

Short Communication

Anticorrosive Activity of 2-Hydroxybenzaldehyde-thiosemicarbazone for AISI 1020 Carbon Steel in Acid Medium

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Thiosemicarbazones belong to a widely pharmacologically and technologically used class of compounds. The heteroatoms (N and S) and double bond in their structure enable them to act as inhibitory agents - an alternative to corrosion control. This work synthesised 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6) aiming at its anticorrosive activity against AISI 1020 carbon steel in acid medium; the electrochemical methods Potentiodynamic Polarization and Impedance Electrochemical Spectroscopy were used to investigate it. Results showed great anticorrosive efficiency (94%), even at low concentration ($40 \cdot 10^{-5} \text{ mol L}^{-1}$). This effect was confirmed by the determination of the double-layer capacitance (C_{dl}), which provided information about the protective film formed on the metal surface. The adsorption process obeyed the Langmuir adsorption isotherm and the K_{ads} value from the investigation of THIO-6 adsorption mechanisms on metal surfaces indicated that corrosion inhibition occurred through chemisorption, which identifies it as an effective corrosion inhibitor agent.

Keywords: Carbon steel, Electrochemical impedance spectroscopy, Potentiodynamic polarization, Acid corrosion

1. INTRODUCTION

Corrosion is a spontaneous process that causes great damages mainly in metal surfaces; therefore, industry spends a lot to restrain it. There are several methods to terminate or minimise corrosion; however, organic corrosion inhibitors are being widely researched to substitute the ones that harm health [1].

Several substances may act as corrosion inhibitors, but molecules with heteroatoms, such as nitrogen, oxygen and sulphur, aromatic rings and multiple bonds are more efficient since the non-ligand electrons of heteroatoms, and π electrons of aromatic rings and multiple bonds can interact with

the target surface [2]. This interaction can occur through chemical (chemisorption) or physical adsorption (physisorption), in which inhibitors form a protective film over the metal surface that reduces the corrosion rate [3].

The efficiency of organic inhibitors depends on adsorption rates and coating capacity, in which the adsorption depends on the molecular structure, metal surface load and electrolyte type. Inhibitors must be soluble or dispersible to prevent corrosion underwater. Otherwise, they will not be able to inhibit corrosion; despite having all other conditions to be good inhibitors, they may speed the corrosion process [4].

Thiosemicarbazones belong to an interesting class of compounds, especially when it comes to corrosion inhibition since there are sulphur and nitrogen heteroatoms with non-ligand electrons in their structures. They are simple to synthesise and require mild reaction conditions. Studies have shown their ability to form chelates with metals, which proves their capacity to be corrosion inhibitors. Several reports in literature have indicated that thiosemicarbazones act as corrosion organic inhibitors, and how promising alternative for corrosion control they can be [5-7]. Thus, this work aimed at synthesising 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6), and evaluating the anticorrosive activity using the electrochemical methods Potentiodynamic Polarization (PP) and Impedance Electrochemical Spectroscopy (IES).

2. EXPERIMENTAL

2.1. Synthesis of inhibitor

The preparation of THIO-6 was done from equimolar quantities of 2-hydroxybenzaldehyde and thiosemicarbazide, in ethanol as solvent and catalytic quantities of concentrated sulphuric acid, at room temperature, under 6 h of magnetic agitation. Reaction was monitored by thin-layer chromatography, using ethyl: hexane acetate (7:3) as eluent. The product was recrystallized from ethanol and yielded 84%. *Characterisation*: white solid, melting point: 243-244 °C (literature [8]: 245 °C); NMR ¹H (DMSO-d₆, δ): 11.31 (NH), 9.92 (OH), 8.38 (CH=N), 7.90 (H-6), 7.23 (H-4), 6.91 (H-3), 6.83 (H-5).

2.2. Electrochemical tests

Electrochemical tests were performed in electrochemical cells with three electrodes: the reference electrode from Ag/AgCl, the counter electrode from platinum and the working electrode from AISI 1020 carbon steel with following composition (%): C: 0.17, P: 0.04, S: 0.05, Mn: 0.30, and the remainder Fe, with 0.64 cm² superficial area, 7.86 g/cm³ density and 0.5 g equivalent mass. Measurements were carried out using PGSTAT 302N Autolab potentiostat/galvanostat, and the results were analysed using software NOVA 1.9. Firstly, HCl 1 mol.L⁻¹ solution (blank) was evaluated, and then other THIO-6 solutions were tested at the following concentrations: 10.10⁻⁶ mol L⁻¹, 30.10⁻⁶ mol L⁻¹, 15.10⁻⁵ mol L⁻¹, 30.10⁻⁵ mol L⁻¹ and 40.10⁻⁵ mol L⁻¹. In all experiments, the working electrode was to reach the stable open-circuit potential.

2.2.1. Potentiodynamic Polarization test

Potentiodynamic anodic and cathodic polarization curves were performed using a scan rate equal to 1 mV s^{-1} from -200 mV up to $+200 \text{ mV}$ around the open circuit potential [9]. Data collecting and the test control were done using NOVA 1.9 from Autolab software package.

2.2.2. Impedance Electrochemical Spectroscopy test

In IES test, measurements were done as open circuit potential (E_{ocp}) over frequency range from 10 kHz to 100 MHz , amplitude of 10 mV peak-to-peak, using AC signal. Data collecting and the test control were also done using NOVA 1.9 from Autolab software package.

3. RESULTS AND DISCUSSION

The THIO-6 was prepared through a condensation reaction of 2-hydroxybenzaldehyde and thiosemicarbazone in acid medium, using ethanol as solvent in good yield (84%) (Figure 1).

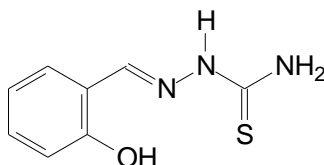


Figure 1. Chemical structure of 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6).

THIO-6 was chosen to be studied due to promising anticorrosive activity results [9] earlier obtained for 4-hydroxybenzaldehyde-thiosemicarbazone: 97% and 90% efficiency at $10 \cdot 10^{-3} \text{ mol L}^{-1}$ concentration against AISI 1020 carbon steel in $\text{HCl } 1 \text{ mol L}^{-1}$ medium, through PP and IES, respectively. Eventually, the hydroxy substituent group at position 2 of the aromatic ring favours the thiosemicarbazone chelate effect against metals that constitute carbon steel. THIO-6 tests were performed at concentration range of $10 \cdot 10^{-6} \text{ mol L}^{-1}$ to $40 \cdot 10^{-5} \text{ mol L}^{-1}$, as Experimental part.

3.1. Electrochemical tests

3.1.1. Potentiodynamic Polarization

PP enabled the evaluation of anticorrosive activity from current densities of each sample. Treating data obtained from those tests allowed the measurement of Tafel curves, $\log i_{\text{curr}}$ x current-potential curve; also, inhibition efficiency values were calculated with equation 1 [3,10].

$$EI(\%) = \frac{i_0 - i_1}{i_0} \times 100 \tag{1}$$

where i_0 and i_1 are current densities of corrosion in the absence and presence of the inhibitor, respectively.

Curves were superimposed to compare tested thiosemicarbazone at various concentrations; they showed a rise in the corrosion inhibition percentage when the inhibitor concentration increased in the electrolytic solution (Figure 2). Analysis of Tafel curves showed that THIO-6 may act as a mixed inhibitor with slightly cathodic tendency at lower concentrations. The decline, mainly observed in the anodic and cathodic side under the rise of the inhibitor concentration, indicates a smaller current in the system in the presence of the inhibitor when compared to its absence (blank). In addition, this compound acted as adsorption inhibitor, this means that more molecules are adsorbed on the metal surface with the concentration increases, promoting better surface coverage [3].

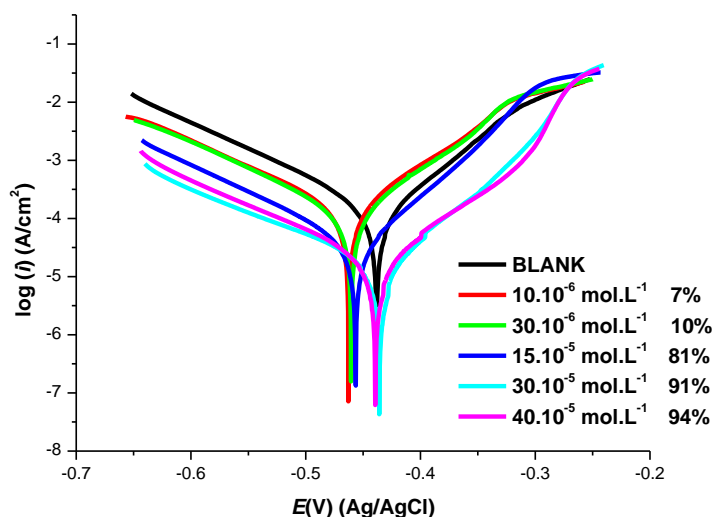


Figure 2. Polarization curves of AISI 1020 carbon steel in 1 mol L⁻¹ HCl in the absence and presence of varying concentrations of 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6).

Table 1. Electrochemical parameters obtained from Potentiodynamic Polarization for AISI 1020 carbon steel in HCl 1 mol L⁻¹ solution in the absence and presence of THIO-6 at various concentrations.

THIO-6 (mol L ⁻¹)	OCP (mV)	-E _{corr} (mV)	i _{corr} 10 ⁻⁴ (A cm ⁻²)	β _a (mV/dec)	-β _c (mV/dec)	η (%)
blank	-456	444	1.91	102.02	96.01	0
10.10 ⁻⁶	-457	463	1.78	134.90	89.29	7
30.10 ⁻⁶	-453	462	1.71	127.74	93.43	10
15.10 ⁻⁵	-443	456	0.35	95.05	66.47	81
30.10 ⁻⁵	-440	436	0.16	115.29	69.96	91
40.10 ⁻⁵	-446	444	0.11	94.62	69.99	94

Inhibition efficiency values for each concentration of THIO-6, obtained from the PP test for AISI 1020 carbon steel in HCl 1 mol L⁻¹ solution, are shown in Table 1, as well as the respective potential corrosion (E_{corr}), the corrosion current density (i_{corr}), and the anodic (β_a) and cathodic (β_c) Tafel constants, obtained by the Tafel plots. Through of the i_{corr} values obtained in presence and absence of THIO-6 was possible calculate the inhibition efficiency, where, the best corrosion inhibition of 94% at 40.10⁻⁵ mol L⁻¹.

3.1.2. Impedance Electrochemical Spectroscopy

Nyquist graph is an alternative representation of frequency response, using the load transfer function, ranging frequency from zero to infinite [12]. Thus, Nyquist graphs of the carbon steel electrode in HCl 1 mol L⁻¹ with and without the addition of THIO-6 at different concentrations are shown in Fig. 3. Nyquist plots show a single capacitive semicircle for the blank and inhibitor agent solutions, and it can be observed that the semicircle increases with the THIO-6 concentration. This indicates that the corrosion of carbon steel in acidic mediums is controlled by a charge-transfer process [12].

Equation 2 was used to calculate inhibition efficiency [1,10]. Table 2 also shows values of electrochemical parameters obtained from IES tests. Inhibition efficiency results confirmed that THIO-6 efficiency rises due to concentration increase, reaching a 94% of corrosion inhibition at 40.10⁻⁵ mol L⁻¹, such as, the PP results.

$$EI_{EIE}(\%) = \frac{R_{ct} - R_{ct}^0}{R_{ct}} \times 100 \tag{2}$$

where R_{ct} and R_{ct}^0 are the charge transfer resistances, in inhibitor presence and absence, respectively.

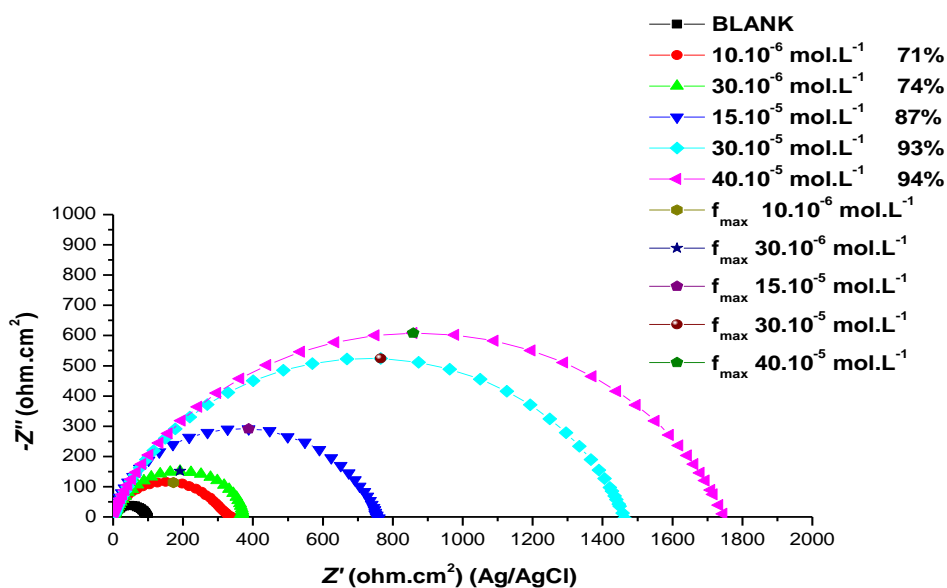


Figure 3. Nyquist graphs of AISI 1020 carbon steel in 1 mol L⁻¹ HCl in the absence and presence of varying concentrations of 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6).

The increase in the charge transfer resistance (R_{ct}), pushed by THIO-6, is probably due to the formation of a barrier on the metal surface. Both charge transfer and frequency decreased because of a smaller current in the system; thereby inhibitors formed a protective film on the metal-solution interface. To obtain information about the protective film, equation 3 was used to calculate the double layer capacitance (C_{dl}) (Table 2) [3,11].

$$C_{dl} = Y_0(\omega_{max})^{n-1} \tag{3}$$

where f_{max} is the maximum frequency and R_{ct} is the charge transfer resistance.

Table 2. Electrochemical parameters obtained from EIS plots for THIO-6 at various concentrations against AISI 1020 carbon steel in HCl 1 mol L⁻¹ solution.

THIO-6 (mol L ⁻¹)	R_s (Ω)	R_p ($\Omega.cm^2$)	f_{max} (Hz)	Y_0 ($\mu F.cm^{-2}$)	N	C_{dl} ($\mu F.cm^{-2}$)	η (%)
Blank	-	96.19	-	-	-	-	-
10.10 ⁻⁶	1.35	336.46	15.85	58.4	0.848	29.0	71
30.10 ⁻⁶	1.15	366.70	15.85	58.2	0.826	26.1	74
15.10 ⁻⁵	1.24	753.92	10.00	30.6	0.896	19.9	87
30.10 ⁻⁵	0.17	1457.28	7.90	28.1	0.793	12.5	93
40.10 ⁻⁵	0.17	1745.20	6.30	28.0	0.808	13.8	94

Fig. 4 illustrates the equivalent circuit used to analyze all the EIS spectra, representing a single charge transfer reaction, corroborating with the experimental results [11,14-16].

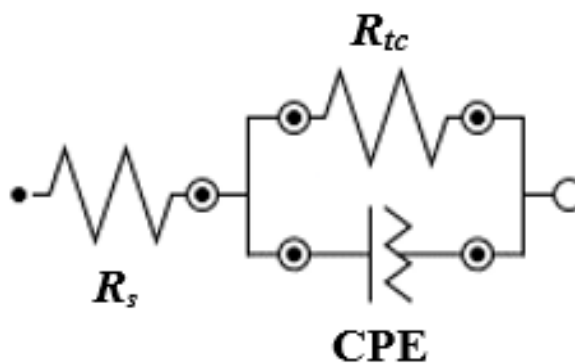


Figure 4. The equivalent circuit model used to fit the EIS experimental data.

Bode plot for carbon steel in acidic media with and without THIO-6 is shown in Fig. 5. At low frequencies, Z_{mod} is a metric that can be used to compare the corrosion resistance of different concentrations of inhibitor. An increase in Z_{mod} leads to better inhibitory performance [16].

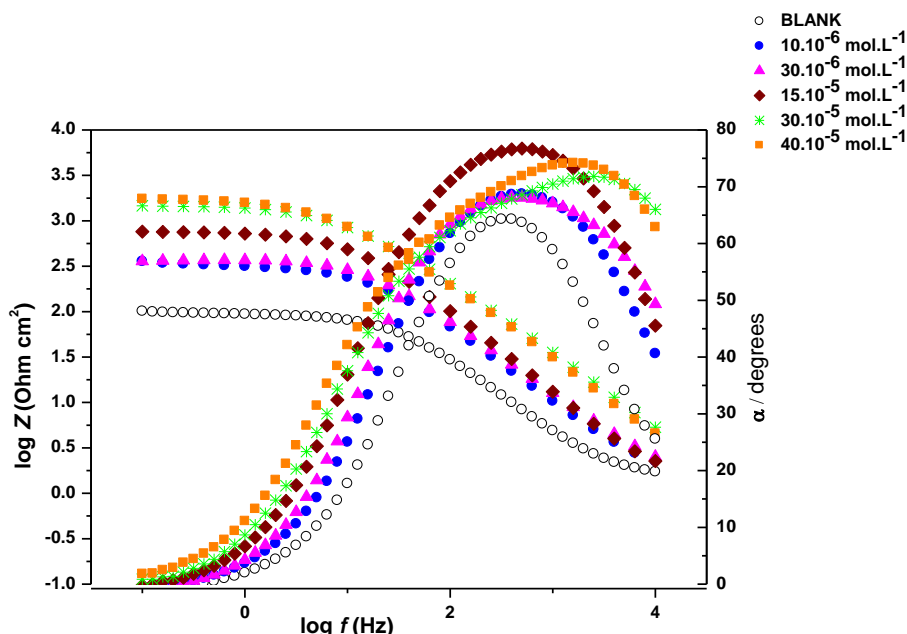


Figure 5. Bode plot of carbon steel obtained in 1.0 mol L⁻¹ HCl in the presence and absence of 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6).

Considering Table 2, there was a decrease in the double layer capacitance (C_{dl}) as THIO-6 increased because inhibitors can work as electrical capacitors, forming a protective film on the metal surface which impede or hinder the charge transfer in the system, thus inhibiting corrosion.

The adsorption mechanism of THIO-6 over a metal surface was investigated through isotherms, among which Langmuir was the most adequate; therefore, the equilibrium constant value (K_{ads}) was calculated using equation 4 [3,10], which represents the Langmuir isotherm.

$$C_{inh}/\theta = 1/K_{ads} + C_{inh} \tag{4}$$

where C_{inh} is the inhibitor concentration (mol L⁻¹) and K_{ads} the adsorption equilibrium constant.

Langmuir isotherm enabled the calculation of Gibbs adsorption free energy (ΔG_{ads}), as follows in equation 5. Electrochemical parameters obtained from this calculation: $A = 1.04$; $B = 8.64 \cdot 10^{-6}$; $K_{ads} = 38.98 \cdot 10^3$; $R^2 = 0.99968 \text{ J k}^{-1} \text{ mol}^{-1}$; $\Delta G_{ads} = -36.00 \text{ kJ mol}^{-1}$. Langmuir isotherm plot for THIO-6 is shown in Fig. 6.

$$\Delta G_{ads} = -RT \ln (55.5 K_{ads}) \tag{5}$$

where R is gas universal constant, T is temperature (K), 55.5 is water molar concentration (mol L⁻¹) in solution, and K_{ads} is the adsorption equilibrium constant.

The calculation of Gibbs adsorption free energy (ΔG_{ads}) enables the determination of whether the anticorrosive activity is happening via bond formation, through donation of electrons from the inhibitor to the metal surface (chemisorption, $\Delta G_{ads} > 20 \text{ kJ mol}^{-1}$), or whether it is an electrostatic interaction between electrons from the inhibitor and the metal surface (physisorption, $\Delta G_{ads} < 20 \text{ kJ mol}^{-1}$). The obtained data indicates that THIO-6 is adsorbed over the metal surface through chemisorption since $\Delta G_{ads} = -36 \text{ kJ mol}^{-1}$; also, this is reinforced by the high K_{ads} value as it indicates a strong interaction between the inhibitor and metal surface when compared to literature, that is $\Delta G_{ads} = -$

$37.15 \text{ kJ mol}^{-1}$ and $K_{\text{ads}} = 5.85 \cdot 10^4$ to 4-hydroxybenzaldehyde thiosemicarbazone [9], and the negative value of ΔG_{ads} means that the adsorption process is spontaneous [17].

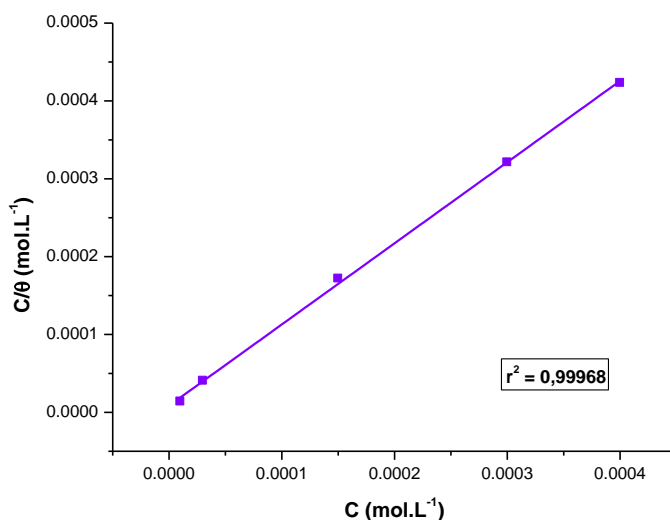


Figure 6. Langmuir isotherm plot for adsorption of the 2-hydroxybenzaldehyde-thiosemicarbazone (THIO-6) on the carbon steel surface in HCl 1.0 mol L^{-1} .

4. CONCLUSIONS

Data taken from PP and IES tests showed that 2-hydroxybenzaldehyde-thiosemicarbazone can act as a mixed corrosion inhibitor at a more efficient than 4-hydroxybenzaldehyde-thiosemicarbazone since it presented 94% inhibition at lower concentration of $40 \cdot 10^{-5} \text{ mol L}^{-1}$, whereas 4-hydroxy-substituted, 90-97% at $10 \cdot 10^{-3} \text{ mol L}^{-1}$. In addition, THIO-6 demonstrated ΔG_{ads} values coherent with spontaneous and strong interaction through chemisorption, which shows a possibly effective corrosion inhibitor agent.

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References

1. L. Li, C. Dong, L. Liu, J. Li, K. Xiao, D. Zhang, and X. Li, *Mater. Lett.*, 116 (2014) 318.
2. K. Shalabil, Y.M. Abdallah, Hala, M. Hassan, and A.S. Fouda, *Int. J. Electrochem. Sci.*, 9 (2014) 1468.
3. S. Safak, B. Duran, A. Yurt, and G. Türkoglu, *Corros. Sci.*, 54 (2012) 251.
4. A. Yildirim, and M. Çetin, *Corros. Sci.*, 50 (2008) 155.
5. C. Jayabalakrishnan, and A. Manimaram, *J. Adv. Res.*, 3 (2012) 233.
6. B. Xu, W. Yang, Y. Liu, X. Yin, W. Gong, and Y. Chen, *Corros. Sci.*, 78 (2014) 260.

7. B. Xu, L. Ying, X. Yin, W. Yang, and Y. Chen, *Corros. Sci.*, 74 (2013) 206.
8. R.M. El-Shazly, G.A.A. Al-Hazmi, S.E. Ghazy, M.S. El-Shahawib, and A.A. Asmy, *Spectrochim. Acta Part A*, 61 (2005) 243.
9. C.M. Goulart, A. Esteves-Souza, C.A. Martinez-Huitle, C.J.F. Rodrigues, M.A.M. Maciel, and A. Echevarria, *Corros. Sci.*, 67 (2013) 281.
10. V.V. Torres, R.S. Amado, C.F. Sa, T.L. Fernandez, C.A.S. Riehl, A.G. Torres, and E. D'Elia, *Corros. Sci.*, 53 (2011) 2385.
11. V.V. Torres, V.A. Rayol, M. Magalhães, G.M. Viana, L.C.S. Aguiar, S.P Machado, H. Orofino and E. D'Elia, *Corros. Sci.*, 79 (2014) 108.
12. K.C. Emregül, E. Duzgun, and O. Atakol, *Corros. Sci.*, 48 (2006) 3243.
13. K.C.R. Ferreira, R.F.B. Cordeiro, J.C. Nunes, H. Orofino, M. Magalhães, A.G. Torres, and E. D'Elia. *Int. J. Electrochem. Sci.*, 11 (2016) 192.
14. K. Tebbji, N. Faska, A. Tounsi, H. Oudda, M. Benkaddour, and B. Hammouti, *Mater. Chem. Phys.*, 106 (2007) 260.
15. M.V. Fiori-Bimbi, P.E. Alvarez, H. Vaca, and C.A. Gervasi, *Corros. Sci.* 92 (2015) 192.
16. H.M. Abd El-Lateef, *Corros. Sci.*, 92 (2015) 104.
17. A. Spinelli, and F.S. Souza, *Corros. Sci.*, 51 (2009) 642.

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