

8-Hydroxyquinoline as an Effective Corrosion Inhibitor for 7075 Aluminium Alloy in 3.5% NaCl Solution

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The inhibition of the corrosion of aluminium alloy in 3.5 wt.% NaCl solution by 8-hydroxyquinoline has been studied using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electrochemical microscopy (SECM) and scanning electron microscopy (SEM). Inhibition efficiency was found to increase up to 96% in presence of 8-Hydroxyquinoline + H₂O at 5.52 mmol/L. Values of inhibition efficiency calculated from potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) are in good agreement. The adsorbed film on aluminium alloy surface containing inhibitor was confirmed by the SECM, SEM results. The results obtained showed that the 8-Hydroxyquinoline could serve as an effective inhibitor of the corrosion of aluminium alloy in 3.5% NaCl solution.

Keywords: 8-hydroxyquinoline, Aluminium alloy; Corrosion inhibitor; EIS; SECM; SEM

1. INTRODUCTION

Metals and alloys used in many oil wells are susceptible to corrosion in aqueous media. Aluminium alloy, the most widely used among them, is also highly susceptible to corrosion, especially in aqueous media [1]. Aluminium alloy is widely used as a construction material for pipe work in the

oil and gas production, such as downhole tubular, flow lines, and transmission pipelines in the petroleum industry. [2].

Therefore, protective measures should be required to prevent the metal loss due to corrosion by using chemical and other means. One of the best known methods for corrosion protection is the use of inhibitors as no special equipments required, low cost, and easy operation. It is highly desired that new inhibitors for Aluminium alloy are non-toxic and environment-friendly. Most of the well-known inhibitors are organic compounds containing nitrogen, oxygen, and/or sulfur atoms; heterocyclic compounds; and delocalized π -electrons. It is generally accepted that organic molecules inhibit corrosion via adsorption at the metal solution interface [3-6], making the adsorption layer to function as a barrier, and isolating the metal from the corrosion [7- 9].

8-Hydroxyquinoline is a monoprotic bidentate chelating agent. It is usually prepared from quinoline-8-sulfonic acid and from a Skraup synthesis from 2-aminophenol. The complexes as well as the heterocycle itself exhibit antiseptic, disinfectant, and pesticide properties, functioning as a transcription inhibitor. Its solution in alcohol is used in liquid bandages. It once was of interest as an anti-cancer drug [10, 12].

The present study investigates the inhibiting effect of 8-Hydroxyquinoline (figure 1). Inhibition effect of 8-Hydroxyquinoline on the corrosion of aluminium alloy in 3.5% NaCl solution was studied by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. Meanwhile, the steel surface was examined by scanning electrochemical microscopy (SECM), and scanning electron microscopy (SEM) techniques.

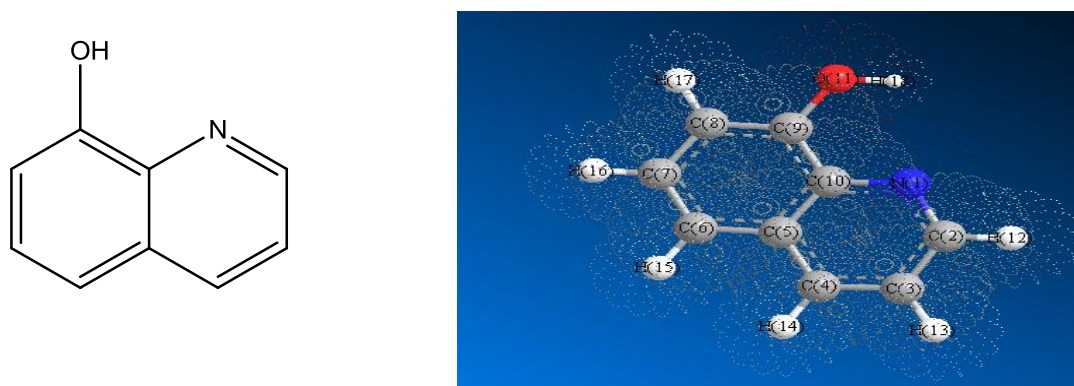


Figure 1. Structures of 8-hydroxyquinoline (IUPAC name: 8-Quinolinol).

2. EXPERIMENTAL

2.1. Preparation of inhibitor

8-hydroxyquinoline was purchased from Kelong Company of analytical grade. It was further mixed with distilled water in 2 mmol/L, 5.52 mmol /L and in distilled water + ethyl alcohol 2 mmol /L, 5.52 mmol/L to prepare 4 different solutions for the study. 8-hydroxyquinoline is an organic compound with the formula C_9H_7NO . It is a derivative of the heterocycle quinoline by placement of an

OH group. This light yellow compound is widely used commercially, although under a variety of names.

2.2. Materials and Solutions

Aluminium alloy having the following chemical composition (wt %): C 0.31; Si 0.19; Mn 0.92; P 0.010; S 0.008; Cr 0.2; Fe balance were used for all studies. Aluminium alloy coupons having dimensions of 10 mm × 10 mm × 3 mm were used for the electrochemical study. The specimens were welded with copper wire and covered with epoxy resin. The specimens were metallographically polished according to ASTM A262, degreased, and dried before experiment. The test solution of 3.5% NaCl was prepared by analytical grade NaCl with double distilled water. All experiments were performed in unstirred solution.

2.3. Electrochemical measurements

The electrochemical experiments were performed by using three electrode cell, connected to Potentiostat/Galvanostat CHI604D. Zview software package was used for data fitting. Aluminium alloy was used as working electrode, platinum electrode as an auxiliary electrode, and saturated calomel electrode (SCE) as reference electrode. Aluminium alloy was used as working electrode, platinum electrode as an auxiliary electrode, and saturated calomel electrode (SCE) as reference electrode. All potentials reported were measured versus SCE. Tafel curves were obtained at a scan rate of 1.0 mVs⁻¹. EIS measurements were performed under potentiostatic conditions in a frequency range from 100 kHz to 0.01 Hz, with amplitude of 10 mV AC signal. The experiments were carried out when the electrochemical system was in steady state in 3.5% NaCl saturated with CO₂ in absence and presence of different concentrations of 8-hydroxyquinoline. Prior to the electrochemical measurement, a stabilization period was allowed to attain a stable value of E_{corr} .

2.4. Scanning Electrochemical Microscopy (SECM)

A model of scanning electrochemical microscopy CHI900C was used. The instrument was operated with a 10 μm platinum tip as the probe, an Ag/AgCl/KCl (saturated) reference electrode, and a platinum counter electrode. The tip and substrate are part of an electrochemical cell that usually also contains other (e.g., auxiliary and reference) electrodes. All potential values are referred to the Ag/AgCl/KCl (saturated) reference electrode. The measurements of line scans were generated with the tip at ~ 10 μm from the specimen surface in all the cases. The scan rate was 80 μm/step.

2.5. Scanning Electron Microscopy (SEM)

The electrodes were immersed in the test solution (3.5% NaCl) in the absence and presence of corrosion inhibitor to observe the effect of corrosion and inhibition. The Aluminium alloy electrodes

were then dried at ambient temperature. Micrographs of abraded and corroded Aluminium alloy surfaces and those after inhibitor addition were taken using a SEM model TESCAN VEGA II XMH instrument.

3. RESULTS AND DISCUSSION

3.1. Electrochemical measurements

3.1.1. Electrochemical Impedance Spectroscopy (EIS)

Impedance spectra for Aluminium alloy in 3.5% NaCl in absence and presence of different concentrations of 8-hydroxyquinoline are shown in the form of Nyquist plots (figure 2a).

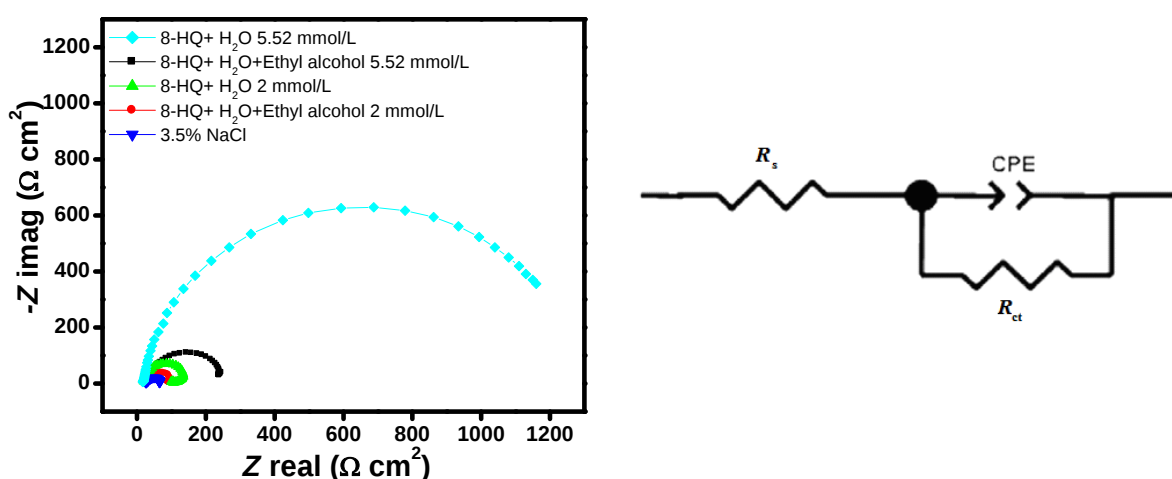


Figure 2. Electrochemical impedance plots for (a) Nyquist (b) equivalent circuit in absence and presence of 8-hydroxyquinoline for Aluminium alloy.

Although the appearance of Nyquist plots remained the same, their diameter increased after the addition of 8-hydroxyquinoline to the corrosive solution. This increase was more and more pronounced with increasing inhibitor concentration indicating the adsorption of inhibitor molecules on the metal surface [13]. However, after the addition of 8-hydroxyquinoline, the impedance modulus of the system gradually increased and was a maximum in the case of 8-hydroxyquinoline + H₂O at 5.52 mmol/L. The impedance diagram (Nyquist) contains depressed curves with the center under the real axis with one capacitive loop in the high frequency (HF) zone. As usually indicated in an EIS study, the HF capacitive loop is related to the charge-transfer resistance process of the metal corrosion and the double-layer behavior, and these loops are not perfect semicircles. The charge transfer resistance increased with increase in concentration of inhibitor [14-18]. The curve in the Nyquist plot is depressed, which we attribute to surface roughness and the resulting distortion of the double layer.

The model used for fitting consists of R_s (the resistance of solution between working electrode and counter electrode), R_{ct} , and the constant phase angle element (CPE) as shown in figure 2b. The

double layer usually behaves as a constant-phase element (CPE) rather than as a pure capacitor. The CPE is substituted for the capacitor to fit the curve more accurately. The capacitance values were calculated using the equation [17, 18]:

$$Z_{\text{CPE}} = Q^{-1} (j\omega)^{-n} \quad (1)$$

where Q is the magnitude of the CPE, j is the imaginary unit, ω is the angular frequency ($\omega = 2\pi f$, the frequency in Hz), and n is the phase shift which can be used as a gauge of the heterogeneity and gives details about the degree of surface inhomogeneity (roughness). Depending on the value of n , CPE can represent resistance ($n = 0$, $Q = R$), capacitance ($n = 1$, $Q = C$), inductance ($n = -1$, $Q = L$) or Warburg impedance ($n = 0.5$, $Q = W$). In fact, when n is close to 1, the CPE resembles a capacitor, but the phase angle is not 90° . It is constant and somewhat less than 90° at all frequencies. The inhibition efficiency is calculated using charge transfer resistance (R_{ct}) as follows,

$$\eta\% = \frac{R_{\text{ct(inh)}} - R_{\text{ct}}}{R_{\text{ct(inh)}}} \times 100 \quad (2)$$

Where $R_{\text{ct(inh)}}$ and R_{ct} are the values of charge transfer resistance in presence and absence of inhibitor in 3.5% NaCl respectively. At different concentrations 8-hydroxyquinoline showed increase in value of R_{ct} with respect to blank 3.5% NaCl solution. The increase in R_{ct} values as shown in table 1 is attributed due to increase in resistance and adsorption of inhibitor molecules on aluminium alloy surface [19-22]. Also any significant change in the values of the phase shift, n , was not observed in the absence and in the presence of 8-hydroxyquinoline. To predict the dissolution mechanism, the value of n can be used as an indicator. The values of n , ranging between 0.74 and 0.86, indicate that the charge transfer process controls the dissolution mechanism of aluminium alloy in CO_2 saturated 3.5% NaCl solution in the absence and in the presence of 8-hydroxyquinoline.

Table 1. Nyquist data for aluminium alloy in 3.5% NaCl at different concentration of 8-hydroxyquinoline.

Inhibitor	Conc. (mmol/L)	R_s ($\Omega \text{ cm}^2$)	R_{ct} ($\Omega \text{ cm}^2$)	n	η %	Surf. coverage θ
3.5% NaCl	-	2.4	47	0.76	-	-
8-HQ+ H_2O	2	2.0	70	0.74	32	0.32
8-HQ+ $\text{C}_2\text{H}_5\text{OH}$	2	2.3	82	0.85	42	0.42
8-HQ+ $\text{C}_2\text{H}_5\text{OH}$	5.52	2.4	246	0.82	80	0.80
8-HQ+ H_2O	5.52	1.6	1407	0.86	96	0.96

3.1.2. Potentiodynamic polarization measurements

Electrochemical kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), and anodic (β_a) and cathodic (β_c) slopes are obtained by the anodic and cathodic regions of the tafel plots shown in table 2.

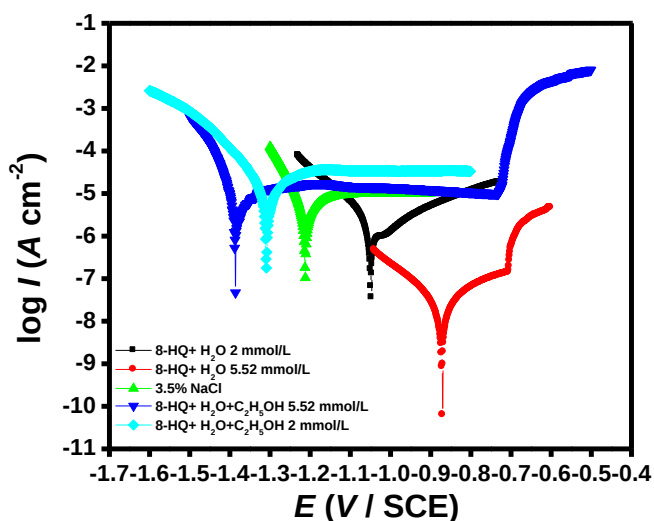
Table 2. Tafel polarization data for aluminium alloy in 3.5% NaCl at different concentration of 8-hydroxyquinoline.

Solution	Conc. (mmol/L)	Tafel data					
		E_{corr} (V vs. SCE)	I_{corr} ($\mu\text{A cm}^{-2}$)	b_a (mV d^{-1})	b_c (mV d^{-1})	η (%)	Surf. coverage θ
3.5% NaCl	-	-1.2	94	46	120	-	
8-HQ+ H ₂ O	2	-1.2	91	134	34	03	0.03
8-HQ+ C ₂ H ₅ OH	2	-1.3	25	18	82	73	0.73
8-HQ+C ₂ H ₅ OH	5.52	-1.3	21	24	83	77	0.77
8-HQ+H ₂ O	5.52	-1.3	06	32	90	93	0.93

The corrosion current density (I_{corr}) can be obtained by extrapolating the tafel lines to the corrosion potential and the inhibition efficiency (η %) values were calculated from the relation:

$$\eta\% = \frac{I_{\text{corr}} - I_{\text{corr(i)}}}{I_{\text{corr}}} \times 100 \quad (3)$$

Where I_{corr} and $I_{\text{corr(i)}}$ are the corrosion current density in absence and presence of inhibitor. The polarization curves for Aluminium alloy in the absence and presence of the inhibitor are given in figure 3. The liberation of H^+ ions is reduced due to addition of the inhibitor. The inhibitor molecules are first adsorbed on the surface and blocked the active sites of the metal surface.

**Figure 3.** Tafel polarization plots for aluminium alloy in absence and presence of 8-hydroxyquinoline.

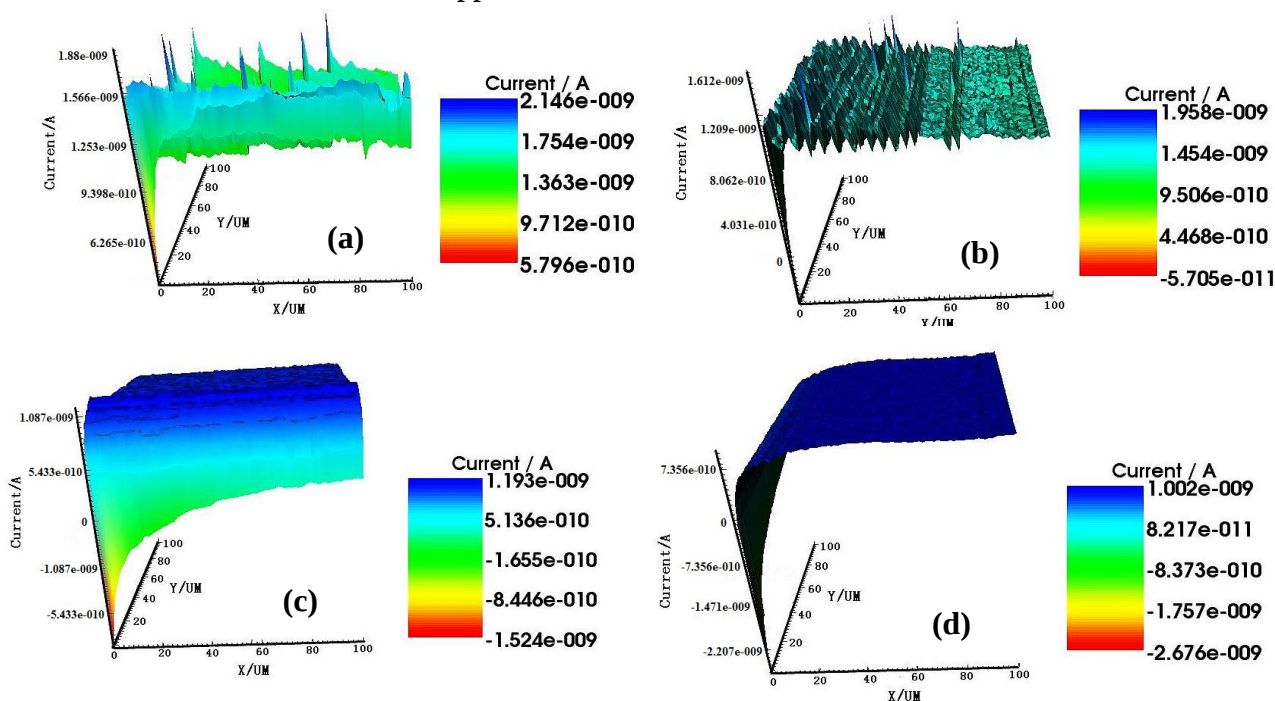
The values of b_a were shifted to higher values and b_c values shifted to lower values with reference to blank in the presence of 8-hydroxyquinoline. This showed that 8-hydroxyquinoline inhibits the corrosion process by controlling anodic and cathodic reactions predominantly of the metal

surface [23]. I_{corr} values decreased with increase in concentration inhibitor. This result confirmed the inhibitive action of 8-hydroxyquinoline towards corrosion of the aluminium alloy. But, analysis of both anodic (b_a) and cathodic (b_c) tafel slope values indicated that both anodic and cathodic reactions were suppressed during the addition of the inhibitor, which suggested that the 8-hydroxyquinoline reduced anodic dissolution and also retarded the hydrogen evolution reaction [24-26].

3.2. Surface Analysis

3.2.1. Scanning Electrochemical Microscopy

The scanning electrochemical microscope (SECM) [29] has been introduced to the corrosion field, giving valuable microscopic information from a corroding surface [30, 31] allowing the measurement of local differences in electrochemical reactivity. The important advantage of the SECM technique is that it operates on both insulating (coated / films) and conducting (non-coated) surfaces, thus allowing one to easily distinguish between the coated and corroded surfaces [32]. Figure 4a-j presents the morphology of the specimens visualized by scanning electrochemical microscope in presence and absence of 8-Hydroxyquinoline. The status of a corroded sample was studied by monitoring the probe (tip potential: 0.5 V vs Ag/AgCl/saturated KCl reference electrode) and the substrate (tip potential: -0.7 V) in test solutions. Corrosion activity is observed from 10 minutes after immersion in the electrolyte solution. When an insulating surface as we used different concentration of 8-hydroxyquinoline with 3.5% NaCl solution is approached in an SECM measurement the diffusion field surrounding the tip is hindered and the tip current decreases as shown in figure 4c-j. This is typical for an insulating surface. On the contrary, an increase in the current is observed when a conductor blank 3.5% NaCl solution without 8-hydroxyquinoline is approached (figure 4a-b). In the absence of 8-hydroxyquinoline the metal surface remains conductive, which are evidenced by an increase in current as the surface is approached.



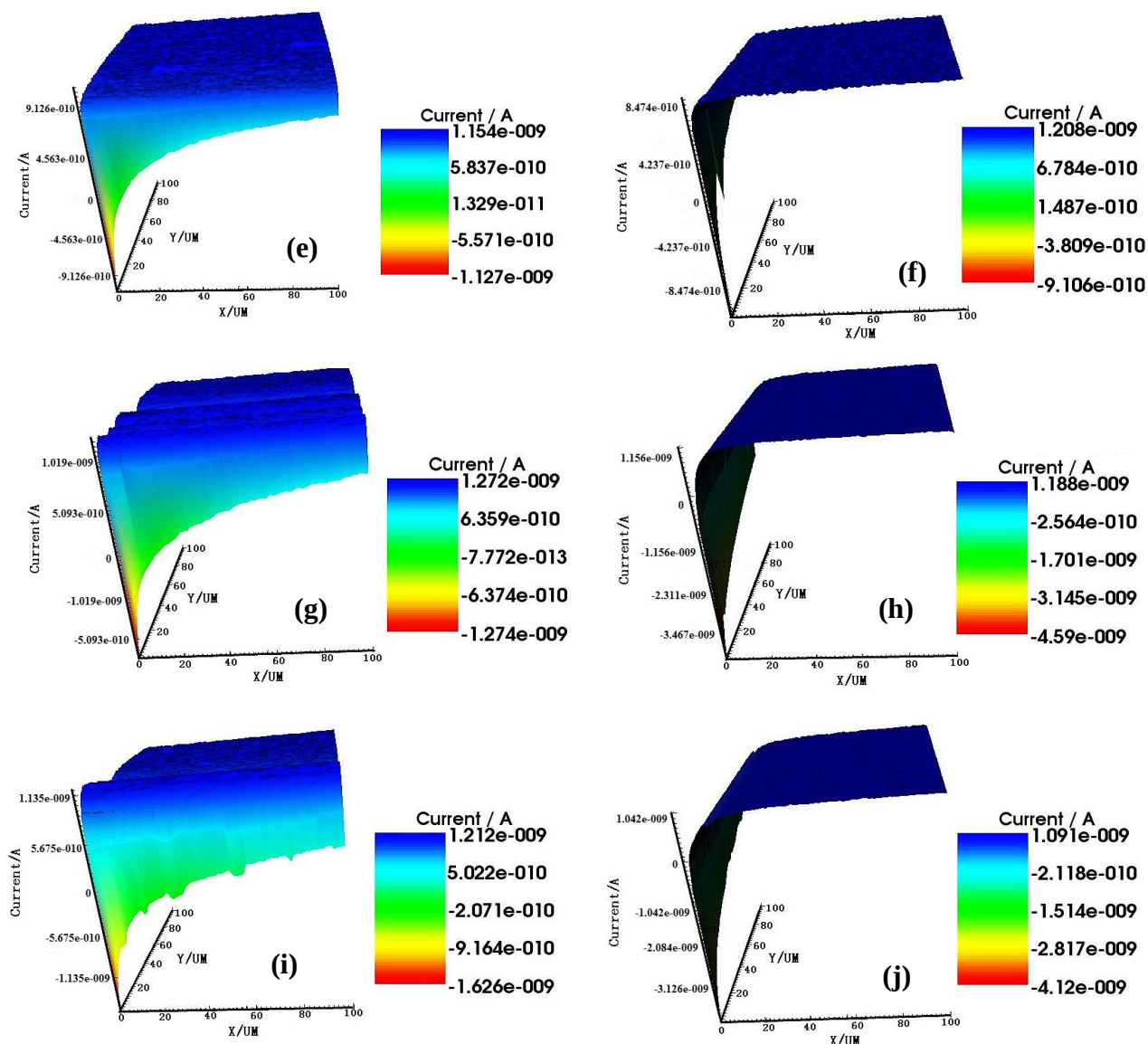
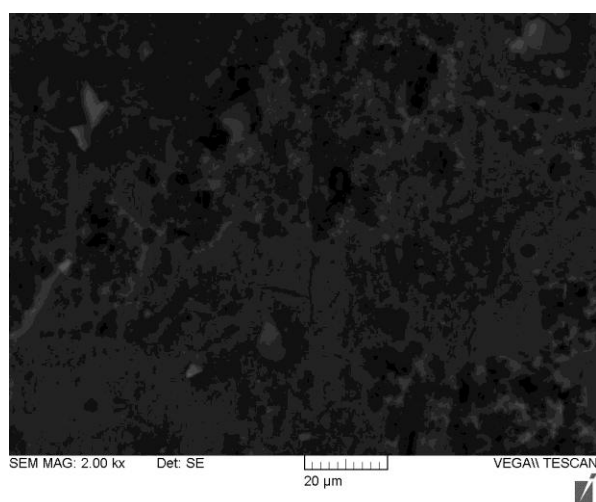
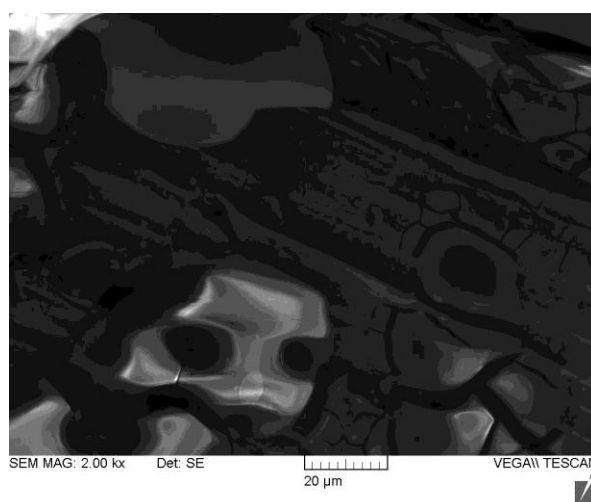
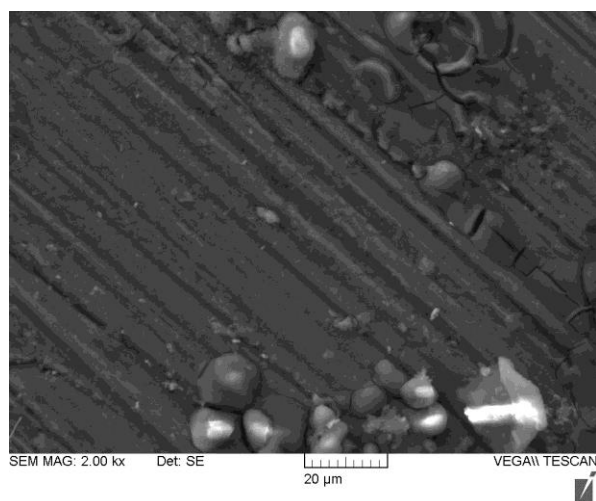
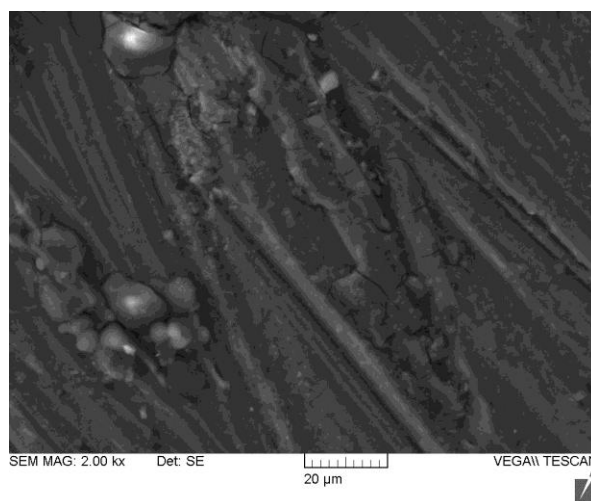


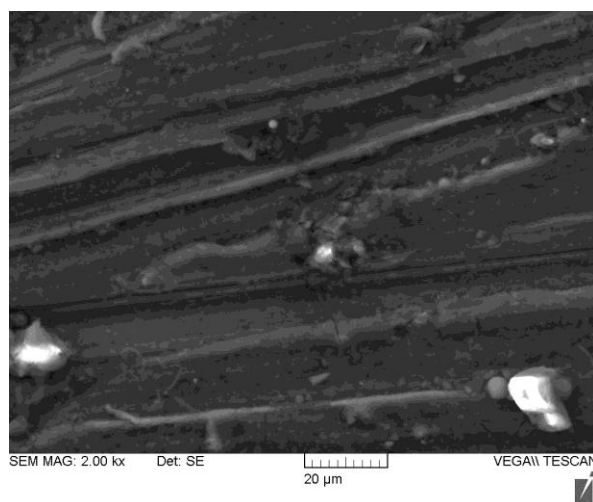
Figure 4. SECM 3-D images for (a) 3.5% NaCl x axis (b) 3.5% NaCl y axis (c) 8-hydroxyquinoline + H₂O 2 mmol/L x axis (d) 8-hydroxyquinoline + H₂O 2 mmol/L y axis (e) 8-hydroxyquinoline + H₂O 5.52 mmol/L x axis (f) 8-hydroxyquinoline + H₂O 5.52 mmol/L y axis (g) 8-hydroxyquinoline + C₂H₅OH 2 mmol/L x axis (h) 8-hydroxyquinoline + C₂H₅OH 2 mmol/L y axis (i) 8-hydroxyquinoline + C₂H₅OH 5.52 mmol/L x axis and (j) 8-hydroxyquinoline + C₂H₅OH 5.52 mmol/L y axis.

When 8-hydroxyquinoline has been added to the solution a gradual transition from a conducting to an insulating surface is seen. Comparing the currents across the corroded sample and the specimens with inhibitor solution, the protection effect of the inhibitor adsorbed on the specimen surface can be validated [33].

3.2.2. Scanning Electron Microscopy (SEM)

Scanning electron microscopy photographs were taken to show the corrosion inhibition is due to the formation of an adsorptive film on the steel surface. The morphology of the specimen surface in figure 5a showed a corroded surface in the absence of inhibitors, there are pits and cracks on the specimen's surface, and the surface is strongly damaged. However, in the presence of 8-hydroxyquinoline, the surface corrosion of aluminium alloy is remarkably decreased. The surface was less corroded and smooth for 8-hydroxyquinoline + H₂O 2 mmol/L, 8-hydroxyquinoline + H₂O 5.52 mmol/L, 8-hydroxyquinoline + C₂H₅OH 2 mmol /L and 8-hydroxyquinoline + C₂H₅OH 5.52 mmol /L as shown in figure 5b, 5c, 5d and 5e. Therefore, a smooth and less corroded morphology of aluminium alloy samples result from exposure to the inhibitor solutions. These results prove that the 8-hydroxyquinoline formed a protective film on the metal surface and can effectively protect aluminium alloy samples from a corrosive environment [30, 31].

**A****B****C****D**



E

Figure 5. SEM images of aluminium alloy specimens in (a) 3.5% NaCl (b) 8-hydroxyquinoline + H₂O 2 mmol/L (c) 8-hydroxyquinoline + H₂O 5.52 mmol/L (d) 8-hydroxyquinoline + C₂H₅OH 2 mmol/L and (e) 8-hydroxyquinoline + C₂H₅OH 5.52 mmol/L.

4. CONCLUSIONS

In this study, corrosion inhibition efficiency of 8-hydroxyquinoline on aluminium alloy in 3.5% NaCl was determined by electrochemical and surface analysis. Electrochemical impedance spectroscopy data reveals increase in R_{ct} values, which accounted for good inhibition efficiency. The SECM and SEM studies confirmed the blockage of metal surface through adsorption process.

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