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Evaluation of *Eulychnia acida* Phil. (Cactaceae) Extracts as Corrosion Inhibitors for Carbon Steel in Acidic Media.

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The process of pickling to remove corrosion products in metal pipes requires the use of an acidic solution together with corrosion inhibitors to protect the metal. However, the use of synthetic/commercial inhibitors has caused environmental pollution and human health problems. As a result, studies have begun to analyse natural extracts from several different plants as potential corrosion inhibitors, as they are generally more innocuous and/or biodegradable. The present study evaluates the effectiveness of aqueous extracts obtained from *Eulychnia acida* Phil. (Cactaceae) as potential corrosion inhibitors for carbon steel in acidic media. The total phenolic compound and flavonoid content of the aqueous extracts of the cactus species was determined prior to the experiments. The inhibition efficiency of the extracts obtained by decoction of the external bark, internal bark and medulla of the cactus stems were evaluated by mass loss, demonstrating an efficiency of 90% at concentrations of 100 and 1000 ppm. The polarization curve tests indicate an efficiency of over 80% inhibition at concentrations of 1000 and 1500 ppm. The results show that metabolites present in the extracts act as corrosion inhibitors and are able to promote surface protection by blocking active sites on the metal.

Keywords: corrosion inhibition, cactaceae (copao), carbon steel, acidic media

1. INTRODUCTION

Carbon steel is one of the most used alloys in industry, though the use of acidic solutions in processes such as pickling and industrial cleaning of pipes, tanks, etc. can cause electrochemical corrosion problems on the metal surface, inducing active dissolution [1-3]. As a result, some chemical substance must be added during pickling to act as a corrosion inhibitor and thus decrease the damaging

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effects of the acid on the metal surface. A corrosion inhibitor is defined as "a chemical substance that decreased the corrosion rate when present in small quantities in the solution" [4-6]**.**

Synthetic or commercial corrosion inhibitors can be classified as inorganic or organic. The formulations of inorganic inhibitors are based on polyphosphates, borates, zinc salts and some stabilising polymers. These can pollute lakes and rivers, beginning a process known as eutrophication [7-8]. Organic inhibitors are highly conjugated molecules containing heteroatoms in their structures, such as nitrogen, oxygen, sulphur, etc. These atoms favour adsorption of the compounds onto the metal surface either by the formation of bonds with the non-bonding electron pairs of the heteroatoms, or by interaction between the metal surface and the cloud of π electrons in the conjugated system, thus forming a layer that decreases the metal corrosion rate [9-10]. Though most of these compounds produce a high level of corrosion inhibition, they represent a risk to human health and the environment. Based on the above, and on the demands of new environmental legislation such as the Law on the Control of Toxic Substances of the United States Environmental Protection Agency (EPA) and the Directives of the Restriction of Hazardous Substances of the European Union, there is an increasing need to develop for environmentally friendly corrosion inhibitors [11].

In recent years, attempts have been made to mitigate the impact on the environment by using compounds of plant origin, which can be biodegradable and of inexpensive, while the associated extraction process creates less pollution than the production of synthetic inhibitors [12-14]. These compounds are known as "green corrosion inhibitors" and are related to secondary metabolites that are biosynthesised by plants [15-17]. Numerous organic compounds from plant extracts have been studied as corrosion inhibitors for different metals, with inhibition efficiencies above 85% [18-22]. Therefore, the secondary metabolites, either mixed or as isolated compounds, are posited as potential corrosion inhibitors for exploitation on an industrial scale, also leading to the production and conservation of different species or the reuse of plant waste products.

Based on the above, the present study aims to investigate the inhibiting properties on carbon steel corrosion of aqueous extracts of *Eulychnia acida* (Copao), a species of the Cactaceae family, endemic to the Mediterranean region of Chile. Copao fruit are sold and used by make homemade alcoholic drinks. Through a study carried out by the INIA (2005), initiatives have been set up to domesticate and exploit the fruit commercially, focusing on the food industry, as its secondary metabolites have antioxidant properties and are biodegradable [23]. In a study by Jiménez-Aspee *et al.* [24] the main components of Copao fruit were separated and characterised using high pressure liquid chromatography (HPLC) coupled with mass spectrometry (MS). The main component of the extract include *Isorhamnetin-3-O-[α-rhamnopyranosyl-(1→6)-ß-glucopyranoside]* and *Isorhamnetin dirhamnoside hexoside*, which are glycosidic flavonoids that together with other components of the extract give it an antioxidant property. Taking this antioxidant property into account, the present study analyses the potential properties as a corrosion inhibitor for carbon steel in acidic media presented by extracts obtained from this plant.

2. METHODOLOGY

2.1. Materials

The natural extracts were obtained from arms of plants of the species *Eulychnia acida* Phil. (Cactaceae), known commonly as Copao. *Eulychnia acida* is an arborescent cactus with a single central trunk from which the arms emerge measuring from 1.5 to 4 m in height [25]. The species is endemic to northern Chile, growing in central valleys and on north-facing hillsides between 27º 50' S and 32º 14' S. The samples used in this study were collected in March 2015 close to the towns of Los Vilos (31°52'18.70''S; 71°28'4.90''W, 3 m.a.s.l.) and Illapel (31°33'07''S; 71°06'32''W, 443 m.a.s.l.). Though the species is commonly infected by the holoparasitic plant *Tristerix aphyllus* Miers ex DC. (Barlow & Wiens) (Loranthaceae), the present study used only non-infected individuals. A total of 10 non-infected individuals of *E. acida* were collected at each collection site. The samples consisted of a 1 m long section of the arm selected at random from each individual. These arm sections were cut from the plants, stored in plastic boxes and taken to the laboratory within 48 hours, where they were stored at -15 º C.

A36 carbon steel test probes were used for the corrosion tests; their composition is shown in Table 1.

Table 1. Composition of the A36 carbon steel.

C	**Si**	**Mn**	**P**	**S**	**Cr**	**Ni**	**Mo**
0.185	0.136	0.388	0.014	0.008	0.003	0.002	0.002
Al	**Cu**	**Co**	**Ti**	**V**	**W**	**Sn**	**Fe**
0.037	0.012	0.001	0.001	0.002	0.009	0.001	Remainder

2.2. Extract preparation

The external bark, internal bark and medulla were separated from the samples. The latter two structures were treated as a single unit denominated "pulp" in this study. The external bark and the pulp were dried at 60ºC for 48 hours. 100 g of each dry sample was then ground in a mortar and deionised water was added to a final volume of 500 ml. The mixture was then heated and boiled for 10 minutes with constant stirring. Finally, the mixtures were filtered and concentrated at low pressure; the solid and dry extract was refrigerated until analysis.

2.3 Extract characterisation

2.3.1. Determining of total phenol content (TP).

Total phenolic content was determined by UV-Visible spectrophotometry with the Folin-Ciocalteu [26] colorimeter technique using gallic acid as standard: 4 mg of each extract was dissolved in a 50 ml volumetric flask with deionised water. A 0.5 ml aliquot was taken of this solution and added

to a light-protected vial. After this, 750 µL of 1N Folin-Ciocalteu reagent were added and after 5 minutes 750 µL of 20% sodium carbonate were added. The resulting solution was left to rest for 2 hours at room temperature and the absorbance of the samples was measured at λ = 760 nm. The calibration curve (R^2 = 0.996) was prepared with a solution of 0.1 g/L gallic acid, the standards (concentration range of 0-4 mg/L) were protected from light. 250 µL of 1N Folin-Ciocalteu reagent were added to each flask. They were then shaken and 750 µL of 20% sodium carbonate were added. The solutions were made up to a final volume of 2 ml and the reaction was left to develop for 2h. The results were expressed in milligrams of gallic acid equivalent per gram of extract (mg AGA/g extract).

2.3.2. Determining total flavonoids (TF).

Total flavonoid content was measured in accordance with the method reported in the literature [27]: 4 mg of extract were dissolved in 50 ml of deionised water. A 0.5 ml aliquot of each extract was taken and placed in a vial. 75 µL of 5% sodium nitrite were added and the reaction was left for 5 minutes. 150 µL of 10% aluminium chloride hexahydrate and 500 µL of 1M sodium hydroxide were then added and the reaction was again left for 5 minutes. The resulting solution was brought to a final level of 2.5 ml with deionised water. The absorbance was measured at a wavelength of λ = 310 nm. The results are expressed in mg of quercetin equivalent /g of extract (mg QE/g extract).

2.4. Mass loss assays

The mass loss tests assays were carried out in accordance with ASTM G31-72 [28], using sheets of A36 carbon steel measuring 3.0 x 3.0 x 0.2 cm. The steel surface was polished with SiC papers up to 1000G, washed with deionised water and degreased with acetone. The sheets were then submerged in 0.1M HCl in the presence and absence of the aqueous Copao bark and pulp extracts for 48 hours. Two different concentration levels were evaluated: 100 ppm and 1000 ppm. After the immersion period, the test probes were cleaned with deionised water and pickling was performed in accordance with current standards. The corrosion rate was calculated as the difference in mass, and the efficiency of the inhibitors was calculated using equation 1. Each assay was performed in triplicate.

$$\eta\% = \frac{W_o - W}{W_o} \times 100 \qquad \text{(eq.1)}$$

η%= Inhibition efficiency.

W_0 = Mass loss in the absence of the extract.

W = Mass loss in the presence of the extract.

2.5. Surface analysis

The steel surface was examined under a Hitachi SU3500 scanning electron microscope. Carbon steel probes measuring 1 cm^2 were submerged for 48 hours in 0.1M HCl in the presence and absence of the aqueous extract at 1500 ppm.

2.6. Electrochemical assays

In order to evaluate the Copao extracts as corrosion inhibitors, potentiodynamic polarization curves were performed. The A35 carbon steel test probes were used as working electrodes after polishing with 120 – 320 – 400 and 600G carbon-silicon sandpaper, washing with deionised water and degreasing with acetone. The test probes were coated with epoxy resin, leaving an exposed area of 1.0 x 1.0 cm^2. A saturated calomel electrode was used as reference electrode and platinum wire was the counter-electrode. Measurements were taken in 0.1M HCl varying the extract concentration (0 – 100 – 500 – 1000 and 1500 ppm). Prior to each polarisation, the open circuit potential was left to stabilise for 30 minutes. The polarization curves were used to obtain the corrosion current density for each system by applying Tafel regressions. This data was then used to calculate the inhibition efficiency in accordance with equation 2:

$$\eta\% = \frac{j_{corr,0} - j_{corr}}{j_{corr}} \times 100 \qquad \text{(eq. 2)}$$

$j_{corr,0}$ = carbon steel corrosion current density without inhibitor.

J_{corr} = carbon steel corrosion current density in the presence of Copao extracts.

Once the optimum extract concentration level had been determined, this was used to obtain polarization curves for the steel at different temperatures (25, 35, 45 and 55ºC), in the absence and presence of the Copao extracts. The electrochemical assays were performed in triplicate using an Autolab potentiostat model 302A.

3. RESULTS AND DISCUSSION

3.1. Extraction yield

The efficiency of natural inhibitors is generally attributed to their phenolic content. The decoction process improves extraction yields, as it provides a higher amount of water soluble compounds, though the high temperatures can decompose some extract components, as was demonstrated by Vasconcelos *et. Al* [16]. Table 2 shows the aqueous extraction yields expressed as g of extract per 100 g of dry plant material. It can be seen that the decoction process obtains approximately 20% extraction of soluble substances in boiling water, which is influenced by the polarity of the water and the temperature used. In a prior study by Tan *et al.* [18], the effect of the solvent on extraction yields was studied in a species of Manglar (*Rhizophora apiculata*). The results showed that the higher the polarity index of the solvent, the higher the extraction yield of compounds with phenolic structures.

The aqueous Copao extracts are composed mainly of different secondary metabolites, such as phenols and polyphenols [24, 27]. The phenolic compounds have a large number of different chemical structures, including phenolic acids, polyphenols, tannins, anthocyanins and flavonoids, among others. These can exist freely or form glycosides through covalent bonds with sugars. Their chemical structure is adequate for antioxidant actions and they can also chelate metal ions. These compounds are associated with the corrosion inhibition efficiency of different natural extracts.

In order to determine the total phenolic content (TP) of the Copao extracts, the Folin-Ciocalteu reagent was used. In base media, this reagent reacts with the phenols present in the sample to form blue coloured chromogens that are quantifiable by spectrophotometric methods. The total flavonoid content (TF) was quantified using the colorimeter method with quercetin as standard. The results for extraction yield, TP and TF are shown in Table 2, where no significant differences are seen for the yield figures when obtaining the total aqueous extract from the bark (22.23%) or the pulp (18.95%). The TF figures are also similar for each extract type, with the bark giving 50.13 mg QE/g extract and the pulp 48.57 mg QE/g extract. However, there is a slight difference with TP values, since the bark gives 67.54 mg AGA/g extract, while the pulp gives 58.75 mg AGA/g extract. For both extracts, the flavonoid content is lower than the phenolic compound content, which is to be expected, as flavonoids are a subgroup of phenolic compounds.

Table 2. Extraction yield, total phenolic content (TP) and total flavonoid content (TF).

Extract	Extract yield (g / 100 g dry plant material)	Total phenol content (TP) (mg AGA / g extract)	Total flavonoid content (TF) (mg QE / g extract)
Bark	22.23	67.54 $\pm$ 0.06	50.13 $\pm$ 0.04
Pulp	18.95	58.75 $\pm$ 0.03	48.57 $\pm$ 0.07

3.2. Mass loss assays

Table 3. Data for mass loss on the A36 carbon steel in the presence and absence of the Copao extracts at two concentration levels: 100 and 1000 mg L^{-1} in 0.1M HCl. Assay time: 48 hours.

Extract	Concentration [mg L^{-1}]	OCP (mV / SCE)	V_{corr} (mm año^{-1})	η (%)
Control	-	-592	4.94	-
Bark	100	-478	0.46	90.7
	1000	-500	0.40	91.9
Pulp	100	-486	0.54	89.1
	1000	-480	0.38	92.3

The results of the mass loss assays for carbon steel in 0.1M HCl for 48 hours in the presence and absence of the Copao extracts are shown in Table 3. The corrosion rate (V_{corr}) of the carbon steel decreases significantly in the presence of all extracts, proving that the extracts have an inhibitory effect on the corrosion process of carbon steel in acidic media. This shows that the organic compounds present in the natural extract are able to interact with the steel surface through an adsorption process, blocking the active sites on the metal. The inhibition percentage (η%) is approximately 90% when 100 mg of extract are added per litre of acidic solution. When this concentration is increased 10-fold, the efficiency of both extract types increases approximately 2%, showing that there is again no significant difference between the bark and pulp extracts. In the presence of the extracts, the corrosion potential (OCP) moves slightly towards more anodic values, thus corroborating the improved behaviour of the

material. These results are comparable with those obtained by Faustin et al. [7], since considering the same inhibitor concentration obtained from the extract of *Geissospermum laeve*, the active component of which is geissospermine, a corrosion inhibition efficiency of 92.0% was obtained for C38 steel in 1M HCl.

3.3. Surface analysis

Fig. 1 shows micrographs obtained for the carbon steel test probes after 48 hours of immersion in 0.1M HCl in the presence and absence of 1500 ppm of bark and pulp extract. The micrograph in Fig. 1a is for the steel in the absence of the extracts, in which it can be seen that the steel has suffered a general corrosion attack with the formation of corrosion products (rust). The corrosion product on the steel surface is rough and very porous. In Fig. 1b and 1c, it can be seen that in the presence of 1500 ppm of extract the surface has remained smooth and free of corrosion products, with even the sandpaper lines remaining visible. This again corroborates the adsorption of the organic compounds present in the Copao bark and pulp extracts, thus protecting the carbon steel from corrosion in this highly aggressive environment. These results are concordant with those obtained by M'Hiri et al. [21], who used orange peel extract as an antioxidant to achieve the precipitation of a surface film on carbon steel in acidic media.

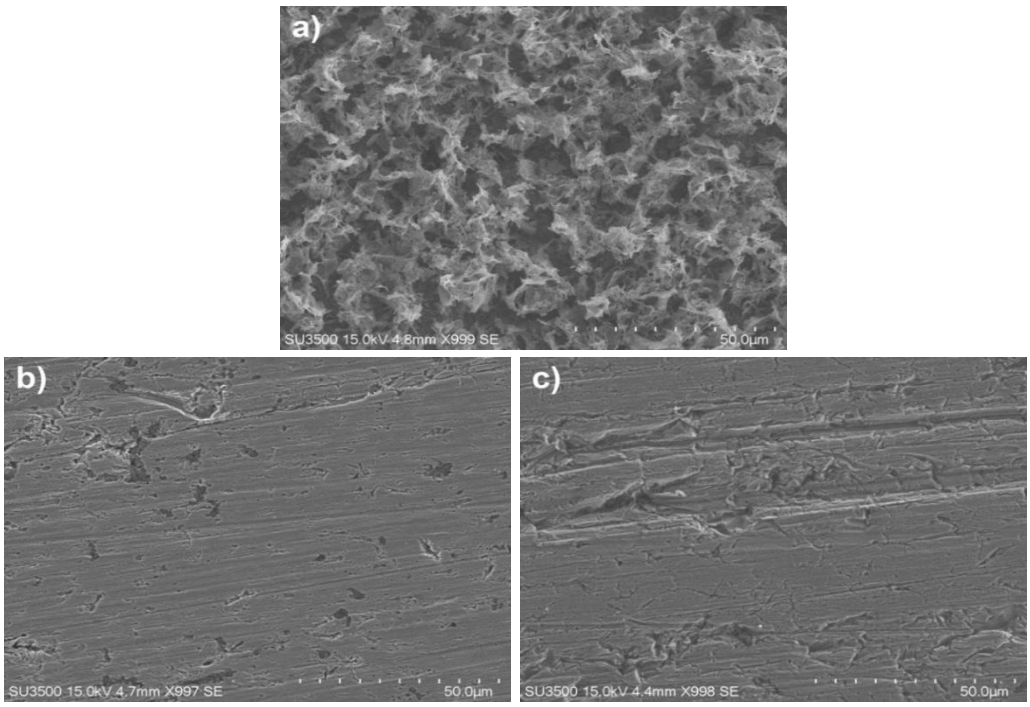

Figure 1. Microphotograph at 1000x of the carbon steel after immersion for 48 hours in a solution of 0.1M HCl. a) steel in absence of extracts, b) steel in the presence of 1500 ppm of Copao bark extract and c) steel in the presence of 1500 ppm of Copao pulp extract.

3.4. Potentiodynamic polarisation curves

Figs. 2a – 2b show the potentiodynamic polarization curves obtained for the A36 carbon steel in 0.1M HCl in the presence and absence of aqueous Copao bark and pulp extracts. Table 4 shows the electrochemical parameters found using the polarization curves: corrosion potential (E_{corr}), corrosion current density (j_{corr}), anodic Tafel slope (β_c), cathodic slope (β_c) and inhibition efficiency (η), as a function of Copao extract concentration. Comparing the corrosion potentials, it can be seen that the presence of the extracts in the acidic solution is able to move the potential to more anodic values. In the literature, an inhibitor is considered anodic or cathodic if it induces a shift in corrosion potential of over 85 mV with respect to the E_{corr} value of the sample in the absence of the inhibitor. In the present study, the shift in potential for the bark extract concentration of 100 mg L^{-1} is approximately 40 mV towards more anodic values and this figure rises to 50 mV when the concentration is raised to 1500 ppm. Therefore, under the present study conditions, the extracts cannot be classified as anodic or cathodic inhibitors, as the difference in potential is very low.

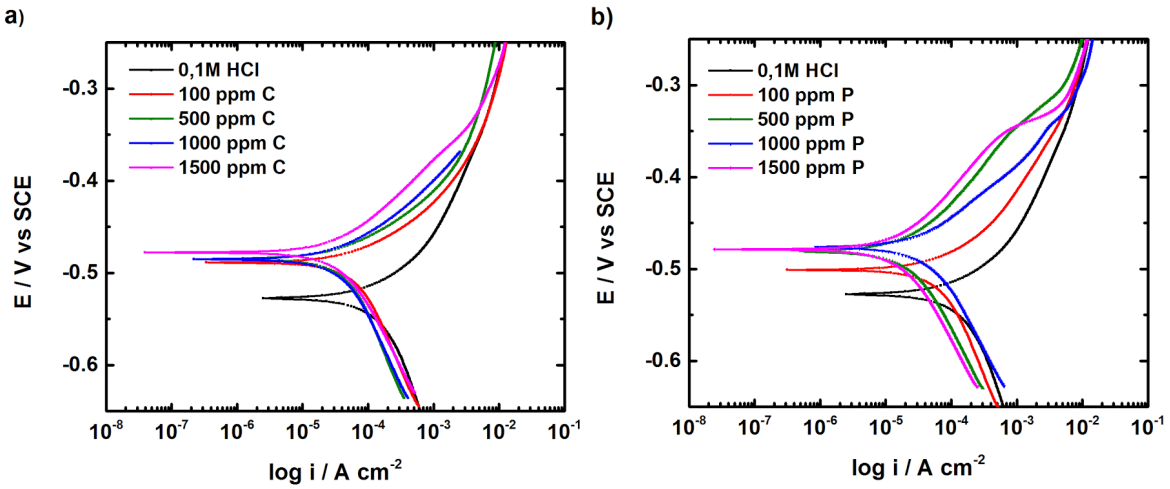

Figure 2. Polarization curves for carbon steel in 0.1M HCl in the presence and absence of Copao extracts at different concentrations (100, 500, 1000 and 1500 ppm) a) aqueous bark extract, b) aqueous pulp extract.

Table 4. Electrochemical parameters for the A36 carbon steel in 0.1M HCl, obtained from the polarization curve in the presence and absence of Copao extracts at different concentrations.

Extract	Concentration [mg L^{-1}]	E_{corr} (mV SCE)	j_{corr} (A cm^{-2})	$ß_a$ (mV dec^{-1})	$ß_c$ (mV dec^{-1})	η (%)
Control	-	-528	200	119	119	-
Bark	100	-489	89	90	148	55.6
	500	-484	49	68	153	75.3
	1000	-485	42	63	133	79.0
	1500	-478	37	64	119	81.7
Pulp	100	-500	131	93	153	34.6
	500	-480	25	83	120	87.5
	1000	-476	40	59	130	80.1
	1500	-479	18	75	121	91.1

Nevertheless, when analysing the corrosion current density values (j_{corr}) calculated from the Tafel slopes, there is a significant decrease in corrosion rate with the increased extract concentration. In both cases a shift is seen in anodic current (metal dissolution) and cathodic currents (hydrogen generation) (Fig. 2a-2b), demonstrating that they act as mixed inhibitors. This behaviour is similar to the use of the inhibitor extracted from *Gundelia tournefortii* in the corrosion process of mild steel in 2.0M HCl and 1.0M H_2SO_4, which acts as a mixed inhibitors, achieving efficiency figures of 93% and 90%, respectively [19].

The anodic Tafel slopes decrease in comparison to the sample without extract, which corroborates that the mechanism of active dissolution of the alloy is different when you add extracts, which is likely due to the formation of complexes on the metal surface. These results are in agreement with those obtained by Zhang et al. [20], who report the use of methionine and its derivatives in the formation of a surface film on 1045 steel through a chemical absorption process, inhibiting the corrosion process on average 95.01% in 0.5M HCl.

The cathodic Tafel slopes show little variation compared to the control slope, meaning that the decrease in cathodic currents is more related to the blocking of active sites on the metal surface and not a change in the proton reduction mechanism.

Fig. 3 shows the Tafel curves for the steel in Copao bark and pulp extracts as a function of temperature, indicating that as the temperature increases, there is a shift in potential towards more negative values and an increase in corrosion current. However, the corrosion inhibitory effect of the extracts tends to remain constant, as the corrosion current in the absence of the extracts also increases (Table 5).

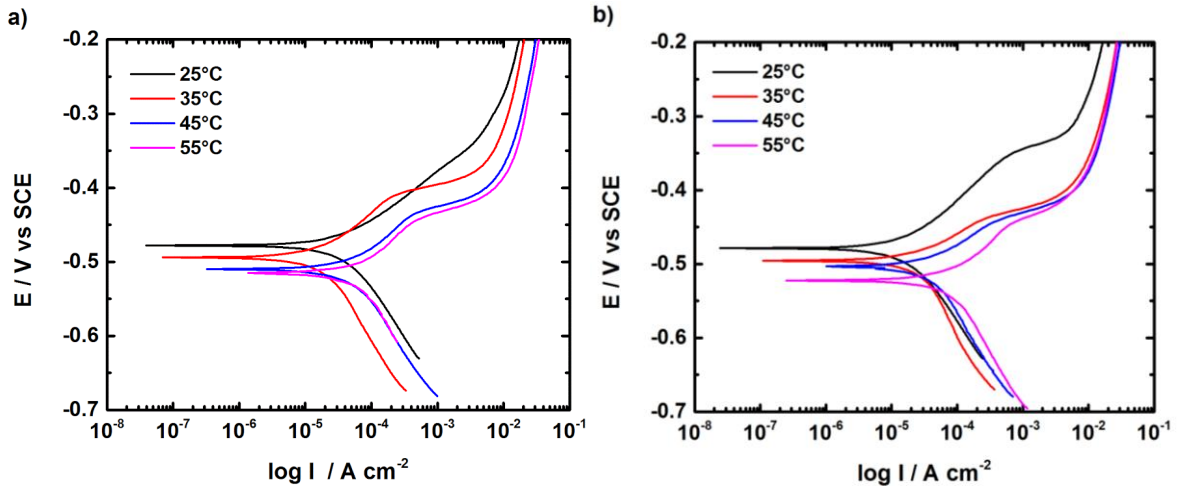

Figure 3. Polarisation curves for Copao extracts: a) bark and b) pulp, at a concentration of 1500 ppm at different temperatures.

The variation in corrosion rate with regard to temperature can be used to calculate the apparent activation energy of the carbon steel corrosion process in the presence and absence of the Copao extracts by applying the Arrhenius equation (eq. 3):

$$I_{corr} = A \exp\left(-\frac{E_a}{RT}\right) \quad \text{(eq. 3)}$$

I_{corr} = corrosion current density.

A = Arrhenius pre-exponential factor.

E_a = apparent activation energy.

R = universal gas constant.

T = absolute temperature.

Table 5. Variation in corrosion potential, corrosion current and inhibition efficiencies of the Copao extracts with temperature.

Temperature (ºC)	Extract	E_{corr} (mV / SCE)	J_{corr} ($\mu A\ cm^{-2}$)	η (%)
25	Control	-528	200	-
	Bark	-478	37	81.7
	Pulp	-479	18	91.1
35	Control	-514	490	-
	Bark	-482	32	93.5
	Pulp	-496	24	95.1
45	Control	-524	830	-
	Bark	-509	43	94.8
	Pulp	-503	34	95.9
55	Control	-543	1400	-
	Bark	-515	56	96.0
	Pulp	-522	69	95.1

Fig. 4 presents the variation in corrosion current as a function of the inverse temperatures in order to determine the activation energy of the process. The increase in temperature accelerates the carbon steel corrosion process in the presence and absence of the Copao extracts. The correlations give a linear regression coefficient close to one. It can be seen in the graph that 1500 ppm of aqueous bark or pulp extract modifies the activation energy of the corrosion process, which is reflected in the change in slope between the carbon steel without extracts and in the presence of the extracts. Using the Arrhenius equation, the apparent activation energy of the A36 carbon steel corrosion process in acidic media and in the absence of the extracts is calculated at a value of 40.59 kJ/mol, while in the presence of 1500 ppm of bark extract the value decreases to 19.03 kJ/mol, and to 19.30 kJ/mol in the presence of 1500 ppm of pulp extract.

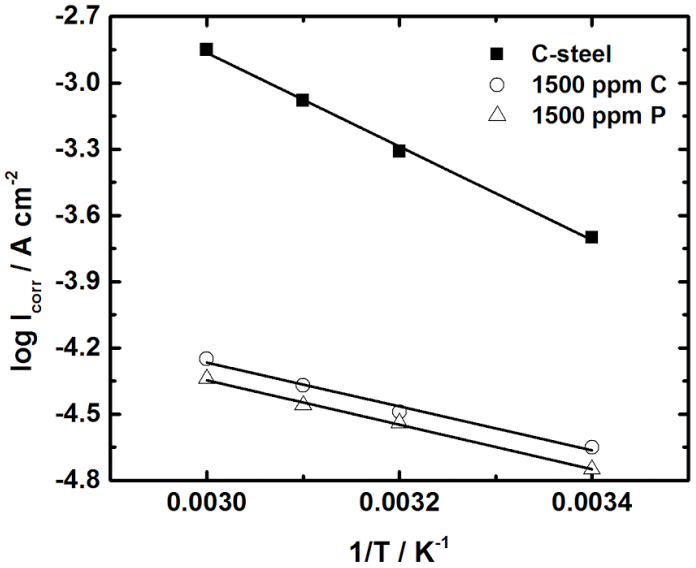

Figure 4. Linear fit to determine the activation energy of the carbon steel corrosion process in the presence and absence of the Copao extracts.

The decrease in activation energy in the presence of the corrosion inhibitor extracts is related to a chemisorption process that is likely due to the formation of complexes between the Fe^{2+} cations and the components of the extracts on the surface of the metal [29]. Similar results were obtained by Souza et al. [13], who used *Ilex paraguariensis* extracts to decrease the E_a of the corrosion of steel in 1M HCl, assuming a mechanism of chemisorption. Similarly, Al-Senami et al. [17] report that *Cucumis Sativus* (cucumber) pell extract inhibited carbon steel corrosion in 1M HCl by 82%, using the E_a value to confirm that the adsorption process is spontaneous and endothermic.

4. CONCLUSION

It has been shown that aqueous Copao extracts act as natural corrosion inhibitors for A36 carbon steel in 0.1M HCl.

Considering that the bark and pulp extracts showed no significant differences regarding phenolic and flavonoid content, or in terms of corrosion inhibition efficiency, the separation of the plant parts can be discarded, thus simplifying the extraction method.

The inhibition efficiency of the extracts obtained by decoction of the external bark, internal bark and medulla of the cactus arms was evaluated by mass loss, giving a figure of around 90% at concentrations of 100 and 1000 ppm, and using polarization curves the efficiency of the extracts was over 80% inhibition at concentrations of 1000 and 1500 ppm. Therefore, the metabolites present in the extracts act as corrosion inhibitors and are able to induce protection of the surface by blocking active sites on the metal.

The SEM analysis revealed the formation of a smooth surface on the C-steel in the presence of the Copao extract compounds, which was most likely due to the formation of a strong chemisorptive bond between the Copao extract compounds and the C-steel surface.

The efficiency of the extract in inhibiting the corrosion of C-steel in 0.1M HCl increased with higher extract concentrations and remained relatively constant with changes in temperature. The apparent activation energy (Ea) for the dissolution of C-steel decreased in the presence of the Copao extract.

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