Beet Root Extract as a Corroison Inhibitor for Mild Steel in 1.0 M HCl Solution

A.M.Nagiub*, H.F.Y.Khalil**,M.H.Mahross*, B.N.A.Mahran*** and M.M.B.El-Sabbah**

Abstract— The effect of aqueous beet root extract (BRE) on the corrosion of mild steel in 1.0 M HCl solution was investigated using both gravimetric and electrochemical techniques. The impact of temperature was also determined at temperature range from 298 to 328 K. A significant increase in the corrosion inhibition was observed with increasing of the BRE concentration. At inhibitor concentration of 0.3034 g/L, the percentage of inhibition reaches 83.79% at room temperature and 71.11% at 328 K. Adsorption study of BRE was found to agree with the Langmuir's adsorption isotherm. The values of free energy of adsorption, heat of adsorption and activation energy were calculated. Polarization results showed that BRE acted as mixed type inhibitor. Surface analysis (UV-VIS spectra, SEM and EDAX) were also carried out to establish the mechanism of corrosion inhibitor on mild steel in HCl medium.

Index Terms— beet root, corrosion inhibition, natural products, surface morphology.

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1 INTRODUCTION

Mild steel is the most commonly used steel. It is used in the industry as well in the different everyday objects. However, it is highly tending to rusting in many environments, particularly in HCl medium. In order to prevent or minimize corrosion inhibitors can be used. The inhibitor will reduce or inhibit the corrosion by either chemisorption on the metal surface or reacting with metal ions and forming a barrier-type on its surface [1-11]. Environmental restriction of application of inhibitors has reoriented researchers to prefer natural compounds called green corrosion inhibitors. Natural plants were added in form of extracts, oil or pure compounds, may play major role to keep the environment healthier, safely and under pollution control [12-16]. Extracts of naturally occurring products that are biodegradable in nature, contain mixture of compounds, these compounds usually having nitrogen, oxygen and sulphur which will work as corrosion inhibitor for metals. Recently, the use of different herbal compounds as corrosion inhibitors have been widely used, of these some data has been reported for the use of Anise, Caraway, Cumin and Hibiscus as corrosion inhibitors [17-23]. In this study, the effect of aqueous BRE (BRE) on the corrosion inhibition of mild steel exposed to 1.0 M HCl solution will be investigated using both gravimetric and electrochemical techniques. The effect of temperature will also be determined

2 EXPERIMENTAL

2.1 Materials

Mild steel specimens tested in the present study are in the form of sheet. The chemical analysis of used mild steel is given in Table (1). Before immersion Mild steel sheets in the test arrangement each of them are set up by cleaning with emery paper from 250 to 1200 grit, to get a smooth surface, washing with deionized water and after that degreased with acetone, washed again with deionized water then dried with Nitrogen. An aqueous extract of beet root was prepared by grinding 10 g of beet root with deionized water, filtering the suspended impurities, and making up to 100 mL. The extract was used as corrosion inhibitor

Table 1
CHEMICAL COMPOSITION OF WILD STEEL BY WT %

C	**Si**	**Mo**
0.0826	0.100	0.00211
Co	**Cu**	**Pb**
0.000574	0.00375	0.00282
Mn	**P**	**Al**
0.369	0.0262	<0.0001
Nb	**Ti**	**Fe**
0.00175	0.00048	< 99.35
S	**Cr**	**Ni**
0.00791	0.00531	0.0163
V	**W**	**As**
0.00251	0.0158	0.0123

2.2 Methods

Weight loss measurements were carried out by weighing the mild steel sheets before and after immersion in 500cm^3 HCl solutions for different time intervals in the presence and absence of different beer roots concentrations. Experiments were also performed at temperature range (298-328K). Duplicate experiments were performed in each case and the mean value of the weight loss was determined. The potential of the mild steel electrode was measured against saturated calomel electrode (SCE) as a reference electrode exposed to 1.0 M HCl solution in absence and presence of different concentrations of

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the inhibitor. The electrochemical cell used in potentiodynamic polarization consists of (three electrodes), working electrode (mild steel), reference electrode (saturated calomel electrode (SCE)) and platinum wire used as counter electrode. The exposed area of working electrode to solution was (1Cm²). For the anodic and cathodic potentiodynamic polarization (Tafel plots) the entire potential scan was programmed to take place within ± 250 mV of the corrosion potential .The measurements were conducted at scanning rate of 0.2 mV/s. Scanning electron microscope (SEM) (Joel JSM 5600LV) equipped with Oxford Instruments 6587 EDX microanalysis detector was used to get the samples images. UV-Vis. spectroscopic measurements were conducted using a spectrophotometer, Unicam; model UV4-200.

3 Results and discussion

3.1 Gravimetric Methods (Weight Loss Measurements)

Several factors are believed to greatly affect the performance of organic corrosion inhibitors, of theses, adsorption sites availability (N, S, O, P), charge density, molecular size, mode of interaction with metal surface and the formation of metallic complexes [25]. Weight loss of mild steel electrode was determined at various time intervals in absence and presence of different concentrations of BRE. The obtained weight-loss time curves are represented in Fig1 at 25 °C.

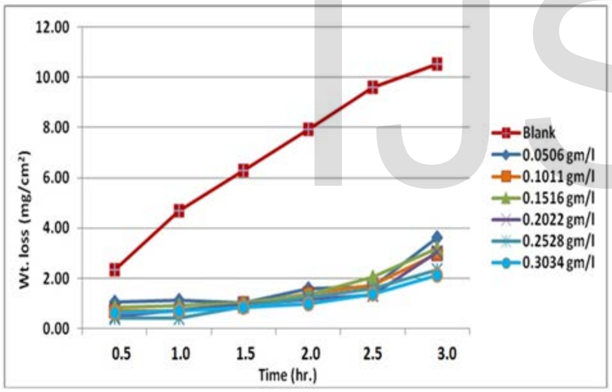


Fig (1): Variation of weight loss with time for the corrosion of mild steel in solution 1.0MHCl containing various concentrations of BRE at 25 °C.

It is clear that the weight-loss of mild steel electrode in the presence of different BRE varies linearly with time, and having lower corrosion rate than those obtained in blank solution. The linearity obtained may indicate the absence of insoluble surface film during corrosion and the inhibitors were fast adsorbed onto the metal surface and, therefore, impeding the corrosion process [26]. The corrosion rate (C.R.), the inhibition efficiency (IE %) and the surface coverage (θ), that represents the part of metal surface covered by inhibitor molecules, was calculated using the following equations:

$$I.E.\% = (1 - ((C.R.)inh.)/(C.R.)free\ ) \times 100 \quad (1)$$

$$\theta = (1 - ((C.R.)inh.)/(C.R.)free\ ) \quad (2)$$

Where (C.R.)free and (C.R.)inh are the corrosion rate in the absence and presence of inhibitors respectively. The calculated values of (C.R.), I.E. % and θ for different concentrations of BRE at 25 °C are listed in Table (2). It is clearly obvious that the corrosion rate decreases with increase in the inhibitor concentration. This observed trend may result from the fact that adsorption and surface coverage increase with the increase in concentration. It is also observed that the inhibition effeciency increases as the added inhibitor concentrations were increased. It reaches 83.79 % for 0.3034 gm/L of BRE.

Table 2

Calculated values of the corrosion rate, degree of surface coverage and Inhibition efficiency for mild steel in 1.0 M HCl solutions in absence and presence of different inhibitor concentrations

Conc. gm/l	C.R.	θ	% I.E.
BLANK	6.89	---	---
0.0506	1.68	0.75	75.55
0.1011	1.41	0.79	79.44
0.1516	1.56	0.77	77.29
0.2022	1.28	0.81	81.30
0.2528	1.15	0.83	83.31
0.3034	1.11	0.84	83.79

3.2 Adsorption considration

The inhibitor molecules can be adsorbed on the metal surface by different modes according to different adsorption isotherms. Different adsorption isotherms have been tested graphically by fitting the experimental data. The value of correlation coefficient (R^2) was used to determine the best fit isotherm. According to the obtained results Langmuir adsorption isotherm was found to best describe the system. According to this isotherm, θ is related to the C and adsorption equilibrium constant $K_{ads.}$, via the following equation [27].

$$C/\theta = (1/K(ads.)\ ) + C \quad (3)$$

Fig 2 shows the relation between plots of log (C/θ) versus C. A straight line with slope around one was obtained. Accordingly, the adsorption of BRE on mils steel surface exposed to HCl obeys Langmuir adsorption isotherm. Meanwhile, the obtained results showed that both R^2 values and the slopes are very close to unity which may suggest the strong adherence of the adsorbed inhibitors to the assumptions of Langmuir [28]. The equilibrium constant of adsorption obtained from the slopes of the Langmuir isotherms were used to calculate the free energy for the adsorption of different BRE on the surface of mild steel. The free energy of adsorption of different BRE on the metal surface is related to the equilibrium constant of adsorption according to equation (4):

$$K(ads.) = (1/55.5)\ exp(-\Delta G(ads)/RT) \quad (4)$$

Where R is the universal gas constant, $\Delta G_{ads.}$ is the free energy of adsorption and 55.5 is the concentration of water in solution (mol

L^{-1}) [29].

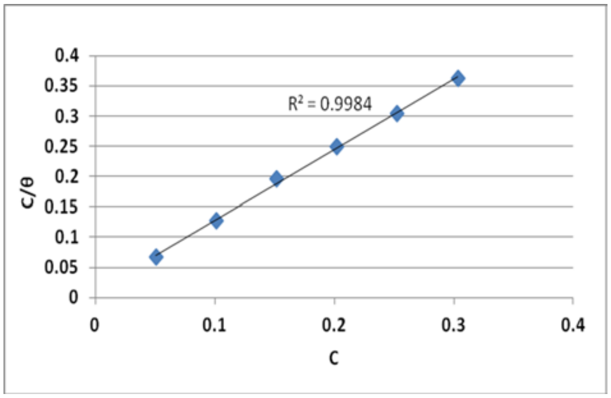


Fig (2): Langmuir adsorption isotherm for the investigated inhibitor on mild steel.

The value of (ΔG°_{ads}) for adsorption of extract inhibitor was found to be -48.25 kJ mol^{-1}. The negative sign of free energy of adsorption of BRE at mild steel surface indicating that the adsorption is a spontaneous process and chemisorption are taking place. The heat of adsorption of BRE on mild steel surface was calculated using Equation (5).

$$Q_{ads.} = 3.303R[(log\theta_2/(1-\theta_2) - \log(\theta_1/(1-\theta_1)] \times [(T_1 \times T_2)/(T_{2-}T_1)] \quad (5)$$

Where θ_1 and θ_2 are the degree of surface coverage at temperatures T_1 and T_2 respectively. Mean value of Q_{ads} (-19.16 kJ mol^{-1}) was obtained from the experimental data of BRE at the temperature studied. Such negative value indicating that the adsorption of BRE on mild steel is exothermic. Also has been interpreted to imply a reduction in the degree of surface coverage with rise in temperature [30]. It can also be stated that since the reaction was carried out at constant pressure, values of Q_{ads} should approximate those of enthalpy of adsorption (ΔH°_{ads}) [31].

3.3 Thermodynamic consideration

In order to invistigate the stability of the adsorbed layer on mild steel surface and to evaluate the activation parameters of the corrosion process, weight loss measurements were carried out in the temperature range of 289 – 328 K in the absence and presence of 0.2528 gm/L of BRE during 3 hours of immersion time. Results obtained are shown in Fig (3) and Table (3). The data clearly shows that the inhibition effeciency of BRE is inversly proportional to temperature which could be due to the acceleration of dissolution process of mild steel and partial desorption of the inhibitor from the metal surface with temperature [32].

Table 3
Calculated values of the corrosion rate, degree of surface coverage and inhibition efficiency in 0.2528 g/L of BRE in 1.0 M HCl at different temperatures

Temperature K	C.R.	θ	% I.E.
298	1.15	0.83	83.31
308	1.37	0.80	80.07
318	1.64	0.76	76.07
328	1.99	0.71	71.11

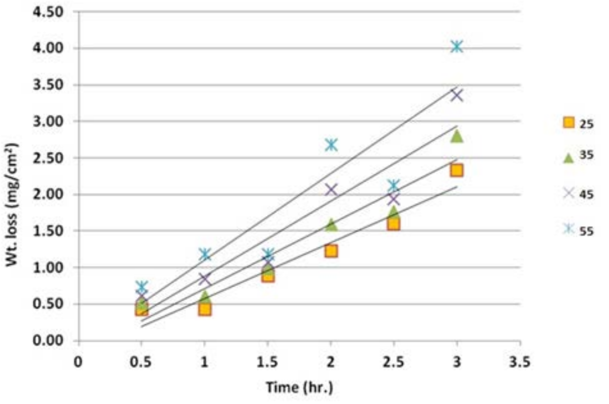


Fig (3): Variation of weight loss with time for the corrosion of mild steel in 0.2528 g/L of BRE in .0 M HCl at different temperatures.

In an acidic solution the corrosion rate is related to temperature by the Arrhenius equation [33]:

$$\mathrm{Log}(C.R.) = [(-Ea)/2.303RT] + \log A \quad (6)$$

Where (C.R.) is the corrosion rate, E_a is the apparent activation energy, R is the molar gas constant, T is the absolute temperature and A is the frequency factor. Fig. (4) shows the plot of log C.R. versus 1/T. Linear plots were obtained for BRE.

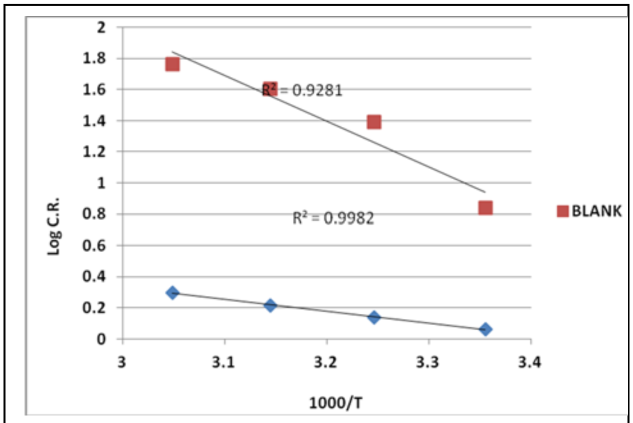


Fig (4): Arrhenius plots for mild steel in 1.0 M HCl in absence and presence of 0.2528 g/L of BRE.

Inspection of the obtained data showed that, activation energy little increased in inhibited acid (14.85 kJ/mol) compared to free acid (13.47 kJ/mol). This was attributed to an appreciable decrease in the adsorption process of the inhibitor on the metal surface with increase of temperature and corresponding increase in the reaction rate because of the greater area of the metal that is exposed to HCl solution.

3.4. Open Circuit Potential Measurements

Results given in Fig (5) illustrate the open circuit potential curves (OCP) for mild steel in 1.0 M HCl solution in absence and in presence of different concentrations of BRE. In almost for BRE there is always a general tendency for the OCP to drift with time towards more stable values at which it tends to be stabilized after 30 mins. Addition of inhibitor molecules to the aggressive medium produces a positive shift in immersion potential (E_{im})and steday state potential (E_{ss}.) As the concentration of the inhibitor increases, the corrosion potential was shifted to more noble direction, Ess values are higher than the values obtained for solution without inhibitor.

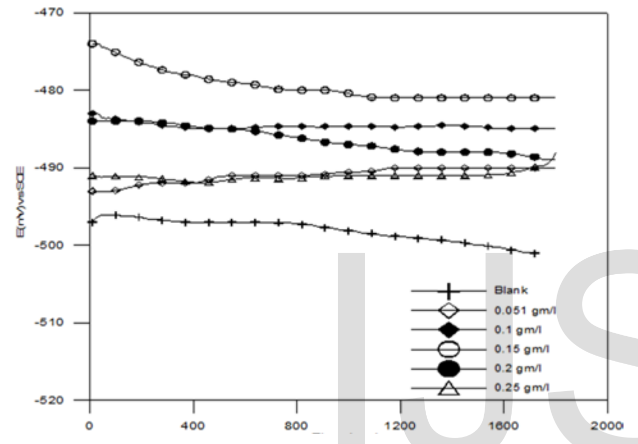


Fig (5): Potential-time curves for mild steel in 1.0M HCl (blank) and different concentrations of BRE.

3.5. Rate of Oxide Film Thickening

In 1979, Abd El-Kader and Shams El-Din developed a theory for film thickening on the surface of metal and alloy [34]. The fundamental of the theory is based on the condition that when the anodic reaction is the rate limiting step for an electrochemical reaction consists of simultaneous anodic (film formation) and cathodic (oxygen reduction) couple. Accordingly straight lines will be obtained for the data in form of potential-log (time) curves (equation 7).

$$E = constant + 2.303[\delta/\beta]\ \log t \qquad (7)$$

Where (E) electrode potential with respect to a saturated calomel electrode, (t) was the time from the moment of immersion in solution, (δ) was the rate of oxide film thickening per decade of time and β was given by equation (8):

$$\beta = [nF/RT]\alpha\delta t \qquad (8)$$

In equation (8), (α) is a transference coefficient similar to that found in electrochemical kinetic rate expressions ($0.0 < \alpha < 1$), and (δ') is the width of the activation energy barrier to be traversed by the ion during oxide formation, R is the gas constant and T is the absolute temperature. The theory was successfully applied different metals and alloys in different environments [35-37]. The values of the rates of oxide film thickening obtained from these studies were in good agreement with the data obtained by other independent techniques, such as ellipsometry and impedance [34].

When appling this theory in our study, the curves of Fig (6) shows that the potential of metal-electrode varies linearly with the logarithm of the immersion time. For the slope of the E-log t lines, the values of the rate of thickening of the oxide per unit decade of time (δ) in solution of various concentrations of BRE can be calculated by equation (7). Fig (6) and the values in Table (4) suggest that film thiecking was obtained as indicated by enoblements of the The open potential curves (OCP) of all concentrations. Also the rate of oxide film thickening in the solution of different extracted natural products was independent of their concentration. It may also conclouded that the presence of these natural compounds has a little specific effect on the oxide growth, in the sense that they neither allow dissolution nor they seem to be incorporated in the oxide film formation [34].

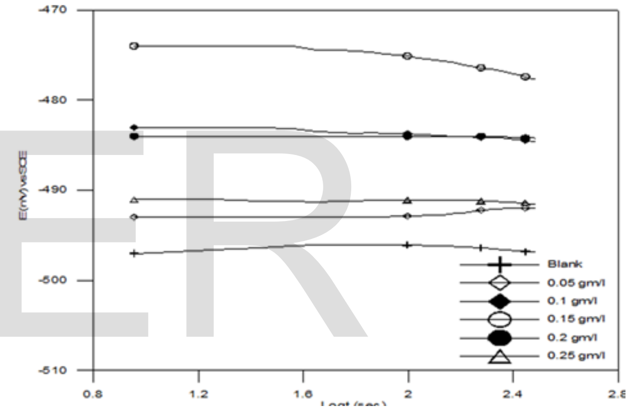


Fig (6): Potential-Log t curves for mild steel in 1.0M HCl (blank) and different concentration f BRE at 25 °C.

Table 4

Values of slopes of E (mV) vs. log t lines and the rate of oxide film thickening (δ) (nm\log t) for corresponding the mild steel in 1.0M HCl and different concentration of BRE.

Test solution	Slope	Rate (nm/log t)δ'
Blank	**0.184**	**0.005**
0.05 gm/l	**0.958684**	**0.220**
0.1 gm/l	**1.153405**	**0.024**
0.15 gm/l	**2.925641**	**0.029**
0.2 gm/l	**0.132632**	**0.074**

3.6. Potentiodynamic Polarization Measurements (Linear and Tafel Polarizations)

The electrochemical effect of BRE concentration on mild steel expsoed to 1.0 M HCl solution was studied using linear and

Tafel polarizaton technique. Corrosion inhibition effeciencies (I.E. %) was also clacuted using ellectrochemical teqniques. The corrosion kinetic parameters obtained form tafel polarization mesurments are tabulated in Table (5). Table 5 shows that the polarization resistance ($R_{p)}$, Tafel slopes constants (β_a, β_c), corrosion potential (E_{corr}), Corrosion current density (I_{corr}), corrosion rate (C.R.) and inhibition efficiencies (I.E.%) are function of the concentration of BRE.

Table 5
Polarization parameters for mild steel in 1.0M HCl and different concentration of BRE

	Blank	BRE (gm/l)				
C	1M	0.05	0.1	0.15	0.2	0.25
IE (%)	-	76.6	86.6	87.3	92	95
C.R. (mpy)	2099	494.2	284	267.4	168.7	106
Icorr (uA/cm2)	2292	536	308	290	183	115
Ecorr (mV)	-474	-463	-464	-470	-473	-487
Bc (mV/decade)	169	191.7	138.5	178.6	147	237.9
Bca(mV/decade)	119	162.9	131.9	160	107	276
Rp (ohm)	48.7	71.4	95.3	126.5	147.1	483

Fig 7 shows that Tafel lines are shifted to more negative and more positive potentials for the cathodic and anodic process, relative to the blank curves. This means that the additive effects both anodic dissolution of the metal and cathodic evolution of hydrogen (i.e. mixed-type inhibitor). It is clear from Fig (7) that both the cathodic and the anodic reaction are inhibited and the inhibition increases as the inhibitor concentration increases. In addition, the slopes of the cathodic and anodic Tafel lines are approximately constant and independent on the inhibitor concentration. This behaviour suggests that the inhibitor molecules affect the corrosion rate of mild steel without changing the metal dissolution mechanism [38]. Also, the addition of inhibitor molecules causes a decrease in I_{corr}., taht increases with increasing inhibitor concentration indicating that the additive compound can be used as corrosion inhibitor of mild steel. The values of inhibition effeciency increased significantly with increase of inhibitor concentration indicated that a higher coverage of inhibitor on the surface was obtained in a solution with higher concentrations of inhibitor.

It is of interest to note that, the values of (I.E.%) given by polarization are slightly different than that obtained by weight-loss measurements. This difference can be attributed to the fact that the first method gives instantaneous corrosion rate whereas the second method gives average corrosion rates, also the difference may be attributed to the difference in the time required to form an adsorbed layer of inhibitor on metal surface that can inhibit corrosion [39].

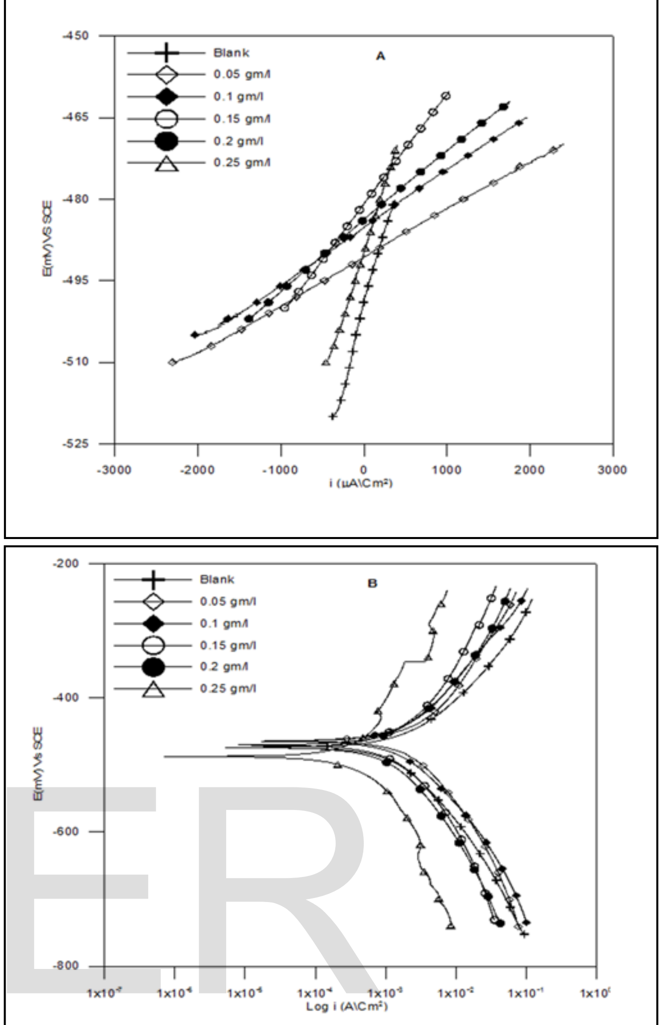
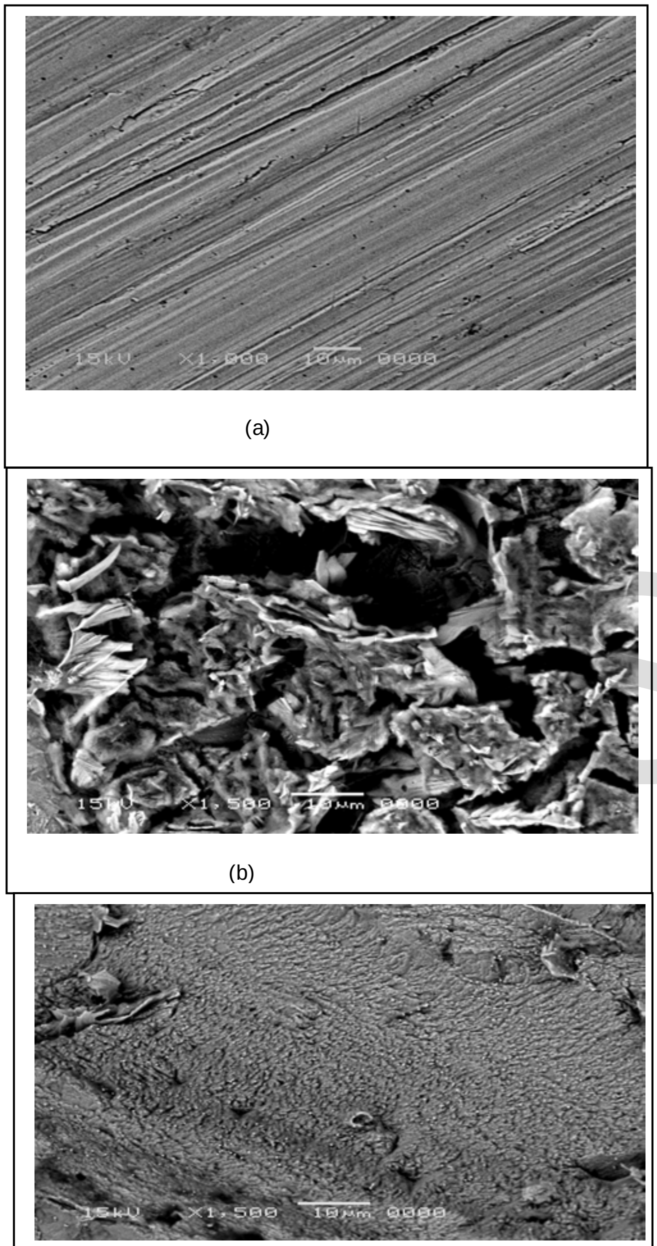


Fig (7): Linear (A) and Tafel plots (B) polarization curves of mild steel 1.0M HCl (blank) and different concentrations of BREed at 25 °C.

3.7. Surface Morphology of the Metal Electrodes

The barrier effect of the corrosion products of a metal in a given environment depends on the characteristics and properties of the film produced. Thickness, uniformily, compactness, porosity, solubility, fragility and adherence will condition the corrosion rate and morphology of attack to the underlying metal. Fig (8 A) illustrates the morphology of surface of polished mild steel electrode before exposure to corrosion media (blank). The specimens were subjected to microscopic examination at x 1000. The micrograph shows a characteristic inclusion, which was probably an oxide inclusion. Fig (8 B) shows SEM image of the surface of the studied mild steel electrode specimen after immersion in 1.0 M HCl solution for 24 hours. The micrograph reveals that, the surface was strongly damaged. The corroded areas are shown as black grooves in the specimen with gray and white zones, which correspond to the dandruff of iron oxide. It suggested an uncovered surface in acid and metal electrode severally corroded. The highly oxidized phase perhaps formed in air when desiccated under no protection for the surface. Fig (8 A,B and C) shows the SEM image which describe the morphology of mild steel electrode before exposure to 1.0 M HCl (A), after 24 hours of immersion in the solution of 1.0 M HCl (B) and with addition of BRE (C). The surface roughness of the mild steel appears lower with addition of the inhibitor than that without addition. This indicating a protective layer of adsorbed inhibitor preventing acid attack.



(a)

(b)

(c)

Fig (8): SEM image of polished mild steel surface (A), SEM image of mild steel exposed to 1.0 M HCl (B) and SEM image of mild steel exposed to 1.0 M HCl having BRE(C).

It is important to take into consideration the percentage of the elements present on the surface of the mild steel. The EDX analysis of the surface reveals the presence of oxygen and iron, suggesting therefore the presence of iron oxide / hydroxide Figs (9-11)and Table (6). The presence of the peaks of carbon, nitrogen, chloride, silicon and sulpher is explained by the adsorption of the inhibitor BRE on the products of corrosion of the mild steel.

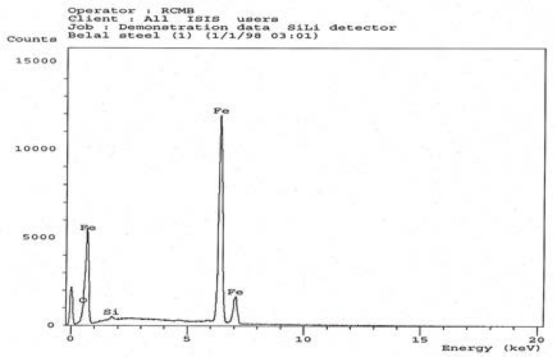


Fig (9): EDAX examination mild steel**.**

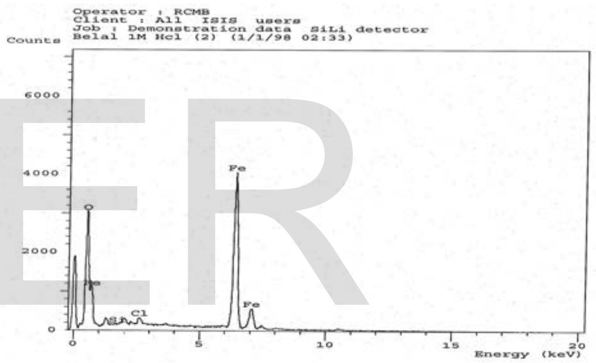


Fig (10): EDAX examination of mild steel immersed in 1.0 M HCl for 24 hours.

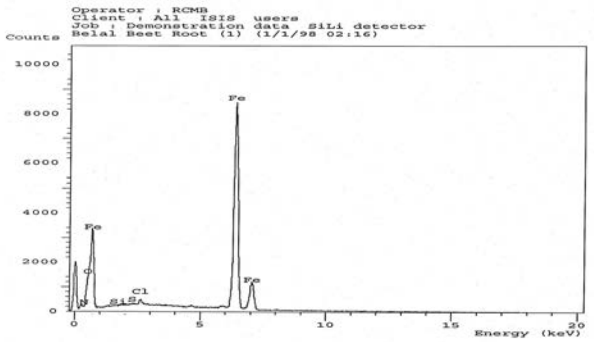


Fig (11): EDAX examination of mild steel immersed in 1.0 M HCl in presence of 0.0506 g/L BRE.

Table 6

EDX analysis for mild steel, mild steel exposed to HCl and

Mild steel exposed to HCl and BRE.

specimen	Fe %	O %	Cl %	Si %	S %	N %
Pure Mild steel	**99.1**	**0.990**	---	---	---	---
Mild steel in 1M HCl	**68.72**	**30.763**	**0.453**	**0.067**	---	---
Mild steel in 1M HCl +BRE	**80.913**	**16.580**	**0.120**	**0.020**	**0.110**	**2.560**

3.8. Ultraviolet and analysis Visible Spectrophotometer:

The active ingredient in an aqueous BRE is mainly betanin. The red color of the extract is due to betanin [40].The inhibition mechanism of BRE (Betanin) is believed to be as a result of complex formation between Fe^{+2} and Betanin. The formed complex is adsorbed on the metal surface and thereby isolating the metal from further corroding attack. To provide an evidence for formation of complex , UV-VIS spectra of solutions in presence of 1.0 M HCl and BRE in absence (Blank) and in presence of mild steel sample was investigated. The results shown in Fig (12) reveals that, the absorbance peaks (330 and 535 nm) occurred in the visible region for BRE decreased or disappeared after adsorption inhibitors on mild steel surface reducing the concentration of BRE. In the same time,there are two significant peaks at different wavelenthes after addition of BRE to mild steel electrode have been obseerved ,which may indicate a new structure unit formed and degradation of the original structure of BRE [41].

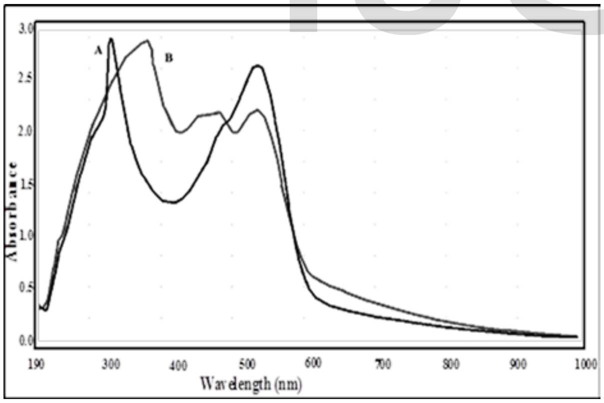


Fig (12): Electronic absorption spectra of BRE (blank) and (A) and in presence of mild steel electrode (B).

4 PROPOSED INHIBITION MECHANISM.

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 [42]. The adsorption of an inhibitor depends on many factors, of these, its chemical structure, its molecular size, the nature and charged surface of the metal, and distribution of charge over the whole inhibitor 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. These ions replace solvent molecules from the metal surface, and their centers reside at the inner Helmholtz plane. This phenomenon is termed specific adsorption, contact adsorption. The anions are adsorbed when the metal surface has an excess positive charge in an amount greater than that required to balance the charge corresponding to the applied potential. The exact nature of the interactions between a metal surface and an aromatic molecule depends on the relative coordinating strength towards the given metal of the particular groups present [43].

An adsorption isotherm describes the equilibrium between the concentration of certain species in the phase in which it is present and in the metal-electrolyte phase. So, adsorption equilibrium can be written as :

$$ORG_{(aq)} + X\ H_2O_{(ads)} \rightarrow ORG_{(ads)} + XH_2O_{(aq)}$$

Where ORG is the organic compound adsorbed and deadsorbed at the same speed on the metal surface. The adsorption phenomenon occurs in an aqueous solution containing the organic compound [$ORG_{(aq)}$]. This involves the displacement of a certain number of water molecules (χ) by the organic compound which is adsorbed on the electrode surface [$H_2O_{\ (ads)}$].

5 CONCLUSIONS

The BRE extract acted as efficient inhibitor for the corrosion of mild steel in 1.0 M HCl. The inhibition efficiency decreased as the temperature was increased. Inhibition effect was performed via the adsorption of BRE on the mild steel surface which follows Langmuir adsorption isotherm. The negative sign of ΔG°_{ads} of BRE at mild steel surface indicates a spontaneous and chemisorption process. The electrochemical parameters such as $E_{corr.}$,b_a and b_c indicate that the BRE act as mixed-type inhibitors. Obtained results in this study suggest the possiblity of config the complex on the mild steel surface.

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