Research Article

Inhibition Effect of Glycerol on the Corrosion of Copper in NaCl Solutions at Different pH Values

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The inhibitory effect of glycerol on copper corrosion in aerated NaCl (0.5 M) solutions at three pH values (4, 7, and 10) was evaluated. Inhibition efficiency was assessed with conventional electrochemical techniques: open circuit potential, potentiodynamic polarization, and electrochemical impedance analysis. Glycerol reduced the corrosion rate of copper in NaCl solutions. The best inhibition effect ($\eta \approx 83\%$) was produced in alkaline (pH 10) chloride media. This effect can be ascribed to increased viscosity and the presence of copper-glycerol complexes.

1. Introduction

As worldwide biodiesel production increases so does production of the byproduct glycerol [1, 2]. For every gallon (3.78 L) of biodiesel produced approximately 0.3 Kg glycerol results. By 2016, the global biodiesel market is expected to be 37 billion gallons [3], consequently resulting in production of 11.1 billion kilograms of glycerol. This looming glycerol glut means that new uses for glycerol need to be found or conversion processes developed to convert it into more valuable chemicals [4]. Finding new uses for glycerol would also help to lower the cost of biodiesel, the main factor behind decreasing production rates. Electrochemical studies have shown glycerol to be useful as an additive in electrochemical baths for coating formation [5–7]. It has also been used in combination with traditional corrosion inhibitors to improve efficiency, but very few studies have focused on glycerol alone as a corrosion inhibitor. Shaker and Abdel-Rahman [8] reported that the corrosion rate of copper decreases at higher glycerol proportions in water-glycerol solutions. The authors

show that the reactions were controlled by diffusion. A key aspect of glycerol is its viscosity and its potential to form a metal-glycerol complex. Viscosity in water-glycerol solutions increases as glycerol concentration increases [9]; therefore, an increase in viscosity can also be expected to decrease mass transfer of ions. A decrease in oxygen concentration can affect the cathodic reaction. In alkaline solutions, glycerol is known to form a Me-glycerol complex (Me = Zn, Fe, and Cu) [10, 11] which may act as a barrier to inhibit corrosion of metals. The present study aim was to evaluate the inhibitory effect of glycerol (Figure 1) alone on corrosion of copper exposed to NaCl solutions at three pH values.

2. Experimental Procedure

Deionized water and reagent grade NaCl, HCl, and NaOH were used to prepare NaCl solutions with three different pH values. Glycerol (99.5%) was purchased from Sigma-Aldrich (CAS 56-81-5). Samples were cut from a pure (99.999%)

FIGURE 1: Chemical structure of glycerol.

copper rod (Goodfellow, 5.0 mm diameter) and embedded in epoxy resin. A bar cross section was exposed to the NaCl solution. Before each exposure, the sample was abraded with a series of different grade emery papers (up to 1200), rinsed with water and ethanol, and dried with hot air.

All electrochemical measurements were done using a standard three-electrode cell configuration. Electrochemical experiments were run in the following order: open corrosion potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic scan. All experiments were carried out using a Gamry PCI4 Potentiostat/Galvanostat/ZRA instrument with CMS 100 and 300 software. OCP was measured for 15 min prior to each impedance experiment, which was done at 10 kHz to 20 mHz with a 10 mV peak-to-peak amplitude using ac signals at OCP. The potentiodynamic scan was begun immediately after EIS by scanning from -0.25 to 0.25 V versus OCP at a 1 mVs^{-1} sweep rate. A standard calomel electrode (SCE) was used as a reference in all electrochemical experiments. Impedance data were examined for causality, stability, and linearity with the Kramer-Kronig relationship using the method described by Boukamp [12] and adapted in the Gamry Echem analyst software.

A scanning electron microscope (SEM, Philips XL30 ESEM) was used to examine any inhibitory effect of glycerol on copper corrosion. Samples examined with SEM were abraded with emery paper (up to 2000), polished with a $0.25 \mu\text{m}$ diamond solution, rinsed with water and acetone, and dried with hot air. Copper samples were immersed for 120 hours in 0.5 M NaCl (pH 7) solution with and without 2 M glycerol.

3. Results and Discussion

The OCP (E_{oc}) recorded as a function of time for copper in NaCl (0.5 M) with and without different glycerol concentrations at three pH values shows that overall the presence of glycerol at pH 4 shifted the OCP towards negative potentials (Figures 2(a)–2(c)). The drop in OCP during the first 200 seconds is frequently ascribed to dissolution of a native oxide

previously formed on the copper surface as a result of contact with the atmosphere. A shift to the negative region is also an indication of an active surface. The general behavior of E_{oc} at pH 7 consisted of a shift to noble potentials and was similar with or without glycerol (Figure 2(b)). At pH 7, increasing glycerol concentration had no effect on OCP. At pH 10, glycerol concentration had a clear effect on E_{oc} , causing it to move gradually toward the positive potential region and indicating formation of corrosion products or adsorption of species onto the copper surface.

The polarization curves for copper in NaCl (0.5 M) solutions with and without glycerol in different concentrations at three pH values showed how the Cu corrosion potential (E_{corr}) changed slightly from negative to positive as a function of pH (Figures 3(a)–3(c)). This trend coincided with the shift observed for OCP at all pH values. The cathodic branch of the polarization curves exhibited behavior typical of a reduction reaction with mass transfer limitations. Reduction of dissolved oxygen with formation of hydroxide [13], or reduction of water molecules, is commonly responsible for the cathodic reaction [14]. Another cathodic reaction in acid is the reduction of oxygen to form water molecules. Reduction of hydrogen is an unlikely cathodic reaction because hydrogen is more active than copper in the electromotive series. In the present results, neither pH nor glycerol concentration affected the shape of the cathodic branch (Figures 3(a)–3(c)), indicating that pH and glycerol did not influence cathodic reaction type. Glycerol concentration did reduce cathodic current very slightly, a reaction more noticeable at pH 10. This reduction may be explained by reduction of mass transfer due to increased viscosity as glycerol concentration increased.

No significant change was observed in the polarization curve anodic current at pH 4, indicating that the anodic reaction was unaffected by addition of glycerol. Glycerol's effect became apparent at pH 7 and even more obvious at pH 10. In all cases, a linear portion of the polarization curve was not easily determined. Extrapolation of both sides of the polarization curves to calculate corrosion parameters is preferable, although occasionally just one side is used, mainly when a Tafel linear region is too small or is difficult to observe

FIGURE 2: Open circuit potential (OCP) for Cu in NaCl (0.5 M) solutions with and without glycerol at three pH values: (a) pH 4, (b) pH 7, and (c) pH 10.

[15]. Therefore, in the present study the cathodic branch was chosen to calculate corrosion parameters using the Tafel extrapolation method [16, 17]. Of note is that at pH 10 the anodic branch exhibited a major reduction in anodic current as glycerol concentration increased. The corrosion parameters calculated from extrapolation of the cathodic branch showed that, at all pH values, corrosion current decreased as glycerol concentration increased (Table 1). The percentage inhibition efficiency was calculated using corrosion current and the following equation [18, 19]:

$$\eta_T (\%) = \frac{i_{\text{corr}}^0 - i_{\text{corr}}}{i_{\text{corr}}} \times 100, \quad (1)$$

where i_{corr}^0 is the corrosion current measured in a NaCl solution in absence of glycerol and i_{corr} is the corrosion current measured in a NaCl solution containing glycerol as inhibitor.

The best inhibition efficiency was attained at pH 10, possibly due to formation of a layer of copper-glycerol complexes near the copper surface, effectively reducing the reaction area and producing an inhibitory effect [11]. The two main copper-glycerol complexes are $\text{CuGl}(\text{OH})_3^{-2}$ and $\text{CuGl}_2(\text{OH})_2^{-2}$, where Gl^- is a glycerol anion [20].

In the example shown in Figures 4(a)–4(c), the calculated Kramer-Kronig data fit well in both the Bode and Nyquist diagrams. Residual error was within 0.5%, and goodness-of-fit was 24.86×10^{-6} . However, residual error was generally

FIGURE 3: Polarization curves for Cu in NaCl (0.5 M) solutions with and without glycerol at three pH values: (a) pH 4, (b) pH 7, and (c) pH 10.

$<0.5\%$ for both acid and neutral NaCl solutions. Residual error in alkaline (pH 10) solutions (with and without glycerol) was $<1.5\%$. This increase in residual error was probably caused by formation of copper-glycerol complexes on the copper surface. An increase in error reported in the literature was ascribed to passive film formation [21]; in this study, goodness-of-fit in all solutions was on the order of 10^{-6} .

The Nyquist impedance plots for copper in NaCl (0.5 M) solutions with and without glycerol at three pH values show a depressed semicircle the diameter of which can be obtained by extrapolating toward the low frequency value limit ($\omega \rightarrow 0$), which increases with addition of glycerol (Figures 5(a)–5(c)). Semicircle diameter is correlated to the polarization resistance (R_p) value, which is

considered inversely proportional to corrosion rate. Then, independent of the equivalent circuit used to model the EIS data, the glycerol's inhibitory performance can be observed by comparing R_p from the diameter of the impedance spectra. Various equivalent circuits have been reported for modeling impedance data of copper in NaCl solutions [20–22]. The equivalent circuit shown in Figure 6 was used in analysis of the Nyquist plots because it has been used to study coating for corrosion protection, pitting corrosion [22], or copper corrosion in the presence of inhibitors [23–26]. Fitting the equivalent circuit model produced estimated parameters (Table 2). R_s represents the solution resistance, while CPE_1 and CPE_2 are constant phase elements that absorb inhomogeneities of the double layer capacitance and

TABLE 1: Electrochemical parameters determined by Tafel extrapolation of the cathodic branch of the potentiodynamic polarization curves for copper in aerated NaCl (0.5 M) with and without glycerol at three pH values.

pH	Glycerol (M)	E_{corr} mV versus SCE	I_{corr} $\mu\text{A}\cdot\text{cm}^{-2}$	b_c $\text{mV}\cdot\text{d}^{-1}$	b_a $\text{mV}\cdot\text{d}^{-1}$	η_r %
pH 4	0.0	-243	5.27	-335	61.9	Blank
	0.1	-270	2.97	-201	66.7	43.6
	0.5	-275	2.69	-207	65.1	48.9
	1	-277	2.89	-208	65.9	45.1
	2	-281	1.98	-209	62.6	62.4
pH 7	0.0	-212	11.2	-575	64.1	Blank
	0.1	-206	6.57	-442	72.8	41.3
	0.5	-228	5.88	-313	103.0	47.5
	1	-217	5.19	-384	82.7	53.6
	2	-215	3.03	-215	93.2	72.9
pH 10	0.0	-208	9.7	-750	81.3	Blank
	0.1	-186	3.9	-261	161.3	60
	0.5	-203	2.3	-203	206.4	76.2
	1	-185	2.1	-208	205.0	78.1
	2	-213	1.6	-209	200.0	83.2

TABLE 2: Electrochemical impedance parameters obtained by fitting the Nyquist plots for Cu in aerated NaCl (0.5 M) with and without glycerol at three pH values.

0.5 M NaCl (pH)	GC (M)	R_s ($\Omega\text{ cm}^2$)	R_{p1} ($\Omega\text{ cm}^2$)	CPE_1 Y_0 ($\Omega^{-1}\text{ cm}^{-2}\text{ S}^{n_1}$)	n_1	R_{p2} ($\Omega\text{ cm}^2$)	CPE_2 Y_0 ($\Omega^{-1}\text{ cm}^{-2}\text{ S}^{n_2}$)	n_2	W Y_0 ($\Omega^{-1}\text{ cm}^{-2}\text{ S}^{0.5}$)	η_z (%)
4	0	15.0	106	3.9×10^{-5}	0.88	60.6	8.9×10^{-4}	0.45	6.0×10^{-5}	bk
	0.1	17.7	105	6.9×10^{-5}	0.82	81.9	8.4×10^{-4}	0.46	5.3×10^{-5}	10
	0.5	17.4	175	7.1×10^{-5}	0.83	56.1	7.2×10^{-4}	0.46	3.4×10^{-5}	28
	1	23.2	200	2.6×10^{-5}	0.93	15.7	4.6×10^{-4}	0.48	2.8×10^{-4}	28
	2	16.6	247	4.2×10^{-5}	0.88	62.9	5.6×10^{-4}	0.48	1.4×10^{-4}	46
7	0	16.7	5002	6.6×10^{-6}	0.989	3.27×10^{-3}	1.2×10^{-4}	0.49	5.1×10^{-2}	bk
	0.1	15.2	6569	8.2×10^{-6}	0.980	2.0×10^{-3}	7.9×10^{-5}	0.51	3.1×10^{-2}	23
	0.5	16.1	7871	7.4×10^{-6}	0.980	4.9×10^{-3}	3.9×10^{-5}	0.55	5.4×10^{-2}	36
	1	16.0	13590	1.0×10^{-5}	0.934	2.4×10^{-3}	3.3×10^{-5}	0.47	1.1×10^{-1}	63
	2	16.6	14660	6.2×10^{-6}	0.980	3.0×10^{-3}	2.5×10^{-5}	0.20	1.2×10^{-1}	65
10	0	15.8	6190	47.9×10^{-6}	0.60	835.5×10^{-3}	5.9×10^{-6}	0.92	123.9×10^{-3}	bk
	0.1	15.0	13560	37.3×10^{-6}	0.38	292.5×10^{-3}	13.9×10^{-6}	0.82	12.8×10^{-3}	54
	0.5	15.4	22540	35.8×10^{-6}	0.32	15.6×10^{-3}	13.6×10^{-6}	0.91	1.3×10^{-3}	72
	1	19.6	27530	30.6×10^{-6}	0.30	2.65×10^{-3}	12.96×10^{-6}	0.90	0.1×10^{-3}	77
	2	19.7	36750	29.0×10^{-6}	0.32	2.2×10^{-3}	11.6×10^{-6}	0.90	0.2×10^{-3}	83

GC = glycerol concentration.

improve model fit. The characteristic parameters of the constant phase elements are Y and n . Estimated R_p from the semicircle diameter corresponded to the impedance of an anodic reaction occurring in two stages with magnitudes represented as $R_{p1} + R_{p2}$ [27]. Although an exact difference between both resistances has been neither fully understood nor fully described [28], a number of studies use these parameters for modeling corrosion behavior of copper in the presence of an inhibitor. Inhibition efficiency was calculated

using polarization resistance ($R_{p1} + R_{p2}$) and the following equation [19, 29]:

$$\eta_z (\%) = \frac{R_p - R_p^0}{R_p} \times 100, \quad (2)$$

where R_p^0 is the polarization resistance measured in a NaCl solution in the absence of glycerol and R_p is the polarization

FIGURE 4: Typical Kramer-Kronig analysis results for Cu in NaCl (0.5 M, pH 10) solution containing glycerol (2 M). (a) Nyquist diagram, (b) Bode diagram, and (c) residual error ($\Delta Z/Z$) for the real and imaginary components of the impedance data.

resistance measured in a NaCl solution containing glycerol as inhibitor.

The fit was generated using the equivalent circuit in Figure 6. Typical results of fitting analysis are shown in Bode (Figure 7(a)) and Nyquist (Figures 7(b)-7(c)) plots (symbols represent measured data and solid lines represent fitted curves). In general, there was a good fit between the calculated and experimental impedance data.

The most significant parameters are total polarization resistance ($R_p = R_{p1} + R_{p2}$), the constant phase element, which represents the double layer capacitance (CPE_1), and inhibition efficiency. Other parameters also exhibit glycerol's inhibitory effect but are less notable. Polarization resistance increased and $CPE_{1,2}$ values decreased in response to pH

levels and glycerol concentration (Table 2). The R_p and CPE behaviors agree with the potentiodynamic polarization measurement results, and the values of both parameters suggest the presence of a film thickening process that could act as a barrier to corrosion and thus be responsible for the inhibitory effect. Presence of a film was more evident at pH 10; indeed, the best agreement between the inhibition efficiency values determined by the Tafel extrapolation of the cathodic current and the impedance data was observed at pH 10. These findings support the assumption of formation of a copper-glycerol complex on the copper surface.

Comparison of the inhibition efficiency obtained by potentiodynamic polarization and the impedance data shows that both results follow the same trend. The very slight

FIGURE 5: Nyquist plot for Cu in NaCl (0.5 M) at four glycerol concentrations as a function of three pH levels: (a) pH 4, (b) pH 7, and (c) pH 10.

difference in values was probably caused by differences in measurement time [30]. The order of the electrochemical measurements was open circuit potential, impedance, potentiodynamic polarization, meaning the layer of adsorbed molecules during each measurement would be slightly different. However, impedance was most effective at demonstrating glycerol's inhibitory effect on copper corrosion.

Micrographs (SEM) of copper samples exposed to 0.5 M NaCl at pH 7 with and without added glycerol showed no visible indications of ion chloride attack on the copper surface in the presence of glycerol (Figure 8(a)). In contrast, the copper exposed to NaCl in the absence of glycerol exhibited evidence of localized corrosion, such as micro- and macropitting across the entire copper surface (Figure 8(b)).

FIGURE 6: Equivalent circuit model used to fit the impedance data from the copper/NaCl (0.5 M) interface with and without glycerol.

FIGURE 7: Equivalent circuit fit for Cu in 0.5 M NaCl (pH 10) + 0.5 M glycerol; (a) Nyquist, (b) phase, and (c) modulus.

FIGURE 8: SEM micrographs of copper surface after 120 hours of immersion at room temperature (a) in aerated 0.5 M NaCl (pH 10) + 2 M glycerol and (b) in aerated 0.5 M NaCl (pH 10).

These observations agree with the electrochemical results and confirm that glycerol effectively inhibits copper corrosion.

4. Conclusions

Glycerol inhibits corrosion of copper in aerated NaCl (0.5 M) solutions. Inhibition efficiency increases with increasing glycerol concentration and is especially notable at high pH values. Glycerol does not affect the anodic or cathodic reactions, suggesting that increased viscosity reducing mass transport apparently explains the reduction in corrosion rate from acid to neutral solutions. The reduced anodic corrosion rate at pH 10 is probably due to two causes: an increase in solution viscosity and presence of a film on the copper surface, most likely composed of copper-glycerol complexes. SEM images confirm the effectiveness of glycerol as an inhibitor of copper corrosion in NaCl solutions.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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References

- [1] J. C. Thompson and B. B. He, "Characterization of crude glycerol from biodiesel production from multiple feedstocks," *Applied Engineering in Agriculture*, vol. 22, no. 2, pp. 261–265, 2006.
- [2] M.-Y. Seo, J.-W. Seo, S.-Y. Heo et al., "Elimination of by-product formation during production of 1,3-propanediol in *Klebsiella pneumoniae* by inactivation of glycerol oxidative pathway," *Applied Microbiology and Biotechnology*, vol. 84, no. 3, pp. 527–534, 2009.
- [3] X. Fan, R. Burton, and Y. Zhou, "Glycerol (byproduct of biodiesel production) as a source for fuels and chemicals—mini review," *Open Fuels and Energy Science Journal*, vol. 3, pp. 17–22, 2010.
- [4] F. Yang, M. Hanna, and R. Sun, "Value-added uses for crude glycerol—a byproduct of biodiesel production," *Biotechnology for Biofuels*, vol. 5, p. 13, 2012.
- [5] B. Y. Johnson, J. Edington, and M. J. O'Keefe, "Effect of coating parameters on the microstructure of cerium oxide conversion coatings," *Materials Science and Engineering A*, vol. 361, no. 1-2, pp. 225–231, 2003.
- [6] I. A. Carlos, M. A. Malaquias, M. M. Oizumi, and T. T. Matsuo, "Study of the influence of glycerol on the cathodic process of lead electrodeposition and on its morphology," *Journal of Power Sources*, vol. 92, no. 1-2, pp. 56–64, 2001.
- [7] C. Siva Kumar, V. S. Rao, V. S. Raja, A. K. Sharma, and S. M. Mayanna, "Corrosion behaviour of solar reflector coatings on AA 2024T3—an electrochemical impedance spectroscopy study," *Corrosion Science*, vol. 44, no. 3, pp. 387–393, 2002.
- [8] M. A. Shaker and H. H. Abdel-Rahman, "Corrosion of copper metal in presence of binary mixtures," *The American Journal of Applied Sciences*, vol. 4, no. 8, pp. 554–564, 2007.
- [9] J. B. Segur and H. E. Oberstar, "Viscosity of glycerol and its aqueous solutions," *Industrial & Engineering Chemistry*, vol. 43, no. 9, pp. 2117–2120, 1951.
- [10] E. Radoslovich, M. R. Raupach, P. G. Slade, and R. M. Taylor, "Crystalline cobalt, zinc, manganese, and iron alkoxides of glycerol," *Australian Journal of Chemistry*, vol. 23, no. 10, pp. 1963–1971, 1970.
- [11] H. Koyano, M. Kato, and H. Takenouchi, "Electroless copper plating from copper-glycerin complex solution," *Journal of the Electrochemical Society*, vol. 139, no. 11, pp. 3112–3116, 1992.
- [12] B. A. Boukamp, "Linear Kronig-Kramers transform test for immittance data validation," *Journal of the Electrochemical Society*, vol. 142, no. 6, pp. 1885–1894, 1995.
- [13] K. F. Khaled, "Studies of the corrosion inhibition of copper in sodium chloride solutions using chemical and electrochemical measurements," *Materials Chemistry and Physics*, vol. 125, no. 3, pp. 427–433, 2011.
- [14] E.-S. M. Sherif, "Inhibition of copper corrosion reactions in neutral and acidic chloride solutions by 5-ethyl-1,3,4-thiadiazol-2-amine as a corrosion inhibitor," *International Journal of Electrochemical Science*, vol. 7, no. 4, pp. 2832–2845, 2012.

- [15] E. McCafferty, "Validation of corrosion rates measured by the Tafel extrapolation method," *Corrosion Science*, vol. 47, no. 12, pp. 3202–3215, 2005.
- [16] M. A. Amin and M. M. Ibrahim, "Corrosion and corrosion control of mild steel in concentrated H_2SO_4 solutions by a newly synthesized glycine derivative," *Corrosion Science*, vol. 53, no. 3, pp. 873–885, 2011.
- [17] F. Zucchi and I. H. Omar, "Plant extracts as corrosion inhibitors of mild steel in HCl solutions," *Surface Technology*, vol. 24, no. 4, pp. 391–399, 1985.
- [18] H. Amar, A. Tounsi, A. Makayssi, A. Derja, J. Benzakour, and A. Outzourhit, "Corrosion inhibition of Armco iron by 2-mercaptobenzimidazole in sodium chloride 3% media," *Corrosion Science*, vol. 49, no. 7, pp. 2936–2945, 2007.
- [19] S. Hong, W. Chen, H. Q. Luo, and N. B. Li, "Inhibition effect of 4-amino-antipyrine on the corrosion of copper in 3wt.% NaCl solution," *Corrosion Science*, vol. 57, pp. 270–278, 2012.
- [20] E. Norkus, "Diffusion coefficients of Cu(II) complexes with ligands used in alkaline electroless copper plating solutions," *Journal of Applied Electrochemistry*, vol. 30, no. 10, pp. 1163–1168, 2000.
- [21] A. K. Iversen, "Stainless steels in bipolar plates—surface resistive properties of corrosion resistant steel grades during current loads," *Corrosion Science*, vol. 48, no. 5, pp. 1036–1058, 2006.
- [22] A. Królikowski and J. Kuziak, "Impedance study on calcium nitrite as a penetrating corrosion inhibitor for steel in concrete," *Electrochimica Acta*, vol. 56, no. 23, pp. 7845–7853, 2011.
- [23] E. M. Sherif and S. Park, "Inhibition of copper corrosion in 3.0% NaCl solution by N-phenyl-1,4-phenylenediamine," *Journal of the Electrochemical Society*, vol. 152, no. 10, pp. B428–B433, 2005.
- [24] E. M. Sherif and S. Park, "2-Amino-5-ethyl-1,3,4-thiadiazole as a corrosion inhibitor for copper in 3.0% NaCl solutions," *Corrosion Science*, vol. 48, no. 12, pp. 4065–4079, 2006.
- [25] E.-S. M. Sherif, "Effects of 2-amino-5-(ethylthio)-1,3,4-thiadiazole on copper corrosion as a corrosion inhibitor in 3% NaCl solutions," *Applied Surface Science*, vol. 252, no. 24, pp. 8615–8623, 2006.
- [26] K. F. Khaled, "Guanidine derivative as a new corrosion inhibitor for copper in 3% NaCl solution," *Materials Chemistry and Physics*, vol. 112, no. 1, pp. 104–111, 2008.
- [27] P. R. Seré, J. D. Culcasi, C. I. Elsner, and A. R. Di Sarli, "Relationship between texture and corrosion resistance in hot-dip galvanized steel sheets," *Surface and Coatings Technology*, vol. 122, no. 2-3, pp. 143–149, 1999.
- [28] E. M. Sherif, R. M. Erasmus, and J. D. Comins, "Inhibition of copper corrosion in acidic chloride pickling solutions by 5-(3-aminophenyl)-tetrazole as a corrosion inhibitor," *Corrosion Science*, vol. 50, no. 12, pp. 3439–3445, 2008.
- [29] V. V. Torres, R. S. Amado, C. F. de Sá et al., "Inhibitory action of aqueous coffee ground extracts on the corrosion of carbon steel in HCl solution," *Corrosion Science*, vol. 53, no. 7, pp. 2385–2392, 2011.
- [30] B. El Mehdi, B. Mernari, M. Traisnel, F. Bentiss, and M. Lagrenée, "Synthesis and comparative study of the inhibitive effect of some new triazole derivatives towards corrosion of mild steel in hydrochloric acid solution," *Materials Chemistry and Physics*, vol. 77, no. 2, pp. 489–496, 2003.