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Cornus Sanguinea leaves alcoholic extract as corrosion inhibitor for carbon steel in acidic solutions

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Abstract

In recent years finding environmentally friendly and affordable sources to mitigate corrosion has become demanding in many industries due to the increased awareness related to environmental issues. Due to their readily availability, biodegradability, low toxicity and relatively low cost, plant extracts have been shown to be an effective alternative for corrosion protection of different metals in various environments. This work reports on the performance of the alcoholic extract of *Cornus sanguinea* leaves (CSL) as a green corrosion inhibitor for carbon steel (CS) immersed in 1 M HCl solution. Weight loss and potentiodynamic polarization techniques have been used to investigate the corrosion rate (CR) of the CS samples immersed in the 1 M HCl solution with and without the addition of various concentrations of the CSL alcoholic extract. The addition of 250 mg/L CSL alcoholic extract resulted in the highest corrosion inhibition efficiency (CIE) (i.e. 91.68%) at 25 ºC. The polarization curves showed that the CSL alcoholic extract acts as a mixed-type inhibitor. A significant decrease of the CIE of the CSL alcoholic extract was observed when increasing the temperature in the range 25–55 ºC.

Keywords: *Cornus Sanguinea, carbon steel, alcoholic plant extract, potentiodynamic polarization, green corrosion inhibitor*

1. Introduction

The addition of different types of compounds (i.e. corrosion inhibitors) is one of the most effective methods to reduce the corrosion susceptibility of steel in acidic solutions. The presence of heteroatoms (i.e. N, O, and S), in addition to benzoic rings, double and triple bonds facilitates the adsorption of these compounds on the metal surface (Chen et al. 2022; Ardakani et al. 2021; Belkaid et al. 2012). Although many of these compounds have shown high CIE in acid environments their toxicity, synthesis procedure and cost limit their application in several areas. Plant extracts are relatively inexpensive and can be obtained through different types of extractions mainly as aqueous or alcoholic extracts (Abd-El-Nabey et al. 2020; Alrefaee et al. 2021; Badawi and Fahim 2021; S. Bilgic 2021; S.. Bilgic 2022; Chaubey et al. 2021; Coiai et al. 2021; El Hassouni et al. 2022). *Cornus sanguinea* is a deciduous shrub which belongs to the *Cornaceae* family. To the best of our knowledge, *Cornus sanguinea* leaves extract has not been previously tested as corrosion inhibitor. This paper reports on the CIE of the CSL alcoholic extract for CS immersed in 1 M HCl solution using weight loss and potentiodynamic polarization measurements. The effect of temperature (in the range 25–55 ºC) on the CR of the CS samples immersed in 1 M HCl solution, with and without additions of the CSL alcoholic extract was also studied.

2. Materials And Methods

2.1 Preparation of the CSL alcoholic extract

The leaves of *Cornus sanguinea* were washed with water and then dried for 3 days at 50 ºC. The dried leaves were ground in a blender, and then were extracted for 3 hours in 80% ethanol with reflux. At the end the mixture was filtered, and the extract was stored at 2 ºC.

2.2 Sample and solution preparation

The composition (in wt.%) of the CS samples used in this study is: 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. The samples for weight loss measurements were cylinder-shaped (5 cm long and with a diameter of 0.8 cm), while for the electrochemical measurements 15 mm diameter disc-shaped samples, with a 0.785 cm^2 exposed area to the solution were used. Prior to the measurements the surface of the samples was polished with emery papers (i.e. 180, 240, 320, 500, and 1000 grit), rinsed with double distilled water and degreased with acetone in an ultrasonic bath for 5 minutes. The corrosion environment was 1 M HCl with

and without additions of 25–250 mg/L (i.e. 25, 50, 100, and 250 mg/L) of the CSL alcoholic extract.

2.3 Weight loss measurements

The CS cylinders were weighted first and then immersed for 14 h, at 25 ± 0.5 ºC in 250 mL beakers that contain 1 solution with and without addition of the CSL alcoholic extract. After the immersion time, first the surface of the samples was rinsed with double distilled water, degreased with acetone, and reweighted. The weight loss of the CS cylinders was calculated by the mass difference before and after the exposure to the solution. The experiments were caried out in duplicates for each concentration. The weight loss was used to calculate CR as:

$$\mathrm{CR} = \frac{\mathrm{W}}{\mathrm{St}} \quad (1)$$

where W is the average weight loss of the CS cylinders before and after immersion, S is the total surface of the CS cylinder, and t is the immersion time. CIE(%) was calculated by the following equation:

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

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

2.4 Electrochemical measurements

A 1 L glass cell (IS-CCS Corrosion Cell Set from PalmSens), a saturated calomel reference electrode (SCE), platinum counter electrode, and the working electrode (disc-shaped CS samples) were used to perform the electrochemical measurements with a WaveNow potentiostat form Pine Research. The CS samples were first immersed for 30 minutes in the corrosion environments and the open circuit potential (E_{OC}) was measured. Then, potentiodynamic polarization was performed in the potential range ±120 mV *vs*. E_{OC}, with a scan rate of 0.1 mV/s. The effect of temperature was tested only for the optimum concentration in the temperature range 25–55 ºC. The CIE(%) of the CSL alcoholic extract was calculated as:

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

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 CSL alcoholic extract, respectively.

3. Results And Discussion

3.1 Weight loss measurements

Table 1 presents the CR and CIE(%) values of the CS samples calculated from the weight loss before and after immersion in 1 M HCl solution at 25 ºC, with and without additions of CSL alcoholic extract.

Table 1. Weight loss results of CS samples immersed in 1 M HCl solution with and without additions of CSL alcoholic extract.

Concentration (mg/L)	CR ($g/m^2 \cdot h$)	CR (mm/y)	CIE (%)
Blank	2.18	2.42	–
25	1.05	1.16	51.98
50	1.02	1.13	53.12
100	0.94	1.05	56.70
250	0.64	0.71	70.81

The addition of 25–250 mg/L of the CSL alcoholic extract decreased the CR of the non-inhibited CS samples from 2.18 to 0.64 mm/y. This can be attributed to an increased isolation of the CS samples from the corrosion environment with increasing extract's concentration. Increasing inhibitor concentration resulted in increased CIE(%) of the alcoholic extract, reaching 70.81% for 250 mg/L of the CSL alcoholic extract added.

3.3 Electrochemical measurements

Figure 1 shows that the E_{OC} of the CS samples stabilized (no significant change) within 5 min of immersion. The E_{OC} values of the CS samples were impacted by the concentration of the inhibitor, shifting to less negative potentials in the presence of the CSL alcoholic extract.

3.3.1 Effect of inhibitor concentration on the corrosion rate of CS

The influence of CSL alcoholic extract on the CR of the CS samples in 1 M HCl solution was also studied with potentiodynamic polarization measurements, as shown in Figure 2. The addition of the CSL alcoholic extract shifted the corrosion potential (E_{corr}) towards less negative values with respect to the value of the blank solution. The decrease of the current density on both sides of the polarization curves indicates that the inhibitor affects both the anodic and cathodic corrosion reactions, behaving as a mixed-type inhibitor.

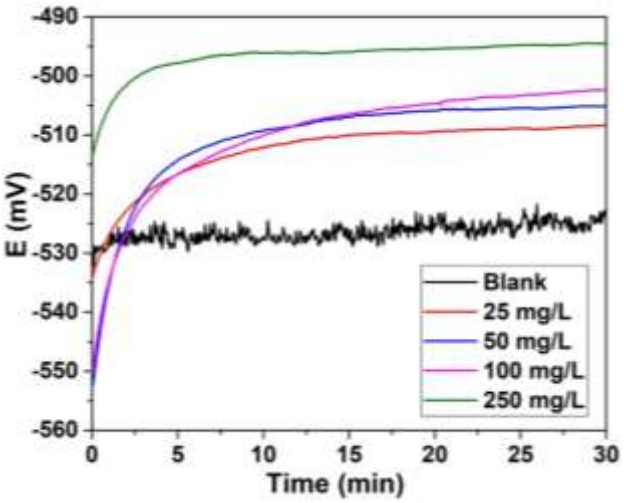

Figure 1. Variation with time of the E_{OC} of CS samples in acidic solutions with and without addition of the CSL alcoholic extract.

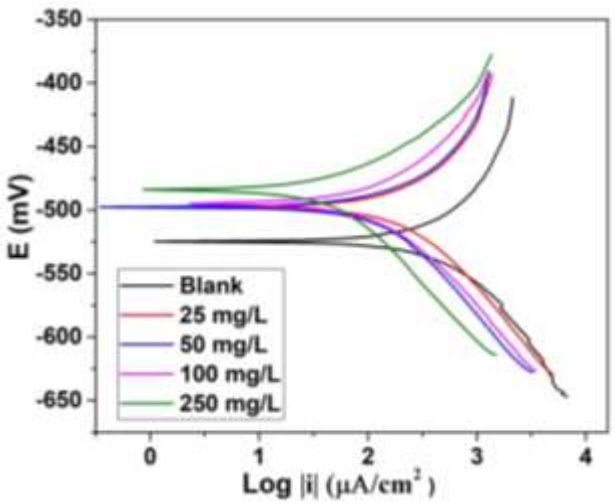

Figure 2. Potentiodynamic polarization curves of CS in acidic solution with and without addition of the CSL alcoholic extract.

A significant decrease of the i_{corr} of the non-inhibited samples with the addition of CSL alcoholic extract (from 630.96 to 52.48 μA/cm^2 in the presence of 250 mg/L of the CSL alcoholic extract) is seen in Table 2. Higher concentrations of the RAL alcoholic extract (i.e. 500 mg/L, results are not displayed), did not further decrease the CR of the CS samples, indicating that 250 mg/L is the optimum concentration. The highest value of CIE(%) was calculated to be 91.68%. The corrosion inhibition performance of the CSL alcoholic extract can be attributed to the possible adsorption of flavonoids such as Ampelopsin 3-O-glucoside, Quercetin 3-O-galactoside (hyperoside), that are found to be present in this extract (Tenuta et al. 2022).

3.3.2 Effect of temperature on corrosion rate of CS

The corrosion resistance of the CS samples in 1 M HCl solutions, with and without addition of the optimum concentration of the CSL alcoholic extract, was also studied in the 25–55 °C range, using the potentiodynamic polarization technique.

As shown in Table 3, the CR of the CS samples immersed in the 1 M HCl solution containing the optimum concentration of the CSL alcoholic extract at 25 and 55 ºC increased significantly from 0.61 to 23.14 mm/y, respectively. Meanwhile, CIE(%) decreased from 91.68 to 27.56%, respectively. These changes revealed a low corrosion inhibition performance of the CSL alcoholic extract at higher temperatures, probably due to the desorption of the compounds found in the CSL alcoholic extract.

Table 2. Kinetic parameters obtained from potentiodynamic polarization curves of CS 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)	CIE (%)
Blank	630.96	-528.15	6.566	7.32	–
25	239.88	-497.91	2.496	2.78	61.98
50	169.82	-496.75	1.767	1.97	73.08
100	123.03	-494.55	1.280	1.43	80.50
250	52.48	-486.80	0.546	0.61	91.68

Table 3. The effect of temperature on the corrosion of CS samples immersed in 1 M HCl solution with and without addition of 250 mg/L CSL alcoholic extract.

	25 ºC		35 ºC		45 ºC		55 ºC	
	CR (mm/y)	**CIE (%)**	**CR (mm/y)**	**CIE (%)**	**CR (mm/y)**	**CIE (%)**	**CR (mm/y)**	**CIE (%)**
Blank	7.32	–	9.21	–	17.16	–	31.95	–
250 mg/L	0.61	91.68	1.33	85.55	6.09	64.52	23.14	27.56

4. CONCLUSIONS

In this study, weight loss and electrochemical measurements were used to study the corrosion inhibition efficiency of the *Cornus sanguinea* leaves alcoholic extract for carbon steel in 1 M HCl solution. Both methods performed at 25 ºC, showed that the corrosion inhibition efficiency of the CSL alcoholic extract increased with increasing its concentration in the 25–250 mg/L range. The highest corrosion inhibition efficiency (i.e. 91.68%) was obtained in the presence of 250 mg/L extract (the optimum concentration). Potentiodynamic polarization curve measurements revealed that the corrosion inhibition efficiency of the alcoholic extract decreased with the increase of temperature within the 25–55 ºC range, revealing the weak performance of the inhibitor at higher temperatures. Polarization curve data shows that CSL alcoholic extract can simultaneously suppress the cathodic and anodic corrosion reactions of carbon steel in acid medium, and therefore it can be classified as mixed-type corrosion inhibitor.

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