Adsorption and Protection of Low C-Steel Corrosion in 1M Hydrochloric acid Medium using Hyoscyamus Muticus Plant Extract

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ABSTRACT

The using of Hyoscyamus Muticus plant extract for corrosion inhibition of low C-steel in 1 M hydrochloric acid using chemical methods(mass reducing method, gasometric method), electrochemical methods(electrochemical impedance spectroscopy (EIS), Tafel polarization methods, electrochemical frequency modulation) and spectral methods (scanning electronic microscope (SEM), atomic force microscope (AFM)). From results the rise of the resistance of charge transfer (R_{ct}) with concentration increasing of the extract helps the extract components to adsorb on the surface of metal. From The polarization curves the using of extract deviate the reduction and oxidation reactions into less current density. These deviations confirm that Hyoscyamus extract anodic and cathodic inhibitor. The dissolution reaction rate measured by mass reduced data modified the later results. We found that the %IE rose with rising of both concentration of inhibitor and temperature. The Hyoscyamus extract is adsorbed on the low C-steel surface according to Temkin equation. Finally, the results show the Hyoscyamus extract adsorption type is chemisorption.

Keywords: Hyoscyamus Muticus, adsorption, corrosion, inhibition, low C-steel, HCl.

INTRODUCTION

Hydrochloric acid (HCl) solutions are widely used for acid cleaning; industry acid pickling, oil well acidizing and acid descaling [1–4], but hydrochloric acid medium has been aggressive effect on substances. The inhibitor substances use is to protect the metal versus acid corrosion. Corrosion is the reaction of a metal with corrosive surrounding [5, 6]. The factors affecting corrosion processes are the type of metal, the behavior of the media and the surface between metal and media, such as the aggressive species in medium, liquid movement, the metal dissolution mechanisms and the species discharge at the metal surface [5].The testing of plant extracts as cheap, safety, on-hand and renewable sources of inhibitors. The plant extracts include of different of organic compounds containing hetero atoms and some [7–12] have been to act as metal dissolution inhibitors in various corrosive mediums. Low carbon steel is a main substance in the construction, which is widely used in many industries for the handling of various solutions [13]. Hydrogen chloride solution is very aggressive to many materials [14].

The different industries interruption due to metal deterioration become increasingly expensive and can cost much money for reducing and change of upkeeps [15]. So, we need the using of substances has inhibiting

effect to protect the materials which used in different fields of application. The formation of thin layer resulting from interaction of organic compounds on the metal (mixed inhibitors) while in case of inorganic inhibitors may block anodic or/and cathodic sites [16–18].Using of extracts of plant as inhibitors in acidic solutions, as, Cannabis [19], caffeine [20]. This study test the Hyoscyamus extract role on the dissolution mechanism of low C-steel in1M HCl acid medium. The Hyoscyamus extract role is measured using gasometric method, mass loss method, polarization diagrams, EIS technique, SEM technique and AFM technique. The happening of inhibition is investigated by the attractive parameters of Hyoscyamus extract on low C-steel after dipping in the hydrochloric acid medium.

MATERIALS AND METHODS

The low carbon steel specimens with dimensions 20x 20 x 2 mm and its composition in table 1.

Table 1: Main components (weight %) of the low C-steel

Component	Carbon	Mn	Phosphorus	Silicon	Iron
Wt (%)	0.046	0.90	0.007	0.002	Rest

The used solution corrosive medium is 1M HCl (34%), purchased from Al-Gamhoria & Co. for chemicals materials. The preparation of test solutions used bidistilled water. The inhibitory solution was prepared from the dilution of the Hyoscyamus extract (1000ppm), at different concentrations.

Gasometric method: The hydrogen evolution method is a useful technique that calculates the amount of hydrogen producing during a corrosion process. The used bottle must contact through a plastic tube to a burette initially, the air volume in the burette was measured. Finally, medium low carbon steel specimen was immersed in the test solution and the reaction bottle was enclosed. The amount of H_2 gas was measured by the decreasing of the aqueous solution level in the burette at fixed time intervals.

Mass loss method: "Medium low carbon steel specimens were mechanically abraded up to 1200 grades emery paper and degreased with acetone, rinsed with bidistilled water two times and finally dried between filter paper. After weighting accurately, the specimens were immersed in 100 ml of 1 M HCl with and without different concentrations of Hyoscyamus extract. After different immersion time (30, 60, 90, 120, 150 and180 min) the low carbon steel samples were taken out, washed with bidistilled water, dried and weighted accurately. The experiments were done triplicate and the average value of the weight loss was taken. The average weight loss of the three parallel low carbon steel sheets could be obtained at required temperature. The inhibition efficiency (%IE) and the degree of surface coverage (θ) of the investigated inhibitors on the corrosion of low carbon steel were calculated as follows [21]:

$$IE \% = \theta x\ 100 = [(W_o – W)/ W_o] x\ 100 \quad\quad\quad (1)$$

where W_o and W are the values of the average weight loss in the absence and presence of the inhibitor, respectively".

Polarization curves: The working electrode voltage was beginning at - 700 to + 700 mV vs. SCE. SO, Tafel slopes, exchange current density (i_{corr}) and corrosion voltage (E_{corr}) were calculated.

EIS method: using alternative current signals at the open circuit potential in the frequency values from 100 kHz to 0.5 Hz to calculate the corrosion impedance results that analysis by suitable equivalent circuit (CPE).

Electrochemical Frequency Modulation (EFM) technique: Using two waves of 2 and 5Hz [22-24] to give the intermodulation spectra of the electrochemical frequency modulation. The highest peaks were

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used to measure the current density (i_{corr}), the Tafel constants (βc and βa) and the causality factors CF-2 and CF-3[25].

Scanning electron microscopy Technique: SEM technique provide information on morphology, topography and the extent of inhibitor protective layer. The surface morphology of the specimens was examined using Scanning electron microscope VEGA3 TESCAN model.

Atomic Force Microscopy (AFM) Technique: The main advantage of AFM is that the roughness of the metal surface can be calculated which is a measure of the texture of a metal surface. The surface roughness is caused due to deviations of a surface from its ideal form .AFM analysis was carried out using Nano Surf Easyscan 2 Flex AFM instruments (Nanotechnology Center, Mansoura University).

RESULTS AND DISCUSSION

Hydrogen evolution method: The iron oxidation in solution of acid was studied following to the assumption reactions

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2}$$

Followed by the conjugate reduction process

$$2H^+ + 2e^- \rightarrow H_2 \tag{3}$$

The produced H_2 gas volume resulting from the corrosion reaction can be calculated. Results obtained by the hydrogen evolution method (in Fig.1) are matching with other methods including weight loss and electrochemical methods. The hydrogen volume is dependent on time of reaction according to eq (4):

$$V = Kt \tag{4}$$

where V is the H_2 gas volume, time t and K is the corrosion rate. From the table (2), the results indicate that the extract decreased the H_2 gas volume and increase the inhibition efficiency [26].

Table 2: Inhibition efficiency of low C- steel obtained from gasometric method after 120 min in 1 M Hydrochloric acid for different Hyoscyamus extract concentrations at 30°C.

[Inh]. Ppm	hydrogen gas Volume .ml	%I.E
Blank	3.4	-
50	1.2	64.7
100	1.0	70.6
150	0.9	73.5
200	0.8	76.5
250	0.7	79.4
300	0.6	82.4
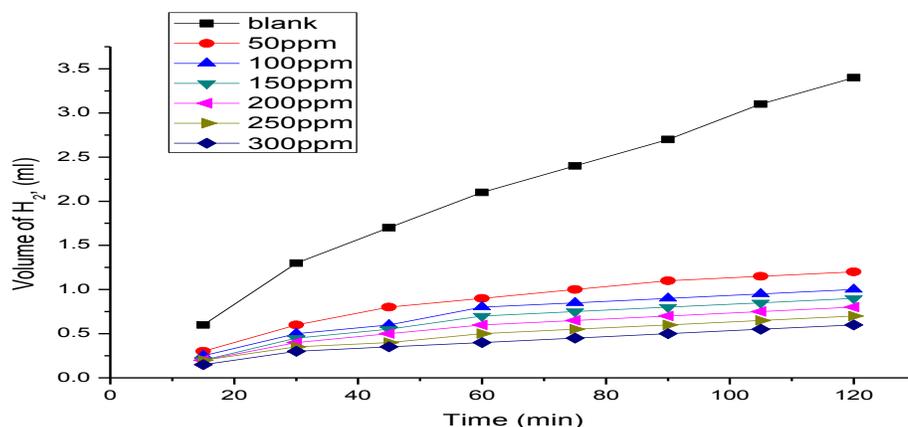
Fig. 1: Hydrogen evolution from low carbon steel dissolution in 1 M HCl
in absence and presence of Hyoscyamus extract at 30°C.

Weight-loss measurements: The losing in mass of low C- steel is measured, at different time periods, without and with of various extent of Hyoscyamus extract. The relationship between mass reduction and time are shows in figure 2 for Hyoscyamus extract. The corrosion inhibition efficiency is affected by the concentration of inhibitor. The curves for different inhibitor concentrations were fall below of the corrosive media. The rising in concentration of the inhibitor give a decreasing of mass reduction and rising of the metal corrosion protection. Experimental data show that the Hyoscyamus extract is considers as inhibitory substance for low C- steel corrosion in 1M HCl medium. Also, the covered surface area (Ө) and inhibition efficiency due to the thin layer, founded by Eq. (1), that raise with raising the extract extent. The data recorded in table 3.
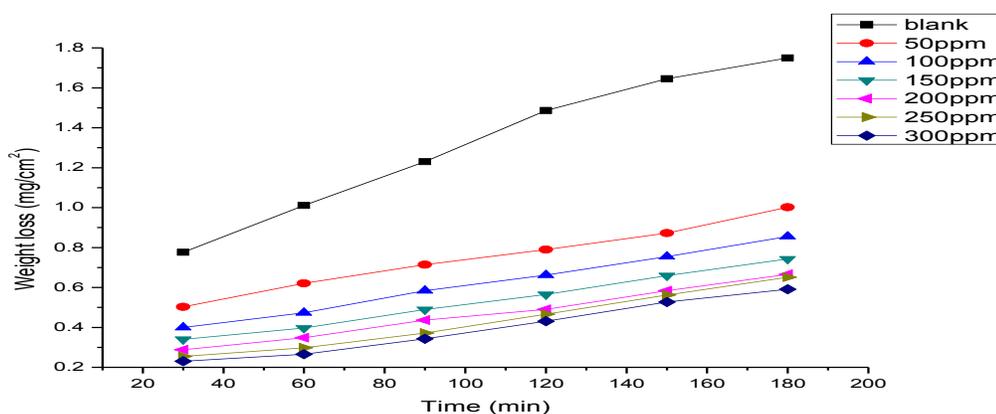
Figure 2: Curves of mass losing versus time for the corroded low carbon steel in 1M hydrochloric acid
without and with the various Hyoscyamus solution concentrations at 30°C

Table 3: Percentage of protection and coverage of surface degree of Hyoscyamus extract
for the low C- steel dissolution in Hydrochloric acid from mass reduction data at
various concentration of Hyoscyamus extract at 30ºC.

[inh.], ppm	Hyoscyamus extract	
	% IE	Ө
50	47.5	0.475
100	55.2	0.552

150	58.6	0.586
200	62.4	0.624
250	64.2	0.642
300	66.6	0.666

Adsorption isotherm: The equations of adsorption utilizing in expresses the manner and interaction of the low carbon steel with an inhibitor. Temkin equation which are represented in Figures(3)used to calculate θ degree for Hyoscyamus extract The essential data on the interaction of the metal surface with the inhibitor can be modified by the adsorption equations, and the type of the inhibitors on metal is influenced by (i) the metal properties (ii) the inhibitor chemical composition and (iii) the electrolyte type [27]. The covered surface area (θ) was calculated at many inhibitor concentrations in 1 M hydrochloric acid media. The best fitting obey the Temkin adsorption isotherm [28].

$$\Theta_{coverage} = (2.303/a) \log C + (2.303/a) \log K_{ads} \qquad (5)$$

Where θ is the coverage of surface degree, K_{ads} is the adsorption constant, C is the concentration (mol L^{-1}) of the extract and "a" (heterogeneous factor of surface of metal) . The values obtained of "a" , K_{ads} and $\Delta G°_{ads}$ are given in table 4.
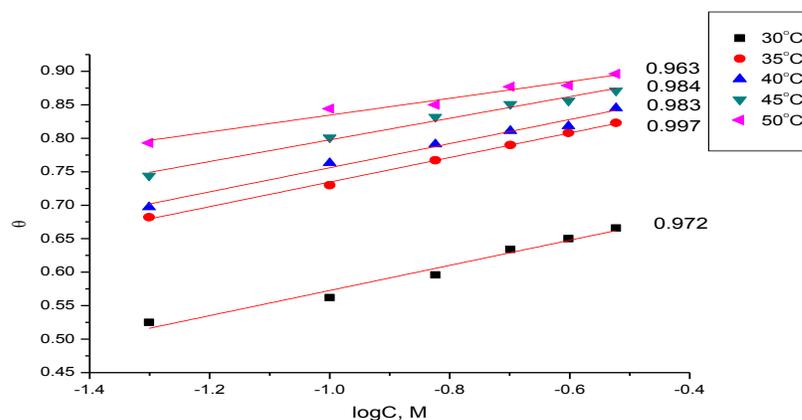
Figure 3: The diagram of Temkin adsorption of Hyoscyamus plant extract on the surface of low carbon steel in 1 M HCl at different temperatures

Table 4: Some parameters from Temkin isotherm for low C-steel in 1M hydrochloric acid for Hyoscyamus plant extract compound at 30°C.

Temp., K	$K_{ads} \times 10^5$ M^{-1}	a	$-\Delta G°_{ads}$ kJ mol^{-1}	$\Delta H°_{ads}$ kJ mol^{-1}	$+\Delta S°_{ads}$ J mol^{-1} k^{-1}
303	0.1	12.3	33.1		1092
308	1.0	12.6	38.5		1092
313	1.6	12.8	39.6	298.1	1079
318	8.7	14.3	43.8		1075
323	449.6	18.4	53.6		1089

From these results we can confirm that, the extract adsorption on the metal through the unshared electrons of hetero atoms. The inhibition strength of corrosion is depending on the nature of adsorbed film (molecular structure). The adsorption equilibrium constant K_{ads} calculated from the Temkin equation is utilized to calculate the adsorption energy of ΔG^0_{ads} as follows:

$$K_{ads} = \frac{1}{55.5} \exp\left[\frac{-\Delta G°_{ads}}{RT}\right] \qquad (6)$$

55.5 is the water molar concentration in the solution in M^{-1}

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From Table (4),ΔG^o_{ads} depend on temperature. The value of ΔG^o_{ads} confirm the inhibitor adsorption is spontaneous and strength of the thin film on the metal. The ΔG^o_{ads} values about -20 kJ mol^{-1} or less negative are suppose (physical adsorption) and those about -40 kJ mol^{-1} or more negative are distinguish adsorption of inhibitor molecules through a coordination bond (chemical adsorption) [29].The calculated ΔG^o_{ads} values are closer to and higher than -40 kJ mol^{-1}distinguish that the adsorption of inhibitor on metal in hydrochloric acid solutions is chemical adsorption. The unshared electrons pairs of hetero atoms may donated to vacant metal orbital's to form a thin layer[30]. From (Table 4), the Temkin parameters can indicate the inhibition mechanism. As, the values of ΔH^o_{ads} calculated were higher than (100 kJ mol−1), this indication of chemisorptions[31]. However, the decreasing of ΔG^o_{ads} indicating the temperature rising lead to reduction of adsorbed surface area of the extract on the metal and this follows to the mass reduction method data[32]. From the van't Hoff equation;

$$\ln K_{ads} = \Delta H^o_{ads}/RT + constant \qquad (7)$$

ΔH^o_{ads} can be also deduced from the plot of ln K_{ads} versus 1/T giving straight lines with slopes of ΔH^o_{ads} / R retaliation, the entropy of adsorption can be measured from equation (8):

$$\Delta G^o_{ads} = \Delta H^o_{ads} - T \Delta S^o_{ads} \qquad (8)$$

The calculated ΔH^o_{ads} and ΔS^o_{ads} were listed in table 2. From the data, it shows that the calculated ΔH^o_{ads} value is positive which indicate that the adsorption process is endothermic. "The higher and positive values of ΔS^o_{ads}, indicating that the small molecules or ions such as H_2O, Cl^- interact with the surface atoms of low carbon steel are shifted by Hyoscyamus extract molecules that raises the disorder of the medium . From the basic equation of thermodynamic, indicating the spontaneity of the inhibitor adsorption process on the metal which lead to raising the disorder" [33].

Effect of temperature: The corrosion rate of low carbon steel in 1M HCl and with concentrations of Hyoscyamus extract was tested in range of temperature from 303 to 323K by mass reduction method. From table 5, both of the rate of corrosion and the percentage of inhibition for Hyoscyamus extract were increases By raising of temperature, for Ivanov [34]assume that the increase of %IE with raising the temperature as the change in the nature of the adsorption pattern; at lower temperatures the adsorption of inhibitor is physically, while chemisorption is preferred at higher temperatures.

Table 5: data efficiencies of inhibition , surface coverage degree (θ) and rate of the low C-steel dissolution in hydrochloric acid using mass reduction method with different Hyoscyamus extract concentrations at various temperatures

Conc, ppm	303 K			308 K			313 K			318 K			323 K		
	θ	%IE	C.R x10^{-3}	θ	%IE	C.R. x10^{-3}	θ	%IE	C.R. x10^{-3}	θ	%IE	C.R. x10^{-3}	θ	% IE	C.R. x10^{-3}
50	0.475	47.5	7.1	0.682	68.2	8.2	0.697	69.7	9.9	0.744	74.4	11.4	0.793	79.3	14.0
100	0.552	55.2	5.5	0.730	73.0	6.3	0.763	76.3	7.5	0.801	80.1	8.3	0.844	84.4	10.0
150	0.586	58.6	4.7	0.767	76.7	5.8	0.791	79.1	7.2	0.832	83.2	8.1	0.850	85.0	9.8
200	0.624	62.4	4.1	0.790	79.0	5.0	0.811	81.1	5.9	0.851	85.1	6.6	0.877	87.7	8.0
250	0.642	64.2	3.9	0.808	80.8	4.8	0.818	81.8	5.8	0.856	85.6	6.4	0.879	87.9	7.7
300	0.666	66.6	3.6	0.823	82.3	4.4	0.845	84.5	5.0	0.871	87.1	5.6	0.896	89.6	6.7

Kinetic –thermodynamic corrosion parameter: The dissolution reaction parameters were measured from equation of Arrhenius (9):

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log k$_{corr}$ = -E$_a^*$/2.303RT + log A   (9)

where

R = universal gas constant,

E_a^* = energy of activated complex,

 T =kelvin's temperature, and

A = Arrhenius factor.

From Table (6), The magnitude of(E$_a^*$)[slope X 2.303 X R]for the metal in corrosive medium in absence and presence of different Hyoscyamus extract concentrations calculated from drawing of k$_{corr.}$ Logarithm against reciprocal temperature plots are shown in fig.4. Table 6 shows that the activation energy in hydrochloric acid decreases in the Hyoscyamus presence. "This was due to tardily rate of inhibitor adsorption with a resultant closer approach to equilibrium during the experiments at higher temperatures according to Hoar and Holliday [35]. But, Riggs and Hurd [36] explained that the reduction in the activation energy of corrosion at higher levels of inhibition arises from a shift of the net corrosion reaction from the uncovered part of the metal surface to the covered one". For the activated complex, the enthalpy change (ΔH*) and entropy change are calculated from Eq.(10):

$$k_{corr} = (RT/Nh)exp(\Delta S^*/R)exp(-\Delta H^*/RT)$$ (10)

Where k$_{corr.}$ is the metal corrosion rate, h is Planck's constant, N is Avogadro's number. Figure (5) indicate a draw of (log k/T) versus (1/T) with Hyoscyamus extract in hydrochloric acid. Straight lines are give (slopes=(ΔH*/2.303R) and intercepts are[log (R/Nh + Δ**S***/2.303R)]written in (Table 6).

Table 6: Kinetic parameters for activated state of low C-steel without and with
Hyoscyamus extract concentrations in 1 M hydrochloric acid

Conc ppm	E$^*_a$ kJ mol^{-1}	ΔH* kJ mol^{-1}	-ΔS* J mol^{-1}K^{-1}
Blank	50.6	48.0	121.6
50	29.7	27.1	197.1
100	29.6	27.0	199.4
150	29.0	26.4	202.3
200	27.6	25.0	208.3
250	26.8	24.2	211.1
300	24.0	21.4	220.9
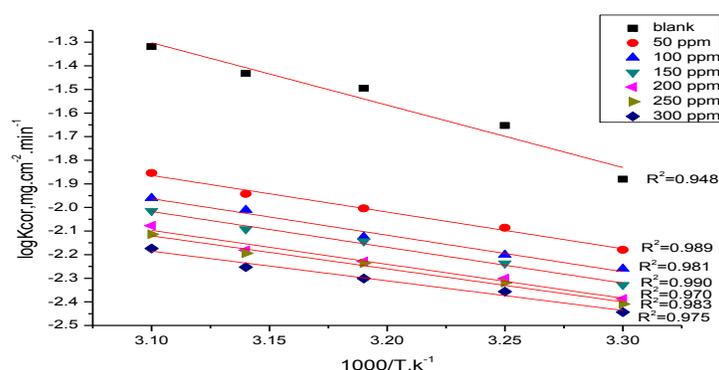
Figure 4: Diagram of Arrhenius (1/ T versus log K$_{corr}$) for dissolution of low C- steel in 1 M HCl
without and with different Hyoscyamus extract concentrations.

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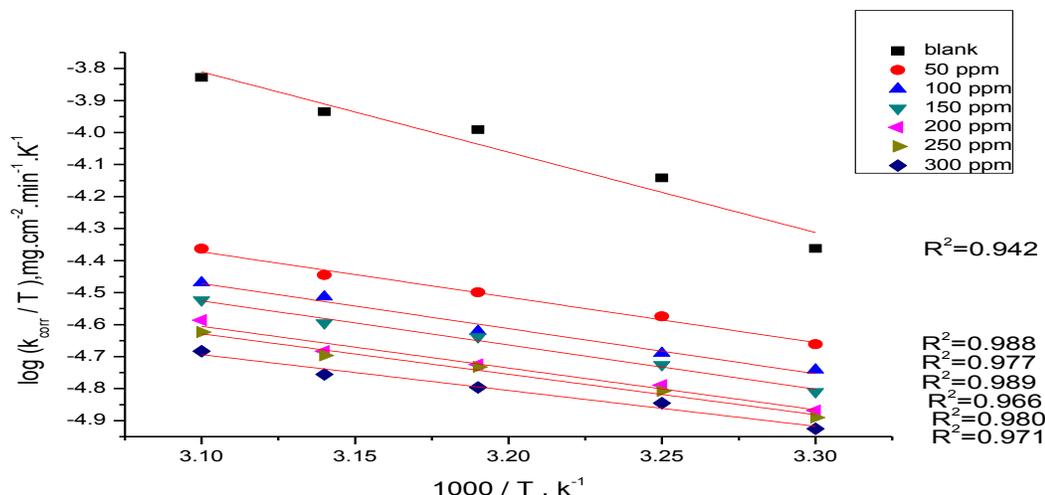
Fig. 5: Diagram of (log k_{corr} / T) versus 1/ T for dissolution of low C- steel in hydrochloric acid without and with different Hyoscyamus extract concentrations.

The activation energy is decreased with rise concentration of inhibitor (Table 6), and then the adsorption is chemical adsorption. The + ve(ΔH^{*}) indicate the extract adsorption is endothermic.The -ve activation entropy with and without the extract shows that in the rate determining step, the association of unstable coordinated compound is more than the dissociation [37].

Electrochemical Frequency Modulation Technique (EFM): EFM is safely dissolution method that detected the current magnitude without knowing of Tafel constants, and with only a small signal of polarizing [38]. Figure 6 shows the EFM spectrum of metal in hydrochloric acid solution with various Hyoscyamus extract concentrations. The harmonic and intermodulation peaks are clearly visible and are much larger than the background noise. The two large peaks, with amplitude of about 75 µA, are the response to the 40 and 100 mHz (2 and 5 Hz) excitation frequencies. It is important to note that between the peaks there is nearly no current response (<100 nA). The experimental EFM data were treated using two different models: complete diffusion control of the cathodic reaction and the "activation" model. For the latter, a set of three non-linear equations had been solved, assuming that the corrosion potential does not change due to the polarization of the working electrode[39].The higher peaks were utilized to measure the Tafel slopes (β_c and β_a) the dissolution current density (i_{corr}), and the causality factors (CF-2 and CF-3). These constants were shown in table 7. The using of Hyoscyamus extract with different concentrations to the corrosive medium reduce the current density of corrosion, meaning that Hyoscyamus extract act as inhibitor by adsorption process. The causality factors resulting from experimental method are equal to the expected values (2 and 3). The %IE$_{EFM}$ raises by higher concentrations of extract and measured using Eq.(11):

$$\%IE_{EFM}=[1-(i_{corr}/i^{o}_{corr})]\times100 \qquad\qquad (11)$$

where i^{o}_{corr} and i_{corr} are corrosion current densities without and with of inhibitor, respectively. Figure 6 indicate the EFM spectrum of low C-steel in HCl medium with various Hyoscyamus extract concentrations.
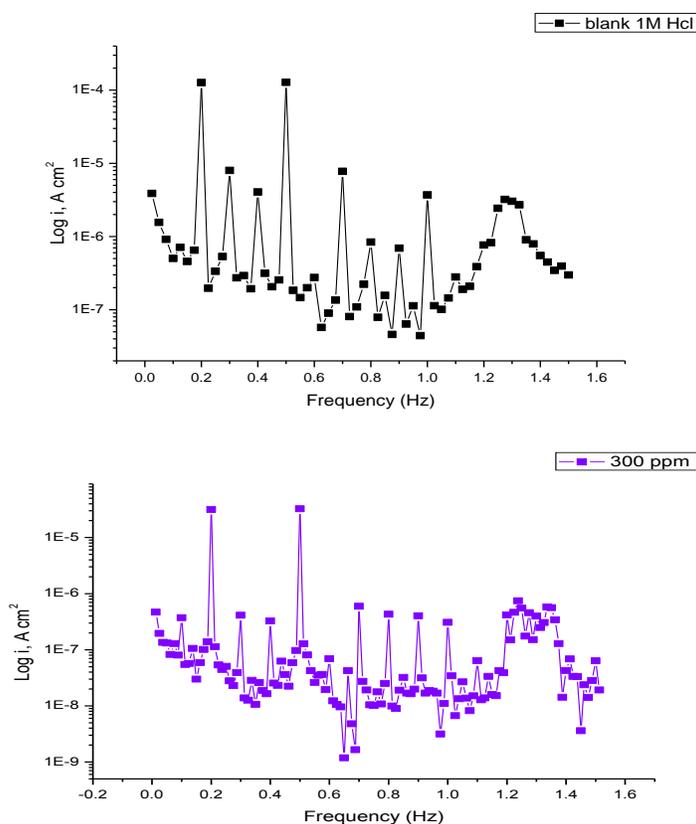
Figure 6: EFM spectrums for the dissolution of C-steel in 1M HCl in absent and presence many Hyoscyamus extract extent.

Table 7: EFM parameters for low C-steel in the absence and presence of many Hyoscyamus concentrations in 1M HCl at 25°C.

[inh.] ppm	$i_{corr,}$ μAcm^{-2}	β_c , $mVdec^{-1}$	β_a , $mVdec^{-1}$	CF-2	CF-3	C.R , mpy	Θ	%IE
Blank	354.2	275.4	134.5	2.06	2.44	161.8	-	-
50	344.6	206.8	102.9	2.09	3.31	157.5	0.027	2.7
100	320.6	43.4	36.7	1.82	2.32	146.5	0.095	9.5
150	221.7	235.7	104.2	2.15	3.06	101.3	0.374	37.4
200	175.2	120.3	85.0	1.87	3.23	80.1	0.505	50.5
250	148.7	101.0	83.2	1.81	1.79	68.0	0.580	58.0
300	50.3	107.9	97.7	2.18	1.96	23.0	0.858	85.8

Electrochemical impedance spectroscopy (EIS): Figure 7 indicate the resistance curves for low C-steel in 1M hydrochloric acid medium without and with concentrations of extract. The rising in the diameters of Semicircles with the using of different concentrations from Hyoscyamus extract indicating the rising of protective film resistance to the polarization process. The Nyquist plots do not produce perfect semicircles due to the irregularity of frequency [40] resulting from the surface asymmetric and the roughness of the surface. The impedance rise with the rise Hyoscyamus extracts concentration. The addition of Hyoscyamus improves the R_{ct} value in corrosive medium. The double layer capacitance is decrease with higher concentration of Hyoscyamus, Due to the adsorbed Hyoscyamus extract molecules forms protective

layer that impede the corrosive species motion into the metal surface[41]. From the results, the raising of the protective percent resulting from the R_{ct} rising with higher concentration of extract.
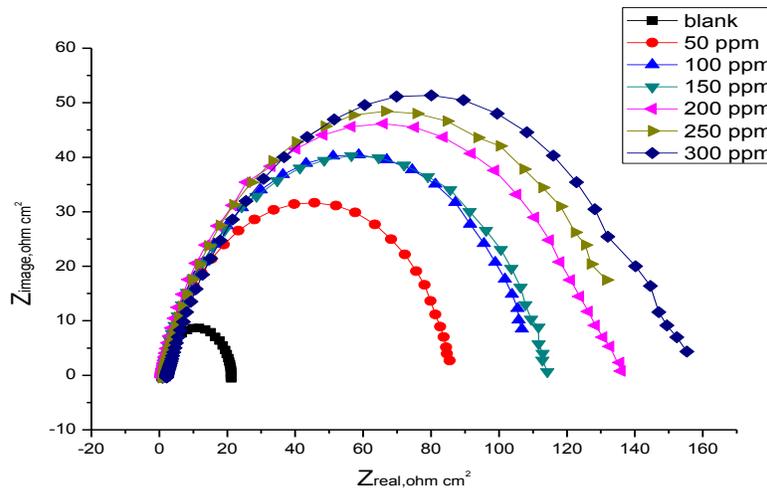
Figure 7a: The Nyquist diagram for the low C-steel dissolution in hydrochloric acid without and with Hyoscyamus extract concentrations at 25 ^{o}C
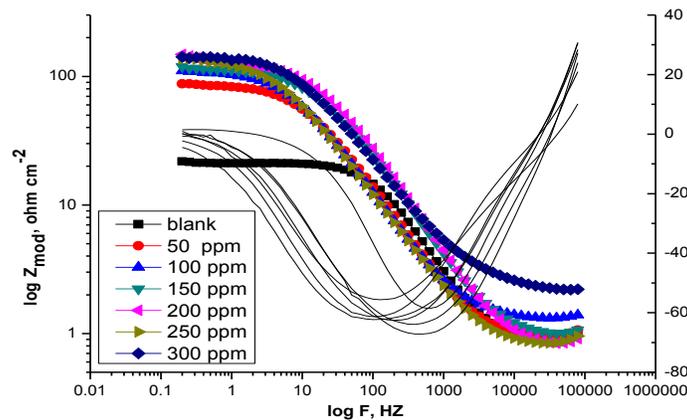
Figure (7b): The Bode diagram for the low C-steel dissolution in hydrochloric acid without and with various Hyoscyamus extract concentrations at room temperature
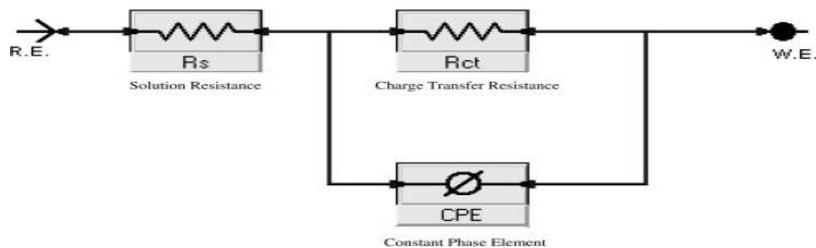
Fig. 8: Equivalent circuit for fitting EIS data for low carbon steel in 1M hydrochloric acid solutions

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From Fig.8, The equivalent electrical circuit utilized for fitting the results. The CPE model give better fitting more than uniform double layer capacitor [42].The double layer capacitance, C_{dl}, Y_0 and n were measured by eq.(12) [43]:

$$C_{dl} = Y_0 \omega^{n-1}/ \sin [n(\pi/2)] \qquad (12)$$

where Y_0 is the CPE value, $\omega = 2\pi f_{max}$, f_{max} is the angular frequency, n is the exponential .The similarity of all curves shape indicating that there is no changes in the mechanism of corrosion [44]. From table 8, The CPE/C_{dl} decrease due to a decreasing of dielectric factor and/or an rising in the double layer thickness [45,46]. The protective percent can measured from equation (13) [47]:

$$\% IE_{EIS} = [1 - (R^\circ_{ct}/ R_{ct})] \times 100 \quad (13)$$

where R^o_{ct} and R_{ct} are the resistance of charge moving values in extract free and inhibitory solution respectively.

Table 8: Parameters measured by EIS method for low C-Steel in 1M hydrochloric acid without and with Hyoscyamus extract concentrations at 25^oC.

[inh.] ppm	R_S, Ωcm^2	Y^o, $\mu\Omega^{-1} s^n cm^{-2}$	n	R_{ct}, $\Omega\ cm^2$	C_{dl}, $\mu F cm^{-2}$	Θ	%IE
Blank	0.906	460.8	0.922	20.2	310.4	-	-
50	0.927	412.6	0.836	84.6	235.6	0.761	76.1
100	1.306	328.2	0.836	108.9	170.8	0.815	81.5
150	0.974	320.4	0.836	110.8	166.5	0.818	81.8
200	0.811	181.5	0.820	127.7	79.4	0.842	84.2
250	0.807	140.1	0.805	135.3	53.6	0.851	85.1
300	2.218	118.0	0.762	145.5	33.2	0.861	86.1

Potentiodynamic polarization curves: Figure 9 give the curves of potentiodynamic polarization for low C-steel corrosion in one molar hydrochloric acid with and without Hyoscyamus extract extent at 25ºC.The magnitude of the density of reaction current ($i_{corr.}$), the corrosion voltage($E_{corr.}$), Tafel constants (β_a and β_c), the covered surface area(Θ) and the protection percent were written in Table(9). The protective percent and covered surface are measured from eq.(14):

$$\% IE_p = [(i^o_{corr} - i_{corr}) / i^o_{corr}] \times 100 = \theta \times 100 \qquad (14)$$

where i^o_{corr} and i_{corr} are the free and inhibited current densities, respectively. From table 10,The addition of Hyoscyamus extract lowers i_{corr} appreciably with slightly change in potential of corrosion process .From the figure 9, the parallel Tafel plots, given that the reduction of protons process is activation controlled without change the discharge of hydrogen ions mechanism.
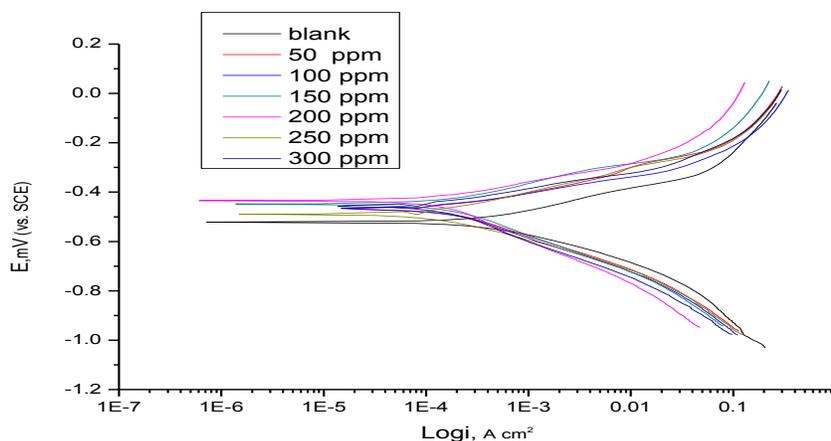
Figure 9: Corrosion polarization plots for the low C-steel in 1M hydrochloric acid without and with Hyoscyamus extract concentrations at 25 ^{o}C

Table 9: Dissolution voltage (E_{corr}), current density (i_{corr}), Tafel constants (β_c, β_a), and covered surface area (θ), and protective percent (%IE_p) of low C- steel in hydrochloric acid at r.t for Hyoscyamus extract.

[inh.] ppm	- $E_{corr,}$ mV (vs.SCE)	$i_{corr,}$ μA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	C.R, mpy	θ	% IE
0	522	375	114.0	96.3	171.3	-	-
50	467	203	150.1	96.3	92.9	0.459	45.9
100	468	155	142.6	72.4	71.0	0.587	58.7
150	448	148	149.7	92.8	67.6	0.605	60.5
200	444	131	180.2	80.6	60.0	0.651	65.1
250	489	128	116.8	97.1	58.4	0.659	65.9
300	456	125	153.7	72.9	57.0	0.667	66.7

Scanning electron microscopy (SEM) : SEM images indicate uniform and damaged shapes (roughness) for the free metal surface(fig.10 a) ,metal in 1M HCl without and with Hyoscyamus extract (fig.10 b-c) The polished metal surface is more smooth with some pits and grooves but in presence of the acid the surface damaged due to the corrosion reaction ,then the surface was became more roughness. The addition of Hyoscyamus extract decreased the corrosion rate by formation of adsorbed layer so the roughness is decreased.
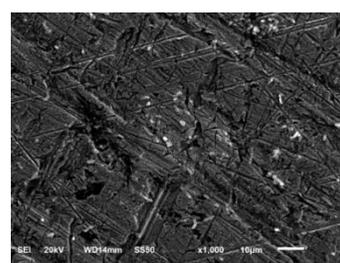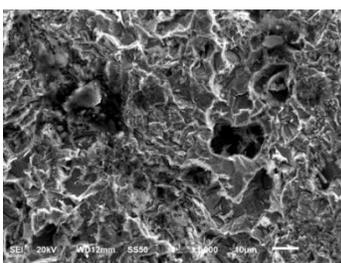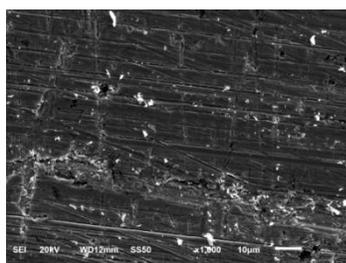
(a)   **(b)**   **(c)**

Fig: 10 : SEM images for low carbon steel (a) free specimen (b) with 1M HCl for 24 h (c) with 1M HCl containing 300 ppm Hyoscyamus extract for 24 h.

Atomic Force Microscopy (AFM): The roughness average values of free metal surface (Fig. 11a), metal in 1M HCl and metal in 1M HCl with Hyoscyamus extract (Fig.11 b, c) were recorded in table 10. The roughness increased in presence of corrosive medium (HCl) due to the corrosion reaction but in the presence of the Hyoscyamus extract the roughness was decreased due to the adsorption of extract on the low carbon steel surface forming protective layer ,indicating that the metal surface was became more smoothly and the corrosion rate was decreased.
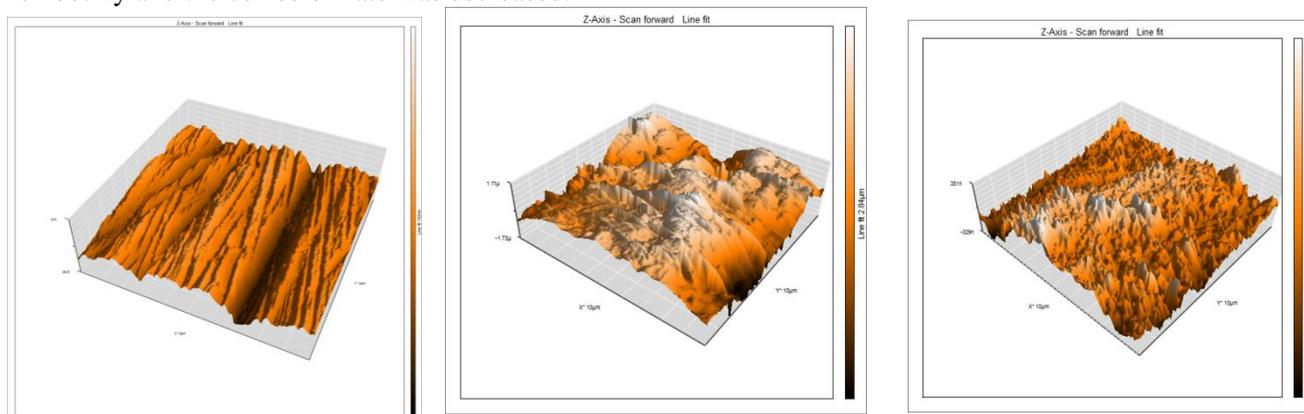
Fig.11: AFM 3D images of for low carbon steel (a) free specimen (b) with 1M HCl for 24 h (c) with 1M HCl containing 300 ppm Hyoscyamus extract for 24 h.

Table 10: AFM parameters for low carbon steel (a) free specimen (b)with 1M HCl for 24 h (c) with 1M HCl containing 300 ppm Hyoscyamus extract for 24 h.

Parameters	A	B	C
The roughness average (Sa)	14.1	392.6	75.9
The mean value (Sm)	-18.0	-17.3	-17.6
The root mean square (Sq)	18.1	493.2	96.1
The valley depth (Sv)	-58.3	-3141.9	-345.1
The peak height (Sp)	40.8	1557.9	447.5
The peak-valley height (Sy)	99.1	4699.8	801.6

Mechanism of inhibition: The charge on the metal surface is positive in acidic medium [48]. Then, the Cl$^-$ ions can be interacting with the metal surface and rise the negative charge on the metal surface. So, the adsorption of protonated Hyoscyamus on the surface take place [30] give reducing the corrosion rate of metal .The adsorption is assumed to take place mainly through the nitrogen and oxygen atoms in Hyoscyamus extract [49].

APPLICATIONS

The results are useful to know the corrosion inhibition, corrosion rate and mechanism of inhibition of low C-steel using Hyoscyamus Muticus plant extract and 1 M hydrochloric acid by chemical methods.

CONCLUSIONS

Hyoscyamus extract has been corrosion inhibitory effect on low C-steel in hydrochloric acid medium. There is good agreement between chemical and electrochemical techniques. Polarization plots data mention that the Hyoscyamus extract is mixed-type inhibitors. Corrosion protection efficiencies of Hyoscyamus extract rise with temperature rising but the energy of corrosion activation was decreased. The adsorption of Hyoscyamus extract follows the Temkin adsorption isotherm (chemisorptions). SEM and AFM techniques give information about morphology, topography and the roughness of the metal surface.

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