Study Of The Performance Of Ruscus Aculeatus Leaves Alcoholic Extract As Corrosion Inhibitor For Carbon Steel In 1 M HCl Solution

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Abstract

The addition of corrosion inhibitors is one of the most widely used methods for the protection of metals and alloys from corrosion in various environments. Although synthetic organic compounds have been found to be highly effective in mitigating corrosion, they are often toxic, non-biodegradable, and rather expensive. Plant extracts are among the environmentally friendly alternatives to replace organic compounds as corrosion inhibitors. This study aims to investigate the corrosion inhibition efficiency of the *Ruscus aculeatus* leaves (RAL) alcoholic extract for carbon steel immersed in 1 M HCl solution, using weight loss and potentiodynamic polarization measurements. The optimum concentration of RAL alcoholic extract, i.e. 200 mg/L, gave a corrosion inhibition efficiency of 91.09% at 25 ºC. Potentiodynamic polarization measurements showed that the RAL alcoholic extract acts as a mixed-type inhibitor with a predominant influence on the anodic corrosion reaction. The corrosion inhibition efficiency of the RAL alcoholic extract decreased at an acceptable rate with increasing temperature in the 25–55 ºC range.

Keywords: Ruscus aculeatus, carbon steel, alcoholic plant extract, potentiodynamic polarization, green corrosion inhibitor

1. Introduction

Plants extracts are among the environmentally friendly alternatives to organic corrosion inhibitors for various metals immersed in different environments (Abd-El-Nabey et al. 2020) (Bilgic 2021). Several aqueous and alcoholic extracts of different parts of plants, including leaves (Alrafai 2022; Zhang et al. 2023), seeds (Abbout et al. 2021; Bhardwaj et al. 2021), roots (Kaya et al. 2023), fruits peels (Aghzzaf et al. 2020) and flowers (Dai and An 2023) have been tested as corrosion inhibitors for carbon steel in acidic environments. The corrosion inhibition efficiency of these extracts is due to the presence of various organic compounds that contain in their structures heteroatoms such as oxygen, nitrogen and sulfur and/or double bonds, which serve as adsorption centers. The adsorbed compounds on the surface of the carbon steel samples isolate them from the corrosion environment. *Ruscus aculeatus* is a naturally occurring bushy sub-shrub belonging to the *Asparagaceae* family. To the best of our knowledge, the *Ruscus aculeatus leaves* (RAL) alcoholic extract has not been previously tested as a corrosion inhibitor for carbon steel in acidic medium. In the present work the corrosion inhibition of *Ruscus aculeatus* leaves (RAL) alcoholic extract for carbon steel immersed in 1 M HCl solution was evaluated by means of weight loss and potentiodynamic polarization. Corrosion studies were performed at 25 ºC. The effect of temperature (in the 25–55 ºC range) on corrosion rate was studied only for the optimum concentration using potentiodynamic polarization.

2. MATERIALS AND METHODS

2.1 Preparation of plant extract

Ruscus aculeatus leaves were washed with water and then dried for 3 days at 50 ºC. The ground dried leaves were extracted for 3 hours in 80% ethanol with reflux. The filtered extract was stored at 2 ºC.

2.2 Samples preparation

Corrosion tests have been carried out on carbon steel with the following composition (wt.%): 0.20% C, 0.22% Si, 0.023% S, 0.014% P, 0.84% Mn, 0.11% Ni, 0.10% Cr, 0.017% Mo, 0.30% Cu, 0.0012% V, 0.0095% N, 0.0002% B and balance Fe. For the weight loss measurements cylindrical-shaped samples 5 cm in length and 0.8 cm in diameter were employed, while for electrochemical measurements disc-shaped samples with a 15 mm diameter were cut and 0.785 cm^2 was exposed to the solution. Prior to the measurements the samples were ground with different emery papers (i.e. 180, 240, 320, 500, and 1000 grit), washed with bidistilled water, and degreased with acetone.

2.3 Solution preparation

The 1 M HCl solution was prepared by diluting a 37% solution HCl provided by Sigma Aldrich. The green RAL alcoholic extract was added in the concentration range of 10–200 mg/L (i.e. 10, 50, 100 and 200 mg/L) to the 1 M HCl solution.

2.4 Weight loss measurements

Cylindrical-shaped samples prepared according to section 2.2 were weighted and then immersed in glass bottles containing 250 mL of the 1 M HCl solution, with and without additions of the RAL alcoholic extract. A water bath was used to keep the temperature constant (25 ± 0.5 ºC). After 14 hours of immersion, the samples were taken out, rinsed with bidistilled water and acetone, and weighted again. To get good reproducibility, experiments were carried out in duplicates. The corrosion rate (CR) of the carbon steel samples were calculated as:

$$\mathrm{CR} = \frac{\mathrm{W}}{\mathrm{St}} \tag{1}$$

where W is the average weight loss of the carbon steel cylinders before and after immersion, S is the total surface of the carbon steel cylinder, and t is the immersion time. The corrosion inhibition efficiency (IE (%)) of the RAL alcoholic extract was calculated as follows:

$$\mathrm{IE}(\%) = \frac{\mathrm{CR}^0 - \mathrm{CR}}{\mathrm{CR}^0} \cdot 100 \tag{2}$$

where CR and CR^0 represent the corrosion rates with and without the addition of the RAL alcoholic extract, respectively.

2.5 Electrochemical measurements

A three-electrode cell from PalmSens, consisting of a working electrode (carbon steel samples), a platinum counter electrode (CE) and a saturated calomel electrode (SCE) coupled to a Luggin capillary as a reference electrode, was used to perform the electrochemical measurements. The working electrode was immersed in the test solutions (with and without additions of RAL alcoholic extract) for 30 min to reach a steady state and the open circuit potential (E_{OC}) was recorded. Polarization curves were recorded from –120 to +120 mV *vs.* E_{OC}, with a scan rate of 0.1 mV/s, using WaveNow potentiostat from Pine Research. The corrosion potential (E_{corr}) and corrosion current density (i_{corr}) were obtained from Tafel extrapolation of the polarization curves. The corrosion inhibition efficiency of the RAL alcoholic extract was calculated as:

$$\mathrm{IE}\ (\%) = \frac{\mathrm{i}^0_{\mathrm{corr}} - \mathrm{i}_{\mathrm{corr}}}{\mathrm{i}^0_{\mathrm{corr}}} \cdot 100 \tag{3}$$

where i_{corr} and i^0_{corr} represent the corrosion current density of the samples in the 1 M HCl solution with and without the addition of the RAL alcoholic extract, respectively. The electrochemical measurements were performed at 25 ± 0.5 ºC. The influence of temperature on the inhibition efficiency of the RAL alcoholic extract is also studied at 35, 45, and 55 ºC, only for the optimum concentration.

3. RESULTS AND DISCUSSION

3.1 Weight loss measurements

The corrosion rates of the carbon steel samples immersed in the 1 M HCl solution at 25 ºC, with and without different concentrations of RAL alcoholic extract, and the respective corrosion inhibition efficiencies, are shown on Table 1.

Table 1. Weight loss results for the carbon steel samples immersed in 1 M HCl solution with and without additions of RAL alcoholic extract.

Concentration (mg/L)	**CR ($g/m^2 \cdot h$)**	**CR (mm/y)**	**IE (%)**
Blank	2.04	2.28	–
10	1.14	1.27	44.19
50	0.81	0.90	60.62
100	0.68	0.75	66.82
200	0.60	0.66	70.85

The corrosion rate of the carbon steel samples decreased with the addition of 10–200 mg/L RAL alcoholic extract, from 2.28 to 0.66 mm/y. Meanwhile, the inhibitor efficiency of the RAL alcoholic extract increased with increasing inhibitor concentration, reaching 70.85% at 200 mg/L extract added. The corrosion susceptibility of the carbon steel samples decreased as more of the inhibitor is adsorbed on their surface, isolating them from the corrosion environment.

3.2 Electrochemical measurements

Figure 1 shows the variations of the E_{OC} with time for the carbon samples immersed in 1 M HCl solution, with and without RAL alcoholic extract additions.

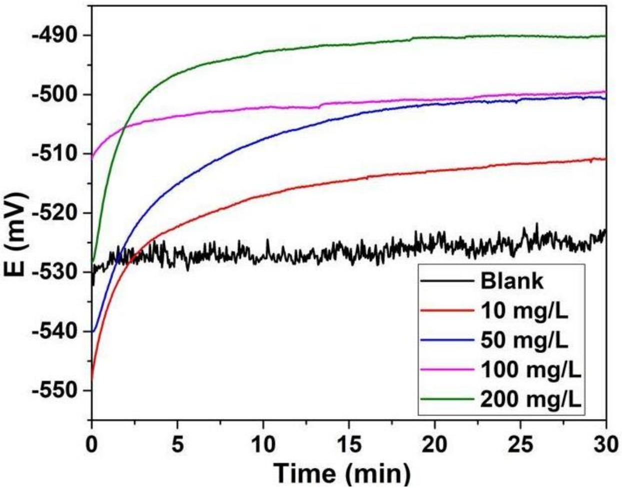

Figure 1. Variation of E_{OC} with time for carbon steel samples in acidic solutions with and without addition of the RAL alcoholic extract.

The E_{OC} of the carbon steel samples stabilized (steady state was achieved) after 5 min of immersion and its value was affected by the solution composition. As shown in Figure 1, E_{OC} shifts towards less negative values with the addition of the RAL alcoholic extract.

3.3.1 Effect of extract concentration on the corrosion rate of carbon steel

Figure 2 presents the potentiodynamic polarization curves of the carbon steel samples immersed in 1 M HCl solution, with and without additions of RAL alcoholic extract. Tafel extrapolation was employed to estimate the kinetic parameters of the cathodic and anodic reactions of carbon steel in the corrosive medium as a function of concentration of RAL alcoholic extract. The obtained values are presented in Table 2. E_{corr} of the inhibited carbon steel samples shifted towards less negative values with respect to the samples immersed in the blank solution. Moreover, i_{corr} significantly decreased with the increasing the concentration of RAL alcoholic extract in the 10–200 mg/L range (from 630.96 to 56.23 μA/cm^2). No significant influence of higher concentrations of the RAL alcoholic extract (i.e. 400 mg/L, results not shown) on the corrosion susceptibility of the carbon steel samples was observed, indicating that 200 mg/L is the optimum concentration. The highest value of corrosion inhibition efficiency was calculated to be 91.09%. Figure 2 shows that the addition of RAL alcoholic extract affects both the anodic and cathodic corrosion reactions (as seen by the decrease in the current densities in both sides of the polarization curves), with a predominant influence on the anodic corrosion reaction. The corrosion inhibition efficiency of the RAL alcoholic extract is attributed to the adsorption of the compounds on the surface of the carbon steel samples.

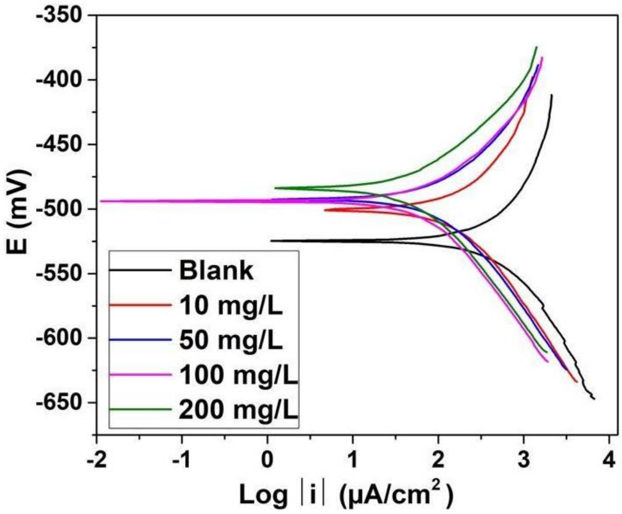

Figure 2. Potentiodynamic polarization curves of carbon steel in acidic solution with and without addition of the RAL alcoholic extract.

Rodrigues et al. (2021) reported that quercetin-O-deoxyhexoside-hexoside apigenin-C-hexoside-C-pentoside isomer II are the main compounds found in the RAL ethanolic extract. These compounds contain heteroatoms, benzoic ring and double bonds that are crucial for the adsorption, and therefore for the effective protection of the carbon steel samples.

Table 2. Kinetic parameters obtained from potentiodynamic polarization curves of carbon steel immersed in 1 M HCl solution, with and without additions of the extract.

Conc. (mg/L)	i_{corr} (μA/cm^2)	E_{corr} (mV)	CR (g/m^2·h)	CR (mm/y)	IE (%)
Blank	630.96	- 528.15	6.57	7.32	–
10	245.47	- 513.81	2.55	2.85	61.10
50	128.82	- 493.16	1.34	1.49	79.58
100	85.11	- 497.17	0.89	0.99	86.51
200	56.23	- 479.66	0.59	0.65	91.09

3.3.2 Effect of temperature on the corrosion rate of carbon steel

Table 3 shows the effect of temperature on the corrosion rate of the carbon steel samples and the respective corrosion inhibition efficiencies, for the optimum concentration of the RAL alcoholic extract. The corrosion rate of the carbon steel samples immersed in 1 M HCl solution containing the optimum concentration of the RAL alcoholic extract at 25 and 55 ºC increased significantly from 0.65 to 13.32 mm/y, respectively.

Table 3. The temperature effect on corrosion processes of carbon steel samples immersed in 1 M HCl solution with and without addition of 200 mg/L RAL alcoholic extract.

	25 ºC		**35 ºC**		**45 ºC**		**55 ºC**	
	CR (mm/y)	**IE (%)**	**CR (mm/y)**	**IE (%)**	**CR (mm/y)**	**IE (%)**	**CR (mm/y)**	**IE (%)**
Blank	7.32	–	10.10	–	17.16	–	31.95	–
200 mg/L	0.65	91.09	1.06	88.52	4.02	76.56	13.32	58.31

Meanwhile, the inhibition efficiency decreased from 91.09 to 58.31 %, respectively.The corrosion rate of the carbon steel samples immersed in 1 M HCl solution containing the optimum concentration of the RAL alcoholic extract at 25 and 55 ºC increased significantly from 0.65 to 13.32 mm/y, respectively. Meanwhile, the inhibition efficiency decreased from 91.09 to 58.31 %, respectively. These changes revealed a low corrosion inhibition performance of the RAL alcoholic extract at higher temperatures, probably due to the desorption of the compounds found in the RAL alcoholic extract from the surface of the carbon steel samples.

4. CONCLUSIONS

The corrosion inhibition efficiency of *Ruscus aculeatus* leaves alcoholic extract for carbon steel in acid medium was studied using weight loss and electrochemical measurements. The inhibitor efficiency increased with increasing the inhibitor concentration reaching maximum value (i.e. 91.09%) for 200 mg/L at 25 ºC. Polarization curves indicated a mixed-type corrosion inhibitor with a predominance in the corrosion anodic reaction. The increase of temperature resulted in decreased performance of the alcoholic extract.

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