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# Asparagine as an Eco-Friendly Corrosion Inhibitor for Copper in Nitric Acid: A Gravimetric and Electrochemical Investigation

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**ABSTRACT**

The corrosion inhibition performance of asparagine (ASP) for copper in 1 M $HNO_3$ solution was investigated using a combined experimental and theoretical approach. The inhibitory effect of ASP was evaluated through gravimetric measurements, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS). The results obtained from weight-loss measurements revealed that the corrosion rate of copper decreased significantly in the presence of the inhibitor, reaching a maximum inhibition efficiency of 94% at $10^{-4}$ M. Electrochemical studies confirmed these findings, showing a considerable decrease in corrosion current density and a marked increase in charge transfer resistance with the addition of ASP. Polarization results indicated that asparagine behaves as a mixed-type inhibitor, affecting both anodic and cathodic reactions. EIS measurements revealed the formation of a protective film on the copper surface, as evidenced by the increase in charge transfer resistance and the decrease in double-layer capacitance. The adsorption of ASP molecules on the copper surface was found to be responsible for the inhibition effect.

**Keywords:** Corrosion inhibitor, Copper, Amino acids, Asparagine, $HNO_3$.

## 1. Introduction

Copper and its alloys are extensively utilized in many industrial fields. Owing to its high electrical and thermal conductivity, copper is commonly applied in heat-transfer equipment and as an electrical conductor in electronic systems. Nevertheless, when it is subjected to aggressive or corrosive environments, copper can deteriorate, resulting in considerable economic losses (Abderrahim et al., 2021; Abderrahim et al., 2018). One of the most effective strategies to mitigate copper corrosion is the use of corrosion inhibitors, and numerous inhibitors have been investigated and developed for this purpose. These substances reduce the corrosion rate by forming a protective layer on the metal surface. Both inorganic (Ahmed et al., 2020; Muñoz et al., 2004) and organic compounds (Ebadi et al., 2012; Farooq et al., 2026) have been reported to be effective inhibitors. However, many conventional inhibitors present environmental and health concerns due to their toxic nature. Consequently, recent research has increasingly focused on the development of environmentally friendly and sustainable corrosion inhibitors. Amino acids are environmentally benign organic compounds that are non-toxic and readily soluble in aqueous solutions. They are also biodegradable and can be synthesized with high purity at relatively low production costs (Loto, 2019). Because of these characteristics, amino acids have attracted attention as potential corrosion inhibitors. Previous studies have shown that organic molecules containing heteroatoms such as nitrogen, sulfur, phosphorus, and oxygen tend to exhibit improved corrosion inhibition performance for copper surfaces (Barouni et al., 2014; Kaya et al., 2016). This effect is mainly due to the electronic structure of copper atoms, which possess partially filled d-orbitals that can interact with electron-donating atoms to form coordination bonds. Structurally, amino acids contain both amine ($–NH_2$) and carboxyl (–COOH) functional groups, together with a side chain that distinguishes one amino acid from another (Akram et al., 2011; Dewangan et al., 2023). The nitrogen and oxygen atoms in these functional groups carry lone pairs of electrons, which can interact with copper atoms at the metal surface. Such interactions promote adsorption of the amino acid molecules and facilitate the formation of protective bonds on the copper surface, contributing to corrosion inhibition. The objective of this study is to investigate the effectiveness of asparagine as a corrosion inhibitor for copper in a nitric acid solution. The inhibitory performance was evaluated using both gravimetric and electrochemical approaches. In particular, weight loss experiments, potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) were employed to determine the inhibition efficiency. Surface morphology analysis was also conducted to support and confirm the results obtained from the gravimetric measurements.

## 2. Experimental

### 2. 1. Materials and Methods

Copper of 99.92% purity was employed in this study. Prior to the experiments, the samples were mechanically polished with emery paper. After polishing, the specimens were carefully degreased by rinsing with distilled water, ethanol, and acetone. The prepared samples were then dried and kept in a desiccator until use. Asparagine (ASP), **Figure 1**, was employed as a corrosion inhibitor.

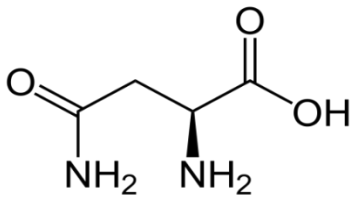


**Figure 1.** Molecular structure of asparagine (ASP).

### 2. 2. Gravimetric Study

Corrosion inhibition studies were performed on copper samples (99% purity) using the mass-loss method. Rectangular specimens (1 cm × 1 cm × 1 cm) were polished with emery paper, washed with distilled water, dried, and accurately weighed before immersion. The samples were then placed in 250 mL of 1 M $HNO_3$ solution for 24 hours at 298 K in the absence and presence of asparagine (ASP) (10-1–10-4 M) as a corrosion inhibitor. After immersion, the specimens were rinsed, dried, and reweighed to determine the mass loss. Each experiment was repeated three times, and the average values were used to calculate the corrosion rate ($V_{corr}$), inhibition efficiency (%IE), and surface coverage (θ).

$$\Delta m = m_1 - m_2 \quad (1)$$

$$V_{corr} = \frac{\Delta m}{S.t} \quad (2)$$

$$\theta = 1 - \frac{\Delta m_{corr}}{\Delta m^{\circ}_{corr}} \quad (3)$$

$$IE(\%) = \frac{V^{\circ}_{corr} - V_{corr}}{V^{\circ}_{corr}} \quad (4)$$

Where:

m1 and m2 represent the masses of the copper samples before and after immersion, respectively. $\Delta m_{corr}$ and $\Delta m^{\circ}_{corr}$ denote the average masses of the specimens before and after immersion, respectively.

### 2.3. Electrochemical Investigations

Electrochemical measurements were performed using a SP150 Bio-Logic potentiostat controlled by EC-Lab software. A conventional three-electrode electrochemical cell was employed, consisting of a saturated calomel electrode (SCE) as the reference electrode, a platinum electrode as the counter electrode, and a copper working electrode with an exposed surface area of 1.75 $cm^2$. Potentiodynamic polarization curves were recorded at a scan rate of 1 mV $s^{-1}$ within a potential range from −300 to +200 mV/SCE, allowing stabilization of the electrical double layer before measurements. Electrochemical impedance spectroscopy (EIS) measurements were carried out at the corrosion potential over a frequency range of 100 kHz to 10 mHz with a 10 mV sinusoidal perturbation.

## 3. Results

### 3.1. Gravimetric Study

The variation in inhibition efficiency (IE%) and corrosion rate ($V_{corr}$) obtained using this method is shown in **Figure 2.**

**Table 1** presents the corrosion parameters derived from weight-loss measurements for copper in 1 M HNO3 solution, in the absence and presence of asparagine. In the blank solution, copper exhibits a high corrosion rate of 22 mg $cm^{-2}$ $h^{-1}$, indicating strong metal dissolution in the acidic medium. The addition of asparagine significantly reduces the corrosion rate and increases both the surface coverage and the inhibition efficiency. The maximum inhibition efficiency reaches 94%, with a corresponding surface coverage of 0.94, suggesting strong adsorption of asparagine molecules on the copper surface. These results indicate that asparagine is an effective corrosion inhibitor for copper in HNO3 solution, probably through the formation of a protective adsorbed film on the metal surface (Debab et al., 2025).

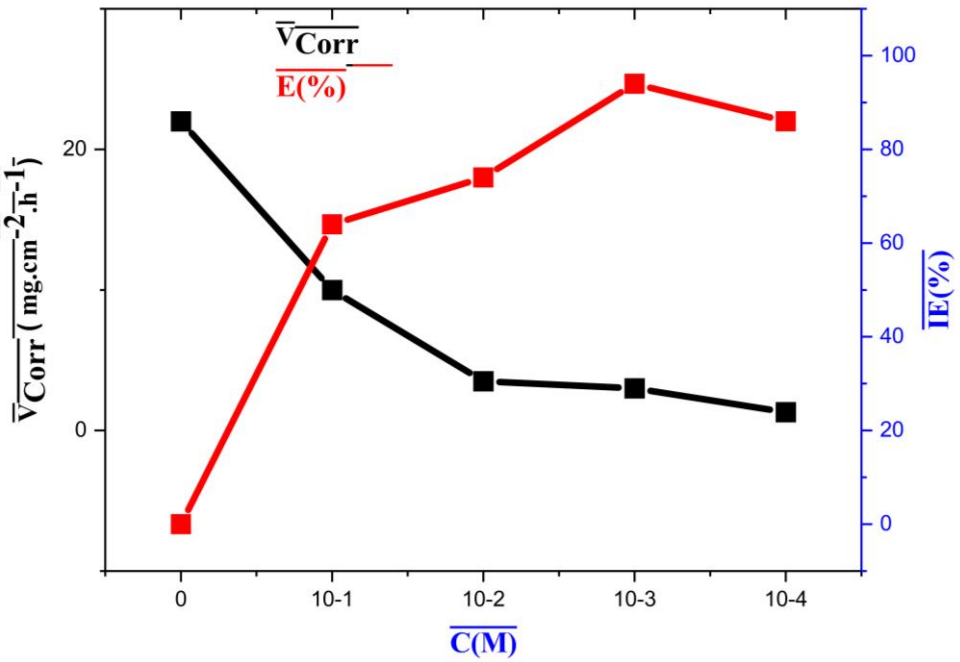


**Figure 2.** Variation of the inhibition efficiency (E%) and corrosion rate ($V_{corr}$) obtained by the gravimetric method in 1 M $HNO_3$ as a function of inhibitor concentration.

**Table 1.** Corrosion parameters derived from gravimetric measurements.

| C (M) | $V_{corr}$ (mg $cm^{-2}$ $h^{-1}$) | θ | IE(%) |
|---|---|---|---|
| **0** | 22 | / | / |
| **$10^{-1}$** | 10 | 0.64 | 64 |
| **$10^{-2}$** | 3.5 | 0.74 | 74 |
| **$10^{-3}$** | 3 | 0.86 | 86 |
| **$10^{-4}$** | 1.3 | 0.94 | 94 |

### 3. 2. Electrochemical Analysis

#### 3. 2. 1. Open Circuit Potential

The evolution of the open-circuit potential (OCP) of copper in 1 M $HNO_3$ solution was monitored in the absence and presence of different concentrations of asparagine ($10^{-1}$-$10^{-4}$ M), and the results are shown in **Figure 3**. In the uninhibited solution, the corrosion potential ($E_{corr}$) stabilizes around −0.028 V/SCE after 1 h of immersion, indicating the establishment of a steady-state corrosion process. In the presence of asparagine, the corrosion potential shifts toward more positive values, suggesting that the inhibitor affects mainly the anodic reaction. This behavior can be attributed to the adsorption of asparagine molecules on the copper surface, which leads to the formation of a protective layer that slows down the dissolution of copper in the acidic medium.

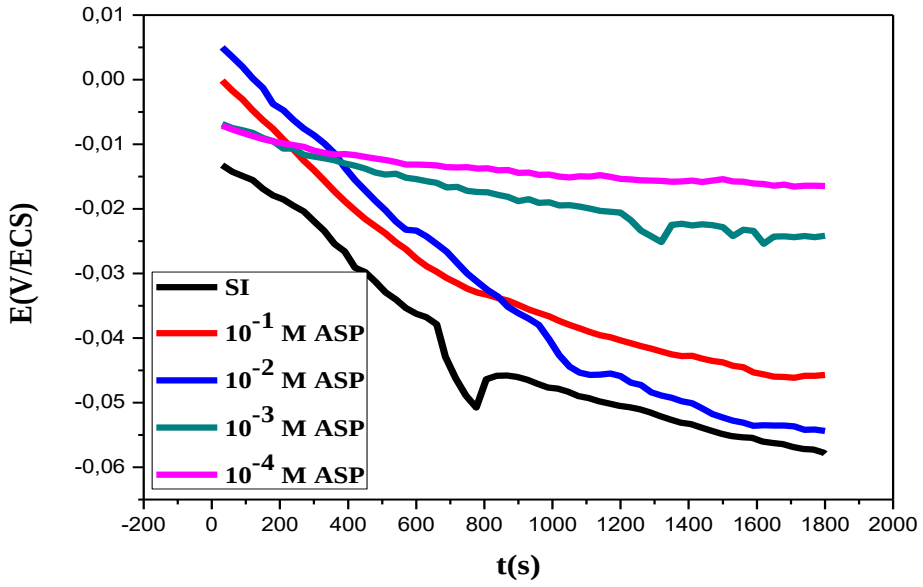


**Figure 3.** Evolution of the open-circuit potential (OCP) of copper immersed in 1 M $HNO_3$ solution in the absence and presence of asparagine.

### 3. 2. 2. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy measurements were performed at the corrosion potential and at different inhibitor concentrations in order to gain a better understanding of the corrosion and inhibition mechanisms of copper in 1 M $HNO_3$ solution. These measurements were used to investigate the corrosion and protection processes occurring at the copper surface in the absence and presence of asparagine (ASP) at various concentrations. The electrochemical impedance diagrams of copper immersed in 1 M $HNO_3$ in the absence and presence of different concentrations of asparagine are shown in **Figure 4a** (Nyquist plots) and **Figure 4b-c** (Bode plots). These diagrams (via **Figure 4a**) reveal the presence of two capacitive loops. The first loop, observed at high frequencies, is attributed to the relaxation process of the electrical double-layer resulting from its charge–discharge phenomenon, which is known to be a rapid process (Amin et al., 2010; McCafferty, 2005). The second loop, appearing at low frequencies, begins with a characteristic behavior associated with Warburg impedance, as reported by other researchers (Ma et al., 2002; Ma et al., 2003). This behavior is generally attributed to the diffusion of soluble corrosion products into the bulk solution and/or the diffusion of depolarizing species from the solution toward the metal/solution interface. The diameter of the capacitive loops increases as the concentration of asparagine decreases. This behavior suggests the formation of a protective barrier on the copper surface, which may be associated with the formation of a Cu(I)–ASP complex adsorbed on the metal surface (Barouni et al., 2010; Fouda et al., 2000).

The Bode diagrams provide additional information about the electrochemical behavior of copper in the studied medium. As shown in **Figure 4b**, a resistive region appears at high frequencies. Furthermore, **Figure 4c** shows the presence of a single time constant for the different concentrations of asparagine (ASP), suggesting that the corrosion process is mainly controlled by a single electrochemical reaction mechanism. The impedance of an electrochemical system can be interpreted by analogy with an electrical impedance.

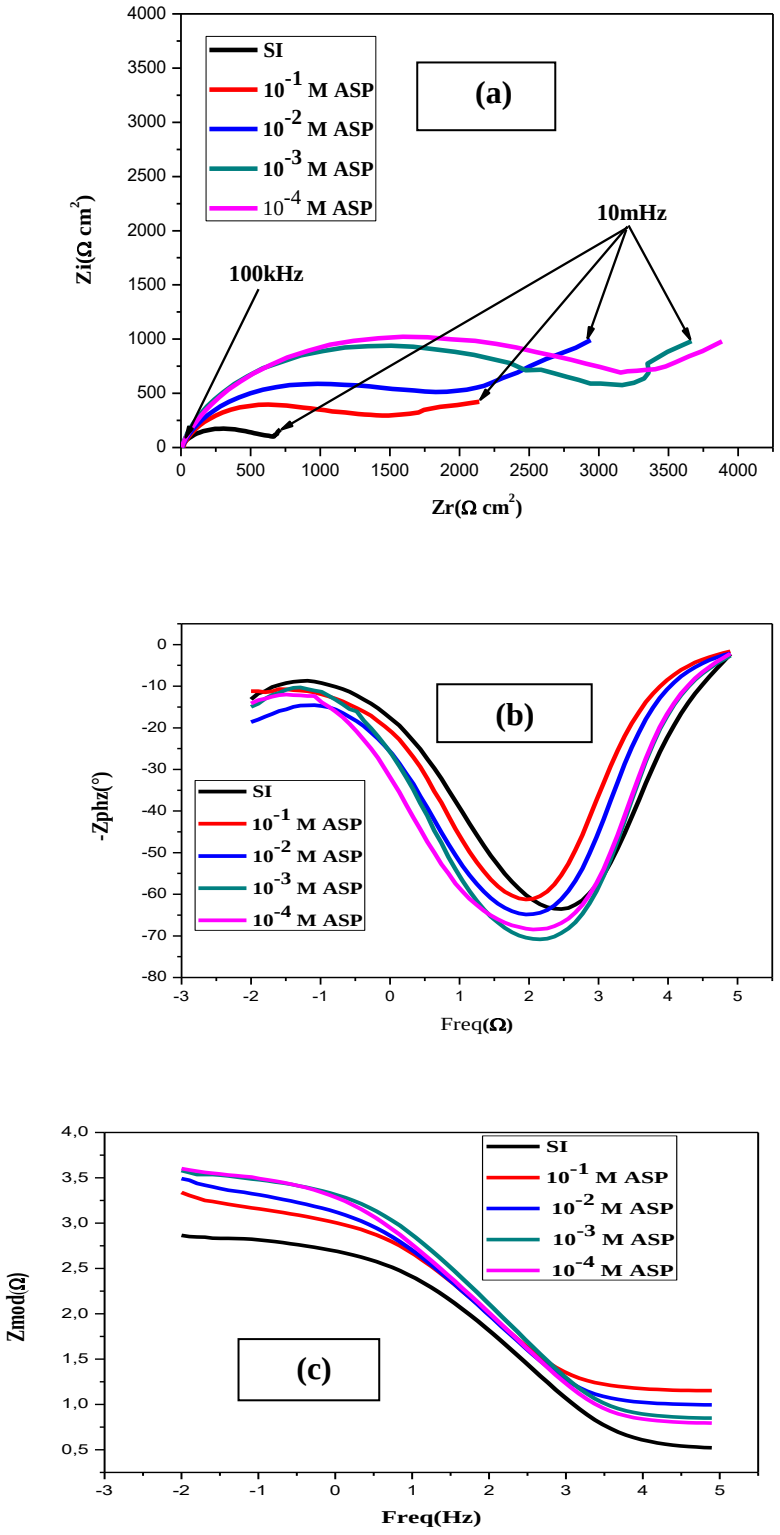


**Figure 4.** Electrochemical impedance diagrams of Cu in 1 M $HNO_3$ in the absence and presence of asparagine at different concentrations: (a) Nyquist plot; (b) and (c) Bode plots.

The various processes occurring at the electrode/electrolyte interface can be represented using an equivalent electrical circuit (EEC). In such circuits, each element connected in series or parallel corresponds to a specific physical process occurring in the system. These models are progressively fitted to the experimental impedance diagrams to extract the parameters necessary to understand the corrosion mechanism. The EEC used to fit the impedance spectra was obtained using the simulation software ZView and EC-Lab and is presented in **Figure 5.** This circuit was employed to model the impedance behavior of copper in 1 M

$HNO_3$ solution both in the absence and in the presence of asparagine. The circuit includes the solution resistance (Rs), the charge transfer resistance (R1), and a constant phase element (CPE1) associated with the double-layer capacitance. In addition, R2 and CPE2 represent the impedance contribution of the adsorbed inhibitor film formed on the copper surface. The parameters $n_1$ and $n_2$ correspond to the heterogeneity factors associated with the phase shift of the constant phase elements. The impedance of the constant phase element (CPE) is defined by the following relation (Selatnia et al., 2018):

$$Z_{CPE} = \frac{1}{Q(jw)^{\alpha}} \qquad (7)$$

Where:

Q ($\Omega^{-1}\cdot s^{\alpha}\cdot cm^{-2}$) represents the magnitude of the constant phase element (CPE); j is the imaginary unit *($j^2 = -1$)*; ω is the angular frequency *($rad\cdot s^{-1}$)*; α is the deviation parameter that characterizes the non-ideal capacitive behavior of the CPE *($-1 \leq \alpha \leq 1$)*.

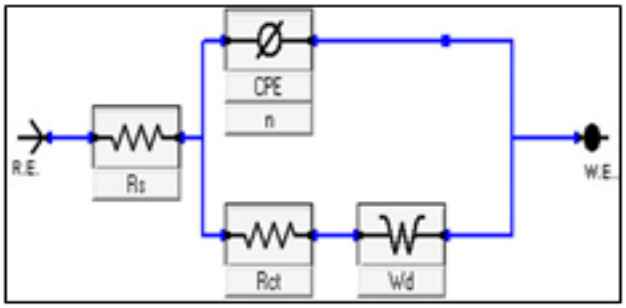


**Figure 5.** Equivalent electrical circuit (EEC) used to fit the electrochemical impedance spectra of copper in 1 M $HNO_3$ solution in the absence and presence of asparagine at various concentrations.

The values of the different electrochemical parameters derived from the equivalent electrical circuit for copper in 1 M $HNO_3$ solution, in the absence and presence of asparagine, as well as the inhibition efficiencies calculated using Equation (8), are summarized in **Table 2.**

$$E(\%) = \left(1 - \frac{R_t}{R_t'}\right) \times 100 \qquad (8)$$

Where $R_t$ and $R_t'$ represent the charge transfer resistances in the absence and presence of the inhibitor, respectively.

The results indicate that the charge transfer resistance (Rt) increases significantly with the addition of the inhibitor, reaching 265.8 $\Omega\cdot cm^2$ at $10^{-4}$ M, which suggests improved corrosion protection. At the same time, the inhibition efficiency (IE%) increases and reaches a maximum value of 94.98%, confirming the strong inhibitive effect of asparagine. The decrease in CPE values and the high n-values indicate the formation of a protective adsorbed film on the copper surface. Overall, the EIS results confirm that asparagine effectively inhibits copper corrosion in 1 M $HNO_3$ solution.

**Table 2.** Electrochemical parameters obtained from the equivalent electrical circuit for copper in 1 M $HNO_3$ solution in the absence and presence of asparagine, along with the calculated inhibition efficiencies.

| (M) | $R_s$ ($\Omega.cm^2$) | $CPE_1$ ($\mu F.cm^2$) | $n_1$ | $Rt_1$ ($\Omega.cm^2$) | $CPE_2$ ($\mu F.cm^2$) | $n_2$ | $Rt_2$ ($\Omega.cm^2$) | IE (%) |
|---|---|---|---|---|---|---|---|---|
| **0** | 5.80 | 0.85 | 0.65 | 10.82 | 9.58 | 0.92 | 1.01 | / |
| **$10^{-1}$** | 3.98 | 0.70 | 0.83 | 21.43 | 7.20 | 0.89 | 3.58 | 49.51 |
| **$10^{-2}$** | 6.65 | 0.64 | 0.69 | 78.30 | 3.90 | 0.93 | 8.6 | 89.98 |

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| **$10^{-3}$** | 7.65 | 0.65 | 0.70 | 79.30 | 2.90 | 0.94 | 14.2 | 92.92 |
| **$10^{-4}$** | 8.13 | 0.004 | 0.91 | 265.8 | 0.69 | 0.91 | 15.2 | 94.98 |

### 3. 2. 3. Polarization Measurements

The polarization curves of copper in 1 M $HNO_3$ solution in the absence and presence of asparagine ($10^{-1}$–$10^{-4}$ M) are presented in **Figure 6**, recorded after 1 h of immersion at a scan rate of 1 mV $s^{-1}$. The addition of asparagine (ASP) causes a noticeable shift in the corrosion potential along with a significant decrease in the corrosion current density, indicating effective inhibition of copper corrosion. This behavior is attributed to the adsorption of inhibitor molecules on the copper surface, which blocks active sites involved in the electrochemical reactions and slows the dissolution process. The electrochemical parameters derived from the polarization curves are summarized in **Table 3.** The inhibition efficiency (IE%) was calculated using the following expression:

$$IE(\%) = \frac{i_{corr} - i'_{corr}}{i_{corr}} \times 100 \qquad (9)$$

where $i_{corr}$ and $i_{corr}'$ represent the corrosion current densities in the absence and presence of the inhibitor, respectively.

In the uninhibited solution, the corrosion current density ($i_{corr}$) reaches 98.96 µA·$cm^{-2}$, indicating a high corrosion rate of copper in a nitric acid medium. The corrosion potential ($E_{corr}$) is measured at −128.17 mV/SCE, which corresponds to the natural corrosion condition of copper in this aggressive environment. The addition of asparagine leads to a significant reduction in the corrosion current density. For example, $i_{corr}$ decreases from 98.96 µA·$cm^{-2}$ to 17.07 µA·$cm^{-2}$ at $10^{-1}$ M and further decreases to 9.036 µA·$cm^{-2}$ at $10^{-4}$ M. This strong decrease indicates that asparagine effectively inhibits the corrosion of copper in nitric acid solution.

The inhibition efficiency (IE%) increases progressively with decreasing inhibitor concentration, reaching 95.75% at $10^{-4}$ M, which represents the highest protective performance among the tested concentrations. This behavior suggests that the inhibitor molecules strongly adsorb on the copper surface, forming a protective film that reduces the active sites available for corrosion reactions. The values of the corrosion potential ($E_{corr}$) exhibit slight shifts in the presence of the inhibitor. Since the displacement of $E_{corr}$ is relatively small (generally less than ±85 mV compared to the blank solution), the inhibitor can be classified as a mixed-type inhibitor, affecting both the anodic dissolution of copper and the cathodic reduction reactions.

Furthermore, the changes observed in the anodic ($B_a$) and cathodic ($B_c$) Tafel slopes indicate that the addition of asparagine modifies the kinetics of both electrochemical reactions. The increase in the Tafel slopes suggests that the inhibitor alters the reaction mechanisms by blocking active sites on the copper surface.

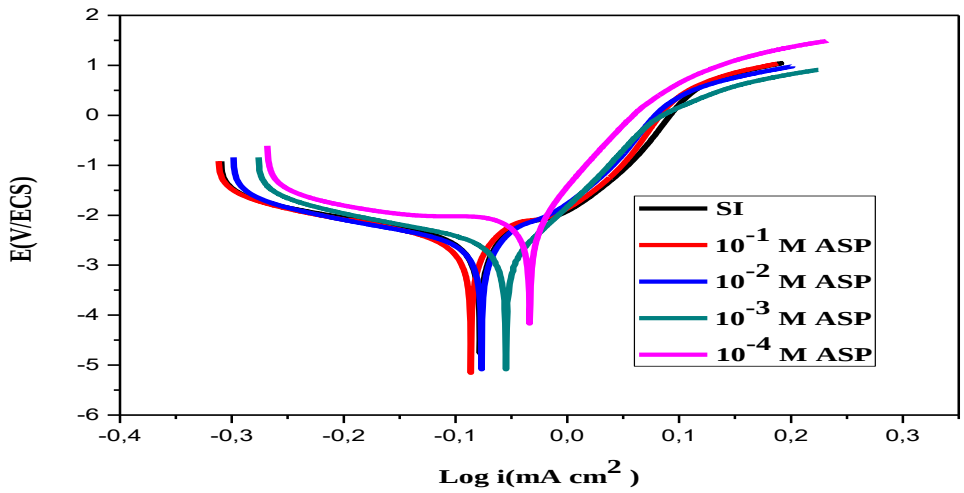


**Figure 6.** Potentiodynamic polarization curves of copper in 1 M $HNO_3$ solution in the absence and presence of asparagine at different concentrations.

**Table 3.** Electrochemical parameters derived from the polarization curves of copper in 1 M $HNO_3$ solution in the absence and presence of asparagine at different concentrations, and the corresponding calculated inhibition efficiencies.

| C (M) | $E_{corr}$ (mV/ECS) | $i_{corr}$ (µA.cm$^{-2}$) | $B_a$ (mV.dec$^{-1}$) | $B_c$ (mV.dec$^{-1}$) | IE (%) |
|---|---|---|---|---|---|
| **0** | -128.17 | 98.96 | 34.8 | 24.9 | / |
| **$10^{-1}$** | -118.88 | 17.07 | 37.3 | 21.3 | 66.19 |
| **$10^{-2}$** | -118.14 | 12.89 | 41.8 | 28.8 | 73.61 |
| **$10^{-3}$** | -143.69 | 10.06 | 52.9 | 42.9 | 80.79 |
| **$10^{-4}$** | -165.82 | 9.036 | 63.6 | 43.03 | 95.75 |

### 3. 3. Optical Microscopy Analysis

Optical microscopy is a technique used to examine the surface condition and morphology of materials. In this study, optical micrographs of the copper surface immersed in 1 M $HNO_3$ solution in the absence and presence of asparagine (ASP) at $10^{-4}$ M were obtained. The surface morphologies are presented in two-dimensional and three-dimensional representations in Figures 7a, a′ and 7b, b′, respectively.

In the absence of the inhibitor (Figures 7a and 7a′), the copper surface exhibits numerous pits of different sizes, accompanied by severe surface degradation, resulting in significant roughness. This damage indicates intense corrosion of copper in 1 M $HNO_3$ solution. In contrast, in the presence of asparagine at $10^{-4}$ M (Figures 7b and 7b′), the copper surface appears much smoother, and no noticeable pits are observed. This behavior confirms the formation of a protective inhibitor film on the metal surface, which effectively reduces the corrosion rate of copper.

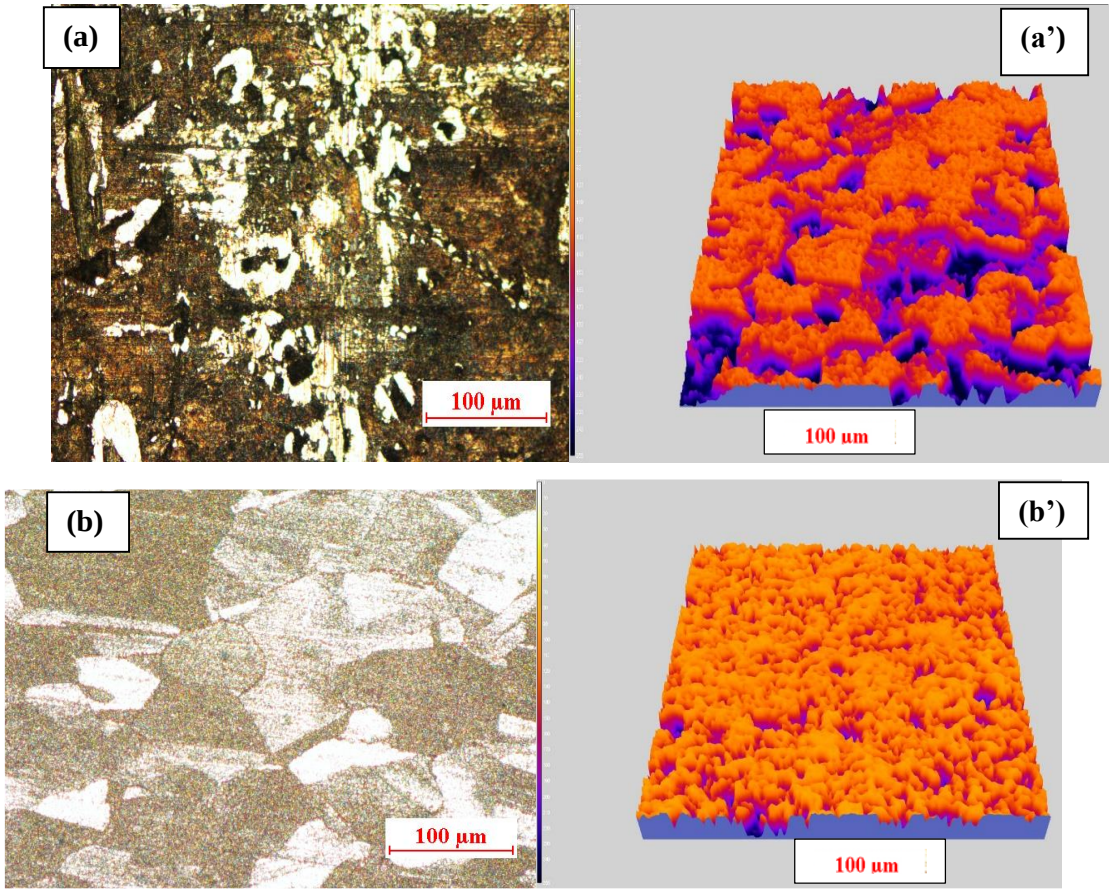


**Figure 7.** Optical microscopy (OM) images of the copper surface after 2 h of immersion in 1 M $HNO_3$ solution: (a, a′) without inhibitor and (b, b′) with asparagine (ASP, $10^{-4}$ M).

## 4. Conclusion

The corrosion inhibition performance of asparagine (ASP) for copper in 1 M $HNO_3$ solution was investigated using gravimetric measurements, electrochemical techniques, and theoretical calculations. The main conclusions can be summarized as follows:

1. Gravimetric results showed that the corrosion rate of copper decreases significantly in the presence of ASP, with an inhibition efficiency reaching 94% at $10^{-4}$ M.
2. Potentiodynamic polarization studies indicated that ASP acts as a mixed-type inhibitor, reducing both anodic dissolution and cathodic reduction reactions.
3. Electrochemical impedance spectroscopy revealed a significant increase in charge transfer resistance (Rt) and a decrease in double-layer capacitance, confirming the formation of a protective adsorbed layer on the copper surface.
4. The adsorption of ASP molecules on copper leads to the formation of a protective film, which blocks the active sites responsible for corrosion and slows the electrochemical reactions.

The results demonstrate that asparagine is an effective and environmentally friendly corrosion inhibitor for copper in nitric acid solution, making it a promising candidate for corrosion protection in acidic environments.

## Conflict of Interest

On behalf of all authors, the corresponding author states that there is no conflict of interest.

## Data Availability

No data was used for the research described in the article.

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