Electrochemical Evaluation of Chrysin Flavonoid as Corrosion Inhibitor for Mild Steel in Sulphuric Acid Solution

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Abstract — Recently research is focused on natural organic compounds as metallic corrosion inhibitors demonstrating good corrosion protection and efficiencies. Steel corrosion behavior in acid media was evaluated in the presence of a pure natural flavonoid metabolite named Chrysin present in different plants. The evaluation of corrosion protection was studied using polarization curves, electrochemical impedance spectroscopy (EIS) and electrochemical current density under potentiostatic conditions. Polarization curves present active dissolution and at high overpotentials two passivation regions were found. Slight corrosion protection was obtained from EIS measurements and potentiostatic curves at three different anodic potentials: -370, +216 and +600 mV, revealed a more stable passive film in the presence of Chrysin at both passive regions. High corrosion protection was obtained on the film formed at +600 mV during the first 4 hours of immersion.

Index Terms — Evaluation, Electrochemical, Chrysin, Steel, Acid.

I. INTRODUCTION

Mild steel is the most common metal used by the oil, petrochemical and construction industries, due to its physical and mechanical properties such as malleability, ductility, hardness, and its low cost [1]. However, corrosion is an electrochemical process that affects metallic materials, degrading its properties [2]. This deterioration mechanism can be controlled by some corrosion prevention measures like synthesized inhibitors [3]-[5].

Several researchers have determined that organic compounds with heteroatoms like nitrogen, oxygen, phosphorous, sulfur, or aromatic rings as functional group in their structure, are capable to reduce the corrosion rate [6-13]. However, several compounds have shown difficulties to be degraded in the environment. Hence, in the development of novel corrosion inhibitors, it has been considered to design non-toxic compounds, some of them have been obtained from natural sources which have been a good alternative [4], [14]-[18].

On the other hand, there are some particular compounds named flavonoids, with several chemical and biological characteristics. These metabolites are synthesized from some plants [19]. Among the most important properties reported for flavonoids are: antitumoral, anticancer and antioxidant, due to the presence of aromatic rings and oxygen in their structure as carbonyl and hydroxyl groups. In fact, these organic compounds have demonstrated the formation of metal complexes [20]-[22], antioxidant properties [23], [24], and some other important properties [25]. This family of molecules has been widely investigated and more than 4000 different flavonoids have been isolated from plants [26], but few flavonoids have been investigated as corrosion inhibitors [27]-[29].

The aim of this work is to study and evaluate the corrosion effect in mild steel from the presence of the Chrysin flavonoid (see Fig. 1), in acidic media and the effect in the passive film formed, using electrochemical techniques in particular electrochemical noise under potentiostatic regime.

II. EXPERIMENTAL PROCEDURE

A. Testing Material

Cylindrical probes of 1018 mild steel 0.6 mm of diameter (0.14% C, 0.90% Mn, 0.30% S, 0.03% P and Fe as balance) with a copper wire spot welded at the top, were encapsulated in a commercial epoxydic resin. The exposed area was 0.28 cm², which was abraded with 600 up to 1200 SiC emery paper to reach a mirror like surface appearance. The testing corrosive solution was made diluting sulphuric acid in distilled water obtaining a concentration of 0.5M H₂SO₄. Chrysin was purchased from Aldrich diluted in distilled water and used without further purification to be added in the corrosive media, to obtain different low, medium and high concentrations (50, 300, 500 ppm). All solutions were prepared under stirring conditions (100 rpm) at room temperature.

B. Electrochemical Techniques

Potentiodynamic Polarization curves (PC), electrochemical noise (EN) and Electrochemical Impedance Spectroscopy (EIS) measurements were performed to evaluate the electrochemical performance of the system. A saturated Ag/AgCl electrode was used as reference and a
graphite rod were used as auxiliary electrode. A fully automated potentiostat/galvanostat from ACM Instruments was used in this study. Each specimen was immersed into the solution for thirty minutes to stabilize the free corrosion potential $E_{corr}$ and PC were polarized and swept from -1000 mV up to +1000 mV, with a scan rate of 1 mV/s.

Electrochemical Impedance Spectroscopy (EIS) measurements were used. For EIS tests, the amplitude applied for the signal was 20 mV. Also, the frequency interval was of 10 KHz to 0.01 Hz. For the EIS measurements, a signal with an amplitude of 20 mV was applied to the electrode and a frequency interval of 10 KHz-0.01 Hz.

The current density/time measurements (CDM) under polarizing conditions, were made gathering the current oscillations using a working electrode, a platinum auxiliary and the reference electrodes, at a sample rate of one second per sample during periods of 1024 seconds, averaging and obtaining one sample current measurement for every minute. A computer controlled coupled to ACM zero-resistance ammeter (ZRA) was used.

Micrographs were obtained from the scanner electron microscope (SEM) Jeol JSM-7600 model, to observe the corrosion attack over the metal surface and the effect of the Chrysin concentration.

III. RESULTS

A. Polarization Curves

The characterization of mild steel in the sulphuric acid solution without and in the presence of Chrysin, was obtained from polarization curves and is presented in Figure 1. In the absence of Chrysin mild steel showed a free corrosion potential around -380 mV and two passivation regions with passivation potentials at +350 mV and +530 mV. Moreover, mild steel in $H_{2}SO_{4}$ system presents few oscillations, around +510 mV, due to instability caused from the breakdown of the first passive film and formation of the second passive film [28]. The uniform corrosion of mild steel in acidic media proceeds when mild steel reacted with hydrogen ions, and oxide films are formed at more positive anodic over-potentials. The current density at the active Tafel region is about 10 mA/cm$^{2}$ with the first passive current density of 300 mA/cm$^{2}$ and, the second more protective passive current density of 0.4 mA/cm$^{2}$ [28], [29].

The shape of polarization curves in the presence of Chrysin at different concentrations present similar shapes in the active Tafel region. The cathodic branch obtained in the active Tafel is represented in Fig. 2. Effect of Chrysin at different concentration in the polarization curves for mild steel in 0.5 M $H_{2}SO_{4}$.

At higher anodic overpotentials the effects are similar but with a passive current density diminishing from 0.7 mA/cm$^{2}$ for the blank sample down to 0.10 mA/cm$^{2}$ for the highest Chrysin concentration and two orders of magnitude lower than the current density registered for steel in the blank solution, and a reduction in metal dissolution (corrosion rate).

B. Electrochemical Impedance

The overall impedance for carbon steel is represented in Nyquist and Bode plots in the presence of different concentrations of Chrysin and presented in Fig. 3. It is possible to observe a depressed capacitive semicircle at higher and mid frequencies associated to active dissolution followed by an inductive loop at low frequencies due to mass transport phenomenon [30]-[34]. The depression in the capacitive semicircle in the higher frequency range can be due to the heterogeneity of the metal surface. Also, the change in the diameter semicircle and the value of the impedance modulus reflects the effect of the inhibitor. The phase angle presents two peaks associated to at least two time constants A left displacement in the phase angle in the frequency range, confirmed the Chrysin inhibitor action and more than one process occurring over the metal surface.

The inductive loop can be attributed to an adsorption-desorption of inhibitor molecules and/or relaxation of $H^+$ adsorbed species, observed for iron in acidic media [35], [36]. This depends on the nature of the acid, the additive, time and potential and the inductive loop disappears after extended immersion periods. To obtain the EIS parameters, experimental data were analyzed and obtained using electrical equivalent circuits and Zview software and the best fitting was obtained through a RCL (see Fig. 4) and results are presented in Table 1.

| TABLE 1: CHANGES IN THE IMPEDANCE PARAMETERS AT OCP OF CARBON STEEL IN $H_{2}SO_{4}$ 0.5 M IN ABSENCE AND IN THE PRESENCE OF DIFFERENT CHRY SIN CONCENTRATIONS. |
|---|---|---|---|---|---|---|
| Conc. (ppm/M) | $R_{e}$ ($\Omega/cm^{2}$) | CPE ($\mu Fcm^{2}$) | $n$ | $R_{ct}$ ($\Omega/cm^{2}$) | L (Henry/cm$^{2}$) | Et (%) |
| 0 | 1.01 | 263 | 0.89 | 8.10 | 6.58 | - |
| 50(2 x 10$^{-5}$) | 1.52 | 230 | 0.85 | 13.85 | 4.85 | 42 |
| 300(1 x 10$^{-5}$) | 1.76 | 153 | 0.91 | 18.24 | 15.31 | 56 |
| 500(2 x 10$^{-5}$) | 1.97 | 184 | 0.90 | 11.16 | 10.94 | 27 |
The inhibitor efficiency (E\textsubscript{i}) % value was calculated from impedance charge transfer resistance data as in the following equation:

\[
CIE \% = (1 - R_{ct} / R_{inh}) \times 100
\]

where \(R_{ct}\) and \(R_{inh}\) are the charge transfer resistance in the absence and in the presence of Chrysin respectively. Also, according to the EIS values at open circuit corrosion potential, poor inhibition was obtained from Chrysin.

C. Potentiostatic Curves

The best inhibitor performance was observed, according to the polarization curves therefore was decided to study the inhibition effect using potentiostatic current density as a function of time. In the passive regions’ films were obtained under polarizing conditions, without and in the presence of Chrysin in solution. A working iron electrode was immersed into the working solutions and polarized to the desired potential (-360 mV active, +216 mV first passive region and +600 mV second passive region) [31], [32].

Fig. 5 presents the current density as a function of time for steel without and with 300 ppm of Chrysin, polarized 20 mV above the corrosion potential (-360mV). The current density oscillations were measured every second and a one minute average minute obtained, was plotted during 24 hour period. The current density in the absence of Chrysin presents and average value around 1 mA/cm\(^2\), with small oscillations around this value all along. In the presence of the mid concentration (300 ppm), current density average values are lower (0.5 mA/cm\(^2\)) with a few very high amplitude oscillations at one, nine and twenty hours of immersion were observed. These transients show decreasing current density values and returning back to the average current density, associated to localized events [33], [34].

In a similar way steel samples were immersed in the acid solution without and with extreme Chrysin concentrations (50 and 500 ppm) in the first passive region (+216 mV) and presented in Fig 6. The steel sample in acid solution without Chrysin presents low amplitude current density oscillations related to film breakdown-repassivations events. At the lower concentration after 6 hours of immersion the current density observed started to oscillate with increasing amplitudes till the end of the experiment, after 20 hours of immersion. This behaviour could be associated to incomplete passive film formation-rupture or inhibitor adsorption-desorption events associated to instabilities in the passive film at this overpotential and metastable transient pitting attack [35]. At the highest Chrysin inhibitor concentration considered (500 ppm), the transients disappeared therefore a more stable oxide film was formed, and an overall current density slightly diminish when compared to steel without inhibitor. The results suggest a small beneficial effect of Chrysin in the stability of the film present over the metal surface [32]-[35].

In a similar way, current density measurements under potentiostatic regime of mild steel in H\textsubscript{2}SO\textsubscript{4} were obtained applying the second passive potential (+600 mV) during 20 hours of immersion presented in Fig. 7. For the steel sample in acid solution in the absence of Chrysin a value around 1 mA/cm\(^2\) is obtained, presenting small amplitude oscillations all along the time of immersion. This behavior is usually observed for uniform corrosion and passive state process [37]. However, the system containing 300 ppm of Chrysin, presents a decrease in the current density average value to...
0.03 mA/cm$^2$ and oscillations were almost non-existent due to the formation of a more stable and protective passive oxide.

[Diagram of current density vs. time for different Chrysin concentrations]

Fig. 6. Current density under potentiostatic regime in the first passive state (+216 mV) for mild steel immersed in 0.5 M H$_2$SO$_4$ containing the extreme concentrations of Chrysin (50, and 500 ppm), during 20 hours at room temperature.

The current density observed for the steel sample in acid media in the presence of 500 ppm Chrysin concentration, showed a decrease of seven to nine orders of magnitude in its current density with some oscillations present, due probably to film breakdown repassivation events during the first four hours. It is also possible that at this high overpotentials Chrysin molecules react forming protective complexants with the Fe$^{2+}$ ions, later on breaking down. After this time the passive current density film suddenly increased to the passive current density from the sample in the absence of the inhibitor [38, 39].

[Diagram of current density vs. time for different Chrysin concentrations]

Fig. 7. Current density under potentiostatic regime at +600 mV for steel immersed in H$_2$SO$_4$ 0.5 M without and with two Chrysin concentrations (300 and 500 ppm) for 24 hours of immersion.

D. Scanner Electron Microscopy

As an example, Fig. 8 shows the SEM micrographs from the surface after the potentiostatic measurements for steel polarised at +216 mV in the presence of 50 ppm of Chrysin. Fig. 8a presents a general view of the passive pitted surface of steel and in figure 8b a detailed magnification showing the porosity of the passive film layer formed in the presence of 50 ppm Chrysin.

[SEM micrographs for mild steel polarised at +216 in the presence of 50 ppm of Chrysin. a) general view of the passive pitted surface of steel; b) higher magnification showing the passive film.

The positive potential applied allowed the homogeneity in the passive film over the mild steel surface in presence of the inhibitor (Fig. 9 a). The compact passive film decreased the localized attach. The stability of this system was observed in potentiostatic plots as smoother shape (see Fig. 5). In Fig. 9 a, is seen two important zones: 1) the passive film and 2) the integrity of mild steel under the passive film.

[SEM micrograph showing a) general view of steel passive film and b) higher magnification of the steel passive film appearance in the presence of 500 ppm Chrysin at +600 mV in acid media.]

Fig. 9. SEM micrograph showing a) general view of steel passive film and 2) higher magnification of the steel passive film appearance in the presence of 500 ppm Chrysin at +600 mV in acid media.
IV. CONCLUSIONS

Steel in acid solution presents active general dissolution and two passive regions at high overpotentials. At free corrosion potential, the presence of Chrysins flavonoid as inhibitor affects the corrosion behavior with a slight reduction in the corrosion rate with a 56% efficiency and mass transport control. In both passive regions its presence affects the passive oxide formed improving the stability according to the potentiostatic curves, diminishing the current density at medium and high concentrations. At the second passive region the passive current density diminishes more than seven orders of magnitude in the first four hours of immersion at 500 ppm Chrysins flavonoid concentration.

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REFERENCES

[1] M. Finigar and J. Jackson, “Application of corrosion inhibitors for steels in acidic media for the oil and gas industry: a review”. Corrosion Science, Vol. 86, 9, pp.17-41, 2014.

[2] W. D. Callister and D. G. Rethwisch. Materials science and engineering Vol. 5. New York, John Wiley & Sons. 2011.

[3] R. J. Fried, “Corrosion inhibitors”. Applied Science Publishers Ltd. 1978.

[4] M. F. L. Bentiss, M Lebrini, M Lagrenée, M Traisne, A. Elfarouk, and H. B. P. Markhali., R. Naderi, M. Mahdavian, M. Sayebani, M. A. Velázquez-González, J. G. Gonzalez-Rodríguez, M. G. Valldareás-Cisneros, J. A. Hernando-Díez. “Use of Rosmarinus officinalis as green corrosion inhibitor for carbon steel in acid medium”. American Journal of Analytical Chemistry, Vol. 5, 2, ID 42143. 2014.

[5] P. M. Dewick, Medicinal natural products: a biosynthetic approach. New York. John Wiley & Sons. 2002.

[6] M. M. Kaspzik, A. Erleiven, and J. Ochocki, “Properties and applications of flavonoid metal complexes.” RSC Advances, Vol. 5, 57, pp. 45853-45877. 2015.

[7] S. A. Van Acker, J. G. Van Balen, D. J. Van den Berg, A. Bast, and W. J. F. Van der Vigth, “Influence of iron chelation on the antioxidant activity of flavonoids”. Biochemical pharmacology. Vol. 56, 8, pp. 935-943.1998.

[8] S. A. Van Acker, W. J. F. Van Der Berg, M. J. L. Tromp, and A. Bast, “Structural aspects of antioxidant activity of flavonoids”. Free Radical Biology and Medicine, Vol. 20, 3, pp. 331-342. 1996.

[9] P. G. Pietta, “Flavonoids as antioxidants”. Journal of natural products, Vol. 63, 7, pp.1035-1042. 2000.

[10] S. D. Banjarnahor and N. Artanti, “Antioxidant properties of flavonoids”. Medical Journal of Indonesia, Vol. 23, 4, pp. 239-44. 2015.

[11] J. K. Prasain, S. H. Carlson, and J. M. Wyss, “Flavonols and age-related disease: risk, benefits and critical windows.” Materia. Vol. 66, 2, 163-171. 2010.

[12] K. V. Sahidhara, M. Kumar, and A. Kumar, “A novel route to synthesis of flavones from salicylaldehyde and acetophenone derivatives”. Tetrahedron Letters. Vol. 53, 18, pp. 2355-2359. 2012.

[13] J. C. Ezhalharis, P Naragaran, J. Christy, and P Prabavathy, “Corrosion Inhibitive and Adsorption Properties of a Flavonoid compound for Mild Steel in Acidic Medium”. Journal of the Korean Chemical Society, Vol. 55, 3, 495-501. 2011.

[14] P. Valavanis, D. Spanoudaki, C. Gikis, and D. Sazou. “Using recurrence plots for the analysis of the nonlinear dynamical response of iron passivation-corrosion processes”. Chaos, Vol. 28, pp.085708. 2018.

[15] M. Y. Díaz-Cardenas, M. G. Valladares-Cisneros, C. Menchaca-Campos, S. Lagunas-Rivera, J. G. Gonzalez-Rodriguez, J. Uruchurtu-Chavarín, “Electrochemical and chemical quantum studies of a natural alkaloid compound: Boldine, as green corrosion behaviour on carbon steel and Copper in sulfuric acid” J. Mater. Environ. Sci., Vol.10, 10, pp.1011-1024. 2019.

[16] A. A. Aksüt, W. J. Lorenz, and F. Mansfeld, “The determination of corrosion rates by electrochemical dc and ac methods—II Systems with discontinuous steady state polarization behavior”. Corrosion Science, Vol. 22, 7, pp. 611-619. 1982.

[17] H. Gabrielli. “Investigation of electrochemical processes by an electrochemical noise analysis. Theoretical and experimental aspects in potentiostatic regime.” Electrochimica Acta, Vol. 31, 8, pp. 1025-1039. 1986.

[18] E. Garcia, J. Uruchurtu, and J. Genesca, “Chaotic analysis of electrochemical noise response of copper,” Anales de Química, Vol. 94, 4-5, pp. 335–341. 1998.

[19] J. Uruchurtu, “Transient Behavior of Pure Aluminum During Noise Analysis”, NACE Conference in Localized Corrosion NACE-9. 1987.

[20] J. Uruchurtu Chavarín, “Electrochemical Investigations of the Activation Mechanism of Aluminium”. Corrosion, Vol. 47, 8, pp. 472-479. 1991.

[21] G. S. Frankel, and N. Sridhar, “Understanding localized corrosion”. Materials Today, Vol. 11, 10, pp.38-44. 2008.

[22] W. J. Lorenz and F. Mansfeld. “Determination of corrosion rates by electrochemical DC and AC methods”. Corrosion Science, Vol. 50, 10, pp. 3799-3805. 2008.

[23] A. Legat, and E. Govekar. “A comparison of spectral and chaotic analysis of electrochemical noise”. Electrochemical Noise Measurement for Corrosion Applications. ASTM. 1996.

[24] A. M. Homborg, T. Tinga, E. P. M. Van Westing, X. Zhang, G. M. Ferrari, J. H. W. de Witt, and J. M., “A Critical Appraisal of the Interpretation of Electrochemical Noise for Corrosion Studies”. Corrosion, Vol. 70, 10, pp. 971-987. 2014.

[25] B. P. Markham, R. Naderi, M. Mahdavian, M Sayebani, and S. Y. Arban, “Electrochemical impedance spectroscopy and electrochemical noise measurements as tools to evaluate corrosion inhibition of azole compounds on stainless steel in acidic media”. Corrosion Science, Vol. 75, 10, pp. 269-279. 2013.