Materials International
Open Access Journal (ISSN: 2668-5728)

Article
Volume 6, Issue 4, 2024, 34
https://doi.org/10.33263/Materials64.034

Performance and Efficiency of *Cirsium arvense* Leaves Extract (CALE) as an Eco-Friendly Inhibitor for Carbon Steel in 1.0 M HCl

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Received: 27.02.2024; Accepted: 6.10.2024; Published: 10.12.2024

Abstract: Current research aims to develop non-toxic, biodegradable, and environmentally friendly inhibitors. This study assessed the ability of *Cirsium arvense* leaf extract (CALE) to inhibit carbon steel corrosion in molar hydrochloric acidic conditions. Using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization (PDP) methods, the inhibitory effectiveness η% of (CALE) was evaluated. The effects of inhibitor temperatures (293-323K) and concentrations (200–800 ppm) were studied. With 600 ppm of (CALE) at 293K, the optimal η% of 94% was obtained. The Nyquist graphs demonstrate how rising (CALE) concentration reduces double-layer capacitance and raises charge-transfer resistance due to the (CALE) molecules' adsorption on the CS surface. A mixed-type inhibitory behavior was demonstrated via potentiodynamic polarization.

Keywords: *Cirsium arvense* leaves extract; corrosion; friendly inhibitors; potentiodynamic polarization.

1. Introduction

Metal corrosion is a common occurrence during metal processing, transportation, and storage. Consequently, acid pickling becomes essential as a preparatory step before surface treatment, removing rust and deposited layers from the metal surface [1,2]. Strongly acidic solutions, such as phosphoric, hydrochloric, sulfuric, and nitric acids, are widely used as pickling solutions in the industrial sector [3-5]. As HCl can be cleaned more quickly at room temperature and in a smaller amount than other acids, it is frequently used to cure metal surfaces. Because it doesn't release effluents, including nitrogen and phosphorus, it is less damaging to the environment [6,7]. On the contrary, the use of hydrochloric acid for pickling also presents limitations due to its tendency to induce corrosion on metal surfaces [8,9].

Inhibitors are still the most efficient, popular, and cost-effective way to prevent the deterioration of metals and alloys [10,11]. Several studies on corrosion inhibition have been performed, including synthetic (organic and non-organic) inhibitors [12,13] and eco-friendly inhibitors [14]. Natural materials, like extracts or essential oils, have drawn much interest lately as low-cost, environmentally friendly corrosion inhibitors. They don't include heavy metals or other harmful substances. Thus, their prospects for the environment are excellent [15,16]. It is reported that the majority of these green inhibitors contain substances such as flavonoids, alkaloids, polyphenols, and other organic compounds with heteroatoms (O, N, S), π system, and functional groups such as -NH-, -N=N-, -C=N-, and R-OH in their molecular structure, which promotes their adsorption on metal surfaces and thus the formation of a film that acts as a barrier between the metal and the corrosive medium [17–20]. According to the literature, the performance of the adsorption process is influenced by the chemical composition of the inhibitor, the presence of an active center, the availability of donor or repellent groups, temperature, solution acidity, soak time, and other parameters [21,22].

This study used electrochemical methods, including electrochemical impedance (EIS) and potentiodynamic polarization (PDP), to examine the inhibitory effect of an extract from the leaves of *Cirsium arvense* on the corrosion behavior of carbon steel in a molar solution of hydrochloric acid. The PDP technique was applied, with temperatures being changed from 293 K to 323K, To investigate how this parameter affected the performance of (CALE).

2. Materials and Methods

2.1. Materials and electrolyte preparation.

Carbon steel (CS) specimens with the following composition (weight %): 0.07 C, 0.19 Mn, 0.03 Si, 0.05 Cr, 0.02 Al, and balance Fe were used in this investigation. Before each electrochemical experiment, the CS electrode was carefully polished with emery papers with different degrees of roughness from N° 220 to N° 2000. The polished electrode was rinsed with distilled water, degreased with acetone, and dried with warm air before use. The electrolyte of this work is a solution prepared from 37% HCl of the brand LOBA Chemie, and it was used to prepare acidic media at a concentration of 1.0 mol/L by diluting it with distilled water.

2.2. Inhibitor (CALE) preparation.

The *Cirsium arvense* leaves were harvested in Morocco's Marrakech region. The fresh leaves were washed to remove dust before drying in the shade for 15 days at room temperature (25°C-27°C). A blender was used to crush the dried material into powder. The extraction was carried out using maceration in ethanol. The powdered sample (25 g) was stirred in 200 mL of ethanol for 48 hours at room temperature while protected from light. At 45°C, a rotary evaporator concentrated the filtered product.

2.3. Electrochemical measurements.

Utilizing electrochemical techniques, the processes and phenomena involved in the corrosion of carbon steel in HCl 1M have been investigated. All electrochemical studies were carried out with a potentiostat of the type OrigaStat 100, which was controlled by the Origamaster5 software. The cell was equipped with three electrodes: a carbon steel working electrode, a platinum counter electrode, and a saturated calomel electrode (SCE) as a reference electrode. A surface area of 0.64 cm^2 of the working electrode was exposed to the electrolyte. By submerging the working electrode in the corrosive medium for 30 minutes with and without (CALE), open circuit potential (OCP) surveillance was carried out.

Using a scan rate of 1 mV/s, the potential was changed from -750 to -100 mV (vs. SCE) to execute the potentiodynamic polarization curves on the carbon steel electrode. The polarization curve test's accompanying electrochemical data, including corrosion current density (icorr), corrosion potential (Ecorr), anode Tafel slope (βa), and cathode Tafel slope (βc), can be obtained using linear extrapolation. The following equation can be used to determine the corrosion inhibition efficiency (η%) of the polarization curve test [23]:

$$(\eta\%) = \frac{Icorr - I'corr}{Icorr} * 100 \qquad (1)$$

where Icorr and I'corr denote the corrosion current densities, respectively, in the presence and absence of CALE.

Electrochemical impedance spectroscopy investigations were conducted by applying a signal amplitude perturbation of 10 mV in the frequency range of 1 KHz to 100 MHz. Using EC-LAB software, the impedance data were assessed, and the findings were typically fitted to a suitable equivalent electrical circuit. Using the following formula, the inhibitory efficiency was determined [24]:

$$(\eta\%) = \frac{R_{ct} - R_{ct0}}{R_{ct}} * 100 \qquad (2)$$

The charge transfer resistance values in the presence and absence of CALE are denoted by R_{ct0} and R_{ct}, respectively.

3. Results and Discussion

3.1. Potentiodynamic polarization curves.

To understand the dynamics of metal corrosion and the impact of extract from *Cirsium arvense* leaves on the corrosion kinetics of carbon steel dissolving, this section of the research attempts to provide some clarification. At 293K and 1.0 mol/L HCl concentration, the polarization curves of the CS electrode are displayed in Figure 1, both with and without varying CALE concentrations. Table 1 lists the corrosion parameters combined with the inhibitor's inhibition efficacy that is being studied.

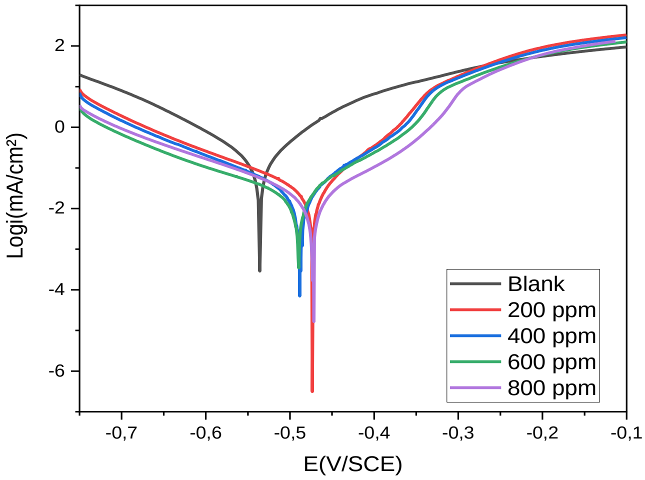

Figure 1. Potentiodynamic polarization curves of CS corrosion in the absence and presence of various concentrations of CALE.

Table 1. Polarization parameters of CS in 1 M HCl solution without and with different concentrations of CALE at 293K.

Concentration ppm	Icorr (µA/cm²)	-Ecorr (mV vs SCE)	βa (mV/dec)	-βc (mV/dec)	η%
Blank	322.8	536.0	99.4	117.7	
200	27.9	473.3	67.5	130.8	91
400	25.3	487.9	81.0	123.5	92
600	19.2	489.9	81.5	146.7	94
800	23.0	472.9	69.2	147.6	93

The study's findings (Figure 1) demonstrate that the corrosion potential values shifted in the anodic direction for all CALE inhibitor doses. The literature states that an inhibitor can be categorized as anodic or cathodic if the displacement of E_{corr} of inhibited solutions relative to the blank solution is larger than 85 mV and that the inhibitor's mixed nature can account for E_{corr} shifts of less than 85 mV [25]. In this investigation, we discovered that the displacement was less than 85 mV and the corrosion potential values did not differ considerably, suggesting that CALE acted as mixed-type inhibitors. Table 1 shows that as CALE concentration rises, a significant decrease in corrosion current density (i_{corr}) results in an increase in inhibition efficiency, which reaches its maximum value (94%) at 600 ppm.

3.2. Electrochemical impedance spectroscopy (EIS).

An effective method for evaluating the adsorption process, electrode kinetics, and surface characteristics is electrochemical impedance spectroscopy (EIS) [26]. EIS measurements were performed in HCl 1M, both with and without varying inhibitor quantities. The CS's Nyquist spectra are displayed in Figure 2. Table 2 is a summary of the values derived from Figure, which include the exponential value of CPE (n), η%, double layer capacitance (Cdl), constant phase element (Qdl), electrolyte resistance (Rs), and charge transfer resistance (Rct).

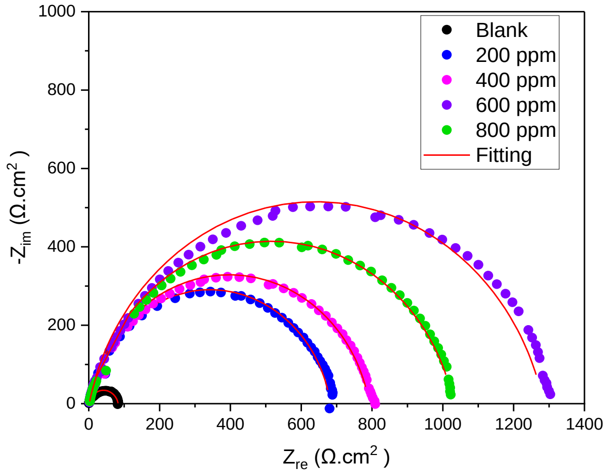

Figure 2. Nyquist plots for CS corrosion in 1.0 M HCl with different concentrations of CALE at 293K.

Figure 2 analysis reveals that all impedance graphs exhibit capacitive loops, demonstrating that charge transfer regulates steel corrosion [27]. The corrosion mechanism of CS remains unaffected by the presence of extract from *Cirsium arvense* leaves. Semicircles' diameters are significantly altered when this inhibitor is added to a corrosive environment; their diameters rise with CALE concentration. The non-perfect capacitive loops in Nyquist plots can be attributed to the inhomogeneities of carbon steel and frequency dispersion [28,29].

Table 2's research demonstrates that while the double-layer capacitance decreases with increasing inhibitor concentration, the charge transfer resistance increases. A drop in the local dielectric constant and/or an increase in the electrical double layer's thickness increases Rct, suggesting a protective layer on the CS surface [30,31].

Table 2 shows that when the amount of *Cirsium arvense* leaves increases, the corrosion inhibition efficiency increases as well, suggesting that the film formed by CALE molecules on the CS surface gets denser and more organized [32]. The percentage can reach 93% when the CALE extract content reaches 600 ppm.

Table 2. Impedance parameters of CS in acidic medium in uninhibited and inhibited medium at 293K.

Concentration (ppm)	Rs ($\Omega.cm^2$)	Rct ($\Omega.cm^2$)	Cdl ($\mu F.cm^{-2}$)	n	Qdl ($\mu\Omega^{-1}$ cm^{-2} Sn)	η%
Blank	0.62	87.78	211.3	0.88	340	
200	1.17	681.2	89.34	0.89	118.3	87
400	1.33	790.9	61.86	0.89	88.3	89
600	0.63	1284	38.23	0.89	63.4	93
800	1.24	1029	55.74	0.89	82.4	91

3.3. Effect of temperature on corrosion inhibition.

Through potentiodynamic polarization, the influence of temperature on the inhibition efficiency of carbon steel in 1M HCl containing 600 ppm of CALE was determined at temperatures ranging from 293K to 323K and in the absence of an inhibitor (Figure 3).

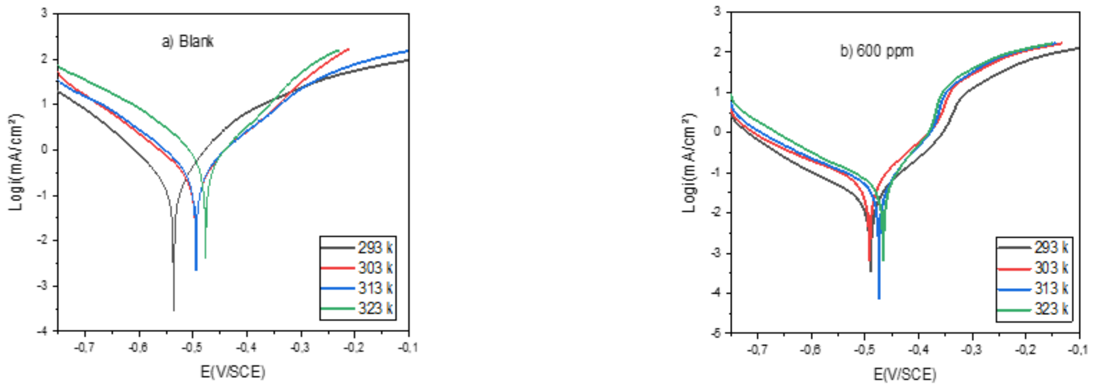

Figure 3. Potentiodynamic polarization curves of CS in the HCl 1M and in HCl 1M + 600 ppm of CALE at different ranges of temperature.

The optimal inhibitor concentration, corresponding to the highest percentage, was determined to be 600 ppm. The corresponding data are displayed in Table 3.

Table 3. Electrochemical parameters of CS in the HCl 1M and in HCl 1M + 600 ppm of CAVE in at different ranges of temperature.

	T (K)	Icorr($\mu A/cm^2$)	-Ecorr(mV vs SCE)	βa (mV/dec)	-βc (mV/dec)	η%
Blank	293	322.8	536.0	99.4	117.7	-
	303	417.6	494.7	106.0	132.9	-
	313	557.7	494.4	121.3	145.3	-
	323	1419.0	476.5	113.7	160.4	-
600 ppm of CALE	293	19.2	489.9	81.5	146.7	94
	303	36.5	491.5	77.2	155.3	91
	313	38.6	473.9	67.1	138.0	93
	323	62.3	466.0	50.3	211.5	95

It is evident that increasing the temperature increases the cathodic and anodic currents of the CS electrode both in the presence and absence of CALE. Table 3 shows that the inhibition effectiveness (η%) increases as the temperature rises, suggesting that CALE functions well as an inhibitor at high temperatures. Its inhibitory efficiency has thereby grown (from 94% to 95%). This indicates that the inhibitor molecules are more likely to adsorb onto the metal surface and block the active corrosion sites [33].

4. Conclusions

The findings of this study demonstrate that *Cirsium arvense* leaf extract (CALE) functions as a potent inhibitor against carbon steel corrosion in 1M HCl. The protective effectiveness of CALE was found to increase with higher concentrations, reaching maximum efficiencies of approximately 94% at 600 ppm and 293K. Moreover, the inhibitory properties of CALE were assessed across a temperature range of 293 K to 323 K. Analysis of the potentiodynamic polarization (PDP) results indicated that CALE acts as a mixed-type inhibitor with a pronounced anodic character. Additionally, the electrochemical impedance spectroscopy (EIS) data corroborated well with the findings from the PDP experiments.

Funding

This research received no external funding.

Acknowledgments

We thank all our colleagues.

Conflicts of Interest

The authors declare no conflict of interest.

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