Corrosion Inhibition of Medium carbon steel in the acidic medium using *Salsola. L.* plant extract

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ABSTRACT

This study included the corrosion inhibition of metal corrosion process of medium carbon steel using (1M H2SO4), The weight loss method has been applied pieces of carbon steel divided to Cubans with dimension (0.4*2*2.4)cm, the samples were polished using carbide silicon paper with dimensions of (180,200, 400,600, 800,1000). The samples were immersed in alcoholic medium at temperature (20℃) for 3 hours. natural inhibitor (Salsola.L.) was used which extracted in aqueous and alcoholic medium, different concentrations (1000، 2000)ppm have been used , the results indicated that highest degree of inhibition for aqueous extract is 93.3% with concentration of (2000)ppm and 90.5% with (1000)ppm at (20C). While the alcoholic inhibitor showed the highest efficiency 92.4% with concentration of (2000)ppm and 88.6% with concentration of (1000)ppm respectively. The structure of inhibitor was studied by infrared spectroscopy and the tested samples were studied by scanning electron microscope

Key words: Salsola. L., Corrosion, Inhibition, Medium Carbon Steel,.

INTRODUCTION

Corrosion is defined as damage to metals and alloys due to their chemical or electrochemical reaction with the surrounding environment. Metals and alloys gradually change, into compounds such as oxides, hydroxides, carbonates and sulphides[1]. Corrosion is the atmospheric oxidation/degradation of metals. It is an electrochemical process by which metallic surfaces react with their environment causing the metal to lose its material properties due to surface deterioration[2], as defined by scientists in the year (1830 A.D) as a complex phenomenon has been studied physically, chemically, electrochemically, kinetically or thermodynamically, the studies proved that to be entirely dependent on mechanical properties of metal[2]. In general, the driving force for the completion of the corrosion reaction is the change in the free energy of the material as a result of their transformation into compounds with a generally lower free energy than their constituent metals[1], therefore they are automatically formed if exposed to the appropriate conditions, the resulting compounds are more stable than the metal which is naturally composed of them [3] .

Process of corrosion of the metal leads to ions generation with some electrons that are consumed by a secondary reaction. When the metal is placed in pure water, some ions will be transferred directly to the solution[4].

$Fe \longrightarrow Fe^{+2} + 2e^- \quad E° = 0.44 \text{ v} \quad ....(1.1) \quad$ oxidation
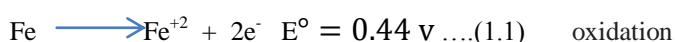
Accumulation of the negative charge on the metal and presence of metal ions in the solution makes the reaction go back:

$Fe^{+2} + 2e^-$ ⟶ Fe $E° = -0.44$ v   ....(1.2) shorthand[4]
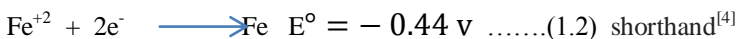
at the end, the equilibrium obtained

Fe ⟶ $Fe^{+2} + 2e^-$ ………….(1.3)
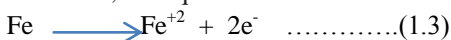
The potential difference depends on the type of metal and the composition of the solution [5,6].

The inhibitors effect on the electrochemical reaction kinetics in the corrosion process, and fixed on the inhibitors on the metal surface, thus the process easy the electrical double layer changes, if same active inhibitors used in the industry is organic compounds, as containing oxygen, nitrogen and sulfur atoms which can lead to adsorption of compounds on the surface of the metal[6].

Also biodegradable green inhibitors that do not contain heavy metals or other toxic compounds are used. Corrosion inhibitors generally control corrosion through the mechanism of these inhibitors, which are applied to the surface of the metal, which acts on the basis of adsorption, On the metal surface [7].Adsorption depends on the charge nature of the metal surface, electronic properties and, properties of solvents, temperature the electrochemical potential[8,9].

This study aimed to estimate the ability of a plant extract to inhibit the corrosion of using metal and to find the difference in the corrosion rate for the static phase at time and different temperatures.

EXPERIMENTAL

1- Samples preparation

The samples were divided to small Cubans with dimensions (2 cm) length and (2.4 cm) width and (0.4 cm) thickness[10]
.

Chemical analysis

The carbon steel samples and the Salsola. L. extract of plant (aqueous and alcoholic) were analyzed spectroscopic ally (Table1), using the atomic absorption spectrophotometer device. (**Note: The device has no ability to measure all elements in the metal and extract**) .

Table 1: Elements analysis data of carbon steel samples

Sequence	Fe	Ni	Zn	Mn	K
Wt %	1.8	0.1	0.1	0.11	17.0

(Table 2) Elements analysis data of the leaves of the plant (aqueous and alcoholic)

Element	Mg	Mn	Zn	Ni	Fe	K	Cu	Cr
Wt %	0.003	0.03	0.5	0.03	99	0.01	0.045	0.032

2- Preparation of Salsola.L. extracts (inhibitor)[11]:

The plant extract was prepared using tap water so as to wash the plant and freeing him from the dust suspended in it limit to ((40-60%) and polar solvents (aqueous and ethanol) as follows: [10].

3-1- The organic extract was prepared as follow (50)gm of the Salsola.L. plant powder in a conical flask(500ml) was mixed with 250 ml of petroleum ether, the mixture was stirred for 72hr using magnetic stirrer and, then the solution was filtered off and dried in oven at (20-30°C) , the filtrate was saved in a glass container and placed in the refrigerator at a temperature of (4)°C.

3-2- The alcoholic extract of the Salsola.L. plant was prepared by the following procedure . (50)gm from the powder that prepared in (3-1) was mixed with 250 ml ethanol 99.9% and stirred for 72hr using the

magnetic stirrer, then the solution filtered and evaporated the filtrate under low pressure using rotary evaporator at (4)°C and the remaining extract (50%) is reserved until use[11,12].

3-3- Prepare aqueous extract the aqueous extract was prepared as mention in (3-2) , was mixed (50gm)with 250 ml of water and stirred for 72hr using the magnetic stirrer. The solution is then filtered off and the filtrate was evaporated under vacuum at (4)°C and the remaining extract (50%) [11,12].

Preparation of the corrosion solution:

By dilution method , 1M concentration of sulfuric acid was prepared[8]

4- Measurement of the weight loss:

All metal samples were placed in 100 ml of (1)M H_2SO_4 and then transferred to a water bath at the required temperature and concentration to the inhibitor for 3hr, then The samples were cleaned and washed with deionized water, and dried with a tissue papers or smoothed papers (type 180-1000 P) and then washed with acetone and dried again. The weight loss was determined in the presence of the inhibitor at concentrations 2000,1000 ppm at (20,30, 40 °C)[13].

RESULTS AND DISCUSSION

1. Method of weight loss

Corrosion rates (CR) were determined in the presence and absence of inhibitor using the following Equation[14] :

$$(CR) = \frac{\Delta W}{A \times t} \quad \text{............ (1.4)}$$

Where (ΔW) weight loss (gm), A: surface area of sample (m^2), t: time of sample exposure for day.

Corrosion rates were obtained in g / m^2 . day (g.m^{-2}d).

The inhibition efficiency was calculated using the equation:

$$\% \text{ IE} = \frac{CR_u - CR_i}{CR_u} \times 100 \quad \text{....... (1.5)}$$

Where CR_u and CR_i are the corrosion rates in the absence of different concentrations of inhibitors, respectively.

The inhibition efficiency (IE%) can be also calculated using the following equation[15]:

$$\% \text{ IE} = \frac{(i\,corr)_a - (i\,corr)_p}{(i\,corr)_a} \times 100 \quad \text{..... (1.6)}$$

Where $(i\,corr)_a$ and $(i\,corr)_p$ is the density of the corrosion current ($\mu A.cm^{-2}$) in the absence of inhibitors, respectively.

Surface cover (θ) can be calculated by the following equation[16] :

$$\theta = \frac{IE}{100} \quad \text{.................. (1.7)}$$

Where: (θ) surface coverage, (IE) inhibition efficiency[17] .

Corrosion rate, inhibition efficiency, corrosion current efficiency and surface coverage were assessed under different conditions. The results were collected in (Table 3,4). It is clear that the rate of corrosion increases with increasing temperature and concentration of sulfuric acid and decreases with increasing of inhibitory concentrations .

(Table 3) Temperature effect upon corrosion rate, density of the corrosion current of medium carbon steel in (1)M of H_2SO_4 and surface coverage in presence of aqueous extract inhibitor

Sample	C_i (ppm)	T $_{(°C)}$	Corrosion rate (g.m^{-2}d)	I_{corr} ($\mu A.cm^{-2}$)	θ	% IE
1.		20	530	450.5	0	0
2.	0	30	900	497.6	0	0
3.		40	1440	682.7	0	0
4.		20	50	42.7	0.905	90.5
5.	1000	30	135	74.6	0.850	85
6.		40	240	114	0.833	83.3
7.		20	35	30.1	0.933	93.3
8.	2000	30	100	55.7	0.888	88.8
9.		40	210	99.6	0.854	85.4

(Table 4) Temperature effect upon corrosion rate, density of the corrosion current of medium carbon steel in(1)M of H_2SO_4 and surface coverage in presence of alcoholic extract inhibitor

Sample	C_i (ppm)	T $_{(°C)}$	Corrosion rate (g.m^{-2}d)	I_{corr} ($\mu A.cm^{-2}$)	θ	% IE
1.		20	530	450.5	0	0
2.	0	30	900	497.6	0	0
3.		40	1440	682.7	0	0
4.		20	60	51.3	0.886	88.6
5.	1000	30	140	77.6	0.844	84.4
6.		40	310	147.4	0.784	78.4
7.		20	40	34.2	0.924	92.4
8.	2000	30	130	72.1	0.855	85.5
9.		40	280	133.1	0.805	80.5

Evaluation of corrosion rate

The weight loss method was used to calculate the corrosion rates in non-inhibitory acid solutions at different temperatures (20, 30, 40°C). The average carbon steel corrosion rate in 1M H_2SO_4 increased from 530 to (1440 g.m^{-2}d) with increasing temperature (20 - 40)°C. And the density of the Corrosion current of the medium carbon steel was increased from (450.5 - 682.7) ($\mu A.cm^{-2}$) with an increase in temperature (20 – 40°C). (Figure 1) shows the increased in the rate of corrosion with increased of temperature, the relationship between temperature as variable and the rate of corrosion and (Figure 2) shows the increased of the density of the corrosion current with increased temperature.
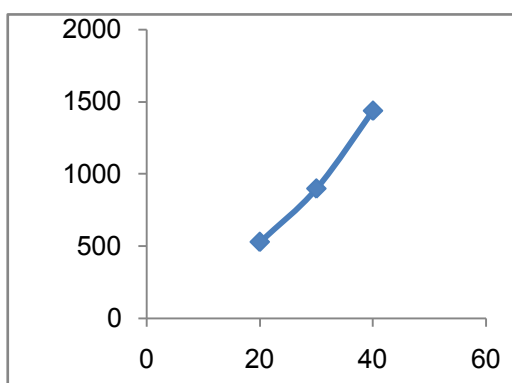

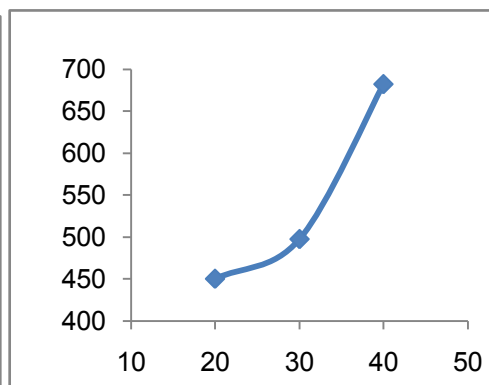**Figure (1) Effect of temperature on the average carbon steel in (1) M of sulfuric acid**

Figure (2) Effect of temperature on the electrolyte current density of carbon medium in (1) M of sulfuric acid

Effect of acid in presence an inhibitor at different temperatures

From (Figures3,4) we notice the effects of temperature on corrosion rate that was expressed for the different inhibitor concentrations The two forms show that the corrosion rate increases with rise of temperature and inhibitor

concentration. When using (1000)ppm an inhibitor at temperatures (20-40°C) ,The highest corrosion rate was (310)g.m^{-2}d at (40°C) when (1000, 2000 ppm) concentration of alcoholic Salsola.L. extract been used ,While the lowest corrosion rate was (50)g.m^{-2}d at 20°C with the aqueous extract.

The concentration of 2000 ppm of the inhibit at different temperatures gave the highest corrosion rate (280) g.m^{-2}d at (40°C) when using extract of the alcoholic. The lowest value of the corrosion rate was (35) g.m^{-2}d at (20°C) with the aqueous extract
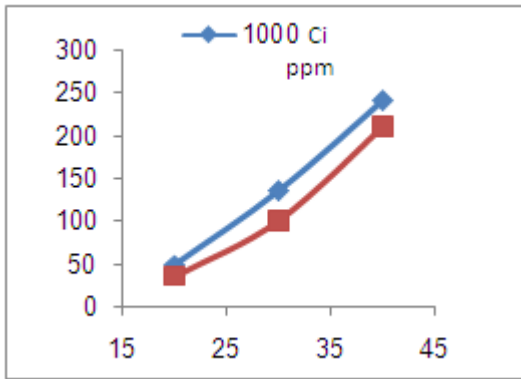
Figure (3) The effect of Temperature medium Carbon steels in (1) M H$_2$SO$_4$ with the presence of aqueous extract
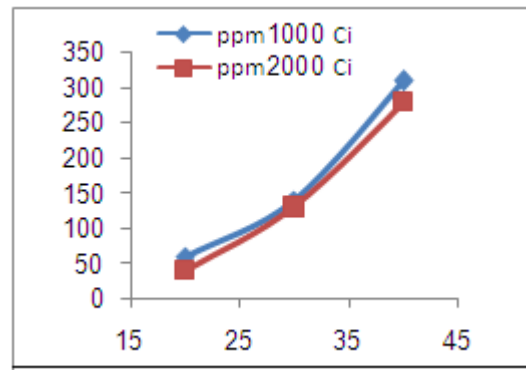
Figure (4) The effect of Temperature effect on corrosion rate of on corrosion rate of medium carbon steels in (1) M H$_2$SO$_4$ with the presence of alcoholic extract.
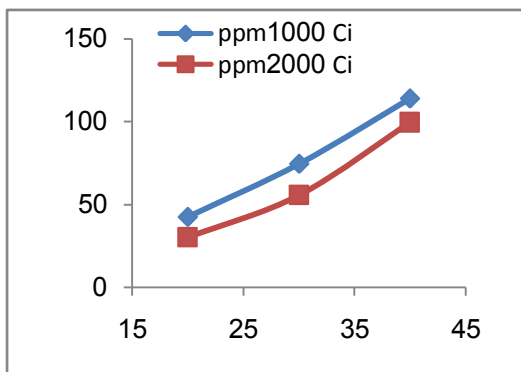
Figure (5) Effect of temperature on density of the corrosion current in(1) M H$_2$SO$_4$ with a aqueous extract
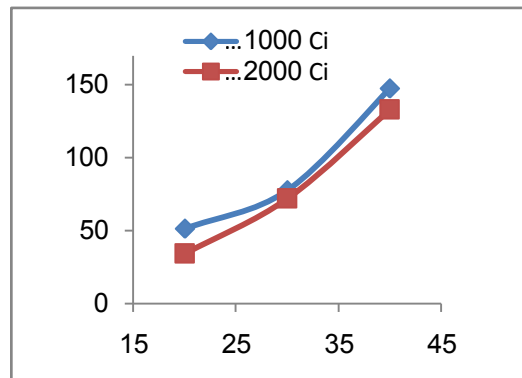
Figure (6) Effect of temperature on density of the corrosion current in (1) M H$_2$SO$_4$ in presence of the alcoholic extract
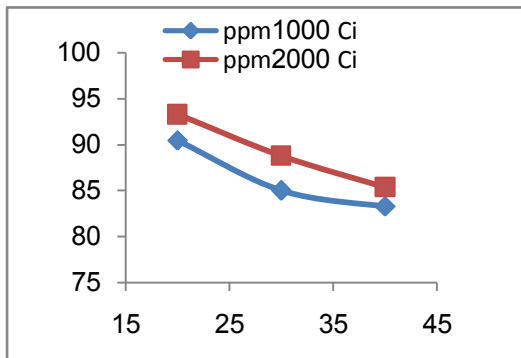
Figure (7) Effect of Temperature on inhibition efficiency in (1) M H$_2$SO$_4$ in presence of alcoholic extract
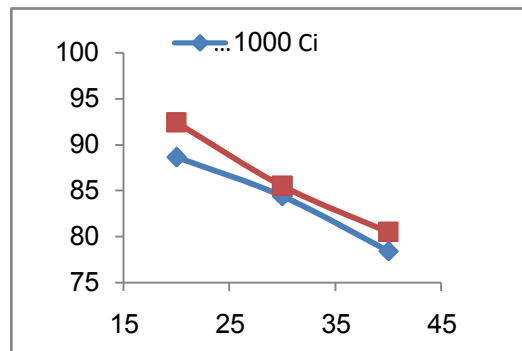
Figure (8) Effect of Temperature on the inhibition efficiency(1) M H$_2$SO$_4$ in presence of aqueous extract
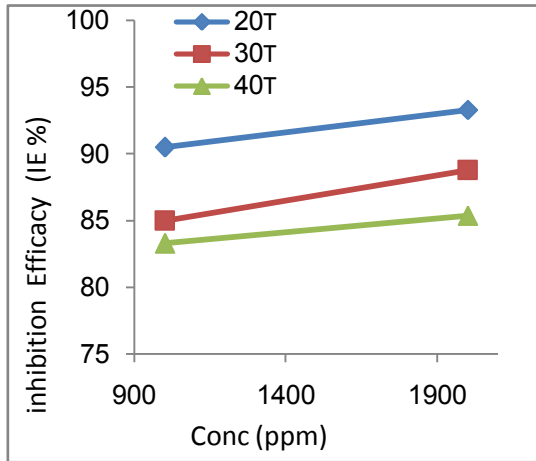
Figure (9) Effect of concentration on inhibition efficiency in (1) M H$_2$SO$_4$ in presence of aqueous extract
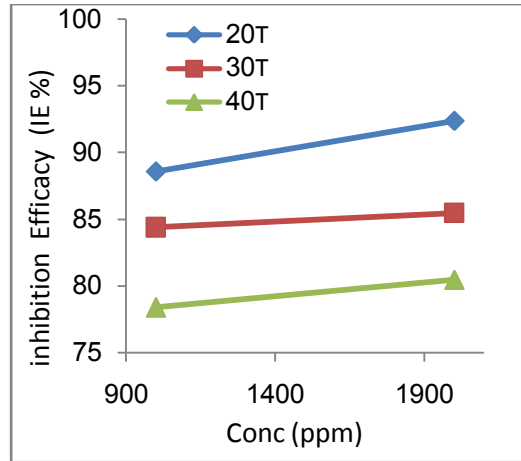

Figure (10) Effect of concentration on inhibition efficiency in (1) M H$_2$SO$_4$ with an alcoholic extract
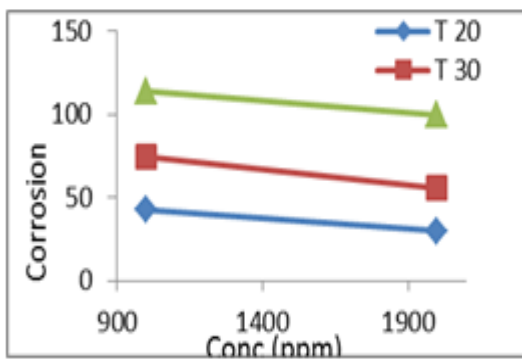

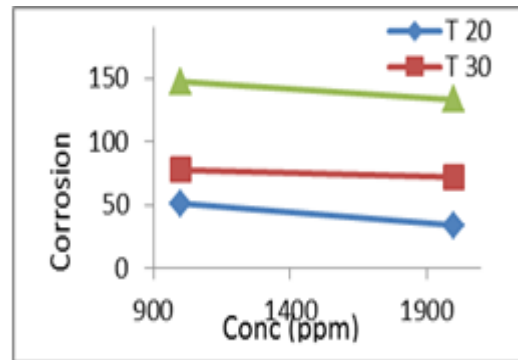**Figure (11) Effect of concentration on density of the erosion current in(1) M H$_2$SO$_4$ with a aqueous extract**

Figure (12) Effect of concentration on density of the erosion current in(1 M H$_2$SO$_4$) with the presence of the alcoholic extract
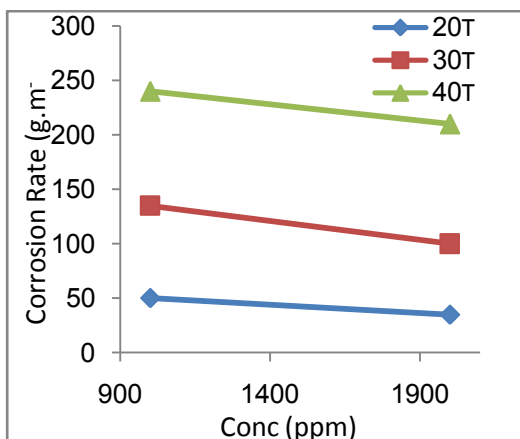

Figure (13) Effect of Concentration on Corrosion rate in (1) M H$_2$SO$_4$ with aqueous extract
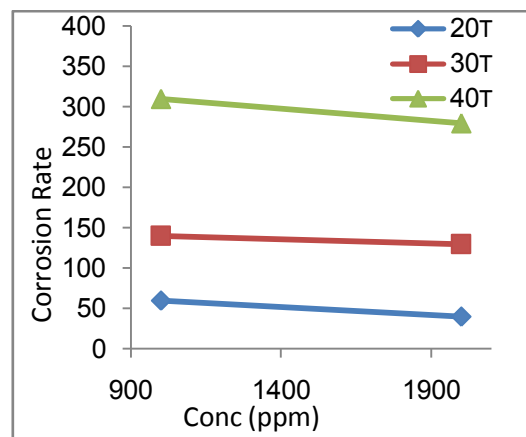

Figure (14) Effect of Concentration on Corrosion rate in (1) M H$_2$SO$_4$ with alcoholic extract .

Scanning electron microscopy studies

The microscopic examination of the surface of the eroded sample in the acid medium showed dark color and that are indicating to corrosion products result from corrosion due to direct exposure to the acid medium. However, with the inhibitors, the damage is much smaller on the surface with clear color. And that because of formation protective layer on the steel surface which prevents the contact between the surface and medium.
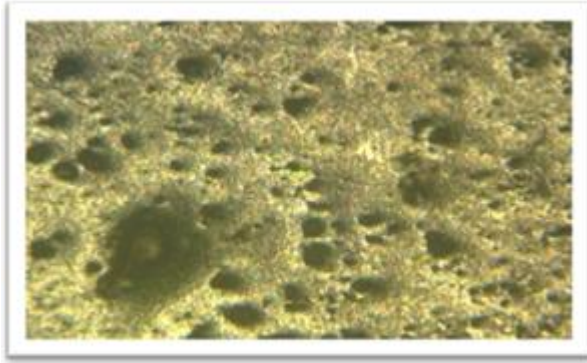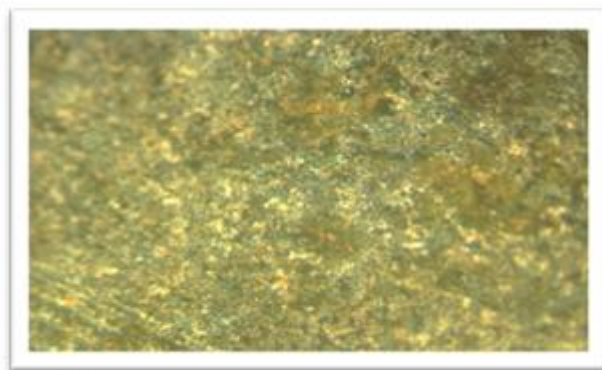
200X

Figure(15) electron Microscopy of medium carbon steel after immersion in the middle of the corrosion medium
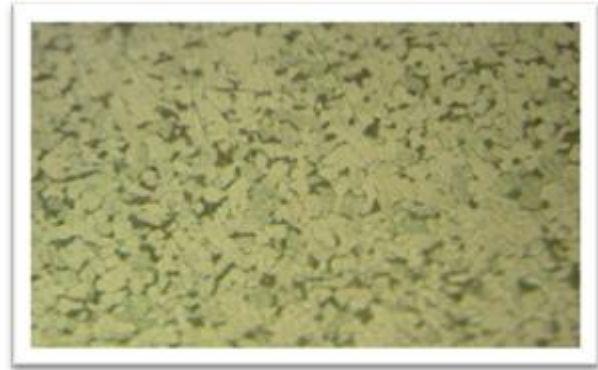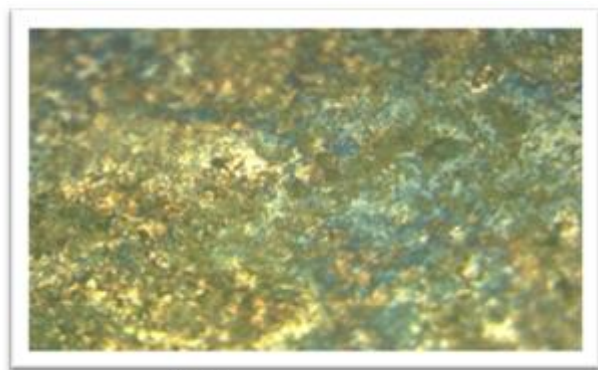

200X

Figure(16) electron Microscopy of medium carbon steel before immersion in the middle of the corrosion medium
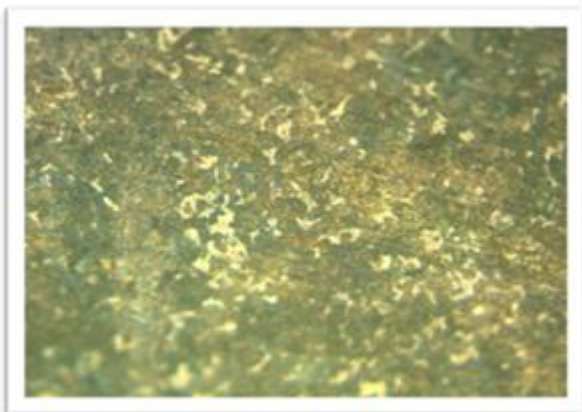

1000ppm

Figure(17) electron Microscopy of steel after corrosion in (1) M H_2SO_4 in the presence of aqueous extract
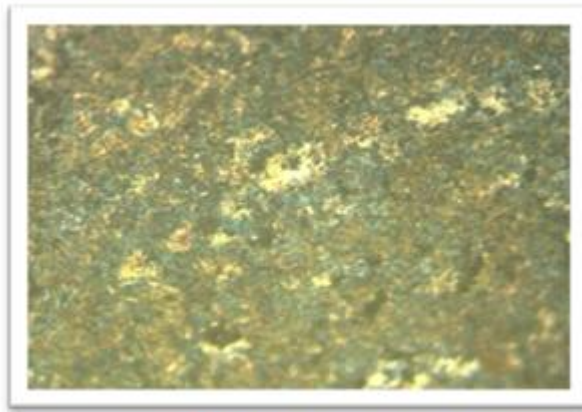

2000ppm

Figure(18) electron Microscopy of steel after corrosion in (1) M H_2SO_4 in presence of aqueous extract

1000ppm

Figure(19) electron Microscopy of steel after corrosion in (1)M H_2SO_4 in the presence of alcoholic extract(1000ppm) extract

2000ppm

Figure(20) electron Microscopy of carbon steel after corrosion in (1)M H_2SO_4 in the presence of alcoholic

Studies of inhibitory structures and infrared radiation

FTIR study of inhibitor composition for the purpose of metal surface protection , plant extract was used and the FT-IR spectra were recorded in order to , elucidate the potential interactions between the adsorbed inhibitor (Salsola.L.) and the surface of carbon steel which are immersed in $(1M)H_2SO_4$. FT-IR results (Table 5) and figure(21) is showed that the stretching frequencies of the inhibitor were shifted to lower values in comparison with the frequencies of the free extract and that maybe as a result . of the reaction between the extract molecules and the surface of the metal[18].

Theses stretching frequencies are assigned to the presence of the alkaloids and flavone's compounds which are responsible for such surface pro11For the purpose of protecting the surface of the metal using plant extracts and finding the best plant that provides protection[18].

Table 5: The important bands for the extract(Cm⁻¹)

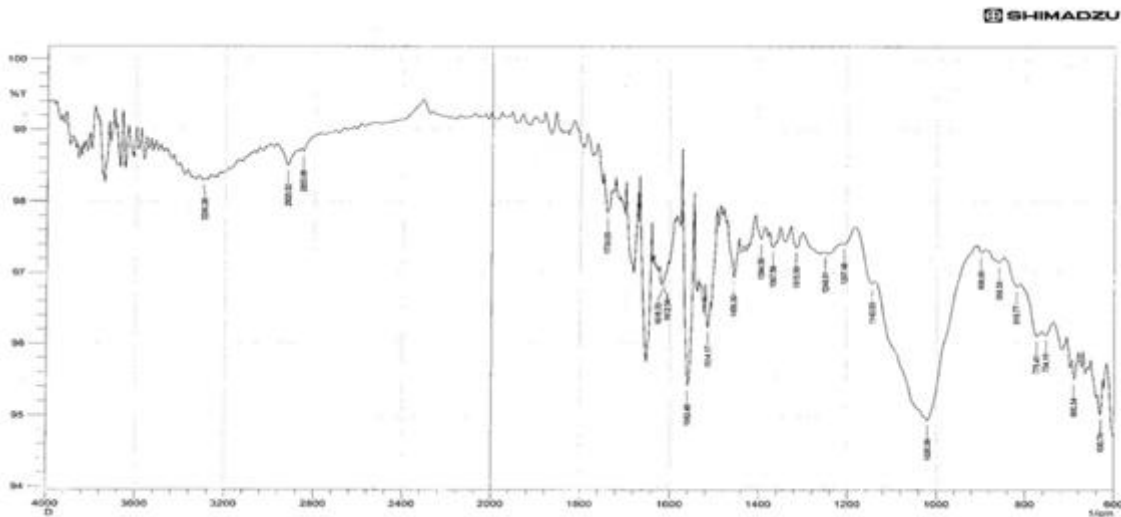|	υ-NH	υ -CH$_3$aliph	υ - CH$_2$aliph	υ -C=O	υ -C=C Ar
Free extract	3298b	2920w	2853w	1739s	1560s
inhibitor	3282b	2918w	2850w	1736s	1560s

B=bond ,w=weak , s=strong

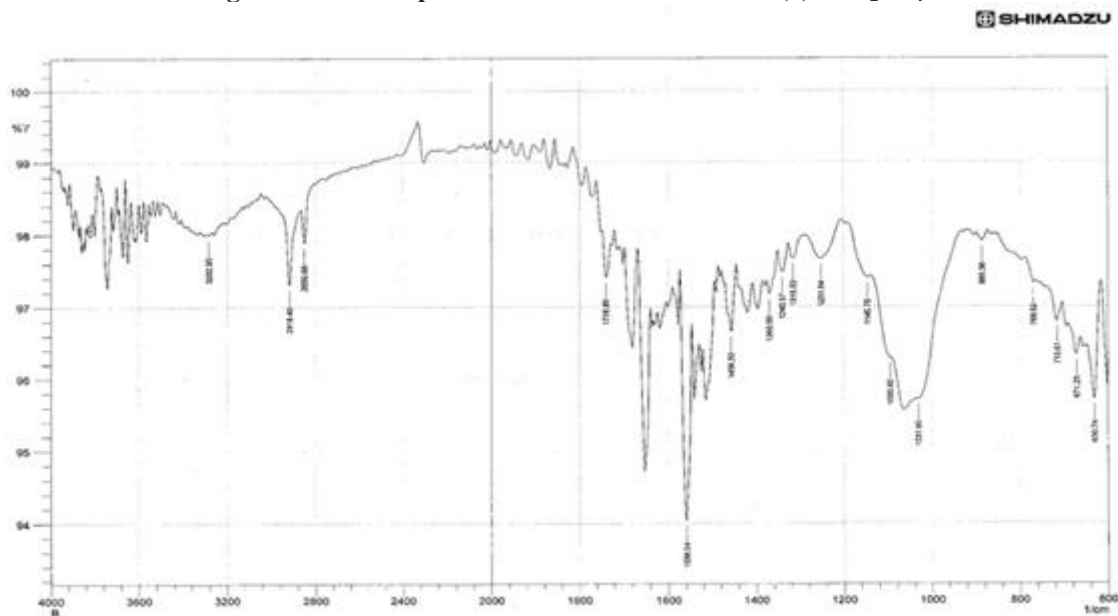**Figure 21: FT-IR spectra of the Salsola. L. extract (1) M H$_2$SO$_4$**

Figure (22) FT-IR spectrum of the extract for the protective layer formed on the metal surface after immersion in 1M H$_2$SO$_4$

CONCLUSIONS

1- Salsola.L. extract acts as a good inhibitor for the corrosion of Carbone-steel in 1 M H$_2$SO$_4$ solution.

2-Inhibition efficiency increases with rise the inhibitor concentration but decreases with rise the temperature.

3-The results obtained from polarization measurements revealed that Salsola.L. extract behaves as a mixed type of inhibitor.

4-Salsola.L. alcoholic extract is better than an aqueous extract at lower concentration.

5-FT-IR show the layers of corrosion inhibition with iron ions on the Carbone medium steel surface especially for the compounds that present in the plant extract.

ACKNOWLEDGEMENT

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