Sumac (*Rhus*) Extract as Green Inhibitor for Steel in Seawater

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ABSTRACT

Sumac extract was tested as green inhibitor for steel in seawater (3.5wt.% NaCl) at room temperature with five concentrations include 4, 6, 8, 12 and 16 mL/L. Corrosion tests were investigated by Potentiostat at 5 mV.sec^{-1} scan rate, and the data measured by Tafel extrapolation method such as corrosion potential, corrosion current density and Tafel slopes. Inhibition efficiencies were calculated and indicated that 8 mL/L was the best concentration for inhibition. Sumac extract was anodic inhibitor type and obeys Langmuir adsorption isotherm with R^2 equal to 0.992. The equilibrium constant of the adsorption-desorption process and the apparent free energy of adsorption also calculated which 0.66313 and - 8.7370 kJ.mol-1 respectively were. FTIR spectroscopy was used to test film formed on steel surface compared with FTIR spectrum of Sumac powder. This test showed the decreasing in intensities of main peaks due to formation Fe^{2+}— organic molecules complexes at functionally groups.

Keywords: Sumac extract; green inhibitor; carbon steel; seawater.

I. INTRODUCTION

Sumac was used as a treatment for half a dozen different ailments in medieval medicine, primarily in Middle-Eastern countries (where sumac was more readily available than in Europe). An 11th century shipwreck off the coast of Rhodes, excavated by archeologists in the 1970s, contained commercial quantities of sumac drupes. These could have been intended for use as medicine, as a culinary spice, or as a dye. Stag horn sumac is a powerful antioxidant. Therefore, sumac extract has been selected in this work to investigate its inhibitive role for carbon steel in seawater.

Sumac is used as a spice, and has been used in cooking for millennia. Parts like leaves, fruits, and seeds of R. coriaria were reported to contain a number of phyto-constituents. The presence of gallotannins (mainly hydrolysable tannins) is a characteristic property of the Rhus genus, mostly R. coriaria species, which is an abundant source of tannins with different isomers and conjugations; besides, it contains other metabolites or phytochemicals, which have been described in various parts of the plant [1-3].

There are not studies about using Sumac extract as inhibitor in spite of its antioxidant activity. This work is attempt to use ethanolic extract of sumac to inhibit steel in artificial seawater at room temperature with five different concentrations include 4, 6, 8, 12 and 16 ml/L using Potentiostat to investigate inhibition protection.

There are many researchers investigated the inhibitive role of green and natural inhibitors for carbon steel in different media [4-12].

II. METHODS AND MATERIAL

Carbon steel was used in this work (chemical composition wt%: 0.121 C, 0.22 Si, 0.44 Mn, 0.014 P, 0.016 S, 0.041 Cr, 0.002 Mo, 0.022 Ni, 0.02 Al, 0.002 Co, 0.055 Cu and Fe remain) obtained by SpectroMAX. Cubic carbon steel (10x10x3 mm) with a square surface area (1cm^2) was used in all experiments. The specimen was mounted by hot mounting using formaldehyde

(Bakelite) at 138°C for 8 minutes to insulate all but one side and make a hole on one side of electrical connection and then the mounted specimens has been grinded with SiC emery papers in sequence of 220, 400, 600, 800, and 1200 grit to get flat and scratch-free surface and polished to mirror finish using polish cloth and alpha alumina 0.5μm and 1μ m, and then washed with distilled water, degreased with acetone and rinsed with distilled water. The base electrolyte was artificial seawater 3.5wt% NaCl solution.

Extraction of sumac seeds was carried out by dissolving 5 g of grounded seeds in 200 mL ethanol. The obtained extract was filtered by using Whatmann filter paper and concentrated to 100 mL. Five volumes of ethanolic extract were used as inhibitor includes 4, 6, 8, 12 and 16 mL/L at room temperatures.

Electrochemical Measurements

Electrochemical cell was composed of platinum counter electrode, prepared carbon steel specimens as working electrode and saturated calomel electrode (SCE) as a reference electrode. ASTM standard cell G5-94 was used. The electrochemical behavior of carbon steel in inhibited and uninhibited solution was studied by WINKING M Lab potentiostat by recording anodic and cathodic galvanodynamic polarization curves. Measurements were carried out by changing the potential $\pm$ 200mV around open circuit potential at scan rate 5 mA.sec^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to the corrosion potential to obtain corrosion parameters.

FTIR Measurements

The film formed on the metal surface (after immersing in an inhibited media for 20 days till drying) was carefully removed and mixed thoroughly with KBr. The FTIR spectra were recorded in Bruker Tensor 27 Fourier Transform Infrared Spectrophotometer.

III. RESULTS AND DISCUSSION

Figure (1) shows the polarization curves for steel 37-2 in seawater at room temperature in absence and presence of Sumac extract with five concentrations (4, 6, 8, 12 and 16 mL/L), these curves indicate the cathodic and anodic regions. At anodic sites, oxidation of iron can occur according to the following equation:

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

While at cathodic sites, many reactions can occur. The main cathodic reduction is reduction of oxygen as follow:

$$O_2 + 2H_2O + 4e \rightarrow 4OH^-$$
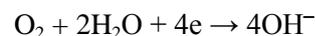
The presence of organic inhibitor (Sumac extract) affects cathodic and anodic reactions where the most organic inhibitors adsorbed on the metal surface by displacing water molecules on the surface and forming a compact barrier. Availability of non-bonded (lone pair) and π-electrons in inhibitor molecules facilitate electron transfer from the inhibitor to the metal. The performance of an organic inhibitor is related to the chemical structure and physicochemical properties of the compound like functional groups, electron density at the donor atom, π-orbital character, and the electronic structure of the molecule [13].

The corrosion data were calculated by Tafel extrapolation method are presented in Table (1) indicate the corrosion potential (E_{corr}) shifted to more noble values after adding natural inhibitor, this means that Sumac extract acts as anodic inhibitor type. The noblest potential was observed in the presence of 8 mL/L equal to -266 mV. The corrosion current density (i_{corr}) was decreased for inhibited media and the lowest value was 0.652 μA.cm^{-2} in the presence 8 mL/L of Sumac extract. Tafel slopes also influenced by Sumac extract, generally the anodic slopes were lower than cathodic slopes. This is infer that the rate of change of current with change of potential was smaller during anodic polarization than that during cathodic polarization due to coverage of anodic sites by green inhibitor (Sumac extract).

The inhibition efficiency IE (%) can be calculated using the equation given below [14]:

$$IE\% = \frac{(i_{corr})_a - (i_{corr})_p}{(i_{corr})_a} \times 100$$

Where $(i_{corr})_a$ and $(i_{corr})_p$ are the corrosion current density (μA.cm^{-2}) in the absence and the presence of the inhibitor, respectively. The data in Table (1) indicate that the inhibitor gave good protection especially in the presence of 8 mL/L. The relationship between IE% and concentration of extract is shown in Fig. (2).

A number of individual aldehydes, fatty acids, long chain alcohols, terpenes and terpenoids, and waxes of commercial or bioactive potential in essential oils and non-polar extractables from selected members of the Rhus genera have been identified [15]. The most compounds have functionally groups represented by carbonyl, hydroxyl and carboxyl groups which may adsorbed on metal surface to form complexes with ferrous ions.

TABLE 1 : Corrosion parameters of steel in seawater in absence and presence of Sumac extract at room temperature.

Conc. mL/L	E_{corr} mV	i_{corr} $\mu.cm^{-2}$	$-b_c$ $mV.dec^{-1}$	$+b_a$ $mV.dec^{-1}$	IE %
0.0	-616	48.76	100.3	85.2	---
4	-488	12.99	88.3	76.9	73.36
6	-438	8.02	90.8	62.7	83.55
8	-266	0.652	132	97.6	98.66
12	-517	1.78	88.5	97.5	96.35
16	-383	0.890	73.1	80.9	98.17
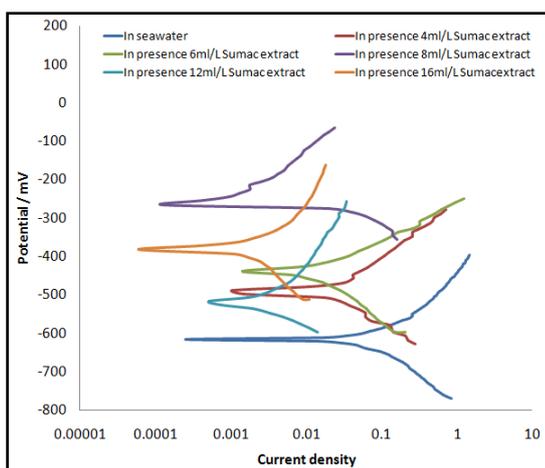
Figure 1: Tafel plots of steel in uninhibited and inhibited seawater at room temperature.
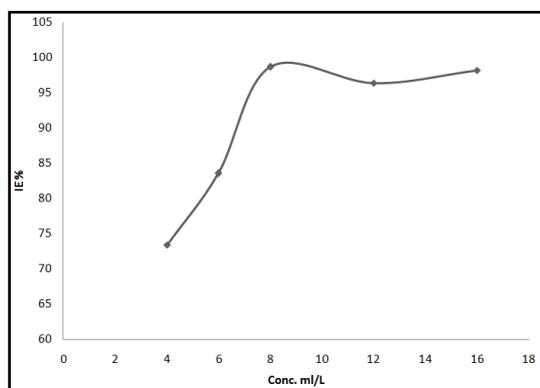
Figure 2: Relationship between concentrations of Sumac extract and inhibition efficiency.

Langmuir isotherm was tested for its fit to the experimental data. The plot of C/θ against C in the presence of Sumac extract is straight line (Fig. 3) indicating that the Sumac extract obeys Langmuir adsorption isotherm which given by the following equation [16]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C$$

where, K_{ads} is the equilibrium constant of the adsorption-desorption process, θ is the degree of surface coverage and C is concentration of inhibitor in the bulk solution. The linear regression coefficient close to unity, hence, adsorption of inhibitor followed Langmuir adsorption isotherm with R^2 value 0.992. The Langmuir isotherm is based on the assumption that each site of metal surface holds one adsorbed species. Therefore, one adsorbed H_2O molecule is replaced by one molecule of the inhibitor adsorbate on the steel surface. The apparent free energy of adsorption (ΔG^o_{ads}) is calculated from the following relation [16]:

$$\Delta G^o_{ads} = -2.303RT \, log 55.5 \, K_{ads}$$
$$where \, K_{ads} = \frac{\theta}{C(1-\theta)}$$

The value of K_{ads} is 0.66313 and ΔG^o_{ads} equal to - 8.7370 kJ.mol^{-1}.

The negative value of ΔG^o_{ads} indicated the spontaneous adsorption of Sumac extract. The value of K_{ads} is relatively small indicating that the interaction between the inhibitor molecules and steel surface is physically adsorbed. This is also supported by lower negative (ΔG^o_{ads}) value.
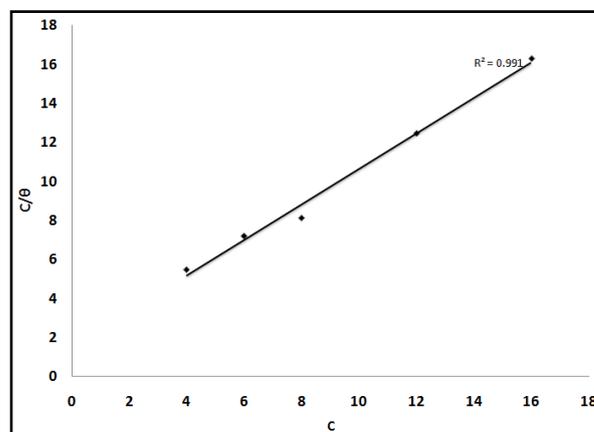
Figure 3: Langmuir adsorption plot for steel in sweater in the presence of Sumac extract with five concentrations.

Fig. (4) shows the FTIR spectra of sumac powder and film formed on steel surface after adsorption the extract on surface. Fig. (4-a) indicates the FTIR spectrum of Sumac powder which appears many peaks.

The main peaks are attributed to C─H aliphatic and aromatic at 2924.18 and 2854.74 cm^{-1}, C═O and conjugated C═C appear at 1741.78 and 1714.77 cm^{-1} respectively. N─H stretch for secondary amine has one band occurs in the range from 3500 to 3300 cm^{-1}.

Many peaks appear between 1500 and 600 cm^{-1} due to ═CH and N─H out of plane (OOP).

Also C─N stretch occurs in the range from 1350 to 1000 cm^{-1}. Figs. (4-b to f) show the FTIR for film formed on steel in presence five concentrations of extract 4, 6, 8, 12 and 16 mL/L respectively. These spectra indicate the decreasing in much intensity due to incorporate the components of Sumac in adsorption with metal ions and formation Fe^{2+}─organic molecules complexes. The lowest intensities were observed in the presence of 8mL/L of Sumac extract, i.e., this concentration represents the best for inhibition.

(a)

(b)

(c)
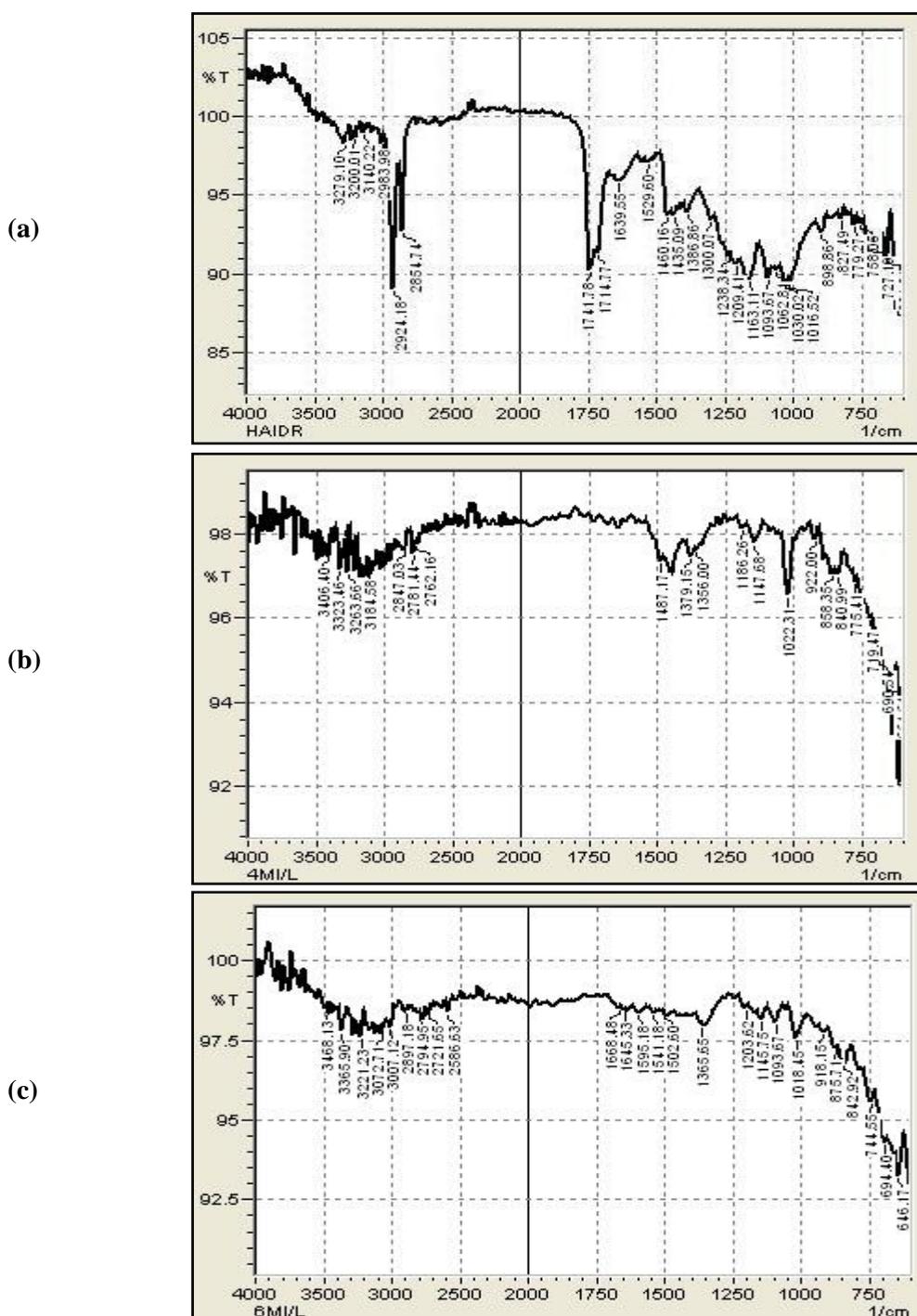
(d)
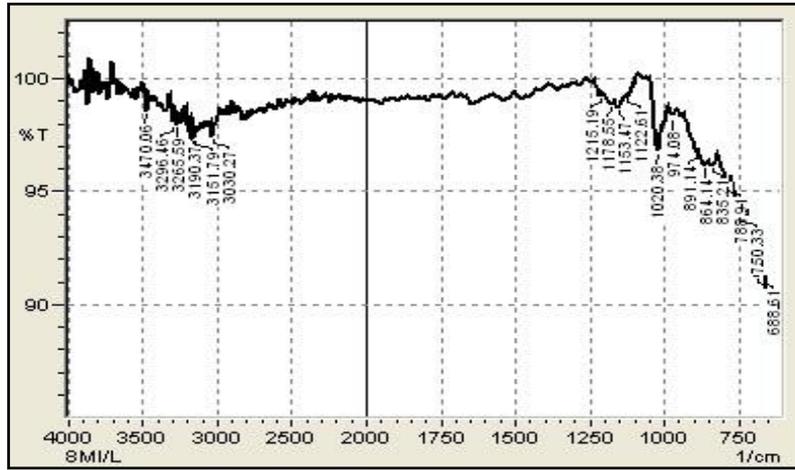
(e)
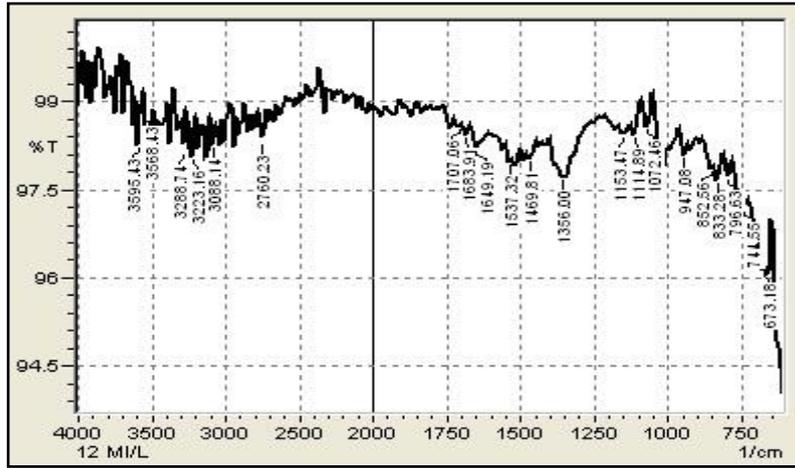
(f)
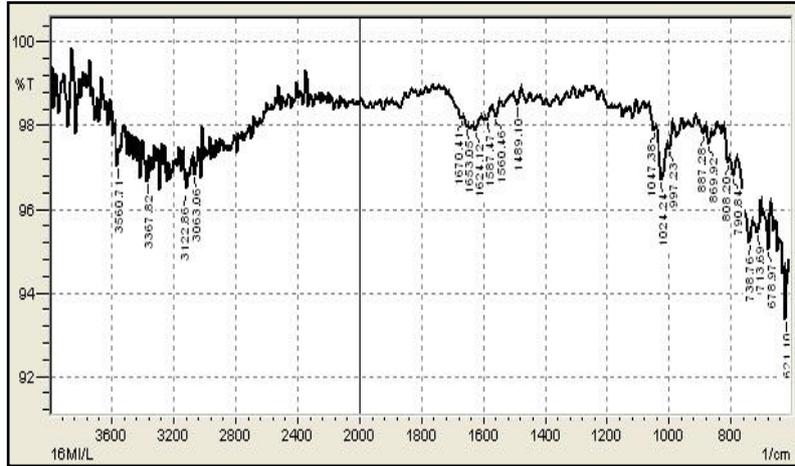
Figure 4: FTIR spectra for Sumac (a), and film formed on steel
surface in corrosive medium in presence
different concentrations of extract.

IV.CONCLUSION

Attempt to use Sumac extract as inhibitor has been investigated for steel in seawater at room temperature by adding five concentrations include 4, 6, 8, 12 and 16 mL/L and the obtained results can be drawn as follow:

1. Sumac extract behaved as anodic inhibitor due to shifting corrosion potentials to more noble values.

2. Inhibition efficiencies indicated that 8 mL/L is the best concentration for inhibition in experimental conditions with IE% equal to 98.66.

3. Sumac extract gave straight line for plot of C/θ against C with linear regression coefficient R^2 equal to 0.992.

4. The equilibrium constant of the adsorption-desorption process and the apparent free energy of adsorption referred to that the interaction between the inhibitor molecules and steel surface is physiosorption.

5. FTIR spectra showed that the inhibitor molecules adsorb to iron ions to form Fe^{2+}—Sumac extract complexes.

V. REFERENCES

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