Orbital
The electronic journal of chemistry

the electronic journal of chemistry

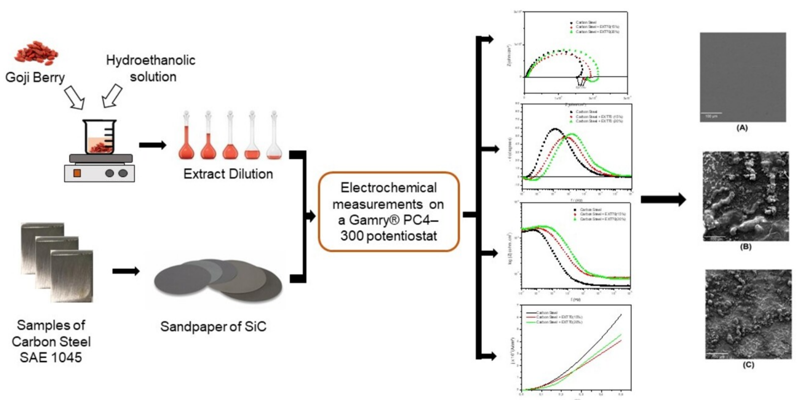
Full Paper | http://dx.doi.org/10.17807/orbital.v13i2.1487

Inhibition Efficiency of Goji Berry Extract Against the Corrosion of Carbon Steel SAE 1045

Danielle Cristina Silva Oliszeski*, Danielle Borges, Guilherme José Turcatel, Carine Vieira, Maico Taras da Cunha, Everson do Prado Banczek, and Paulo Rogério Pinto Rodrigues

Corrosion degrades the surface of metals. Therefore, extracts of natural products are tested as possible corrosion inhibitors, in order to delay or inhibit such processes. These inhibitory substances can act via adsorption, forming a thin protective film that inhibits the anode and/or cathode processes on the surface. This study aimed to test the inhibitory efficiency of goji berry extract (GB) in the corrosion of SAE 1045 carbon steel. The extract was prepared by hydroethanolic extraction and was diluted with 0.5 mol L^{-1} NaCl electrolyte, for electrochemistry tests. The electrochemical impedance spectroscopy and anodic potentiodynamic polarization tests showed that the metal is more resistant to corrosion in the presence of the GB, because higher values of impedance and lower values of current density were obtained in the presence of the GB; the scanning electron microscopy data corroborated the electrochemical test results.

Graphical abstract



Keywords

Anodic polarization
Goji Berry extract
Green inhibitors
Saline solution

Article history

Received 31 March 2020
Accepted 03 May 2021
Available online 28 June 2021

Handling Editor: Sergio R. Lázaro

1. Introduction

Metal pieces are prone to corrosion, which causes financial and environmental damage, e.g., premature wear of parts leading to premature maintenance or even unwanted replacement, causing unplanned shutdown, and consequently, a decrease in profits [1]. The environment is subject to contamination via incorrect disposal of corrosion by-products. There are also costs related to accidents and safety because a part that is damaged loses its efficiency [2-4].

According to ABRACO (Brazilian Corrosion Association), the total annual cost of corrosion (sum of direct and indirect costs) in Brazil is 3% of the GDP (gross domestic product), approximately US $15 billion, and it is estimated that 30% of this value could be saved if the practices that are already known and adequate to control and combat corrosion are adopted [4, 5].

There are several methods that can be employed to prevent the occurrence of corrosive processes, and all are

Departamento de Química – DEQ – Universidade Estadual do Centro-Oeste. Rua Simeão Varela de Sá, 03 – Vila-Carli – Guarapuava – PR – Brazil. *Corresponding author. E-mail: **danielle.dcs@hotmail.com**

based on the treatment of the metal surface. One of the main measures is the application of inhibitors, which are substances added to the corrosive medium to reduce the corrosion rate via the formation of a protective film between the metal and the medium in which it is inserted. Synthetic inhibitors are highly efficient in inhibiting corrosion but are products of the chemical industry and present questionable toxicity to human and environmental life [5, 6].

Due to an increase in ecological awareness, natural products are sought after and can replace traditional ones, reducing the negative impacts of human development and conserving the environment and its resources [7, 8]. In this context, extracts of numerous plant species can be tested as corrosion inhibitors, since the extraction of these compounds is simple and inexpensive. In the literature, there are studies that used extracts of tree bark [4, 7], castor oil [8], cocoa [9], garlic [10], orange leaves [11], rice bran oil [12], and sunflower seed oil among many other fruit extracts, seeds, and plant residues [13-15].

Compositions of plants include carotenoids, tannins, flavonoids, phenolic acids, lignans, stilbenes, and also alkaloids, which are substances reported as corrosion inhibitors in steel, aluminum, zinc, and other metals [6, 16].

The fruit of *Lycium Barbarum* knowen as Goji Berry has antioxidant acitivity attributed to the presente of vitamins C, B1, B2, B6, E, amino acids and carotenoid in this composition, this characteristic makes it a promising candidate to be tested as corrosion inhibitor [17].

The objective of this paper was to evaluate the inhibitory efficiency of Goji Berry extract (GB) in the corrosion of SAE 1045 carbon steel, using electrochemical and morphological analysis techniques.

2. Results and Discussion

The impedance diagrams are shown in Figure 1; only one capacitive arc was observed for all the samples, in the Nyquist diagram in Fig. 1 (A), indicating the occurrence of only one process. Higher impedance values were recorded for the samples in the presence of the inhibitor, showing higher resistance of these samples, which is promoted by the presence of GB organic compounds. Among the concentrations studied, the best response was with a dilution of 20% v/v, due to the higher concentration of organic compounds at this condition.

The presence of an inductive arc for the samples in the presence of the extract is evidenced by the recording of negative imaginary impedance values, and this response may be related to the adsorption behavior of the inhibitors on the metal surface, forming a protective film of corrosion.

The Bode phase angle diagrams in Fig. 1 (B) demonstrate that there is only one time constant, evidencing that only one process is occurring. This constant shifted to higher frequencies in the presence of the inhibitor, showing that the organic compounds in the extract are adsorbed and form a film on the faster responding surface. Higher phase angle values were measured for the 20% inhibitor when compared to the phase angles for the 15% inhibitor, which is in agreement with the higher impedance and resistance to corrosion. The adsorption could be evidenced by the phase angle values less than zero (measured in the Bode diagram) that are associated with the inductive arc, at frequencies in the range between 0.1 and 0.01 Hz.

In Fig. 1 (C), the module diagrams prove the results of the Nyquist and Bode phase angle diagrams, since higher impedance modulus values were determined for carbon steel in the presence of the inhibitor.

The same behavior for EIS tests was observed by Barreto et al. [9], when using cocoa shell extract as an acidic carbon steel inhibitor. They reported that regardless of the presence of the inhibitor, the Nyquist diagram was composed of a single depressed capacitive loop, and that whatever the composition of the solution, the corrosion mechanism remained the same; the maximum phase angle slightly shifted to higher frequencies when the cocoa shell extract was added to the test electrolyte.

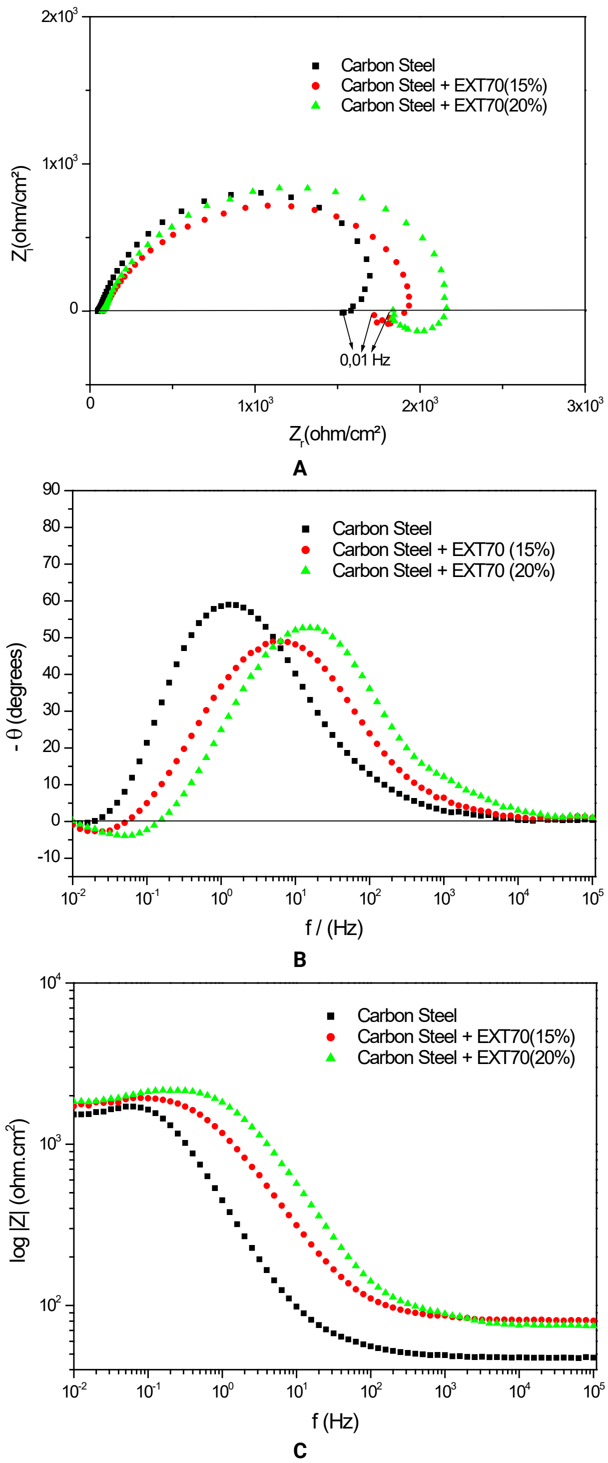


Fig.1. Electrochemical impedance diagrams 1(A) Nyquist, 1(B) Bode phase angle and 1(C) impedance modulus, obtained in NaCl 0.5 molL-1 in the absence and presence of the GB.

The APP curves are shown in Figure 2. The polarization behavior of the samples studied shows that at low overvoltages close to the E_{corr}, the samples containing the GB present low current density values of the order of 10^{-6} A/cm^2, indicating a typically passive behavior; however, this passivity does not persist at higher overvoltages, at which the current density (j) rises abruptly and the system becomes non-passive. However, there is still an inhibitory effect of the GB, indicated by lower current densities than those of the non-GB system, in every anode section studied. For carbon steel in the absence of the GB, the current density increase occurs at an anode surge of 86.9 mV, and for the sample in the presence of 20% GB, this elevation occurs at potentials of 161.9 mV. There is an inflection point in the curve at high elevation, of the order of 250 mV, in relation to 15% and 20% GB, but the j is lower than that of the system without the GB. The EIS measurements were made at the E_{corr}, and the anodic curve behavior regarding the inhibition of the process by the GB is shown in Figure 1 [9,10,16].

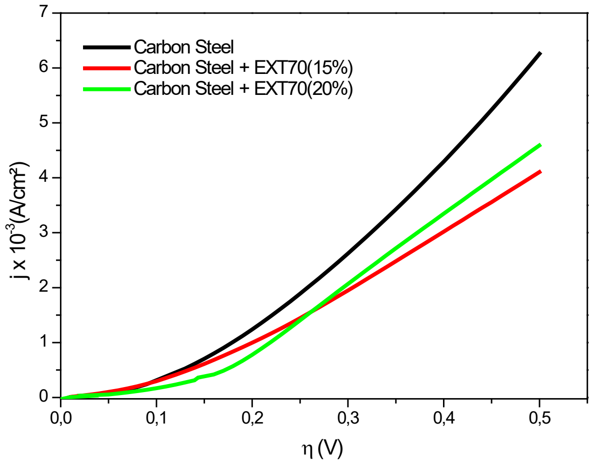


Fig. 2. Anodic potentiodynamic polarization curves in NaCl 0.5 molL^{-1}, in the absence and presence of the GB.

Table 1 presents the values of the j of the anode and the R_{ct} plating curves of the EIS analysis. With these values, using Equations 1 and 2, the IE was calculated and is presented in Figure 3. It was observed that both the efficiencies were potentiated with an increase in the concentration of GB; moreover, the difference in the IE of 15% GB for the polarization measures and EIS analysis was in the order of 4%, and for 20% GB, a 3% difference in the IE was obtained. It should be noted that the behaviors of the IE results for measurements close to the E_{corr} and at an anode overvoltage of 200 mV are equivalent.

Table 1. Current density (j) in η=+200mV and *charge transfer resistance* values (R_{ct}) in E_{corr}.

Sample	j x10^{-3} (A/cm²)	Z_r (ohm/cm²)
Carbon Steel	1,25	1530.45
Carbon Steel + EXT70(15%)	0.988	1911.95
Carbon Steel + EXT70(20%)	0.769	2155.59

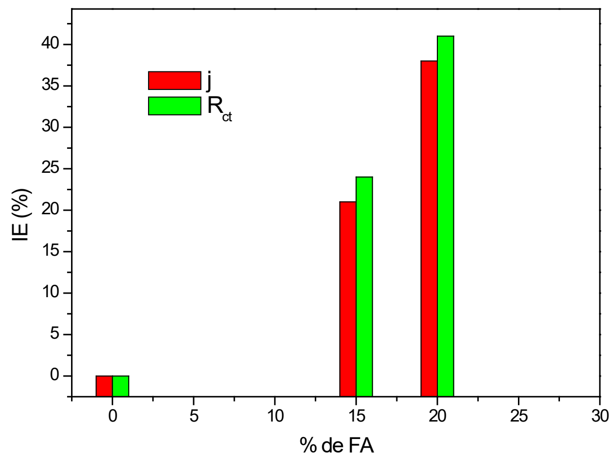


Fig. 3. Percent inhibitory efficiency.

Figure 4 shows the micrographs of the polished substrate, metal polarized in the NaCl medium, and those polarized in the presence of the inhibitor extract at 20% v/v dilution.

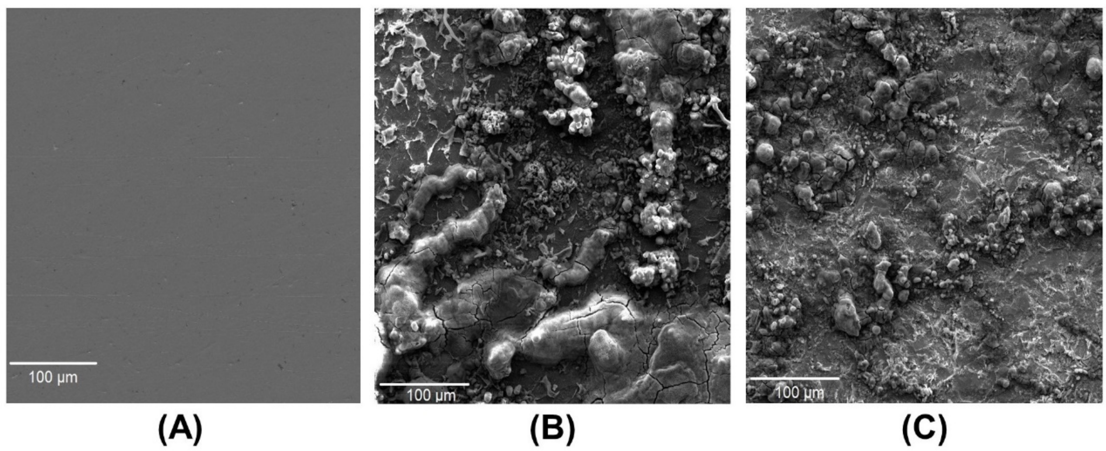


Fig. 4. Scanning electron microscopy of the polished substrate (A), metal polarized in the NaCl medium (B), and sample polarized in the presence of the FA 20% v/v dilution (C).

In Fig. 4 (A), SAE 1045 carbon steel exhibits only one surface treatment, due to which it is uniform and free from any corrosion products. In Fig. 4 (B), there are scales or "islands" (perlíticas/cementitas) that extend throughout the surface of the sample[17]. The same behavior was observed in Fig. 4 (C), but the particle size of the corrosion products is smaller, and the extent is reduced, showing that the corrosive processes are more inhibited in the presence of the 20% v/v extract. SEM data corroborate the assay results shown in Figures 1 and 2 [9, 16, 18].

3. Material and Methods

The Goji Berry extract (GB) was prepared using 5 g of dehydrated fruit (purchased on the local market) and 100 mL of 70:30 hydroethanolic solution. The extraction was carried out at 25 °C under constant stirring for 2 h. Them this GB was diluted to 5, 10, 15, 20 and 25% V/V with distilled water and used to prepare 0.5 mol L^{-1} NaCl solution.

The steel substrate was firstly sanded with SiC #200, #400, #600, and #1200, then, it was washed with a degreaser, dried in hot air and subjected to electrochemical tests.

The electrochemical measurements were performed on a Gamry® PC4–300 potentiostat (three-electrode electrochemical cell using a platinum wire with a large surface area and an Ag/AgCl (saturated) reference electrode as the counter electrode) after 10,000 seconds of stabilization from the open-circuit potential (OCP), known as corrosion potencial (E_{corr}), and electrochemical impedance spectroscopy (EIS) and anodic potentiodynamic polarization (APP). The EIS tests were carried out by potentiometrically applying a disturbance of ± 10 mV in the frequency range of 100 kHz to 10 mHz, with recordings of 10 points per decade. The APP was performed by applying an overvoltage of 1 V in the anode direction of the OCP, with a scanning speed of 0.5 mV s^{-1}. The electrolyte used was a 0.5 mol L^{-1} NaCl solution. The pre-prepared GB extract was used in situ with the NaCl electrolyte at 15 and 20% v/v dilutions.

Inhibition efficiency (IE) was calculated using the anode polarization curves, at 200 mV overvoltage, using Equation 1, where j_a and j_b correspond to the current density values in the absence and presence of the GB, respectively.

$$\text{IE (\%)} = \left(\frac{ja - j\,b}{ja}\right) x100 \qquad (1)$$

The charge transfer resistance values (R_{ct}) at the intercept point of the Z_r axis in the Nyquist diagram were obtained, and the IE was calculated using Equation 2, where $R_{ct}a$ and $R_{ct}b$ are the charge transfer resistance values in the absence and presence of the GB, respectively.

$$\text{IE (\%)} = \left(\frac{Rcta - Rctb}{Rcta}\right) x100 \qquad (2)$$

The surface morphology was analyzed using scanning electron microscopy (SEM) before and after the corrosion tests, with a Tescan® Vega3 equipment having an SE detector and 20 kV tungsten filament, and 10 and 15 mm WD filaments, with a 500-fold increase.

4. Conclusions

The GB under study can be used as a corrosion inhibitor of SAE 1045 carbon steel in 0.5 mol L^{-1} NaCl.

Inhibition of corrosion in the presence of the 20% v/v extract presented higher impedance values and lower current densities, with IE = 38% in the polarization curve and 41% in the Nyquist diagram.

The Nyquist diagram shows an inductive arc in the presence of the inhibitory extract, which is related to the adsorptive process of the organic compounds of GB on the surface of the metal.

The SEM results show that the carbon steel was corroded after its polarization in 0.5 mol L^{-1} NaCl, and that the GB decreases the corrosion, indicating that it can be used as a corrosion inhibitor for this metal in the studied medium.

Acknowledgments

"This study was financed in part by the Coordenação de Aperfeiçoamento de Pessoal de Nível Superior – Brazil (CAPES) – Finance Code 001." The authors are grateful to CNPq (Conselho Nacional de Desenvolvimento Científico e Tecnológico), Fundação Araucária and FINEP (Financiadora de Estudos e Projetos).

Author Contributions

Conceptualization, Danielle Cristina Silva Oliszeski, Guilherme José Turcatel, Everson do Prado Banczek; Methodology, Danielle Cristina Silva Oliszeski, Danielle Borges, Carine Vieira, Paulo Rogério Pinto Rodrigues; Investigation, Danielle Cristina Silva Oliszeski, Everson do Prado Banczek, Resources, Paulo Rogério Pinto Rodrigues; Data Curation, Danielle Cristina Silva Oliszeski, Danielle Borges, Maico Taras da Cunha; Writing – original draft preparation, Danielle Cristina Silva Oliszeski, Writing – review and editing, Danielle Cristina Silva Oliszeski, Danielle Borges, Guilherme José Turcatel, Carine Vieira, Maico Taras da Cunha, Everson do Prado Banczek, Paulo Rogério Pinto Rodrigues; Supervision, Paulo Rogério Pinto Rodrigues; Project administration, Paulo Rogério Pinto Rodrigues. All authors have read and agree to the published version os the manuscript.

References and Notes

[1] Frauches-santos, C. et al. *Rev. Virtual Quim*. **2014**, *6*, 293. **[Crossref]**

[2] Ravichandran, R.; Nanjundan, S.; Rajendran, N. *Appl. Surf. Sci.* **2004**, *236*, 241.**[Crossref]**

[3] de Barros, I. B.; Moscoso, H. Z. L.; Custodio, D. L.; Veiga Junior, V. F.; Bastos, I. N. *Rev. Virtual Quim*. **2015**, *7*, 1743. **[Crossref]**

[4] Meza-Castellar, Pedro et al. *Rev. Ing. Univ. Medellín* 2017, *16*, 15. **[Crossref]**

[5] Available from: **http://www.abraco.org.br/**. Access February 2020.

[6] Raja, P.B.; Sethuraman, M. G. *Mat. Lett*. **2008**, *62*, 113. **[Crossref]**

[7] Elkhotfi, I.; Forsala, Y.; Rakiba, E. M.; Mernari, B. *Port. Electrochim. Acta* **2018**, *36*, 77. **[Crossref]**

[8] Santos, A. M.; de Almeida, T. F.; Cotting, F.; Aoki, I. V.; de Melo, H. G.; Capelossi, V. R. *Mat. Res.* **2017**, *20*, 492. **[Crossref]**

[9] Barreto, L. S.; Tokumoto, M. S.; Guedes, I. C.; de Melo, H. G.; Amado, F.; Capelossi, V. R. *Mater. Res.* **2018**, *21*, e20160309. **[Crossref]**

[10] Barreto, L. S.; Tokumoto, M. S.; Guedes, I. C.; de Melo, H. G.; Amado, F. D. R.; Capelossi, V. R. *Matéria* **2017**, *22*, e11852. **[Crossref]**

[11] Abdel-Gaber, A. M.; Hijazia, K. M.; Younes, G. O.; Nsouli,

B. *Quim. Nova* **2017**, *40*, 395. [Crossref]

[12] Taoui, H.; Bentrah, H.; Chala, A.; Djellab, M. *Mater. Corros.* **2019**, *70*, 511. [Crossref]

[13] Ji, G.; Anjum, S.; Sundaram, S.; Prakash, R. *Corros. Sci.* **2015**, *90*, 107. [Crossref]

[14] Rocha, J. C.; Gomes, J. A. C.P.; D'elia, E. *Corros. Sci.* **2010**, *52*, 2341. [Crossref]

[15] Singh, A.; Lin, Y.; Ebenso, E. E.; Liu, W.; Pan, J.; Huang, B. *J. Ind. Eng. Chem*. **2015**, *24*, 219. [Crossref]

[16] Dahdele, J.; Danaee, I.; Rashed, G. R. *J. Chil. Chem. Soc.* **2016**, *61*, 3025. [Crossref]

[17] Pedro, A. C.; Maurer, J. B. B.; Zawadzki-Baggio, S. F.; Ávila, S.; Maciel, G. M.; Haminiuk, C. W. I. *Ind. Crops Prod.* **2018**, *112*, 90. [Crossref]

[18] Rodrigues, P. R. P. O benzotriazol como inibidor de corrosão para ferros e ligas ferrosas em meios de ácido sulfúrico. [Master's Thesis]. São Paulo: Instituto de Química da Universidade de São Paulo; 1997.

How to cite this article

Oliszeski, D. C. S.; Borges, D.; Turcatel, G. J.; Vieira, C.; da Cunha, M. T.; Banczek, E. P.; Rodrigues, P. R. P. *Orbital: Electron. J. Chem.* **2021**, *13*, 177. http://dx.doi.org/10.17807/orbital.v13i2.1487