Salicornia Extract as Corrosion Inhibitor of Carbon Steel in Acidic Medium

Kadhim F. Al-Sultani

University of Babylon- Iraq
finteelalsultani@yahoo.com

Abstract: The inhibitive effect by salicornia extract for carbon steel in 1M H_2SO_4 solution was investigated using gravimetric methods and electrochemical techniques at room temperature. The results showed that the presence of salicornia extract inhibited the corrosion of carbon steel and that the inhibition efficieucy depended on the concentration of the inhibitor as well as on the time expouser . The dry salicornia extract and the protective film have been analyzed using Fourier transform infrared FTIR spectroscopy. Inhibitive effects of the extract obtained from impedance and polarization measurements were found increase with increase concentration of inhibitor. The adsorption of the inhibitor characteristics were approximated by Langmuir adsorption isotherm at all concentration at 25 ºC. On the other hands, the metallurgical microscopy was used to observations the metallographic.
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Key word: carbon steel, salicornia extract, acidic media, Langmuir isotherm, FTIR, potentidynamic polarization.

1. Introduction

Steel and – based alloys of different grades steel are extensively used in numerous applications where acid solution are widely applied such as industrial acid pickling, industrial acid cleaning and oil-well acidizing acidizing [1]. The usefulness of steel and steel based alloy is constrained by one common problem known as corrosion. Corrosion phenomena, control and prevention are unavoidable major scientific issue that must be addressed daily as for as there are increasing needs of metallic materials in all facets of technological development [2-3]. Among the several methods of corrosion control prevention, the use of corrosion inhibitors is very popular. Corrosive inhibitors are substance which when added is small concentrations to corrosion media decrease or prevent the reaction of the metal with the media. Several investigations have been reported using such naturally occurring substance as corrosion inhibitor for several metals in different media [4-7].

In recent years, a number of eco-friendly compounds such as extract of common plants which contain many organic compounds, e.g., alkaloids, fatty acids, carbohydrates, tannins, pigments and amino acids, have been exploited as green alternative to toxic and hazardous compounds [8]. Most of the effective compounds are use to contain heteroatom such as O,N,S and multiple bonds in their molecules through which they are adsorbed on the metal surface through these heteroatom, protective films are formed [4, 9-11].

The present research reports on the corrosion inhibition and adsorption behavior of extracts from salicornia plant as an environmental benign inhibitor on mild steel corrosion in different media using the weight loss technique. Salicornia (sulicornioideae, chenopodiaceous) is an annual, stem succulent genus with highly reduced leaves and spike – like terminal inflorescences, species always grow in periodically wet saline coastal or in land habitats [12]. Salicornia is grow in west of Iraq in regional between Sudia Arabia, Syria and Iraq, the salicornid represented best food for camels Fig. (1). The salicornioideae family comprises approximately 15 genera and 80 species [13]. Almost all micro – and macronutrient content decrease in the roots and shoots with increasing salt concentration in the growth medium [14].

Fig. (1) Photographs of salicornia (different type)

2. Experimental part

2.1 Preparation of specimens

Commercially available carbon steel was used for all experiments. The specimens having weight percentage composition as follow; 0.35% C , 0.09% Si, 0.06 %Ni, 0.10% Cr, 0.05% S, 0.07% P, 0.12 % Mn,0.03% Mo and the remainder iron. The specimens were of dimensions (2.1*2.1 cm) and thickness 0.4 cm, the steel coupons were immersed in 5% HCl as pickling solution to remove rust and sequentially polished using silicon carbide emery papers 240, 400, 600, 800 and 1000 grits. They were thoroughly cleaned, rinsed in ultrasonic cleaner, dried, and kept in desiccators for further weight loss tests.

2.2 Preparation of salicornia extracts

Salicornia leaves were collected from west of Iraq from of the Kerbala province near of Al- razaz lake. These were cut separately into pieces which were then oven dried at 50 C° for three hours, and ground to power form. Weighed samples extract was prepared by refluxing salicornia powder in doubled-distilled water for two hours. The solution were cooled and then filtration. Concentration of the stack solution was determined by drying a sample and measuring the weight of the residue relative to the volume of the sample taken. From the respective stock solution, inhibitor test solutions were prepared in the concentration range of 1, 1.5 and 3% v/v; the procedure for the preparation of the salicornia extract is similar to those other researchers [15-17].

2.3 Weight loss Measurement

Polished specimens were initially weighed in a digital balance with sensitivity of +0.001 mg at. The weight loss studies were carried out at ambient temperature by immersing previously weighed steel coupons in 150 ml each of blank 1 M H_2SO_4, 3% NaCl and tap water, and test solutions of 1, 1.5 and 3% v/v concentrations of extract for various time before taking weight- loss measurements, the metal specimens were washed with doubled – distilled water, dried with warm air drier and weighed. The weight loss (weight loss per cm^2) was calculated using the following expression:

Weight loss (W) = $\frac{Wi-Wf}{A}$ …… (1)

Where Wi = initial weight (mg), Wf= final weight (mg), A= area (cm^2).

The inhibition efficiency (% IE) of salicornia extract solutions acting as an inhibitor were calculated by using formula as provide below:-

% IE = [1-W1/W2] ×100 …… …….. (2)

Where W1 and W2 are the weight losses (mg) for specimens in the presence and absence of inhibitor respectively.

3- Results and discussion

3-1 Characterization of salicornia extract

The salicornia extract was evaporated to dryness to get solid mass. The FTIR spectra of the solid extract were recorded with (FTIR-8400S SHIMADSO. Japan).

FTIR spectrum is shown in Fig. (2). The groups C=C stretching frequency appeared between (1570.06 – 1597.06 cm^{-1}), indicative of alkenes and aromatic functional groups were presence. The C=0 stretching frequency appeared at (1647.21 – 1718.58 cm^{-1}), this groups attributed to the hemicelluloses and lignin aromatic groups. The C-H stretching frequency appeared at (2850.79-2931.8cm^{-1}) the phenolic O-H stretch appeared at (3417.88- 3491.6 cm^{-1}) [18-19]. Since retention time of compounds is closed to each.

Other and it is very difficult to separate them, hence the total alkaloids extract from salicornia plant was used for corrosion inhibition studies [20]. The FTIR spectrum of the protective film formed on the surface of the metal after immersion in the 1m H_2SO_4 containing 1% of extract is shown in Fig. (3). It is found that the similar functional groups appeared in Figs. (2-3), this proves that the inhibition action was performed by adsorption of plant particles on the carbon steel surface.

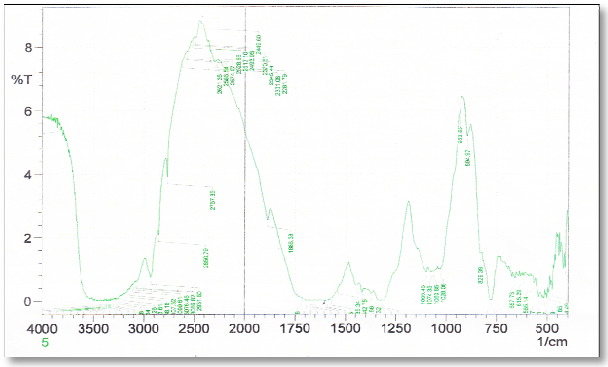


Fig. (2) FTIR Spectra of dry salicornia extract .

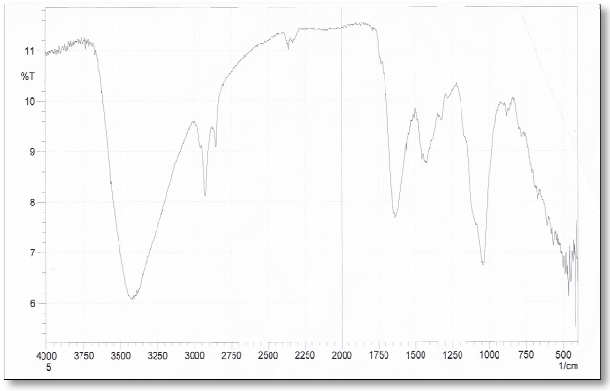


Fig. (3) FTIR Spectra of film formed on metal surfaces after immersion in acidic solution with 3(%v/v)from inhibitor extract for 12 hr .

3-2 Polarization Measurement

The polarization curves of carbon steel immersed in acidic solution in the absence and in the presence of different concentration of salicornia extract at the of 25 C° were summarized in Fig. (4). It is evident that the extract inhibitor brings about considerable polarization of the cathode as well as anode. It was therefore, inferred that the inhibitive action is mixed type, where both the catholic and anodic polarization of the working electrode increase with increase concentration of the inhibitors.

The values $E_{corr.}$ are slightly shifted to more positive values in the presence of increasing concentration of the inhibitors, and the addition of salicornia extract reduces anodic dissolution, retards the hydrogen evolution [17,20,21].

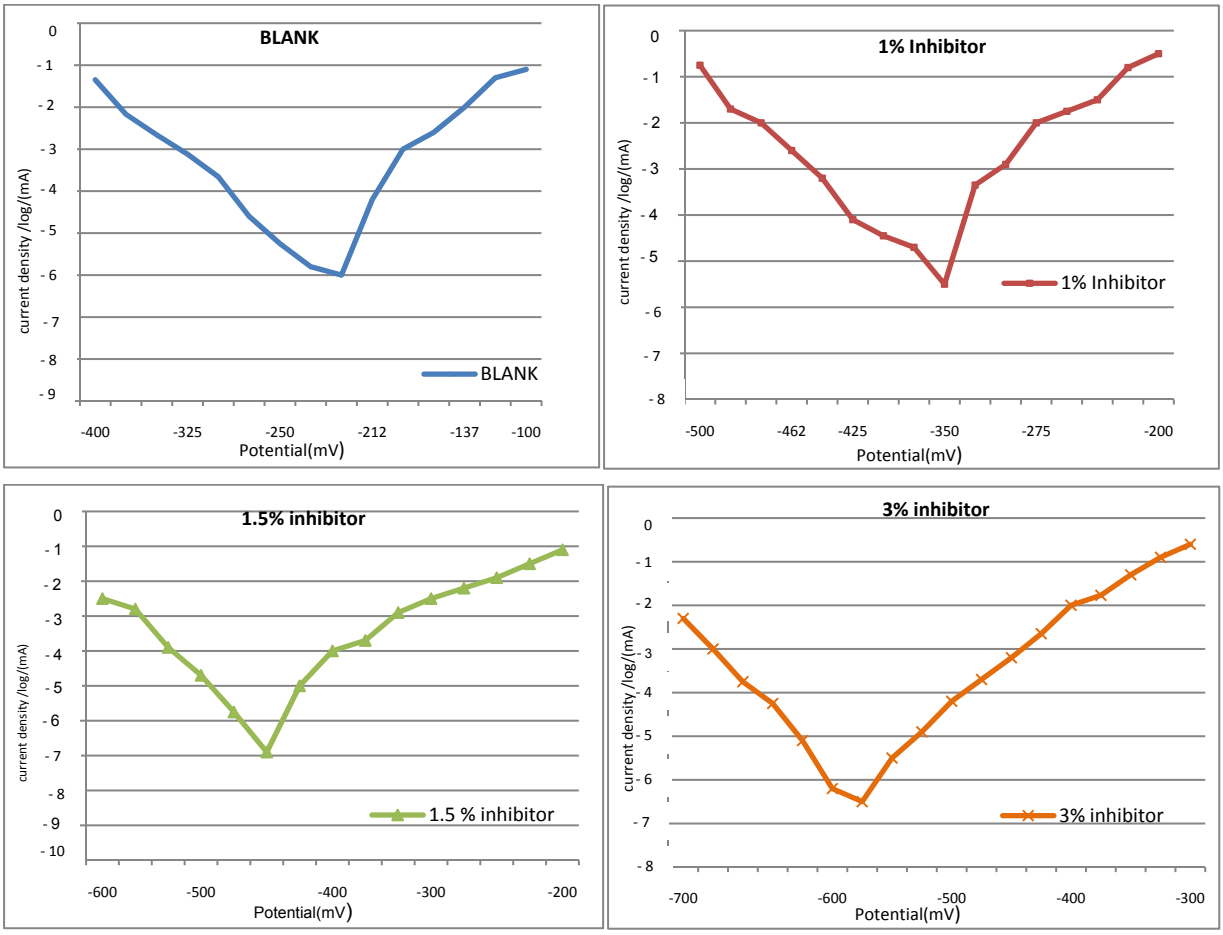


Fig. (4) Polarization Curves for carbon steel in acidic acid with absence and presence of various concentration of inhibitors

3-3 Weight loss Measurement

The weight loss measurement for the carbon steel in 1M H_2SO_4 media in absence and presence of different concentration of salicornia extract was studied in the room temperature. Variation weight loss with of carbon steel exposure in H_2SO_4 solutions containing the inhibitors shows a remarkable decrease in Wight loss compared with solutions without inhibitors Fig.(5). The inhibition process is the result of an adsorptions inhibitors molecule on the carbon steel surface where salicornia extract solutions act as an adsorption inhibitor [22]. Clearly, the inhibition efficiency of salicornia extract increase with exposure time for the inhibitor concentration considered. This indicates that the effectiveness of the inhibitors in retarding. The corrosion rate of carbon steel in the test solutions does not improve indefinitely with increase the inhibitor concentration [16].

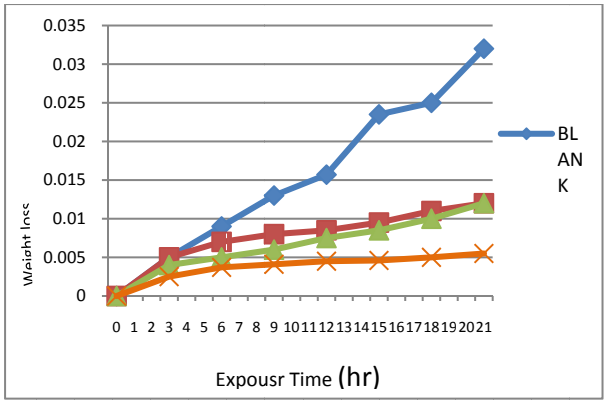


Fig. (5) Variation of weight loss with exposure time for the carbon steel specimen immersed in 1 M H_2SO_4 with different concentration of added inhibitors.

3-4 Mechanism of corrosion inhibition

The effectiveness of organic compounds (salicornia extract) as corrosion inhibitors can be attributed to the a adsorption of the inhibitors molecules through the polar groups to the metal surface, the adsorbed layer on the metal surface acts as a barrier between the corrosive environment and the metal surface. Adsorption isotherms provide information about the interactions among adsorbed molecules themselves as well as their interactions with metal surface [15, 23]. The surface coverage (θ) values for different concentrations of the inhibitor in 1 M H_2SO_4 have been evaluated from the weight loss data. Fig.(6) shows that the inhibition process occurred due to adsorption of active organic compounds on the carbon steel surface. The proved by the linear correlations between $\frac{C}{\theta}$ and C, linear constant of the fitted is close to 1, this indicate that adsorption of inhibitor molecule closely.

$$\frac{C}{\theta} = \frac{1}{K} + c \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where C is inhibitors concentration and K is equilibrium constant for inhibitor molecule absorption on the carbon surface.

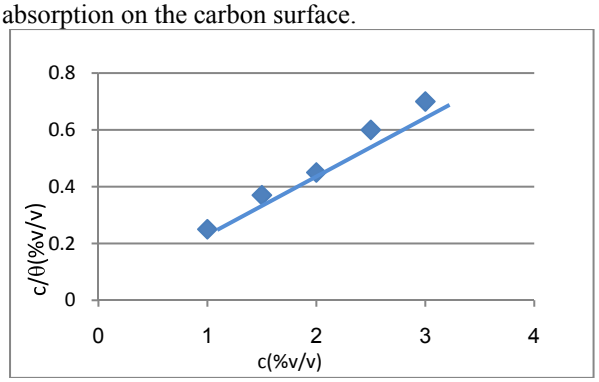
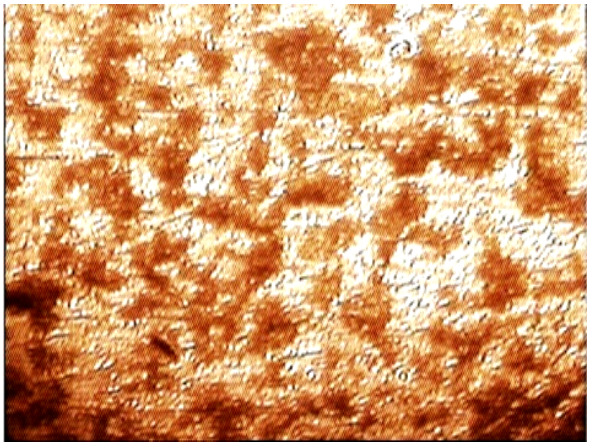


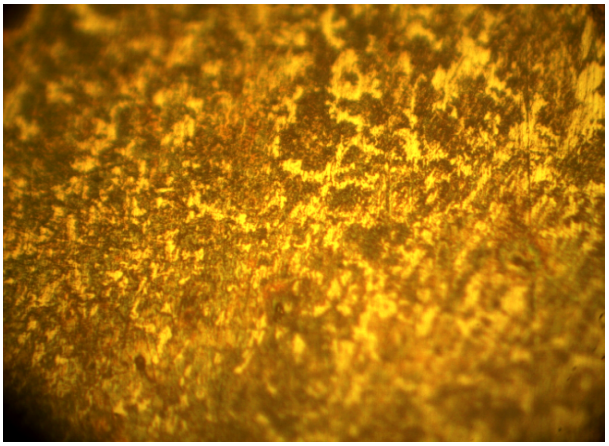
Fig. (6) Langmuir adsorption isotherm for salicornia extract of carbon steel in 1M H_2SO_4 at 25 °C

3-5 Micrographs examination

From Fig.(7) have been shows the micrographs of different slides of carbon steel after immersion in the 1M (H_2SO_4) with the absence and presence of the salicornia extract. From Fig. (7A) observed uniform corrosion of the carbon steel in the test medium without added inhibitors. The micrographs in Figs. (7B,C and D) shows the surface carbon steel in1M(H_2SO_4)with presence different concentration from inhibitors. The surface of specimens is clearly covered with a uniform film of small grains and shows a surface feature with very moderate or minimal corrosive action for the test with the addition of salicornia extract. The corrosion inhibitors adsorb to the metal surface atoms at the metal/solution interface through electrostatic or covalent bond [24]. These observations from the micrographs bear very close correlation with the results obtained from the gravimetric experiments (weight loss).



-A-



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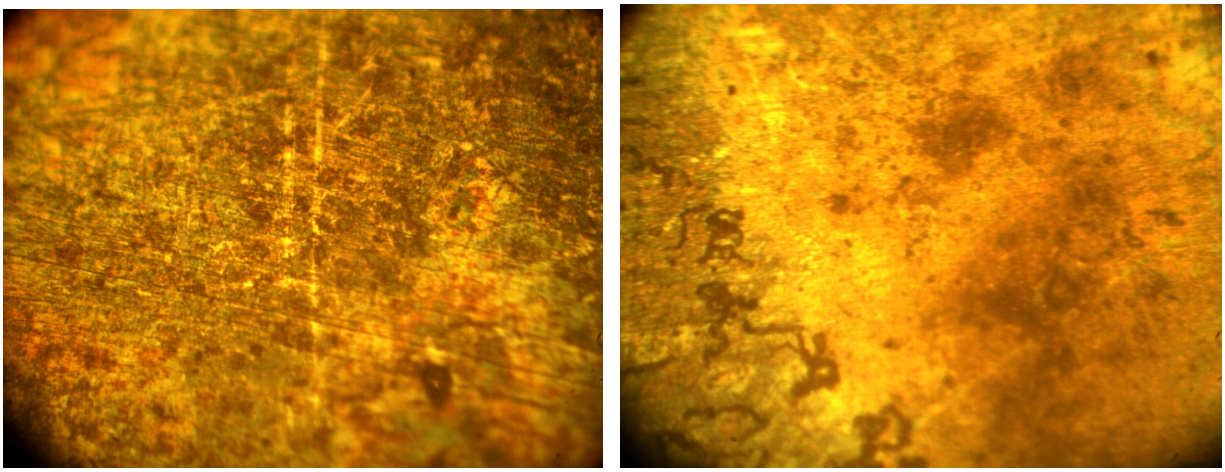

-C- -D-

Fig. (7) : Illustrate the microstructure of carbon steel,(A) before immersion; (B,C and D) after immersion in acidic solution with 1, 1.5 , and 3 (%v/v)from salicornia extract respectively for 12hr.

4- Conclusion

The present study shows that the extracts from saliconia plant acts as an effective and efficient corrosion inhibitor for carbon steel in 1M H_2SO_4. Polarization studies reveals that salicornia extract was mixed- type inhibitor and its inhibition effect increase with increasing extract concentration analysis of FTIR shows that the functional groups contribute to the adsorption extract film onto the surface of the metal. The inhibition activity was due to the adsorption ability of the salicornia extract which was confirmed by Langmuir adsorption isotherms.

Corresponding authors
Kadhim F. Al-Sultani
University of Babylon- Iraq
finteelalsultani@yahoo.com

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