# The Inhibited Effect of Cysteine Towards the Corrosion of Copper in Nitric Acid Solution

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**Abstract:** The detailed study of cysteine (Cys) as corrosion inhibitor for copper in nitric acid solution has been performed through weight loss, electrochemical polarization, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) measurements. The effect of inhibitor concentration, temperature and immersion time against inhibitor action was investigated. Results show that Cys may be used as an efficient inhibitor for copper in nitric acid at higher temperatures (98% at 50°C). Potentiodynamic polarization studies reveal that Cysteine acts as a mixed-type inhibitor without any change in the mechanism of hydrogen evolution. The adsorption of this compound on copper surface obeys Langmuir's adsorption isotherm and has a chemisorptions mechanism.

**Keywords:** Corrosion, inhibition, copper, amino-acids.

## 1. INTRODUCTION

Copper is widely used in industry because of their good thermic conductivity and mechanical properties. Copper is also a relatively noble metal, but it can suffer severe corrosion in aerated acidic media. The use of inhibitor is one of the most practical methods to protect metals from corrosion, especially in aggressive media [1-4]. Organic inhibitors containing nitrogen, oxygen and/or sulfur have been widely used for copper and its alloys [5-9]. Among these organic compounds the most commonly used are benzotriazole [10, 11], benzimidazole [12] and tetrazole [1, 13-15]. Azole compounds exhibited excellent corrosion inhibitors for copper in acidic media, but these are highly toxic. Despite the vast number of corrosion inhibition investigations, there remains relatively few works directed towards the study of non-toxic organic compounds, especially amino acids, as corrosion inhibitors of Cu [6, 16, 17]. Amino acids form a class of non-toxic organic compounds which are completely soluble in aqueous media and produced with high purity at low cost. The literature presents some studies involving amino acids on the corrosion prevention of iron [18, 19], steel [20, 21], aluminum [22, 23], lead [24] and copper [6, 16, 25-27]. Zhang *et al.* studied the inhibitory action of two amino-acid compounds, alanine and cysteine, on copper corrosion in HCl solution [17].

The encouraging results obtained by aminoacids [28] towards copper in nitric acid solution and the selection of cysteine as the good inhibitor of the tested compounds, have incited to develop a detailed study on cysteine. The study was conducted by potentiodynamic polarization, weight-loss and SEM measurements.

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## 2. MATERIALS AND METHODOLOGY

The copper working was of 99% purity. The aggressive solution of 1 mol L$^{-1}$ HNO$_3$ was prepared by dilution of Analytical Grade 65% of mark Taoura with bidistilled water. The amino acid compound tested as inhibitor is the commercial product. The structural formula is shown in Fig. (**1**). Pure copper was immersed in molar HNO$_3$ at various concentrations of Cys ($10^{-5}$ to $10^{-2}$ mol L$^{-1}$).

Before the measurements, the copper specimens were polished successively with emery paper up to 1000 grade, rinsed thoroughly with acetone and bidistilled water. The potentiodynamic polarization curves were recorded using a potentiostat PGP 201 associated to "Volta Master 1", at a scan rate of 60mV/min. The potential ranged from –800 to +500 mV/SCE. The electrochemical measurements were performed in a conventional three electrodes electrochemical cell. Consisting of platinum electrode, as an Auxiliary electrodes, saturated calomel electrode (SCE), as the reference and Cu metal as the working electrode, it had the form of a disc from pure copper of the surface 0.35 cm$^2$.

The electrochemical impedance spectroscopy (EIS) measurements are carried out with the electrochemical system (Tacussel), which included a digital potentiostat model Volta lab PGZ 100 computer at E$_{cor}$ after immersion in solution without bubbling. After the determination of steady-state current at a given potential, sine wave voltage (10mV) peak to peak, at frequencies between 100 kHz and 10 mHz are superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure. The impedance diagrams are given in the Nyquist representation.

Gravimetric measurements were made in intervals of 2, 4, 16 and 24 hours. The solution volume was 75ml. The copper samples used had a rectangular form with face whose

total surface is 12cm$^2$. Mass loss was recorded by an analytical balance with 0.1mg. The sheets obtained from weight loss measurements after 4 hours at 20°C are used in SEM studies.
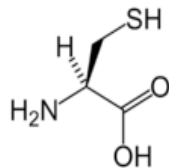
**Fig. (1).** Acide L-2-amino-3-mercaptopropionique L-Cysteine (**Cys**).

## 3. RESULTS AND DISCUSSIONS

### 3.1. Effect of Concentration of Cys

Fig. (**2**) represents the polarization curves of copper in molar nitric acid in the presence of different concentrations of cysteine and absence of inhibitor (blank solution). The extrapolation of straight line allows the determination of the corrosion current density ($I_{corr}$), the corrosion potential ($E_{corr}$) and the cathodic Tafel slope ($b_c$). The values of inhibition efficiency (E%) as function of Cys concentration are given in Table **1**. It is observed that, the corrosion potential $E_{corr}$ shifted to more negative values with the rise of the concentration of Cys. This result indicates that the inhibitors have been adsorbed to cathodic areas. This remark is justified also by the diminution of cathodic current densities while Cys concentration increases in solution. The same results have been reported by other authors [21, 29]. Then, the addition of cysteine as presented in Fig. (**2**) seems that no effect on anodic behaviour is observed but when the curves are presented against the over-potential (E − E$_{corr}$) the effect on anodic process was observed, especially at high inhibitor concentrations. Also, Ismail pointed that cysteine may act according to its protonated form in acidic solution and in its zwitterions structure in neutral solution as shown in the following scheme [30]:
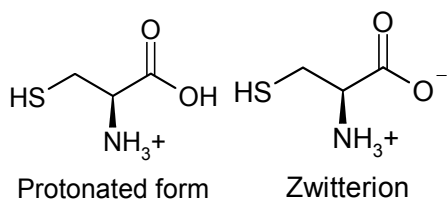
Furthermore, the shape of anodic curves depends on Cyst concentration. That is, with the increase of anodic potentials, the anodic current remains almost constant. This may also postulate that in the presence of Cu$^{2+}$, cysteine interacts to form a copper cysteinate complex (Cu(I) cysteine [27]. In conclusion, both the anodic and cathodic current densities were decreased, indicating that Cyst suppressed both the anodic and cathodic reactions. We may introduce that Cysteine acts as a mixed-type inhibitor with predominance at cathodic potentials. The high performance is attributed to the presence of –SH, NH$_2$, C=O and OH groups, which have a strong affinity for copper, so we may suggest that the inhibitory ability to inhibit copper corrosion is the intramolecular effect of these different groups.

From the electrochemical data gathered in Table **1**, we conclude that the value of $I_{corr}$ decreases with the rise of the concentration of Cys. The high value of $I_{corr}$ is obtained in the blank solution and the less value obtained is related to the presence of Cys at 10$^{-2}$ mol L$^{-1}$. In this case, the corresponding inhibition efficiency is 73%.
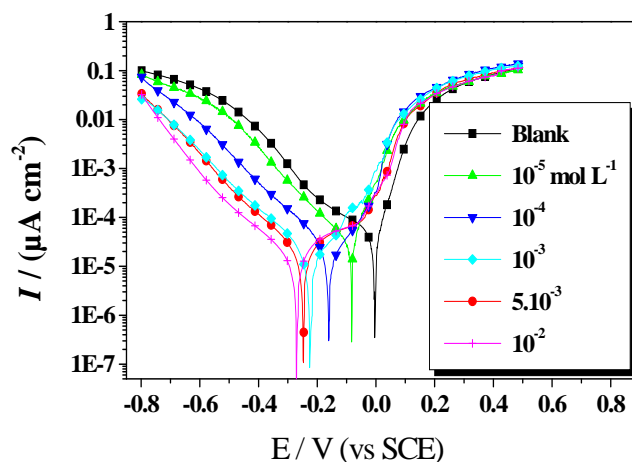
**Fig. (2).** Polarization curves for the effect of Cys concentration on the potentiodynamic behaviour of pure copper in 1 mol L$^{-1}$ HNO$_3$ (T=20°C).

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior. The degrees of surface coverage (θ=E%/100) for different inhibitor concentrations were evaluated by polarization data. Data were tested graphically by fitting to various isotherms. The best fitted straight line is obtained for Langmuir isotherm. Langmuir's isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. The ratio C/θ versus C is plotted linearly, showing that the adsorption obeys to Langmuir isotherm:

**Table 1.**    **Electrochemical Parameters Derived from Fig. (1).**

| Solution | $E_{corr}$/(mV *vs* SCE) | $I_{corr}$/(µA cm$^{-2}$) | $b_c$/(mV dec.$^{-1}$) | E$_I$(%) |
|---|---|---|---|---|
| Blank | -4 | 44.5 | -179 | - |
| 10$^{-5}$M | -84 | 32.5 | -176 | 27 |
| 10$^{-4}$M | -163 | 28.1 | -175 | 37 |
| 10$^{-3}$M | -223 | 18.8 | -177 | 58 |
| 5.10$^{-3}$M | -247 | 13.3 | -175 | 70 |
| 10$^{-2}$M | -268 | 12.1 | -175 | 73 |

$$\frac{C}{\theta} \ = \ \frac{1}{k} + C \tag{1}$$

where *C, k* and *θ* are the concentration of inhibitor, the adsorptive equilibrium constant and the surface coverage, respectively.

The values of linear regression between *C/θ* and *C,* and the parameters of adsorption are determined from Fig. (**3**). The obtained slope 1.35 slowly higher than unity indicates that inhibitor adsorption is not an ideal one as mentioned by Langmuir hypothesis. The coefficient correlation R² is 0.9997. The standard adsorption free energy (*ΔG°*ads) is obtained according to the following equation:

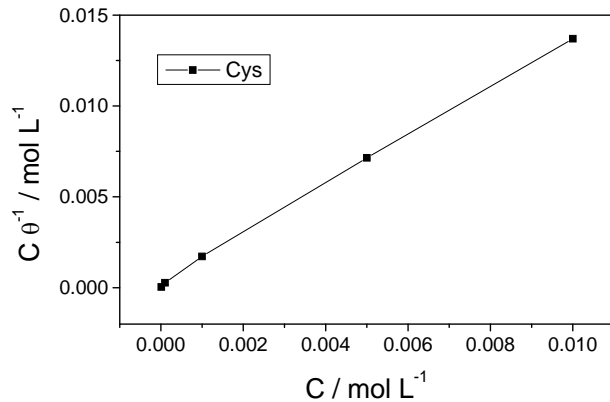$$K = \frac{1}{55.5} \exp(-\frac{\Delta G^\circ}{RT}) \tag{2}$$



**Fig. (3).** Langmuir isotherm adsorption model of Cys on the surface of copper in 1 mol L$^{-1}$ HNO$_3$.

The calculated value of $\Delta G^\circ_{ads}$ = -31.13 kJ mol$^{-1}$. The largest negative value of $\Delta G^\circ_{ads}$ indicates that Cys are strongly adsorbed on the pure copper surface. Literature shows that values which are negative than -30 kJ mol$^{-1}$ indicate chemisorption of Cys molecules [29].

### 3.2. Effect of the Temperature

#### 3.2.1. Wight-Loss Measurements

The effect of temperature on the corrosion behavior of pure copper in molar HNO$_3$ solution without and with Cys at 10$^{-2}$ mol L$^{-1}$ is studied by weight loss method. The corrosion

rates W$_{corr}$ calculated over the temperature range of 20 - 50°C are listed in Table **2**. It's obvious that W$_{corr}$ increases as the temperature increases and consequently (E%) values increased. The increase of (E%) values should be due to the increasing formation rate of Cu$^{2+}$-Cys complex [27, 30]. Therefore, we can suggest that the formation of the complex will increase as a function of temperature.

#### 3.2.2. Polarization Measurements

Fig. (**4**) shows the polarization curves for pure copper in molar HNO$_3$ in the absence and presence of Cys at 10$^{-2}$ mol L$^{-1}$ at different temperatures. The corresponding values of the electrochemical parameters are shown in Table **3**. From the results obtained, we observe that cathodic current-potential curves gave rise to Tafel lines indicating that the hydrogen evolution is activation-controlled. On the other hand, it's clear that the corrosion current density increases with the rise of temperature both in absence and presence of the inhibitor.

The increase in $I_{corr}$ is more pronounced with the rise of temperature for blank solution. In the presence of Cys, the attack of pure copper is highly reduced. It's noted that (E%) depends upon the temperature. The inhibition efficiency increases with the rise of temperature, it reaches 86% at 50°C. The same result was found elsewhere [1, 31, 32].

Fig. (**5**) shows Arrhenius plots of the corrosion rate of 1 mol L$^{-1}$ HNO$_3$ with and without 10$^{-2}$ mol L$^{-1}$ Cys. The values of apparent activation energies E$_a$ and E'$_a$ can be determined from Arrhenius plots according to following relations:

$$I_{corr} = A \exp(\frac{-E_a}{RT}) \ \text{ and } \ I'_{corr} = A \exp(\frac{-E'_a}{RT}) \tag{3}$$

where, E$_a$ = 54.84 kJ mol$^{-1}$ and E'$_a$ = 37.83 kJ mol$^{-1}$are, respectively, the apparent activation energies in absence and presence of Cys. The increase of (E%) as a function of temperature is explained by a specific interaction between the copper surface and the inhibitor [32, 33]. It's also stated that the corrosion process taking place in the presence of efficient inhibitors is characterised by an activation energy whose value is smaller than that of the uninhibited process [1, 32, 34]. This decrease of activation energy may be attributed to the process of chimisorption of Cys on the copper surface [1, 32, 35]. This result is confirmed by the determination of ΔG°ads.
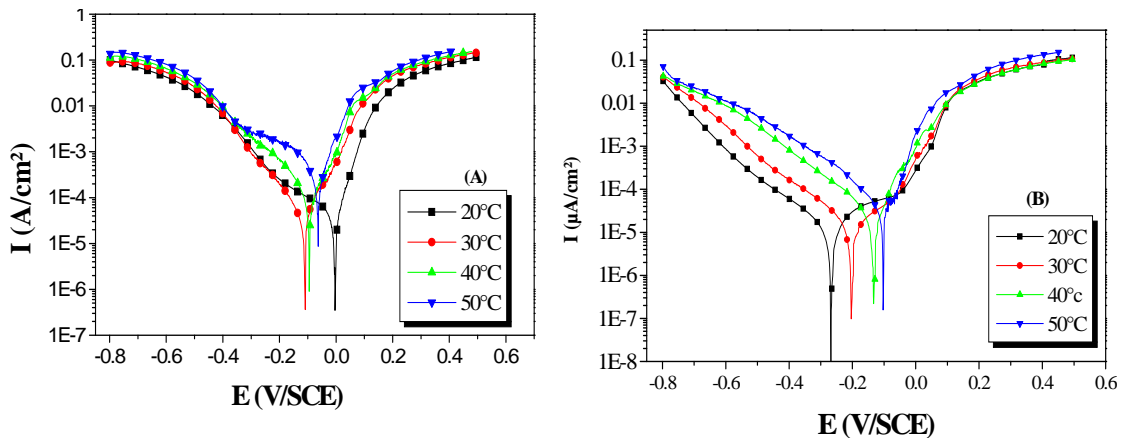


**Fig. (4).** Polarisation curves *I-E* of pure copper in: (**A**) 1 mol L$^{-1}$ HNO$_3$ (**B**) 1 mol L$^{-1}$ HNO$_3$ + 10$^{-2}$ mol L$^{-1}$ Cys at different temperatures.

**Table 2.**    Effect of Temperature on the Cu Corrosion in Molar $HNO_3$ and Added of $10^{-2}$ mol $L^{-1}$ of Cys

| T (°C) | $W_{corr}$ /(mg $h^{-1}$ $cm^{-2}$) | $W'_{corr}$ /(mg $h^{-1}$ $cm^{-2}$) | $E_G(\%)$ |
|---|---|---|---|
| 20 | 0.054 | 0.011 | 80 |
| 30 | 0.10 | 0.019 | 81 |
| 40 | 0.23 | 0.034 | 85 |
| 50 | 2.41 | 0.048 | 98 |

**Table 3.**    Electrochemical Characteristics Derived from Fig. (4)

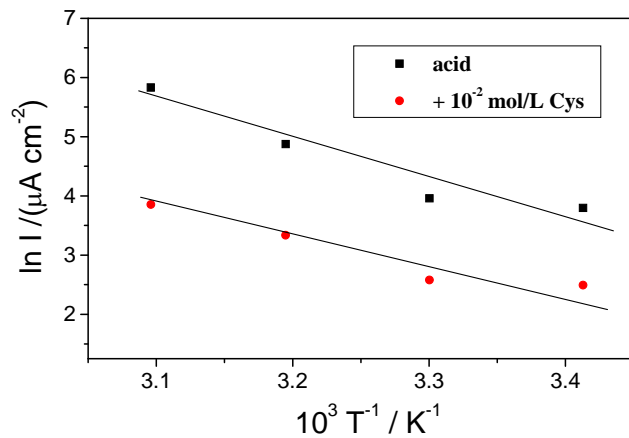| Solution | T (°C) | $E_{corr}$/(mV *vs* SCE) | $I_{corr}$/($\mu A$ $cm^{-2}$) | $b_c$/(mV $dec.^{-1}$) | $E_I(\%)$ |
|---|---|---|---|---|---|
| Blank | 20 | -4 | 44.5 | -179 | - |
| | 30 | -113 | 52.4 | -134 | - |
| | 40 | -95 | 131 | -133 | - |
| | 50 | -69 | 341 | -134 | - |
| Blank + $10^{-2}$ mol $L^{-1}$ Cys | 20 | -268 | 12.1 | -175 | 73 |
| | 30 | -203 | 13.2 | -175 | 75 |
| | 40 | -131 | 28.1 | -175 | 79 |
| | 50 | -105 | 47.2 | -175 | 86 |



**Fig. (5).** Arrhenius plots for pure copper in 1 mol $L^{-1}$ $HNO_3$ solution with and without Cys.

### 3.3. Effect of Immersion Time

Table **4** shows the variation of the weight loss $W_{corr}$ (mg.$cm^{-2}$) of copper at various times of immersion in 1 mol $L^{-1}$ $HNO_3$ at 20°C in the absence and presence of $10^{-2}$ mol $L^{-1}$ mol $L^{-1}$ of Cys. The examination of the data shows that the copper dissolution increased with time and reached a maximum value at 24h. In the presence of inhibitor, we observed that the attack of copper is highly reduced. Table **4** also shows that the inhibition efficiency ($E_R\%$) depends on the time immersion. It increased with time and attained a maximum value (96%) at 24h.

### 3.4. EIS Measurements

The corrosion behavior of copper in acidic solution in the presence and absence of Cyst at $10^{-2}$M, is also investigated by the electrochemical impedance spectroscopy (EIS) at 298 K after 30 min of immersion (Fig. **6**).

The charge-transfer resistance ($R_t$) values are calculated from the difference in impedance at lower and higher frequencies. To obtain the double layer capacitance ($C_{dl}$) the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) is found as represented in equation.

$$C_{dl} = \frac{1}{\omega . R_t} \quad \text{where } \omega = 2\pi f_{max}$$

The inhibition efficiency obtained from the charge transfer resistance is calculated by:

**Table 4.**    Weight Loss of Copper and Inhibition Efficiency of Cyst as Function of Immersion Time
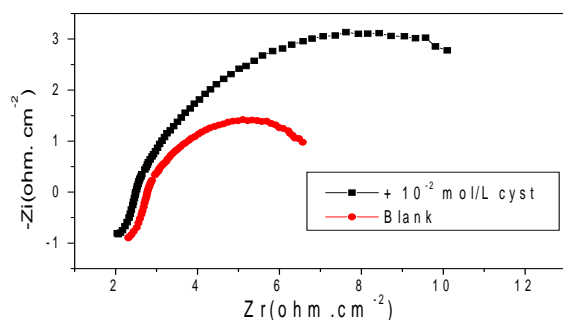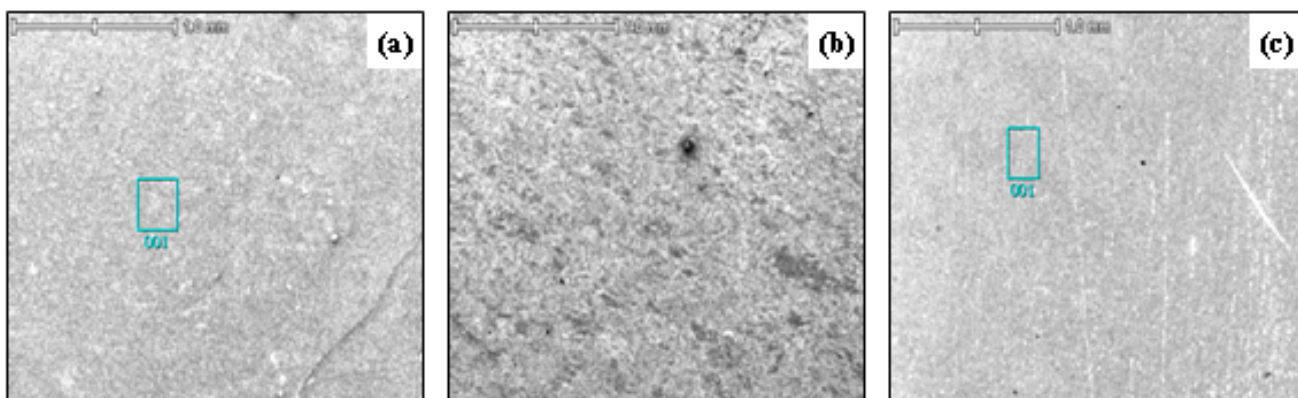
| T (min) | $W_{corr}$ (mg $h^{-1}$$cm^{-2}$) | $W'_{corr}$ (mg $h^{-1}$$cm^{-2}$) | E % |
|---|---|---|---|
| 2 | 0.7 | 0.5 | 28 |
| 4 | 2.6 | 0.53 | 80 |
| 16 | 12 | 1 | 92 |
| 24 | 68 | 2.6 | 96 |

**Table 5.    EIS Data of Copper in Nitric Acid with and without $10^{-2}$M Cyst**

|  | $R_t$ ($\Omega$ cm$^2$) | $C_{dl}$ ($\mu$F cm$^{-2}$) | $f_m$ (Hz) | E% |
|---|---|---|---|---|
| 1 M HNO$_3$ | 3.855 | 165 | 250 | - |
| + $10^{-2}$ M Cyst | 11.776 | 122 | 111 | 67 |

$$E(\%) = \frac{\left[ R_{t/_{inh}} - R_t \right]}{R_{t/_{inh}}}.100$$

$R_t$ and $R_{t/inh}$ are the charge transfer-resistance values with and without inhibitor, respectively.



**Fig. (6).** EIS diagrams of pure copper in free HNO$_3$ and added of $10^{-2}$ mol L$^{-1}$ Cys.

### 3.5. SEM Measurements

Fig. (**7**) shows the copper surface before corrosion and after immersion in nitric acid solution in the absence and presence of Cys at $10^{-2}$ mol L$^{-1}$ after 4h at 20°C.

From Fig. (**7a**), it can be observed that the fresh copper surface was uniform. However, after being corroded in molar HNO$_3$, the copper surface was damaged (Fig. **7b**). It is shown in Fig. (**7c**) that the presence of Cys keeps the quality of the surface similar to that of fresh Cu one. The result showed better corrosion resistance against copper corrosion in the acid media.

### 4. CONCLUSION

We have studied the inhibiting effect of the Cys compound in 1 mol L$^{-1}$ HNO$_3$ on the pure copper by using various methods. The results obtained are in good agreement and are given as follows.

1.    Cysteine was found to be an effective inhibitor for copper in 1M HNO$_3$ solution and its inhibition efficiency increases with its concentration and temperature.

2.    Cys acts as a mixed-type inhibitor and adsorbed on the copper surface according to Langmuir isotherm model.



**Fig. (7).** SEM images of copper surface : **a**) before corrosion, after immersion in nitric acid solution: (**b**) in the absence and (**c**) in the presence of Cys at $10^{-2}$ mol L$^{-1}$ after 4h at 20°C.

The data collected are gathered in Table **5**. As it can be seen from these results, when the concentration of inhibitor increases, $R_t$ increases and $C_{dl}$ tends to decrease. A decrease in the $C_{dl}$ values, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the cysteine acts by adsorption at the metal solution/interface [35].

3.    The inhibition efficiency of Cys increases with immersion time reaching a maximum value (96%) at 24h.

4.    The SEM images confirm the protection of copper corrosion in nitric acid solution by Cys.

### ACKNOWLEDGEMENTS

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