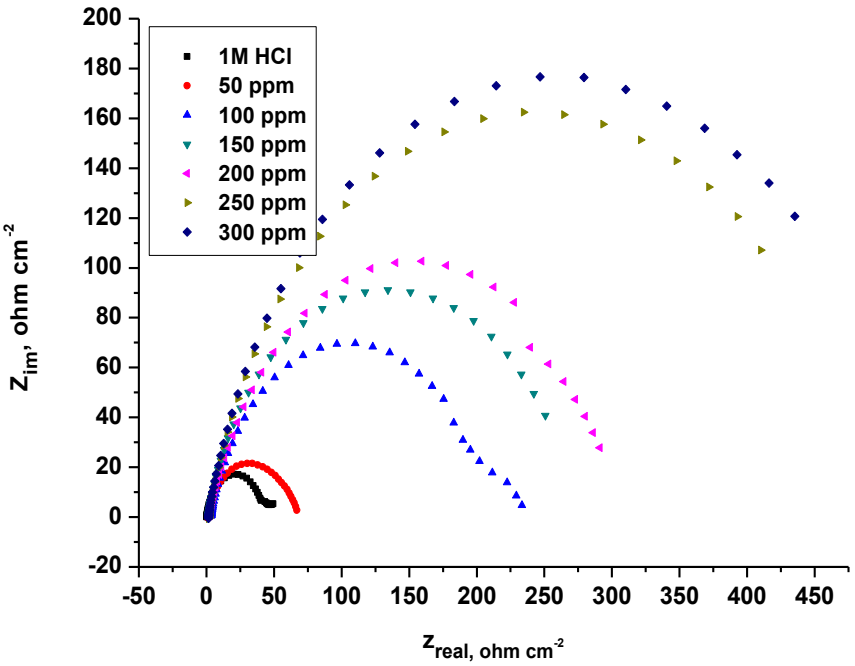


Figure 3: Nyquist plots for carbon steel in 1M HCl at different concentrations of tobacco extract at 25°C

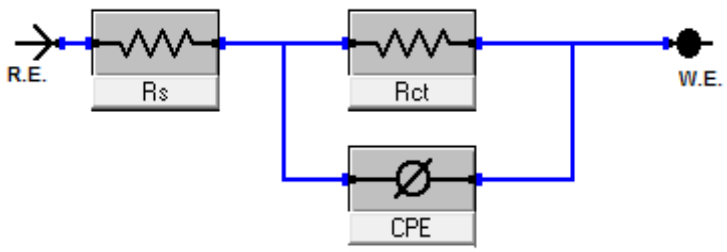


Figure 4: Electrical equivalent circuit used to fit the impedance data.

The R_{ct} values are always higher for higher tobacco extract concentrations than the blank value, revealing the resistance towards the charge transfer reaction, via corrosion reaction. The lower C_{dl} values (Table 3) from the blank as the concentration of the tobacco extract increases confirm the enhancement of adsorption of the inhibitor on the metal surface. The decrease in C_{dl} is attributed to an increase in thickness of the electronic double layer due to adsorption [27]. The adsorption is due to the electronegative hetero atoms present in the organic constituents of the extract on the electropositive metal surface.

Table 3: EIS data of carbon steel in 1 M HCl and in the presence of different concentrations of tobacco extract at 25° C

Conc., ppm	R_S Ω m^2	Y $\mu\Omega^{-1}$ s^n cm^{-2}	n	R_{ct} Ω cm^2	C_{dl} μF cm^{-2}	θ	IE_{EIS} %
Blank	216.5	634.1	0.854	45.12	345.38	----	---
50	1.34	718.5	0.816	62.5	354.1	0.278	27.8
100	3.37	292.2	0.792	198.1	135.4	0.772	77.2
150	1.34	297.8	0.816	252.0	340.7	0.821	82.1
200	2.35	293.8	0.778	291.5	314.4	0.845	84.5
250	1.47	437.1	0.816	446.2	302.4	0.899	89.9
300	1.51	416.9	0.820	472.0	292.3	0.904	90.4

Electrochemical frequency modulation (EFM)

The results of EFM experiments are a spectrum of current response as a function of frequency. The spectrum is called the intermodulation spectrum and examples for corrosion of carbon steel in the absence and presence of 300 ppm concentration of tobacco extract at 25^0C is shown in Fig. 5. The spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (i_{corr}), Tafel slopes (β_a and β_c) and the causality factors (CF-2 and CF-3). The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [28]. As can be seen from Table 4, the causality factors which are very close to theoretical values according to the EFM theory, should guarantee the validity of Tafel slopes and corrosion current densities. The standard values for CF-2 and CF-3 are 2.0 and 3.0, respectively [29, 30]. The corrosion current densities decrease by increasing the concentrations of the extract. The inhibition efficiency, % IE_{EFM} calculated from Equation 5 increases with increasing the extract concentration:

$$\% IE_{EFM} = [1-i_{corr}/i°_{corr}] \times 100 \quad (5)$$

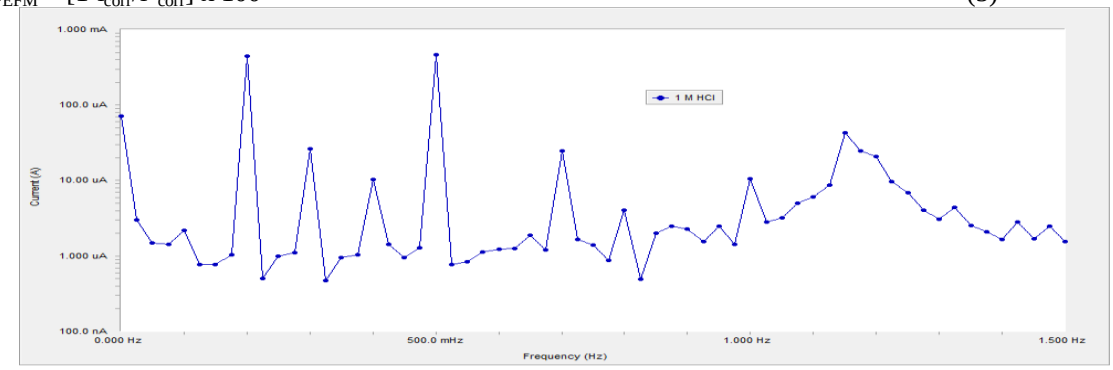


Figure 5: Intermediation spectra for carbon steel in 1 M HCl

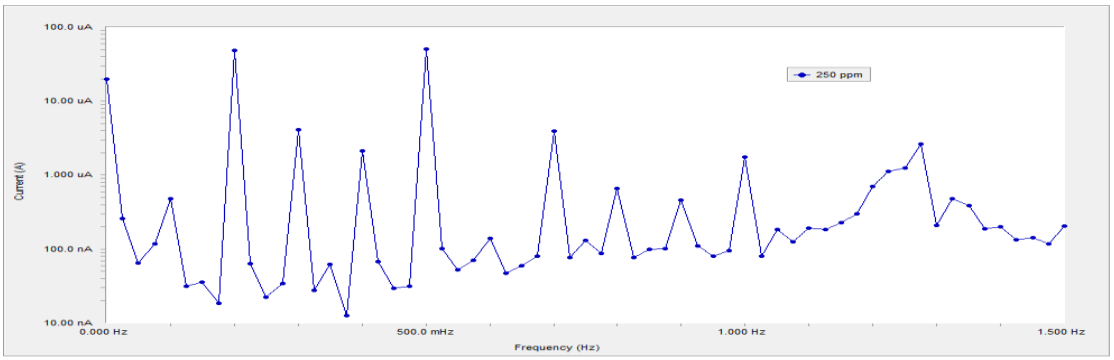


Figure 5: Intermediation spectra for carbon steel in 1 M HCl in the absence and presence of 300 ppm

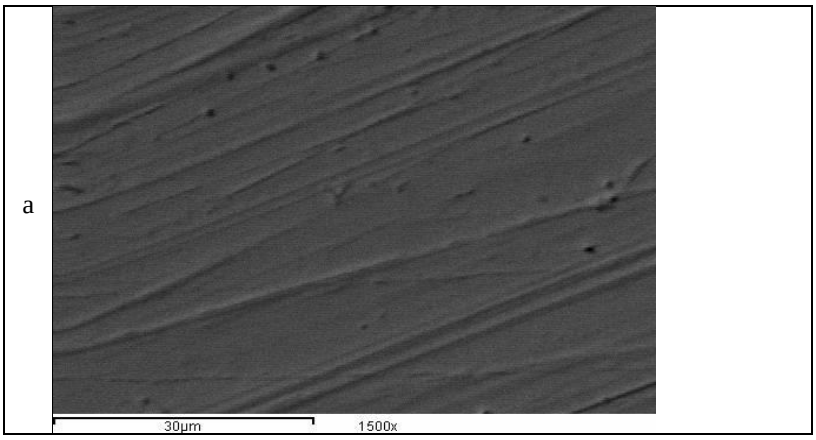
Table 4: Electrochemical kinetic parameters obtained by EFM technique for C- steel in the absence and presence of various concentrations of tobacco extract in 1M HCl at 25^0C

Conc., ppm	i_{corr} μAcm^{-2}	β_c $mVdec^{-1}$	β_a $mVdec^{-1}$	CF-2	CF-3	C.R mmy^{-1}	$\%IE_{EFM}$
Blank	650	112.1	80.7	2.14	3.07	297.2	----
50	530	362.5	110.7	1.91	2.89	242.4	18.5
100	238.2	84.5	159.0	1.93	2.86	108.9	63.4
150	117.1	205.9	85.1	2.05	2.80	53.8	81.9
200	92.3	170.8	92.1	1.97	3.33	42.1	85.8
250	94.9	269.0	132.7	1.92	2.88	43.3	85.4
300	61.8	102.9	98.8	1.94	3.05	28.4	90.5

Surface analysis

Scanning electron microscope (SEM)

Figure 6 shows the SEM photos of carbon steel surface in 1 M HCl. It can be seen from Fig. 6A that the carbon steel samples before immersion seems smooth and shows some abrading scratches on the surface. However, it also appears small black holes, which may be attributed to the defect of steel. The morphology in Fig. 6B shows the carbon steel surface is damaged in some areas. Disclosing that in extract-free solution, the surface is highly corroded. In case of C-steel immersed in 1M HCl solution with tobacco extract, a smooth surface was noticed (Fig. 6C), showing less effective corrosion . In the presence 300 ppm of tobacco extract, there is much less damage on the steel surface, which further confirm the inhibition action. Also, there is an adsorbed film adsorbed on carbon steel surface (Fig. 6C). In accordance, it might be concluded that the adsorption film can efficiently inhibits the corrosion of carbon steel.



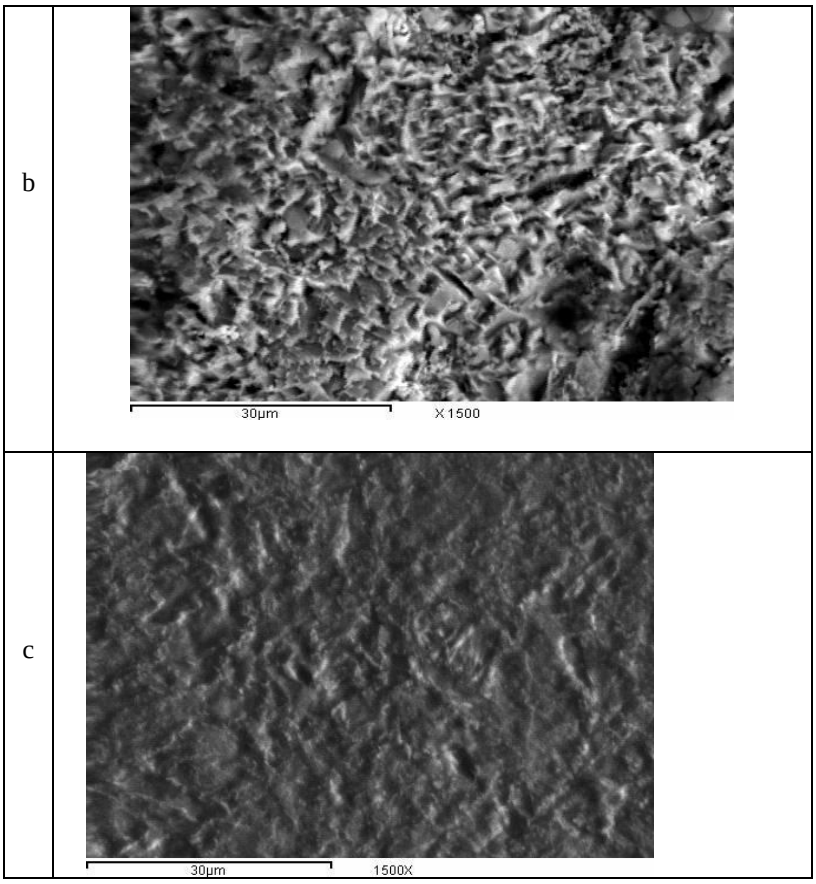
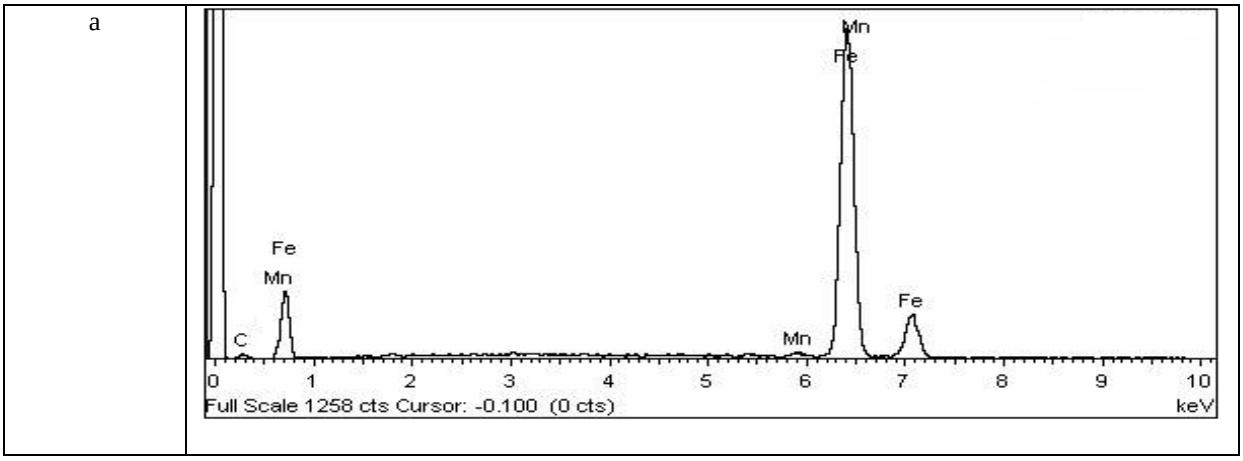


Figure 6: SEM micrographs of C-steel surface (a) before of immersion in 1 M HCl, (b) after 5 h of immersion in 1 M HCl and (c) after 3 h of immersion in 1 M HCl+ 300 ppm tobacco extract at 25°C

Energy dispersive X-ray studies (EDX)

Figure 7a, b and c EDX spectra of the carbon steel surface after immersion in 1 M HCl, for a period of 5 h, in absence and presence of 300 ppm of tobacco extract. Fig (7b) The EDX spectra show the characteristics peaks of some of the elements constituting the steel sample in 1 M HCl without inhibitor. Fig.7c in presence of 300 ppm of tobacco extract the EDX spectra show additional lines of carbon, nitrogen and oxygen, due to the adsorbed layer of the extract that covered the electrode surface. In addition, the Fe peaks are considerably suppressed relative to uninhibited steel surface sample. This suppression of the Fe lines occurs because of the overlying inhibitor film.



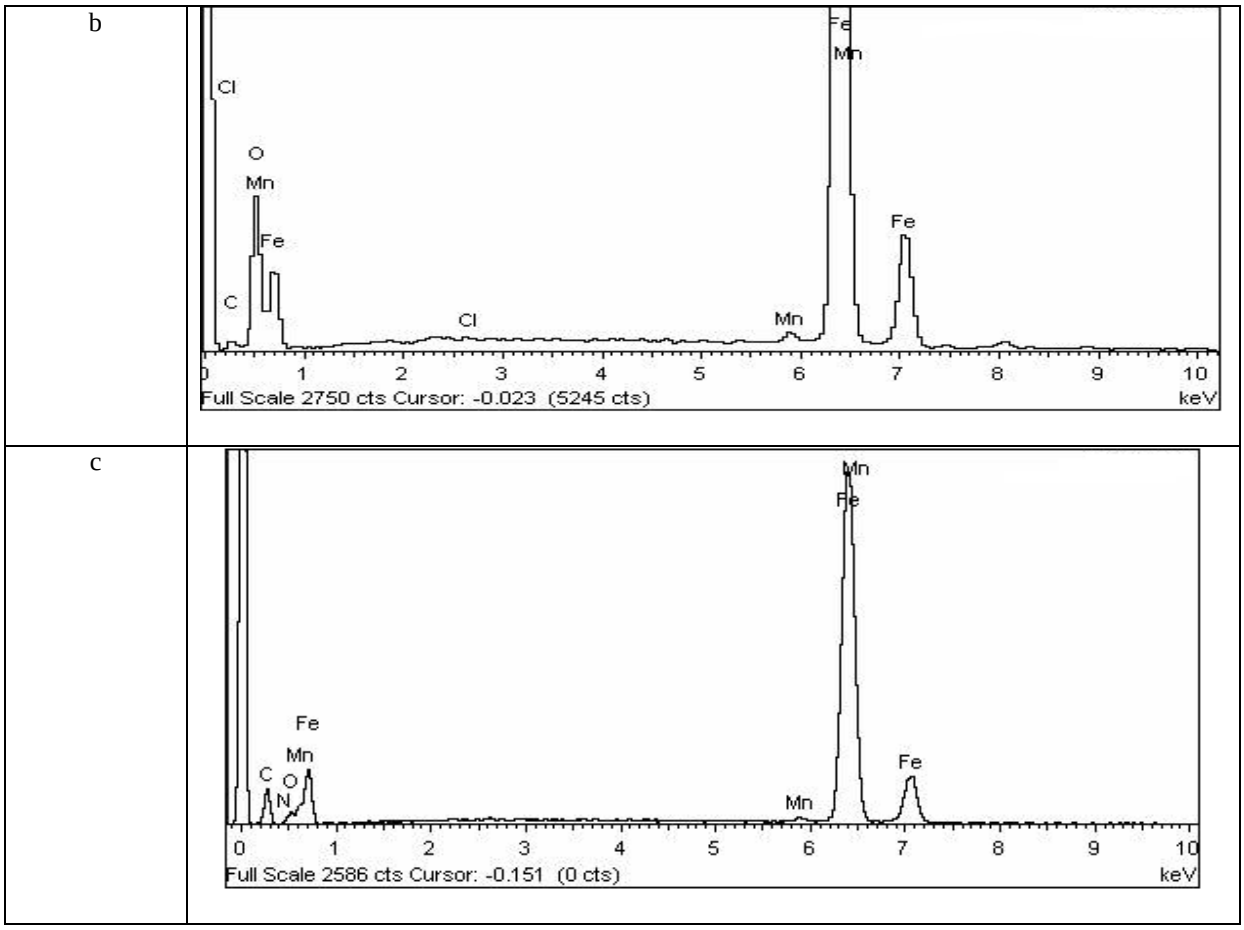


Figure 7: EDX spectra of C-steel surface (a) before of immersion in 1 M HCl, (b) after 5 h of immersion in 1 M HCl and (c) after 3 h of immersion in 1 M HCl+ 300 ppm tobacco extract at 25°C

Table 5: Surface composition (weight %) of carbon steel in absence and presence of 300 ppm of tobacco extract at 25°C

(Mass %)	Fe	Mn	C	O	N	Cl
Pure	94.52	0.61	4.87	-	-	-
blank	57.27	0.56	3.63	30.11	-	0.43
extract	61.54	0.51	18.22	13.89	5.84	

Adsorption isotherms

Basic information on the interaction between inhibitors and metal surface can be provided using the adsorption isotherms [31].The adsorption of an organic adsorb ate metal–solution interface can occur as a result of substitution adsorption process between organic molecules presented in the aqueous solution (Org), and the water molecules previously adsorbed on the metallic surface (H_2O) [32]:

$$Org_{(ads)} + xH_2O_{(ads)} = Org_{(ads)} + xH_2O_{(sol)} \quad (6)$$

Where $Org_{(sol)}$ and $Org_{(ads)}$ are the organic species in the bulk solution and adsorbed one on the metallic surface, respectively, H_2O is the water molecule adsorbed on the metallic surface and x is the size ratio representing the number of water molecules replaced by one organic adsorbs ate. The surface coverage values (θ) were evaluated using corrosion rate values obtained from the weight loss method. The (θ) values for different inhibitor concentrations were tested by fitting to various isothers. The best fit was obtained with Langmuir adsorption isotherm (Fig. 8), given by Eq. (7) [33]:

$C_{inh}/\theta = 1/K_{ads} + C_{inh}$ (7)

Where θ is the degree of surface coverage, C_{inh} is the inhibitor concentration in the electrolyte and K_{ads} the equilibrium constant of the adsorption process. From Fig.8 it can be seen that the linear Correlation coefficient (R) is close to 1 and the slope of straight line is also close to 1, which suggests that the adsorption of tobacco extract from 1 M HCl solution on the carbon steel obeys the Langmuir model and exhibit single-layer adsorption characteristic. From the intercept of the straight line K_{ads} value can be calculated. The equilibrium constant of the adsorption process K_{ads}, is related to the standard free energy of adsorption, $\Delta G°_{ads}$, from the following equation [34]:

$K_{ads}=1/55.5\exp(\Delta G^0_{ads}/RT)$ (8)

The value 55.5 is the concentration of water in solution in mol l^{-1}.The calculated ΔG^0_{ads}values, using Eq. (8), were also given in Table 6.

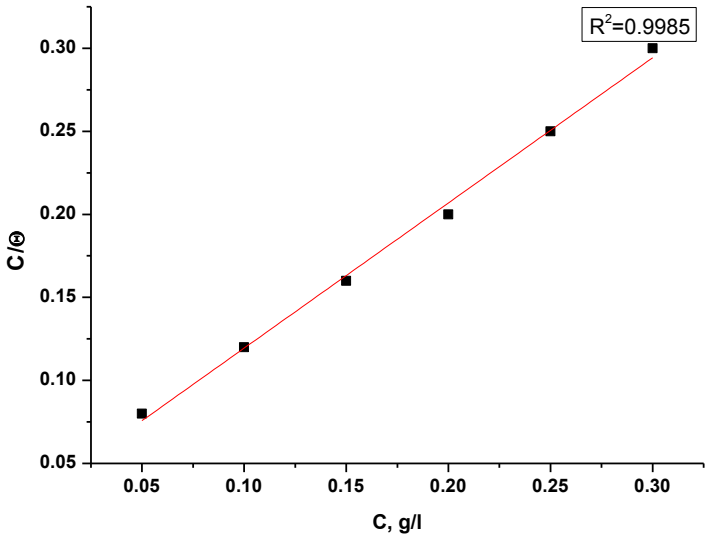


Figure 8: Langmuir adsorption plots for carbon steel in 1 M HCl containing various concentrations of tobacco extract at 25°C

The negative values of ΔG^0_{ads} ensure the spontaneity of the adsorption process and the stability of the adsorbed layer on the steel surface. Erally speaking, the adsorption type is regarded as physisorption if the absolute value of ΔG^0_{ads} was of the order of 20 kJ mol^{-1} lowers. The inhibition behavior is attributed to the electrostatic interaction between the organic molecules and iron atom. With the absolute value of $\Delta G^0_{ads}$is of the order of 40 kJ mol^{-1} or higher, the adsorption could be seen as chemisorption. In this process, the covalent bond is formed by the charge sharing or transferring from the inhibitor molecules to the metal surface [35, 36]. Based on the literature [37], the calculated ΔG^0_{ads} values in this work (Table 6) indicate that the adsorption mechanism of tobacco extract on carbon steel in 1 M HCl solution is typical of chemisorption. The same conclusion was given by Wang et al. [38] and Hassan [39] .The large negative value of ΔG^0_{ads} of tobacco extract indicates that this extract is strongly adsorbed on the steel surface [40,41].

Table 6: Values of adsorption isotherm parameters concentrations of tobacco extract at 25°C

Temp., K	Adsorption isotherm	K_{ads}, $g^{-1}L$	slope	$-\Delta G°_{ads}$, kJ mol
298	Langmuir	33.3	0.99	40.2

Effect of temperature

The effect of temperature on the corrosion rate carbon steel in free acid and in the presence of different concentrations of tobacco extract was studied in the temperature range of 25–45^{0}C using weight loss measurements. The corrosion rate values of carbon steel with and without the addition of this extract in 1 M HCl at various temperatures are listed in Table 6. These data showed that the corrosion rate values decreased as the concentration

and temperature of the tobacco extract increased and hence the corrosion inhibition efficiency increased. This behavior was observed for chemisorption of inhibitors on metal surfaces.

Figure 9 represents Arrhenius plot (as log k versus 1/T) for carbon steel corrosion in 1 M HCl in the absence and presence of various concentrations of tobacco extract. Straight lines were obtained with slope equals to E_a=2:303R: The values of E_a for the corrosion reaction in the absence and presence of tobacco extract were calculated and are presented in Table 7. In examining the effect of temperature on the corrosion process in the presence of the tobacco extract, the Arrhenius equation below was used:

$$\text{Log } k = -E_a/2.303RT + \log A \quad (9)$$

Where k is the corrosion rate, E_a is the apparent activation energy, and A is the frequency factor.

Table 7: Data of weight loss measurements for carbon steel in1M HCl solution in the absence and presence of different concentrations of tobacco extract at different temperatures

Conc., ppm	Temp., °C	Weight loss, Mg $cm^{-2}min^{-1}$	θ	%IE
	25	0.0444	-	-
	30	0.0795	-	-
	35	0.1025	-	-
1M HCl	40	0.1292	-	-
	45	0.2425	-	-
	25	0.0275	0.437	43.7
	30	0.0363	0.544	54.4
50	35	0.0533	0.480	48.0
	40	0.0613	0.526	52.6
	45	0.1075	0.557	55.7
	25	0.0179	0.597	59.7
	30	0.0235	0.704	70.4
100	35	0.0396	0.614	61.4
	40	0.0474	0.633	63.3
	45	0.0772	0.682	68.2
	25	0.0167	0.625	62.5
	30	0.0179	0.775	77.5
150	35	0.0270	0.737	73.7
	40	0.0357	0.724	72.4
	45	0.0525	0.732	73.2
	25	0.0067	0.849	84.9
	30	0.0053	0.934	93.4
	35	0.0063	0.938	93.8
200	40	0.0062	0.952	95.2
	45	0.0086	0.695	96.5
	25	0.0050	0.887	88.7
	30	0.0032	0.960	96.0
250	35	0.0044	0.967	96.7
	40	0.0050	0.961	96.1
	45	0.0075	0.969	96.9
	25	0.0026	0.942	94.2
	30	0.0029	0.959	95.9
	35	0.0032	0.969	96.9
300	40	0.0037	0.972	97.2
	45	0.0041	0.983	98.3

This Table shows the decrease of E_a decelerated the corrosion rate of steel. E_a values of the corrosion process of protected carbon steel are lower than the unprotected carbon steel in 1 M HCl solution. The large decrease in the activation energy of the corrosion process in the presence of the inhibitor indicates the higher inhibition efficiency of the inhibitor. The decrease of the activation energy is due to the adsorption of inhibitor molecules on the metal surface to form stable metal-inhibitor complex (M Inh) [42].

The other thermodynamic parameters (ΔS^* and ΔH^*) were calculated from the linear regression of transition state (Fig.10) using Eq. (10):0k= (RT/Nh) exp (ΔS^*/R) exp (-ΔH^*/RT) (10)
Where k is rate of corrosion, h is Planck's constant, N is Avogadro number, ΔS^* is the entropy of activation and ΔH^* is the enthalpy of activation. A plot of log (k/T) vs. 1/T (Fig. 8) should give a straight line, with a slope of (ΔH^*/2.303R) and an intercept of [log (R/Nh)+ΔS^*/2.303R] Examination of the kinetic values shows that the increase of inhibitor concentration leads to increases of all parameters of corrosion process (Table 7). The positive value of the enthalpy ΔH^*) means that the process is endothermic and it needs more energy to achieve the activated state or equilibrium [43, 44].The negative value of ΔS^* (Table 7) for nicotine extract indicates that activated complex in the rate determining step represents an association rather than a dissociation step, meaning that a decrease in disorder takes place during the course of transition from reactant to the activated complex [45].

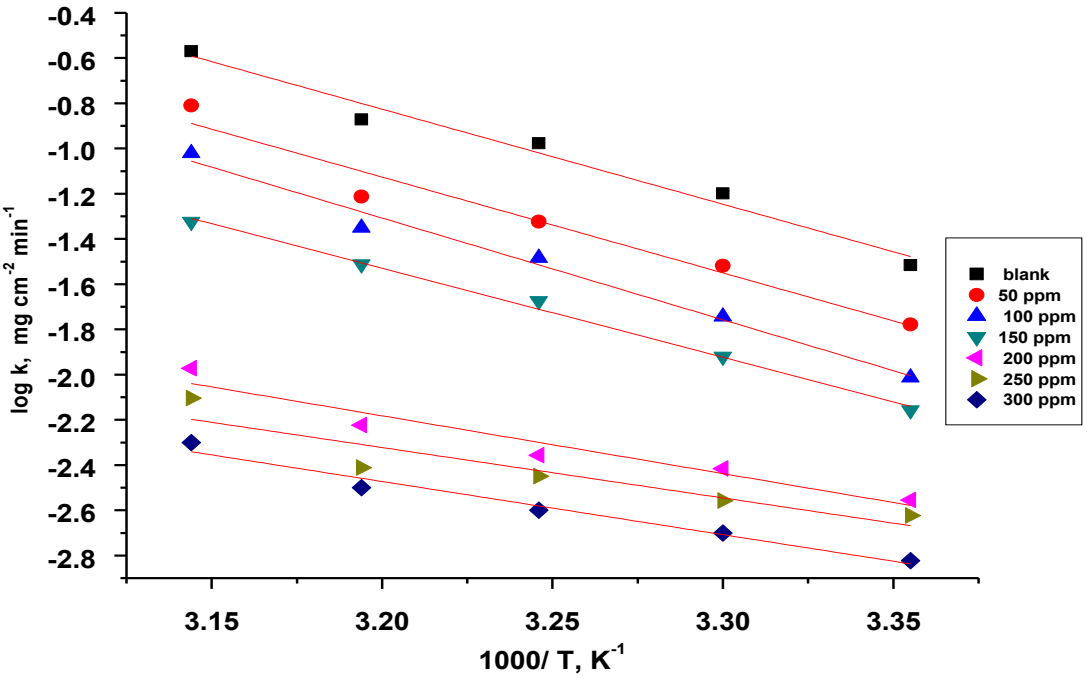


Figure 9: log k (corrosion rate) – 1/T curves for carbon steel in 1 M HCl in the absence and presence of different concentrations of tobacco extract.

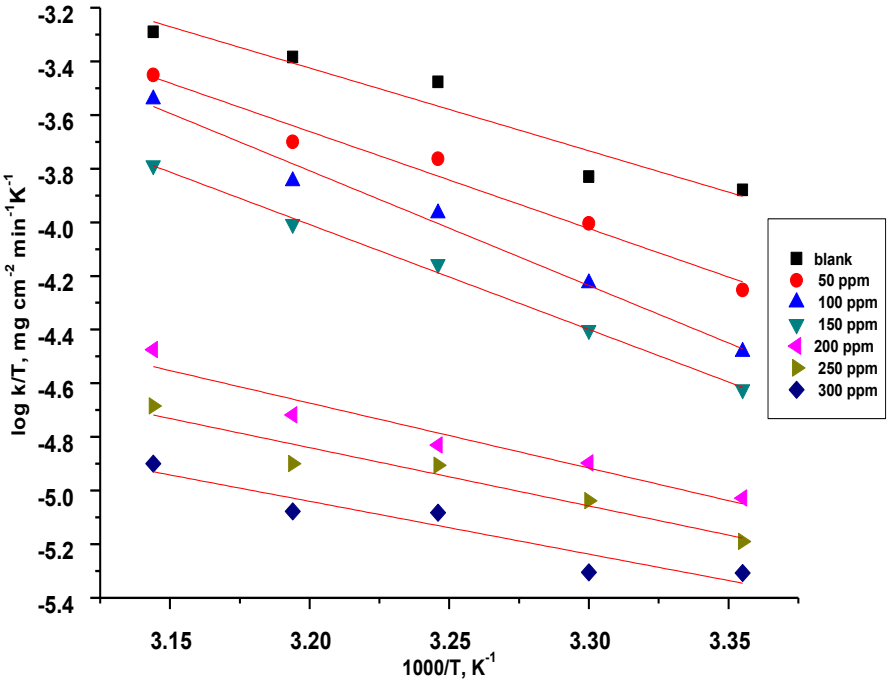


Figure 10: log k (corrosion rate)/T – 1/T curves for carbon steel in 1 M HCl in the absence and presence of different concentrations of tobacco extract

Table 8: Activation parameters for dissolution of carbon steel the absence and presence of different concentrations of tobacco extract in 1 M HCl at 25°C

Activation parameters				
Conc. ppm	E_a^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}	$-\Delta S^*$, J $mol^{-1}K^{-1}$	R^2
1M HCl	80.5	71.4	67.6	0.99741
50	80.4	69.2	46.1	0.95913
100	80.1	76.5	82.1	0.93530
150	75.4	57.4	140.1	0.93687
200	48.9	45.5	142.1	0.93140
250	42.6	40.4	157.1	0.99360
300	38.3	37.6	173.4	0.99878

Mechanism of inhibition

Many of the organic corrosion inhibitors have at least one polar unit with atoms of nitrogen, sulphur, oxygen and phosphorous. It has been reported that the inhibition efficiency decreases in the order to O < N < S < P. Also, iron is well known for its co-ordination affinity to heteroatom bearing legends [46]. The adsorption of organic molecules on the solid surfaces cannot be considered only as purely physical or as purely chemical adsorption phenomenon. The adsorption of the inhibitor molecules on the carbon steel surface can be explained on the basis of the donor–acceptor interaction between π- electrons of donor atoms N and aromatic rings of the inhibitors and the vacant d-orbital's of iron surface atoms. Tobacco extract components may be adsorbed on the metal surface via the chemisorption mechanism, involving the coordinate bonds that may be formed between the lone electrons pairs of the unprotonated N atoms and the empty d-orbital of Fe atoms which enhanced the combination between the inhibitor molecule and electrode surface. Tobacco plants produce large numbers of chemical compounds—including terpenes, alcohols, polyphenols, carboxylic acids, nitrogen-containing compounds, and alkaloids that may exhibit electrochemical activity, such as corrosion inhibition. The many compounds present in the extract make identifying the active inhibitive components difficult, if not impossible. Consequently, the focus of this effort has been to develop an inexpensive natural extraction product that effectively inhibits corrosion. The principle of inhibition is the

adsorption of the phytochemical molecules in the plant on the surface of the metal resulting in the replacement of water molecule at the corroding surface [47, 48]

Conclusions

(1) Tobacco extract acts as a very good inhibitor for the corrosion of carbon steel in 1.0 M HCl. Inhibition efficiency increases with the inhibitor concentration. The adsorption of tobacco extract on carbon steel surface obeys Langmuir adsorption isotherm.
(2) The tobacco extract acts as a mixed-type inhibitor in 1.0 M HCl, and the inhibition of tobacco extract on carbon steel is caused by geometric blocking effect. EIS spectra exhibit one capacitive loop which indicates that the corrosion reaction is controlled by charge transfer process. The presence of tobacco extract in 1 M HCl solutions enhances R_{ct} values while reduces C_{dl} values.
(3) The introduction of tobacco extract into 1 M HCl solution results in the formation of an adsorptive film on the carbon steel surface, which efficiently protects steel from corrosion.
(4) The values of ΔG^{a}_{ds} obtained are low and negative, which reveals the spontaneity of the adsorption process
(5) SEM reveals the formation of a smooth surface on carbon steel in presence of tobacco extract probably due to the formation of an adsorptive film of electrostatic character.

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