Electrochemical evaluation of mucilage and cochineal pigments as a hybrid film coating on aluminum surfaces

L D López-León1, William Sánchez-Ortiz2, A Lobo Guerrero3, Juan A Ruiz-Ochoa4, Liliana Lizárraga-Mendiola1 and Iván E Castañeda-Robles1

1 Cuerpo Académico de Ingeniería Civil Sustentable y Tecnología de Materiales, Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca-Tulancingo km 4.5, 42184, Mineral de la Reforma, Mexico
2 División de Ingeniería Química y Bioquímica, Tecnológico de Estudios Superiores de Ecatepec, Av. Tecnológico S/N, 55210, Ecatepec, Mexico
3 Área Académica de Ciencias de la Tierra y Materiales, Universidad Autónoma del Estado de Hidalgo, Carr. Pachuca-Tulancingo km 4.5, 42184, Mineral de la Reforma, Mexico
4 Facultad de Ciencias de la Ingeniería y Tecnología, Universidad Autónoma de Baja California. Blvd Universitario 1000, Unidad Valle de las Palmas, 22260 Tijuana, Baja California, Mexico

E-mail: ivan_castaneda@uaeh.edu.mx

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Abstract
This work deals with the electrochemical evaluation of a hybrid coating based on mucilage and prickly pear cochineal (Dactylopius coccus) for corrosion protective applications. The Opuntia streptacantha mucilage was extracted by grinding prickly pear cochineal, and three coatings containing mucilage (CM), cochineal-mucilage (CMC), and cochineal-mucilage without Tween 80 (CMC-T) were formulated. The aluminum working electrodes (WE) were coated by immersion and then left to dry for 72 h at room temperature. The formed coats were assessed by electrochemical impedance spectroscopy, electrochemical noise, and potentiodynamic polarization curves after 24, 72, and 168 h of immersion in a 3.5 wt% NaCl solution. These electrochemical measurements were performed in triplicate to check reproducibility. The Tween 80 plasticizer-free cochineal-mucilage-based hybrid coating reveals more excellent protection against corrosion than uncoated aluminum. Optical micrographs were used to set apart the conditions of the hybrid coating after its evaluation, which show the protection of the metallic surface on which it was not coated. Results showed that the hybrid coating has suitable properties as a barrier against corrosion due to its ability to block the aggressive species diffusion by trapping them in the coating structure, which prevents their contact with the metal surface. This property is attributable to better mucilage and cochineal film homogeneity. Also, it acts as a corrosion inhibitor due to its semi-permeable behavior where only water molecules flow through its pores. This hybrid coating showed an excellent corrosion-resistant behavior to be used to protect aluminum.

1. Introduction
The phenomenon of corrosion has significant consequences that can be broken down into two main areas: a) Economic costs: direct costs are estimated at 3.5% of Per capita gross domestic product (GDP), in addition to production stoppages, leaks, product contamination and the application of safety coefficients as indirect costs. It is considered that savings of between 20% and 30% can be obtained if the existing technology for corrosion control and protection methods are adequately applied [1–3]. Aluminum is one of the most widely used materials in light industrial constructions [4]. Chloride-induced corrosion is one of the common causes of metallic structure degradation. Any new mitigation alternative should be effective in several of these process stages. Similarly, methods for slowing corrosion initiation reduces corrosion rates, such as designed electrochemical corrosion inhibitors, and could be implemented to allow functional changes throughout the aluminum interface [5, 6]. The application of coatings is one of the most common methods on aluminum [7]. The most representative example of
corrosion inhibitors used in coatings is the Cr(VI) species. However, they have the main drawback: they are toxic and harmful to the environment and humans [8]. Due to these toxicity issues, replacement is possible using natural organic compounds such as seeds [9, 10], plants and leaf extracts [11], nontoxic synthetic compounds (colorants) [12], rare earth elements [13], and organic compounds [14]. These alternatives are cost-effective, harmless, innocuous, easily obtainable, and environmentally friendly and are required as a green corrosion inhibitor. Consequently, it is necessary to research alternative methods to improve aluminum corrosion resistance. However, there is a growing demand for more economical, functional, and environmentally friendly products that identify possible substitutes for coatings that use lead, mercury, cadmium, and hexavalent chromium [15].

*Nopal (Opuntia ficus indica)* is a cactus of great agronomical importance in Mexico; there are 3 million hectares of native nopal and approximately 233,000 hectares of cultivated nopal; of these, 150,000 hectares are destined for human consumption, with a 139,193-ton annual production [16, 17]. Different nopal species have been studied to determine the chemical compounds present in the plant to understand its properties and applications. Han et al (2002) [18] assessed and related the antioxidant activity mechanisms of *Opuntia ficus-indica* var. *Saboten*, found a high concentration of phenolic compounds (180.3 mg g−1). Camarena-Rangel et al (2017) [19] found flavonoids and phenolic compounds through a phytochemical study of *Opuntia ficus-indica*, *Opuntia megacantha*, and *Opuntia streptacantha callus*. Mazri (2018) [20] studied *Opuntia ficus-indica* juice, finding ascorbic acid, polyphenols, and flavonoids among its components, which presented antioxidant activity due to the phenolic compounds were effective free radical eliminators. Nopal mucilage acted as a corrosion inhibitor for steel in chloride solution [21]. Suarez and González et al (2014) [22] evaluated *Opuntia ficus* extract as a corrosion inhibitor for carbon steel in acidic media, reaching efficiencies as high as 94%. Torres-Acosta et al (2007) [23] evaluated *Opuntia-Ficus-Indica* (Nopal) mucilage as a corrosion inhibitor for steel in chloride-contaminated alkaline solutions. According to the authors, the corrosion resistance improvement was apparently due to a denser oxide/hydroxide film formation on the reinforcing steel when nopal mucilage reacted chemically with the metal, which, in turn, inhibited pit formation when chlorides were added to the electrolyte. Generally, natural polymers have two groups: polysaccharides and proteins [24, 25].

Carmine acid extracted from the grana cochineal is used as a natural colorant of purple–red tones in the food, cosmetic and pharmaceutical industries. The natural dye is a phytophagous insect of the order Homoptera, family Dactylopiidae; it belongs to the genus Dactylopius, lives on cacti of the genera Opuntia and Nopalea, and is known because of its chromatic properties. It is cultivated to obtain commercial carmine concerning the wild cochineal used by hand [26]. Carmine acid is extracted from the insect Dactylopius coccus (cochineal), crystallized in alcohols as red prisms; its function point is not clear, darkens at 120 °C and has Rf 0.17 in 1-propanol: ammonia (d.8809): water (6:3:1) and 0.12 in 1-butanol: pyridine: H2O (3:1:1:1). It has a deep red color in water and is yellow to red in acidic solutions. UV max (water): 500 nm (ε 6800); (0.12 N HCl): 4900–500 nm (ε 5800); (0.0001 N NaOH): 540 nm (ε 3450). Practically insoluble in petroleum ether, benzene, and chloroform [27, 28].

The efficiency of polymeric materials as corrosion-resistant coatings for metals increases when polymeric ligands are modified using corrosion inhibitors. Inhibitor compounds in a polymeric net could be used to create a group of coatings that respond to changes in the coating environment. The goal is to create inhibitors activated by the corrosion process itself, avoiding the exit of corrosive species from the coating. With this restriction, it is possible to reach the dual goal of corrosion protection by a barrier and inhibiting metallic elements. Polarization curves, electrochemical impedance spectroscopy, infrared spectrum, and visual inspection were used. The present work reports the effect of mucilage and cochineal extracts as inhibitors in the formulation of corrosion protection coatings on immersed aluminum. It employs a 3.5% wt NaCl solution using electrochemical techniques, proposing a green and environmentally friendly coating, as it does not contain organic solvents or toxic pollutants.

2. Experimental design

This work is based on a study on the behavior of organic–inorganic hybrid coatings, using mucilage and prickly pear cochineal on aluminum as a protective barrier against corrosion by chlorides. The experimental process consisted of preparing a metal surface to be coated and a blank; obtaining and characterization mucilage and grana cochineal from the nopal; formulation of the coatings, application, evaluation, and analysis of the coating on the aluminum surface in a solution rich in chloride ions. An aluminum electrode with a purity percentage of 99% was used, with an exposed surface of 1 cm². It was polished with CSi abrasive paper of increasing grain size up to #320, rinsed first with distilled water and then with methyl alcohol, and dried by airflow. This procedure was carried out before the immersion coating of the metal surface, subsequent drying of the coating in the environment for 72 h, and subsequent electrochemical testing.
2.1. Obtaining mucilage, treatment of cochineal and formulation of coatings

The *Opuntia streptacantha* cactus, native to central Mexico, was used in this study. Cladodes aged between 2 and 3 years were considered since they contain the highest concentrations of mucilage, according to previous studies [29]. Mucilage extraction was performed according to Sepúlveda *et al* [30]. After removing them, both the mucilage and *Dactylopius coccus* (cochineal) were ground separately in unglazed porcelain mortars to a fine powder. Subsequently, the formulation of the coating was carried out with the following process: in an Erlenmeyer flask, 0.5 g of mucilage, 0.5 g of cochineal, 20 g of deionized water (18 MΩ cm⁻¹), and 0.4 g of glycerol were added; the mixture was heated at 90 °C for 5 min with constant stirring at 1,200 rpm; then it was cooled to 25 °C, followed by the addition of Tween 80 (C₆H₁₂₄O₆); finally, the mixture was stirred for 5 min at 70 °C and 2000 rpm. Three coatings were obtained with variations in the active element of interest (table 1): CM (coating with mucilage), CMC (coating with mucilage and cochineal), and CMC-T (coating with mucilage, cochineal, and without Tween 80).

| Coating | Deionized water, (g) | Mucilage, (g) | Carminic acid, (g) | Tween 80, (g) | Glycerol, (g) |
|---------|---------------------|--------------|-------------------|--------------|--------------|
| CM      | 20                  | 0.5          | —                 | 0.4          | 0.4          |
| CMC     | 20                  | 0.5          | 0.5               | 0.4          | 0.4          |
| CMC-T   | 20                  | 0.5          | 0.5               | —            | 0.4          |

2.2. Electrochemical techniques and test solution

A three-electrode Pyrex® glass electrochemical cell, ASTM G-5 [31], was used for the electrochemical tests, employing a saturated calomel reference electrode (SCE) and a graphite counter electrode. All the potentials in work are referred to as the SCE, which was measured until it reached a stable value, typically 30 min. A 3.5% wt. NaCl solution was employed as an electrolytic solution for the tests, prepared with analytical grade reagents and distilled water, kept at room temperature, naturally aerated, and with a pH equal to 6. Electrochemical measurements were performed in a Potentiostat-Galvanostat model BioLogic 150.

2.2.1. Potentiodynamic polarization curves

For the potentiodynamic bias curves, aluminum was biased from −2.5 V to +2.5 for the value of the corrosion potential \( E_{corr} \) at a scan rate of 1 mV s⁻¹. The corrosion rates were determined by relating the corrosion current density, \( i_{corr} \), with the polarization resistance, \( R_p \), from the Stern-Geary equation [32], for reactions controlled by charge transfer (equation (1)).

\[
I_{corr} = \frac{b_a}{2.303} \times \frac{b_c}{(b_a + b_c)} \times \frac{1}{R_p} = \frac{B}{R_p}
\]

Where \( b_a \) and \( b_c \) are the anodic and cathodic Tafel slopes, respectively, and \( B = (b_a + b_c)/[2.303 (b_a + b_c)] \).

The Tafel slopes’ determination and the potentiodynamic polarization curves were obtained in a reduced category of potentials, that is +/− 60 mV, concerning the \( E_{corr} \), both in cathodic and anodic zones.

2.2.2. Electrochemical impedance spectroscopy (EIS)

A signal of ±10 mV was applied to \( E_{corr} \), in the frequency range between 200 kHz and 0.01 Hz, obtaining 6 points per decade. Inhibitor efficiency values were calculated using equation (2):

\[
I.E. (100\%) = \frac{R_{ct2}}{R_{ct1}} \times \frac{R_{ct1}}{R_{ct2}} \times 100
\]

where \( R_{ct2} \) and \( R_{ct1} \) are the load transfer resistance values with and without the addition of coating, respectively.

2.2.3. Electrochemical noise

For electrochemical noise measurements according to the ASTM-G199 standard [33], the arrangement of two nominally identical working electrodes and one SCE reference electrode was used in a potential range of +/−2.5 for \( E_{corr} \). The potential and current values were recorded at a speed of 1 sample/second; potential and current series were obtained according to time, and the average standard deviations of each series were calculated.

To determine the resistance in noise, \( R_r \), the standard deviation of the noise in current, \( \sigma I \) and voltage, \( \sigma V \) of each run was calculated, and equation (3) was applied (Cottis *et al* 1996, [34]):

\[
R_r = \frac{\sigma V}{\sigma I}
\]
2.3. Microscopic analysis
The coated and uncoated aluminum was analyzed under a light microscope at 40X magnification before and after electrochemical tests. The surfaces were photographed with a camera adapted to the microscope. Micrographs of the segments were studied, and comparisons were made.

2.4. Coating formulations
Three different coatings were made (see table 1), varying the presence of cochineal and Tween 80. The hydrocolloid obtained was placed in Eppendorf tubes to be later placed on the aluminum surface. Aluminum sections were dip-coated and then dried at room temperature to monitor coating thickness for three days. The proposed alternative was formulated based on renewable sources such as nopal mucilage and cochineal. The formulation considered adequate is the one shown in table 1. It was not possible to incorporate different proportions of the order of those added of mucilage, cochineal, glycerol, and Tween 80, because the coatings obtained were too fragile and could not be manipulated, possibly due to the interactions of the cellulosic polysaccharides with the molecules of the matrix that modify the degree of aggregation of the chains and the resistance of the polymeric network.

2.5. Fourier transform infrared spectroscopy
Fourier transform infrared spectroscopy (FT-IR) was carried out using a PerkinElmer Frontier spectrometer with the fully attenuated reflectance technique ATR using a spectral resolution of 4 cm\(^{-1}\) (PerkinElmer, Waltham, MA, USA).

3. Results and discussion
3.1. Polarization curves
The polarization curve was measured to examine the corrosion kinetics of aluminum samples in a 3.5% wt. NaCl solution, in the absence and presence of coatings. Figure 1 presents the polarization curves of Al (blank, uncoated sample), CM, CMC, and CMC-T samples at 298 K. The electrochemical parameters obtained by Tafel analysis are listed in table 2 as the backup information. It can be seen that the addition of CM, CMC, and CMC-T markedly changed the slope of the polarization curves in figure 1. Namely, the oxidation-reduction reactions are restricted by incorporating the CM, CMC, and CMC-T coatings. T in the NaCl solution. This effect implies that the coatings hinder the hydrogen evolution reactions. However, CM, CMC, and CMC-T suppression phenomena are also transferred to the cathodic zone, indicating that oxidation-reduction reactions are blocked in coatings. CMC and CMC-T coatings show a more significant reduction in corrosion potentials, \(E_{corr}\), especially for CMC.

For the Al, CM, and CMC-T cases (Kelly et al, 2003), when applying the reverse sweep, the curve that returns along the same path or for a lower current value establishes that the material does not present a tendency to
localized corrosion [35], that is, that the increase in the current is not due to localized corrosion. However, some other anodic reaction since the area remains constant. However, in the case of CMC coating, the return of the curve is from the front, which indicates that the layer does not break but reaches the potential oxidation reaction of water to occur. This reaction is supported by the extent of the highest corrosion potential observed for the back scan due to the slowing of anodic dissolution kinetics.

In table 2, corrosion potential ($E_{corr}$), corrosion current density ($i_{corr}$), polarization resistance ($R_p$), and corresponding inhibition efficiency (IE) values for different inhibitor concentrations are given as electrochemical parameters. Different inhibitor concentrations calculated inhibition efficiencies from equation (1). Although the anodic and cathodic curves are not symmetrical, the cathodic curves also have regions with a linear ratio between the potential and the logarithm of the current density and zones called Tafel regions. By extrapolating such linear segments from the anodic and/or cathodic curves, and intersecting them to $E_{corr}$, the value of $i_{corr}$ for the metal in an aggressive medium can be determined.

The results for each sample were calculated as the mean ± standard deviation of the triplicate determinations. The percentage error of the current density was found using equation (1), and the corrosion current density ($i_{corr}$) was calculated to validate the data obtained from the curves of the linear polarization resistance and the Tafel slopes of the cathodic and anodic zones. The Stern-Geary coefficient ($B$) is related to the anodic ($b_a$) and cathodic ($b_c$) Tafel slopes.

After performing the corresponding calculations to find the theoretical values of the parameters by applying equation (1), the error percentage is calculated by taking into account the equation (6).

$$\%Error = \left[ \frac{[Theoretical \ value - Experimental \ value]}{Theoretical \ value} \right] \times 100\%$$

(6)

The highest efficiency was the CMC-T coating according to the determined parameters, followed by the CMC and CM. The lowest current density was for the CMC-T. The best behavior against corrosion in environments with chlorides in the study case was for the coating that includes cochineal and mucilage in its formulation without the presence of Tween 80.

### 3.2. Electrochemical noise

The corrosive system is immediately observed in figure 2, which shows the electrochemical noise resistance, $R_n$, response for the different approaches, where the behavior of each of them is immediately observed. Through electrochemical noise techniques and potentiodynamic polarization curves, it was shown that the presence of the coating in the analyzed system revealed a rapid action on metallic surfaces. For the unprotected aluminum, we observe the resistance series, $R_n$, with a small amplitude of the transients due to the speed of generation of the natural film, and it is protected in an accelerated manner. In the first 24 h, the behavior of CMC began with greater amplitude of the transients, generating a more significant attack than the other samples; however, the amplitude reduces without reaching the behavior of Al. In comparison with the results obtained in $R_p$, it is shown that the sample presents an active corrosion potential (more negative). The behavior in the CM and CMC-T systems is very similar with a subtle attack where the transients present small amplitudes when passing. The surface activity is more active over time, showing transients with greater amplitude in short intervals. Comparing with Al they are very similar, clearly corroborated with the $R_p$ technique.

#### 3.2.1. Noise resistance

The resistance values were determined for each of the cases studied (equation (3)): Al, CM, CMC, and CMC-T, as well as in the different immersion times. Figure 3 shows the values obtained, corroborating what is shown in the graphs (figure 2) regarding the behavior of the resistance series. The cases studied with coating presented higher resistance values at 24 h than uncoated aluminum. During this investigation, the behavior of aluminum presents an increased advance of the immersion time with a maximum of 96 h and maintains a similar magnitude in the value at 168 h. In the cases of the CM and CMC coatings, the maximum values of resistance over the uncoated aluminum were at 24 h. During the hours of immersion, these values were reduced, the lowest presented at 168 h. The higher resistance values are present for the case of the CMC-T coating.

### Table 2. Parameters obtained from polarization curves for aluminum immersed in NaCl solution at 3.5% wt. with different coatings.

| Sample     | $E_{corr}$ (V) | $b_a$ (V/decade) | $b_c$ (V/decade) | $i_{corr}$ experimental (A).10$^{-7}$ | $i_{corr}$ theoretical (A).10$^{-7}$ | % Error | IE% from $i_{corr}$ | IE% from $i_{corr}$ | $R_p$ |
|------------|----------------|------------------|------------------|----------------------------------------|----------------------------------------|--------|-------------------|-------------------|------|
| Al (blank) | −0.73          | 0.19             | 0.03             | 61.65                                  | 61.74                                  | 0.09   | —                 | —                 | —    |
| CM         | −0.71          | 0.07             | 0.01             | 32.15                                  | 32.89                                  | 0.02   | 27.68             | 46.73             | —    |
| CMC        | −0.19          | 0.03             | 0.09             | 14.13                                  | 14.89                                  | 0.05   | 87.14             | 75.88             | —    |
| CMC-T      | −0.68          | 0.12             | 0.02             | 11.86                                  | 12.00                                  | 0.01   | 85.91             | 80.56             | —    |
resistance values are present for the case of the CMC-T coating. It indicates the contribution of mucilage, cochineal, and the removal of polysorbate 80 (CMC-T), improves the behavior and resistance in noise resistance values, when compared with aluminum without cover.

3.2.2. Location index
The location index equation (4) is a parameter that evaluates the noise variation in current and compares it with the mean value. This index was calculated through the ratio of the standard deviation in the current ($\sigma_i$) and the root mean square of the current ($I_{rms}$) [36].

$$IL = \frac{\sigma_i}{I_{rms}}$$

Table 3 shows the localization index (IL) for the cases of the coatings. It identifies the type of corrosion present on the surface according to ranges of values reported in the literature [37]: IL values; between 0–0.01 localized corrosion present; 0.1–0.01 mixed corrosion present; and 0.01–0.001 generalized corrosion present. In the case of uncoated aluminum, it initially presented a value corresponding to mixed corrosion, and by increasing the immersion time, it presented values close to 1 corresponding to localized corrosion. The CM coating presented values close to localized corrosion throughout the immersion time. The CMC coating presented a value close to localized corrosion at half the total time immersed in mixed corrosion and increasing the time in localized corrosion. However, for the CMC-T coating, the corrosion phenomenon started with a value close to mixed corrosion, at 96 h to generalized corrosion. At 168 h, it presented a value corresponding to localized corrosion.
Thus, removing the Tween 80 component from the coating formulation caused a more significant effect on surface corrosion resistance phenomena.

For CMC and CMC-T samples at 96 h, when performing the analysis, there is a considerable decrease due to superficial phenomena such as the protection of the coating and generating that the series current density time series present a smaller amplitude; this is observed in figure 2. The resistance time series for these two systems are observed as a continuous straight line, indicating this process and allowing the modification of the corrosion phenomenon different from the initial one. Subsequently, the resistance time series presented greater amplitude in the transients obtained, therefore, the increase in the value of the IL for these cases.

3.3. Electrochemical impedance spectroscopy (EIS)

EIS technique was used to obtain electrochemical characteristics of the corrosion process; also, it was employed to separate the contributions of different phenomena that interfere with and control the corrosion process of aluminum with and without the coating.

EIS Nyquist diagrams of the different systems under study, shown in the graphs (figure 5), were obtained to carry out a quantitative analysis of the impedance spectra. These were simulated with the analogous circuit shown in figure 4.

The system’s EIS results without organic coating can be presented with physical elements in an equivalent circuit. The circuit in figure 4(b) comprises a resistor, $R_s$, representing the solution resistance, and a constant phase element, $CPE_{ct}$, connected in parallel with the charge transfer resistance $R_{ct}$. This circuit is associated with

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**Table 3.** Localization index (LI) values of the aluminum surface with and without coating, at 24, 96, and 168 h of immersion in NaCl at 3.5% wt.

| Time (h) | Al | CM | CMC | CMC-T |
|---------|----|----|-----|-------|
| 24      | 0.144 | 0.921 | 0.804 | 0.391 |
| 96      | 0.326 | 0.964 | 0.385 | 0.087 |
| 168     | 0.731 | 0.791 | 0.945 | 0.891 |

**Table 4.** Electrochemical impedance data for the coated and uncoated steel in a 3.5% NaCl solution.

| System  | $R_s$ (Ω) | $R_{coat}$ (Ω) | CPE$_{coat}$ [mF·s$^{(n-1)}$] | $n_{coat}$ | $R_{ct}$ (Ω) | CPE$_{ct}$ [μF·s$^{(n-1)}$] | $n_{ct}$ | I.E. (%) |
|---------|-----------|----------------|--------------------------------|------------|--------------|-------------------------------|----------|---------|
| Al 24 h | 20.91     | 4202           | 0.16                          | 0.87       | ---          | ---                           | ---      | ---     |
| Al 96 h | 21.22     | 3777           | 0.16                          | 0.85       | ---          | ---                           | ---      | ---     |
| Al 168 h| 20.43     | 3165           | 0.15                          | 0.89       | ---          | ---                           | ---      | ---     |
| CM 24 h | 2.91      | 850            | 0.16                          | 0.83       | 1856         | 7.08                          | 0.85     | 54.20   |
| CM 96 h | 4.47      | 396.4          | 0.37                          | 0.75       | 1085         | 14.11                         | 0.85     | 63.47   |
| CM 168 h| 5.00      | 377.2          | 0.32                          | 0.75       | 915.3        | 38.84                         | 0.83     | 58.79   |
| CMC 24 h| 5.85      | 2104           | 0.12                          | 0.76       | 4792         | 0.26                          | 0.85     | 56.09   |
| CMC 96 h| 4.29      | 1653.2         | 0.26                          | 0.83       | 4256         | 7.44                          | 0.85     | 61.16   |
| CMC 168 h| 5.21     | 966.8          | 0.21                          | 0.80       | 2001.8       | 32.17                         | 0.81     | 51.70   |
| CMC-T 24 h| 3.20    | 4946           | 0.25                          | 0.69       | 10795        | 0.31                          | 0.85     | 54.18   |
| CMC-T 96 h| 5.35     | 3144           | 0.12                          | 0.79       | 7664         | 12.33                         | 0.87     | 58.97   |
| CMC-T 168 h| 4.20   | 2045           | 0.21                          | 0.75       | 5756         | 26.5                          | 0.85     | 64.47   |

Thus, removing the Tween 80 component from the coating formulation caused a more significant effect on surface corrosion resistance phenomena.

For CMC and CMC-T samples at 96 h, when performing the analysis, there is a considerable decrease due to superficial phenomena such as the protection of the coating and generating that the series current density time series present a smaller amplitude; this is observed in figure 2. The resistance time series for these two systems are observed as a continuous straight line, indicating this process and allowing the modification of the corrosion phenomenon different from the initial one. Subsequently, the resistance time series presented greater amplitude in the transients obtained, therefore, the increase in the value of the IL for these cases.
uncoated aluminum in redox reactions in aggressive media. The analogous circuit shown in figure 4(b) generally describes the process at the metal-solution interface. Figure 4(a) shows the resistance of the solution represented by $R_s$, the charge transfer resistance by $R_{ct}$, and a double layer capacitance by $CPE_{ct}$. These are associated with the film formed by the organic coating, in addition to a resistance linked to the coating $R_{coat}$ connected in parallel to a constant phase capacitor $CPE_{coat}$ that represents the heterogeneity of the surface that is produced by the dissolution of aggressive species $[38]$. Impedance parameters were determined by a half-circle suitable method by EC-Lab software (EC-Lab®) using a simple-randomized numerical generator and are presented in table 4.

EIS measurements were performed on a BioLogic SP-150 potentiostat by applying a ±10 mV signal around the $E_{corr}$ value at a frequency interval between 10 kHz and 0.5 Hz. To obtain coating efficiency values, they were calculated using equation (5):

$$I.E. \ (100\%) = \frac{R_{ct2} \times R_{ct1}}{R_{ct2}} \times 100$$

(5)

where $R_{ct2}$ and $R_{ct1}$ are the load transfer resistance values with and without the addition of the coating, respectively.

The values of the constant phase elements obtained for the best fit of the experimental data to the analogous circuit of figure 4 is shown in table 4. It is observed that the coat values for the $CPE_{coat}$ obtained for the different coatings under study depending on the immersion times are very similar (about 0.75–0.85) and can be mainly attributed to the heterogeneity of the electrode surface. In the case of $CPE_{ct}$, it is essential to note that all the calculated $n_{ct}$ are comparable in magnitude, which validates the supposition that these elements are associated with species diffusion $[39]$. The CMC-T system has higher values of resistance and efficiency of organic coating as a function of inversion time than the other systems studied CM, CMC, and the white (without coating).

In the case of $CPE_{ct}$, it is essential to note that all the calculated $n_{ct}$ are similar in magnitude, which validates the assumption that these elements are associated with species diffusion $[39]$. The CMC and CMC-T systems present higher values of resistance and efficiency of the organic coating as a function of the inversion time than the studied CM system and the reference without coating. It is pointed out that the $R_s$ values of different coatings

![Figure 5. Typical Nyquist diagrams were obtained for the system without coating (a) and with the organic coating (b)–(d) on aluminum in a 3.5% NaCl solution.](image)
under study are minor compared to a without covering system due to the microstructure in systems with mucilage is denser and presents holes that provide a diffusion path of the electrolyte to the recovering/substrate interface [40–42].

3.4. Microscopy
The morphology of the coated and uncoated aluminum samples in a 3.5% wt. NaCl solution was observed with a metallographic microscope and a 50X objective (brand, model) (figure 6) before immersion. In the electrolyte and after 168 h of immersion. Subsequently, cleaning was carried out by sonication in deionized water and drying with air. According to the micrographs in figure 6, corrosion products are visible in larger surface areas for uncoated aluminum, with no corrosion damage on the coated metal surfaces. However, hybrid coatings exhibit surface degradation and chloride ions can diffuse through the coating surface using the porosity of the coating as a pathway, causing loss of the coating by delamination.

When the electrolyte reaches the cladding/metal interface, electrochemical reactions begin. All formulations act as a barrier, reducing the diffusion rate of chloride ions and, therefore, localized corrosion damage on the metal surface is reduced. The CMC-T formulation exhibits more acceptable barrier properties, less coating surface damage, and smaller coating-free zones, showing no evidence of coating degradation and excellent adhesion to the metal substrate after testing.

Figure 6. Optical micrographs before and after the electrochemical tests of the uncoated and coated Aluminum surface CM, CMC and CMC-T after 168 h of immersion in a NaCl solution at 3.5% by weight. The arrows indicate some of the pitting (Al), corrosion products (Al and CM), and delamination (CM, CMC and CMC-T) that formed during testing.
3.5. Coating thickness

An ultrasonic thickness measuring tool (Bruker NDT model) was used to determine the coating thickness. Ten measurements were taken at 10 random points on the coated surface, and the average value was calculated; the coating thickness obtained was 18.75 ± 0.01 μm for CMC, 22.12 ± 0.01 μm for CMC, and 21.16 ± 0.01 μm for CMC-T. Three test items of each formulation were evaluated to ensure reproducibility. According to the values obtained, the coating thickness is homogeneous.

3.6. Infrared spectroscopy

Figure 7(a) shows the infrared spectrum (FT-IR) of the mucilage extracted from the nopal (CM). The band at 3255 cm⁻¹ is attributable to carbohydrate O-H bonds of the hydroxyl groups [41]. The C-H stretching vibrations at 2930 cm⁻¹, and small bands at 2882 and 2850 cm⁻¹ are due to C-H and -CH2 stretching of the pyranose and the carboxylic groups, respectively [41]. The C-C stretching bonds are visible at 2100 cm⁻¹. The COO- antisymmetric and symmetric stretching vibrations of carboxylic acid salts of the mucilage were visible from 1615 to 1512 cm⁻¹ [42]. The band at 1400 cm⁻¹ is due to H-C-H bending vibrations. The peaks from 1321 to 988 cm⁻¹ are closely related to the presence of –COOH groups, aromatic proteins, phosphoric groups, and some polysaccharides in pyranose ring conformations, such as the mannose and glucose [43, 44]. On the other hand, the absorption band at 853 cm⁻¹ corresponds to β-D-glucose, while the bands observed at 671 and 550 cm⁻¹ have been assigned to the N–H and O–H out-of-plane vibrations. In this sense, figure 7(b) shows the interaction effect between the cochineal dye and the mucilage extract. The cochineal FT-IR spectrum (C) shows an absorption band at 3350 cm⁻¹ associated with the –OH stretching mode. The bands between 2930 and 2855 cm⁻¹ are due to C-H, -CH2, and -CH3 stretching vibration modes. The band at 1642 cm⁻¹ is from the C=O stretching of the anthraquinone middle ring, while at 1565 cm⁻¹ is observed the C=C stretching of the I ring, the C–O–H scissoring vibration, and the C–H out-of-plane bending. The C=C stretching from I and II aromatic rings and the glucose C–H deformation is present at 1463 cm⁻¹. The C–H and C–O–H deformation and the C–O–H of the groups are present through the band at 1270 cm⁻¹. The band at 1080 cm⁻¹ is due to the scissoring vibrations of the C–O and C–O–H of the glucose and the C–H rocking. The C–H wagging, C–H rotating in-plane bending, and the C=C–C scissor are shown by the
band located at 884 cm\(^{-1}\). The bands that arise between 758 to 532 cm\(^{-1}\) are due to the rocking C–H, out-of-plane bending C–OH, out-of-plane wagging C–H, and several skeletal vibration modes of aromatic systems [45–48]. Table 5 lists the main vibrational modes for the mucilage and the cochineal dye. In addition, the composite formed from the cochineal dye with the mucilage (CMC) shows a different behavior to the CM and the C, indicating a new interaction state between both components. Finally, the effect of removing the polysorbate 80 from the CMC sample is also shown in figure 7(c) (red curve: CMC-T). In this case, a small intensity increment occurred in the bands associated with the CH vibrational modes. This increment could be related to an increment in the polymer composite’s crystallinity by removing the polysorbate 80.

### 4. Conclusion

In this work, we found that high molecular weight organic-inorganic coating is an effective corrosion barrier for pure aluminum in NaCl at 3.5% by weight, with higher efficiency with the coating with mucilage, CM, CMC, and CMC-T. And cochineal without polysorbate 80, CMC-T. The polarization curves showed that the proposed coatings function as mixed-type inhibitors with a more significant effect on the electrochemical reactions in the cathodic branch. From the duration of the corrosion tests, the corrosion potentials, Ec Orr, of the coatings were more positive than with the uncoated material. The resistance value, Rp, of the coating, first decreased and then gradually increased, indicating that the protective effect of the coatings is gradually significant. The presence of coatings on the metallic surface decreases the current density. The electrochemical noise results correlate with the polarization and EIS curves and obtain the localization index, which interprets a better behavior against corrosion by the CMC-T coating. The EIS measurements indicated that the corrosion process was under charge transfer control, agreeing with the efficiency values obtained using polarization curves and EIS electrochemical techniques. IR spectra showed the effect of combining the cochineal with the mucilage, having a close molecular affinity, which helps to improve the structural strength of the organic covering. Combining these compounds in the coatings protects the metallic surface and reduces the attack of chloride ions. Environmentally friendly water-based coatings with fewer volatile organic compounds with low environmental impact were obtained.

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### Data availability statement

The data that support the findings of this study are available upon reasonable request from the authors.
Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

Disclosure statement

The researchers disclosed that no possible conflicts of interest.

ORCID iDs

L D López-León @ https://orcid.org/0000-0001-5871-7707
William Sánchez-Ortiz @ https://orcid.org/0000-0002-8502-2772
A Lobo Guerrero @ https://orcid.org/0000-0001-5816-847X
Juan A Ruiz-Ochoa @ https://orcid.org/0000-0003-0826-3799
Liliana Lizarraga-Mendiola @ https://orcid.org/0000-0001-6320-8923
Iván E Castañeda-Robles @ https://orcid.org/0000-0002-7610-5461

References

[1] Shi X, Xie N, Fortune K and Gong J 2012 Durability of steel reinforced concrete in chloride environments: an overview Constr. Build. Mater. 30 125–38
[2] Michalys P and Vinzilou E 2022 The growing infrastructure crisis: the challenge of scour risk assessment and the development of a new sensing system Infrastructures 7 68
[3] Winston R and Uhlig H H 2018 Corrosion and corrosion control. an introduction to corrosion science and engineering Electrochemistry 4th edn (New York: Wiley) 512
[4] Hufnagel W (ed) 1992 Manual del aluminio 1 2nd edn (Barcelona: Editorial Reverté)
[5] Thakur A and Kumar A 2021 Sustainable inhibitors for corrosion mitigation in aggressive corrosive media: a comprehensive study J Bio Tribol Corros 7 67
[6] Udendy S C, Eke O E and Nnanna L A 2020 Newboudlia laevis leaves extract as tenable eco-friendly corrosion inhibitor for aluminium alloy AA7075-T7351 in 1 M HCl corrosive environment: gravimetric, electrochemical and thermodynamic studies Chemistry Africa 3 305–16
[7] Nyby C et al 2021 Electrochemical metrics for corrosion resistant alloys Sci Data 8 58
[8] Becker M 2019 Chromate-free chemical conversion coatings for aluminium alloys Corros. Rev. 37 321–42
[9] Abiola O K, Otaihe I O E and Kio J O 2009 Gossipium hirsutum L. extracts as green corrosion inhibitor for aluminum in NaOH solution Corros. Sci. 51 1879–81
[10] Fernine Y, Ech-chihbi E, Arrousse N, El Hajjaji F, Bousrafi F, Touhami M E, Rais Z and Taleb M 2021 Ocimum basilicum seeds extract as an environmentally friendly antioxidant and corrosion inhibitor for aluminium alloy 2024-T3 corrosion in 3 wt% NaCl medium Colloids and Surfaces A: Physicochemical and Engineering Aspect 627 127–23
[11] Afreaee S H, Kyong Y R, Chandrabhan V, Quraishi M A and Ebenso E E 2021 Challenges and advantages of using plant extract as inhibitors in modern corrosion inhibition systems: recent advancements J. Mol. Liq. 321 411666
[12] Ogunsipe A O, Ogoko E C and Abiola O K 2020 Corrosion Inhibition of aluminium in 1.0 M HCl by Zinc phthalocyanine sulfonate Journal of Chemical Society of Nigeria 45 533–9 (https://journals.chemsociety.org.ng/index.php/jcsn/article/view/468)
[13] Kozhukharov S and Girginov C 2020 Recent trends of the use of rare earth elements for efficient environmentally compliant corrosion protection of aluminium and its alloys ed P Petkov et al Nanoscience and Nanotechnology in Security and Protection against CBRN Threats. NATO Science for Peace and Security Series B: Physics and Biophysics. (Dordrecht: Springer)
[14] Gobara M, Baraka A, Akid R and Zorainy M 2020 Corrosion protection mechanism of Ce4+/organic inhibitor for AA2024 in 3.5% NaCl RSC Adv. 10 2227–40
[15] Popoola I T 2019 Organic green corrosion inhibitors (OGCs): a critical review Corros. Rev. 37 71–102
[16] Albuquerque J G de, Aquino J D S, Albuquerque J G D, Farias T G S D, Escalona-Buendia H B, Bouquez-Molina E and Arzoubel P M 2019 Consumer perception and use of nopal (Opuntia ficus-indica): a cross-cultural study between Mexico and Brazil Food Res. Int. 124 101–8
[17] Scognamiglio F, Mirabile Gattia D, Roselli G, Persia F, De Angelis U and Santulli C 2019 Thermoplastic starch films added with dry nopal (opuntia Ficus Indica) fibers Fibers 7 99
[18] Eun Hye H, Mi K L, Soyeon L, Sang Ho L, Su Min Y, Heui-Jong Y, Seung-Ho R and Lim Y-H 2020 J. Med. Food 1146–54
[19] Camarena-Rangel N G, Barba De la Rosa A P, Herrera-Corredor J A and Santos-Diaz M D S 2017 Enhanced production of metabolites by elicitation in opuntia ficus-indica, opuntia meyocanthes, and opuntia streptacantha callus Plant cell, tissue, and organ culture 129 289–98
[20] Mazri M A 2018 Cactus Pear (Opuntia spp.) breeding ed J Al-Khayari et al Advances in Plant Breeding Strategies: Fruits. (Cham: Springer)
[21] López-León L D, Juárez-Islas M A, Bassam O, Pérez-Callejas A D and Castañeda-Robles I E 2019 Electrochemical behavior of a cactus mucilage-based corrosion-resistant coating Int. J. Electrochem. Sci. 14 10016–31
[22] Suarez R, Gonzalez-Rodriguez J G, Dominguez-Patino G F and Martinez-Villafana A 2014 Use of Opuntia ficus extract as a corrosion inhibitor for carbon steel in acidic media Anti-Corrosion Methods and Materials. 61 224–31
[23] Torres-Acosta A 2007 Opuntia-Ficus-Indica (Nopal) mucilage as a steel corrosion inhibitor in alkaline media J. Appl. Electrochem. 37 825–41
[24] Ruiz J C and Segura M R 2017 New Polymers for Encapsulation of Nutraceutical Compounds (Hoboken, USA: Wiley)
[25] Hernández E F, Cano-Barrita P F D J, León-Martínez F M and Torres-Acosta, A A 2017 Performance of cactus mucilage and brown seaweed extract as a steel corrosion inhibitor in chloride contaminated alkaline media Anti-Corrosion Methods and Materials 64 529–39
[26] Estudio cromosómico en cuatro tipos de cochinilla (Dactylopius spp.) (Homóptera: Dactylopiidae) del nopal (Opuntia spp.) Tesis presentada como requisito parcial para optar el grado de Maestro en Ciencias, especialista en Fruticultura. Colegio de Postgraduados, San Luis Potosí-México. p 106
[27] Budavari 1996 The Merck index: an encyclopedia of chemicals, drugs, and biologicals (11th ed.). Merck Research Laboratories
[28] Food D 2009 In Europe, it is labelled as CI 75470 on cosmetics and E120 on food products and cosmetic labelling: cochineal extract and carmine declaration. The new rule was published in the Federal Register 74 (No. 2 / Monday, January 5, 2009)
[29] Wanotayan T, Boonyongmaneerat Y, Panpranot J, Tada E and Nishikata A 2018 ISIJ Int. 58 1316
[30] Sepúlveda E, Sáenz C, Aliaga E and Aceituno C 2007 Extraction and characterization of mucilage in Opuntia spp. J. Arid. Environ. 68 534–45
[31] ASTM G5 - Standard Reference Test Method for Making Potentiodynamic Anodic Polarization Measurements. Developed by Subcommittee G01.11, book of standards volume 03.02
[32] Lorenz W 1981 Determination of corrosion rates by electrochemical DC and AC methods Corrosion Science 21 647–72
[33] ASTM G 199-09 2009 Standard guide for electro chemical noise measurement
[34] Cottis R A, Targoose S and Mendoza-Flores J 1996 The Effects Of Solution Resistance on electrochemical noise resistance measurements (Filadelphi: ASTM STP 1277) 93–100 ASTM STP 1277
[35] Kelly R G, Scully J R, Shoesmith D and Buchheit R G 2002 Electrochemical techniques in corrosion science and engineering 1st (Boca Raton, FL: Taylor & Francis) 440
[36] Hladik K and Dawson JL 1982 The measurement of corrosion using electrochemical noise Corros. Sci. 22 231–7
[37] Contreras-Padilla M et al 2016 Physicochemical and rheological characterization of Opuntia ficus mucilage at three different maturity stages of cladode European Polymer Journal 78 226–34
[38] Zhang H and Zuo Y 2008 The improvement of corrosion resistance of Ce conversion films on aluminum alloy by phosphatetreatment Appl. Surf. Sci. 254 4930
[39] Dabala M, Ramous E and Magrini M 2004 Corrosion resistance of cerium based chemical conversion coating on AA5083 aluminum alloy Mater. Corros. 55 381
[40] Li Z and Di S 2017 The microstructure and wear resistance of microarc oxidation composite coatings containing nano-hexagonal boron nitride (HBN) Particles J. of Materi Eng and Perform 26 1551–61
[41] D’Avico L, Beltrami R, Pargoletti E and Cappelletti G 2020 Insight into the release agents/PVD coatings interaction for plastic mold technology Coatings 10 281
[42] Srinath M and Prasad M 2020 Wear and corrosion resistance of titanium carbo-nitride coated Al-7075 produced through PVD Bull. Mater. Sci. 43 1–11
[43] Mariel M, Erick G, Katherine R and José Renán G 2017 Extraction and physicochemical characterization of mucilage from opuntia cochenillifera (L) miller Journal of Chemistry 9 4301019
[44] Bouauoine O, Bourven I, Khalil F and Baudu M 2018 Identification of functional groups of Opuntia ficus-indica involved in coagulation process after its active part extraction. Environ. Sci. Pollut. Res. Int. 25 11111–9
[45] Diaz-Flores L L et al 2005 Preparation and optical properties of SiO2 Sol–Gel made glass colored with carminic acid J. Sol-Gel Sci. Technol. 33 261–7
[46] Marcela-Corina R, Ramona-Crina S, Maria M and Ioan B 2013 Physical–chemical characterization of titanium dioxide layers sensitized with the natural dyes carmine and morin Mater. Sci. Semicond. Process. 16 1351–7
[47] Cañamares M V, García-Ramos J V, Domingo C, and Sanchez-Cortes S 2006 Surface–enhanced Raman scattering study of the anthraquinone red pigment carminic acid Vib. Spectrosc. 40 161–7
[48] Martínez J R, Velázquez-Pérez S E, Serrano G G, Espericueta D L, Ortega-Zarzosa G, Herrera-González A M, Barrientos-Hernández F R and Lobo-Guerrero A 2020 Thermostrochemical behavior of red cochineal dye stabilized with sucrose and embedded in a silica xerogel matrix Physica B 598 412438