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Research

4-NAPHTHYL-3-THIOSEMICARBAZIDE as CORROSION INHIBITOR for COPPER in SEA WATER (3.5% SODIUM CHLORIDE)

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ABSTRACT

The effects of 4-NaTh-3-Thıosemicarbazide on the corrosion of Copper immersed in sea water has been evaluated. The inhibitor efficiency was determined by using three electrochemical techniques, Potential dynamic polarization (PDP), Impedance spectroscopy (EIS), and Open Circuite Potential (OCP) by using Potentiostat Instrument type compact stat (IVIUM) after immersion in sea water contain 3.5% Sodium chloride with presence and without corrosion inhibitor. A good inhibition efficiency is noticed which increases with an increase in corrosion inhibitor concentration. It was obtained that the inhibitor efficiency reached around 95% at 0,001 M from corrosion inhibitor. Both the cathodic and anodic curves are changed markedly in the presence of 4-NaTh-3-Thıosemıcarbazide. The mechanism of inhibition was proposed along the basis of the adsorption of the inhibitor molecules on the copper surface.

Keywords: 4-NaTh-3-Thiosemicarbazide, Copper, Electrochemical impedance spectroscopy, OCP

1. INTRODUCTION

Copper and its alloys are commonly used in manufacturing applications owing to its perfect properties, such as higher electrical conductivity and high thermal conductivity, mechanical strength and durability [1]-[2]. It is understood that the application of copper in a corroded atmosphere induces its corrosion and disintegration [3]-[4]. The investigation, which is the most suitable solution to protecting copper from degradation, also sets that as a concern. Given the past work carried out by various authors, the use of organic compounds is the most competent and financial tool for this reason [5]-[6]. These days' organic compounds are being investigated in different reactive applications as metal corrosion inhibitors [7]-[8]. Many of them are nevertheless toxic and harmful for the environment. Global work is undertaken to find a successful source of corrosion that is biodegradable and non-toxic to the ecosystem. In recent years, the use semicarbazide products (semicarbazones and thiosemicarbazones) are known to have an activity of antiviral, anti-infective and antineoplastic through binding to copper or iron in cells. Semicarbazide is used in preparing pharmaceuticals including nitrofuran antibacterial (furazolidone, nitrofurazone, nitrofurantoin) and related compounds. Thiosemicarbazide and its derivatives are used as corrosion inhibitors for different metallic substrates [9]. Corrosion inhibitors are chemical agents that are commonly used in corrosion systems to guard against degradation of materials. By forming a protective film on the copper surface and reducing the entry of aggressive ions into the concrete matrix, corrosion inhibitors offer protection. Throughout the following sequence are the inhibition capacity of homologous series of organic compounds, including different heteroatoms; P > Se > S > N > O [10]. Potential targets were identified to be other amides and derivatives such as urea (U), thiourea (TU), thioacetamide (TA), and thiosemicarbazide (TSC).

Thiosemicarbazide has been observed to be a potential inhibitor for different metals among various nitrogen and sulphur containing compounds. It has also been confirmed that its inhibitive performance can be significantly enhanced by its derivatives' (Fig.1) with certain aromatic compounds [11]. The very comportment of thiosemicarbazide and its derivatives products has opened a new avenue to examine the applicability for aqueous chloride systems of such compounds as corrosion inhibitors for copper.

The goal of this research was to investigate 4-Naphthyl-3-Thiosemicarbazide in sodium chloride solution as a corrosion inhibitor for copper by using electrochemical techniques of impedance spectroscopy, potentiodynamic polarization, and open circuit potential. All electrochemical techniques were used to calculate the inhibition efficiency of the inhibitors.

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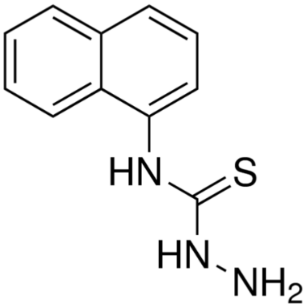

Figure.1 Structure of 4-Naphthyl-3-Thiosemıcarbazide

2. MATERIAL AND METHOD

Cylindrical specimens with a diameter of 0.75 cm were prepared from electrolytic copper (99.9 per cent) and used in the absence and presence of corrosion inhibitors to investigate copper corrosion. The specimens were bound by copper wire from the back, after which they were mounted in epoxy resin with an exposed surface of 0.44 cm^2 (Fig.2). Specimens have been polished using silicon carbide paper successively starting from 600 to 2400 grits to obtain a mirror like a finish. After polishing, the specimens were washed thoroughly with distilled water and dried with hot air.

4-NaTh-3-thiosemcarbazied has been selected and tested as a corrosion inhibitor. The chemically pure compound has been purchased from the Sigma Aldrich Company.

All electrochemical measurements were carried out using a COMPACTSTAT (IVIUM) type electrochemical analyzer instrument, as shown in Figure 3. For performing electrochemical tests three electrode corrosion cells made from 100 mL beaker glass size were used. The working electrode was the copper sample with 0.44 cm^2, a platinum wire was used as the counter electrode, while silver chloride (Ag / AgCl) was used as the reference electrode. All plots have been fitted to 1 cm^2.

Potentiodynamic polarization Copper sample measurements submerged in 3.5 per cent NaCl solution without and inside corrosion inhibitors were performed at a scan rate of 60 mV / min at room temperature. The potential started from a cathodic potential (-0.465 V) against corrosion potential (E_{corr}) and was allowed to sweep in anodic direction up to (0.035) volt above the E_{corr} and the potential scan was reversed to a potential E_{corr} equals. Corrosion parameters: corrosion current (I_{corr}), corrosion potential (E_{corr}) and corrosion rate (CR) were derived from the analysis of polarization plots using the IVIUM software.

The technique of **electrochemical spectroscopy (EIS)** was used to measure the corrosion activity of the copper samples without and inside corrosion inhibitors. Experiments were conducted at room temperature between 10 mHz and 65000 Hz at open-circuit potential over the frequency range. The voltage signal amplitude was 10 mV.

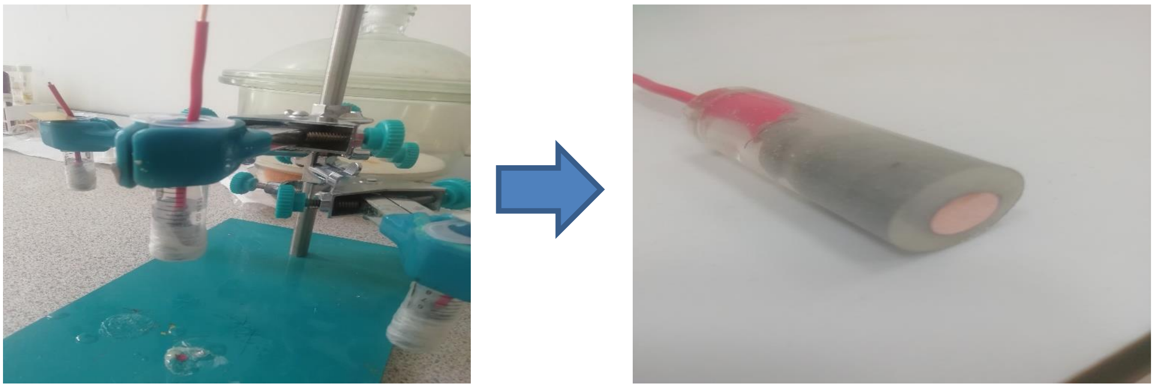

Figure 2. Sample preparation

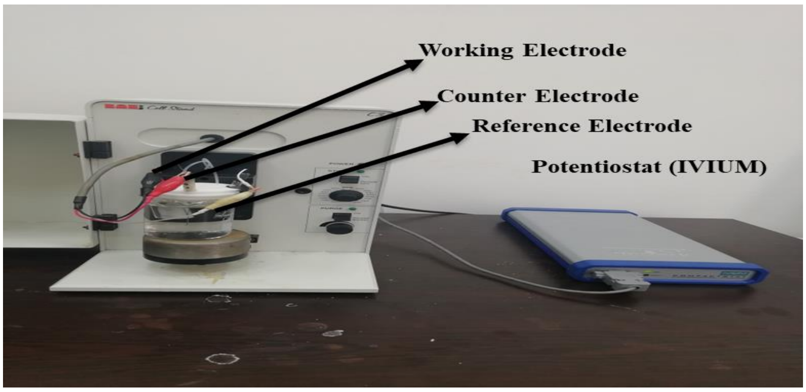

Figure 3. Potentiostat (IVIUM) and Electrochemical cell

3. RESULTS AND DISCUSSION

Fig.4 showed the open circuit potential for copper in 3.5 per cent NaCl, with and without inhibitor concentration. From figure (4) it can be seen that at the beginning of immersion time the value of the open circuit potential is shifted towards less negative meaning, which is believed to be the oxide layer due to figuration. After that, as the duration of immersion increases the value of the open-circuit potential decreases due to the breakdown of copper oxide by reaction as seen below and the creation of CuCl [12].

$$Cu + Cl^{-} \longrightarrow CuCl_{ads} + e^{-} \qquad (1)$$

In addition, it can be seen from Figure (3) that the existence of an inhibitor changed the open-circuit potential to less negative at the end of the experiment due to adsorption molecules on the active part of copper that contribute to the defense of the copper surface at the ingress of Cl-ion.

$$M \longrightarrow M^{+2} + 2e \qquad (2)$$

$$M + Inh_{ads} \longrightarrow [\,M - Inh]_{ads}^{2+.} \qquad (3)$$

Experiments of potentiodynamics polarization were used after the open circuit potential measurements were done. Potential for corrosion (E_{corr}), anodic (ba) and cathodic (bc) Tafel slopes, existing corrosion density ($I_{cor.}$) and inhibition capacity (IE%) were all measured and described in Table (1).

From Fig.5, it can be observed that when the concentration of inhibitors increased, the current density is reduced due to adsorption of inhibitor molecules on the copper surface. The adsorption of inhibitor molecules on the surface makes physical barrier to the mass and charge transfer, giving a high level of protection to the copper surface by hindering the active sites on the copper [13]. In addition, corrosion of potential marginally modified to less negative due to influence of inhibitor concentration and expected adsorption of the inhibitor molecules on the copper surface. It can also be seen from Fig.5 that both anodic and catholic curves shift dramatically with the inhibitor presence. The corrosion inhibitor can be classified as mixed type inhibitor due to shift E_{Corr} to lower than 0.085 V. The maximum displacement in the E_{Corr} with presence inhibitor was 0.04 V [14],[15],[16].

Nyquist and Bode graphs are seen from electrochemical impedance spectroscopy in figure (6), figure (7) respectively. It can be noticed from Fig.6 Nyquist curve for copper without inhibitor contain fading semicircular in the high frequency which is refer to the rudeness and inhomogeneity of electrode [17], while at low frequency the shape of plot is changed to straight line due to the diffusion of soluble copper species from copper surface to bulk solution [17]. Besides Fig.6 the diameter of the semicircle becomes larger with the presence of corrosion inhibitor due to the protection of the surface by corrosion inhibitor molecules can be noticed. From Fig.7 displays Bode graph, the phase angle can be seen increasing with a rise in the inhibitor concentration.

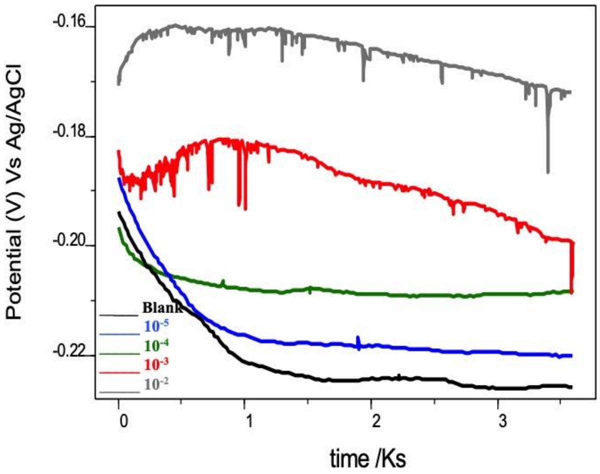

Figure 4. The open circuit potential of copper in 3.5% NaCl solution without and with the addition of different concentrations 4- NaTh-3-TSC

Table 1. Electrochemical parameters of copper corrosion in 3.5% NaCl without and with the addition of different concentrations of 4- NaTh-3-TSC

Conc.Inh.(M)	**$E_{corr,Vvs Ag/AgCl}$**	**j_{corr}, µA/cm2**	**ba, V/dec**	**bc,V/dec**	**CR$_{(mm/year)}$**	**EI%**
Blank	-0.250	8.5	0.068	0.27	0.11	----
10^{-5}	-0.245	6.8	0.047	0.289	0.085	20
10^{-4}	-0.232	1.8	0.065	0.258	0.02	78.8
10^{-3}	-0.224	1.1	0.072	0.298	0.01	87
10^{-2}	-0.210	0.817	0.091	0.295	0.009	90.3

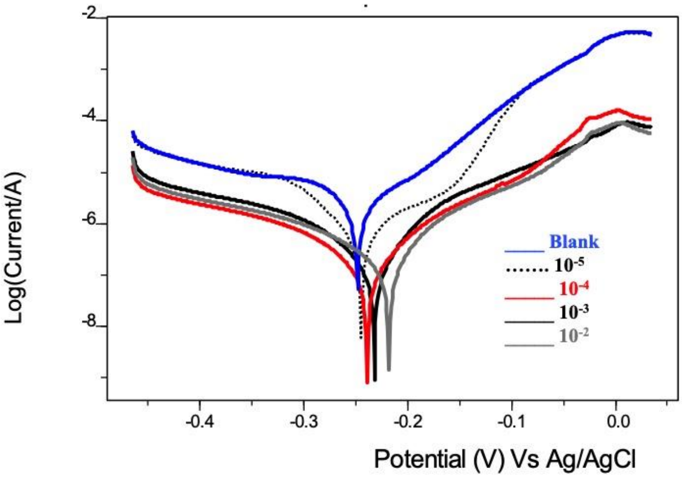

Figure 5. Potentiodynamic polarization curves of copper in 3.5% NaCl solution without and with the addition of different concentrations of 4- NaTh-3-TSC

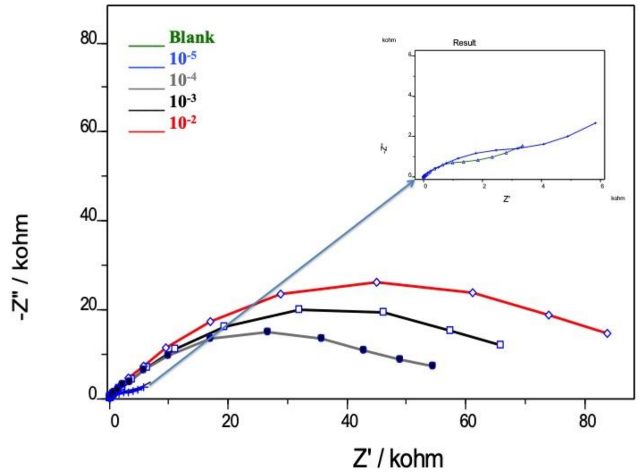

Figure 6. EIS diagrams for copper in 3.5% NaCl in the presence of different concentrations of 4-NaTh-3-TSC Nyquist plots

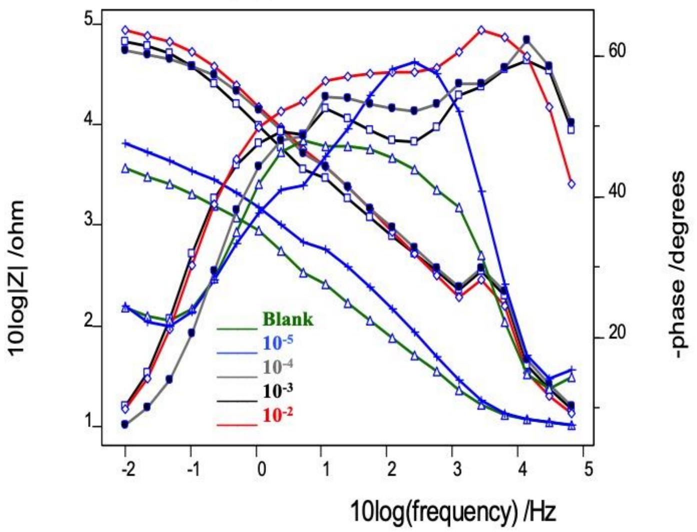

Figure 7. EIS diagrams for copper in 3.5% NaCl in the presence of different concentrations of 4-NaTh-3-TSC Bode phase angle and Bode modules.

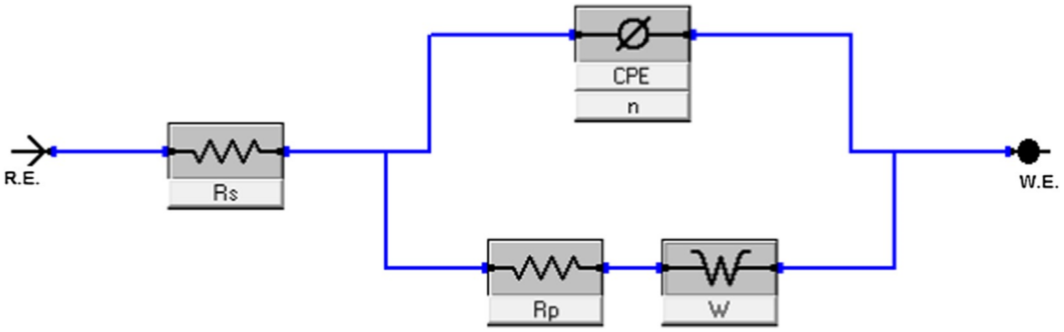

Figure 8. Equivalent circuit corresponding to fitted Electrochemical Impedance Spectroscopy data.

Table 2. Electrochemical impedance spectroscopy parameters for copper in 3.5% NaCl solution without and within the addition of different concentration of 4- NaTh-3-TSC

Conc. Inh.	**R_S, Ω cm2**	**R_P, Ω cm2**	**W, Ω−1 cm−2 s0.5**	**CPE**	**n**	**IE%**
Blank	5.757E+01	3.866E+03	1.128E-03	1.25E-04	0.77	-------
10^{-5}	5.499E+01	4.254E+03	7.689E-04	1.08E-04	0.86	9
10^{-4}	3.277E+02	5.262E+04	1.064E-03	1.47E-05	0.80	92.6
10^{-3}	4.943E+02	7.231E+04	6.379E+01	2.23E-05	0.89	94.6
10^{-2}	3.300E+02	8.995E+04	1.757E-03	1.49E-05	0.82	95.7

The parameters determined from equivalent circuit fitting for electrochemical impedance spectroscopy (Fig.8) and described in table (2). The efficiency of the corrosion inhibitor was calculated using equation, as shown below:

$$\%IE = [(R_p - R_P^{O}) / R_p]. 100 \tag{4}$$

The overall polarization resistance is R_p, R_P^{O} for copper electrode in the presence of a corrosion inhibitor and without the existence of corrosion, respectively. Table 2 indicates that the efficacy of the corrosion inhibitor has improved with an increase in the concentration of the inhibitor and increased the resistance of the protective inhibitor layer (R_p).
The most significant concept in the consumption inhibition cycle is the adsorption of the studied precursor to the metal surface. Diverse adsorption isotherms, including Langmuir, Frumkin, Freundlich, are frequently used to depict the inhibitor adsorption component.

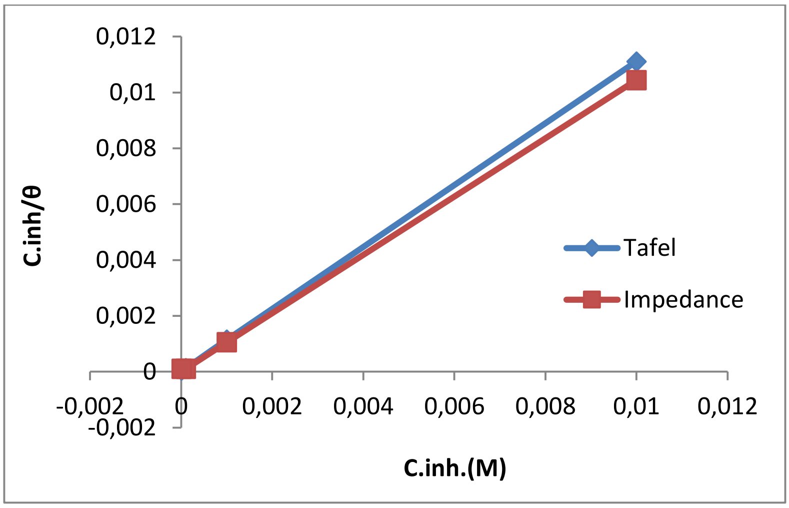

Figure 9. Langmuir adsorption isotherm of 4- NaTh-3-TSC on the copper surface.

Table 3. Langmuir adsorption parameters of 4- NaTh-3-TSC on copper surface in 3.5% NaCl solution

Method	**K_{ads}**	**R^2**	**−ΔGads,kJ/mol**
EIS	25000	0.99999	35.049
PDP	33333	1	35.762

In this work, the Langmuir adsorption isotherm, displayed by equation as shown below, was found to be the most suitable to fit the thread-effects of potentiodynamic polarization and estimates of electrochemical impedance [18].

$$C_{inh}/\theta = (1/K_{ads}) + C_{inh} \qquad (5)$$

where C_{inh} is the concentration of inhibitor, θ is the level of surface inclusion by inhibitor and K is the equilibrium constant of adsorptive.

The got plot of Cinh/θ versus inhibitor fixation (C_{inh}), (Fig.9) is straight showing that the Langmuir adsorption isotherms material to portray the adsorption of 4- NaTh-TSC. Likewise, the interaction coefficient (R2) calculation states that the 4- NaTh-TSC adsorption pursues the isotherm Langmuir. Additionally, this R2 estimate demonstrates that the 4-NaTh-TSC atoms on the terminal surface shaped a monomolecular layer [19]. Furthermore, as shown below, the free adsorption vitality of the Gibbs is determined by the equation:

$$-\Delta G_{ads} = [\ \ln(55.55\ K_{ads})]\ \mathrm{x}\ R\ \mathrm{x}\ T \qquad (6)$$

Where ΔG_{ads} is Gibbs free energy of adsorption, R is the molar gas constant, T the absolute temperature and 55.55 the molar concentration of water.

Table 3. Shows the value of ΔG_{ads}. The Gibbs free energy of adsorption (ΔG_{ads}) was -35.049 kJ mol^{-1} in case (EIS), while in case (PDP) Standard free energy of adsorption (ΔG^o) was -35.762 kJ mol^{-1}. The negative value of ΔG^o indicates the spontaneity of the adsorption reaction of the inhibitors on the copper surface. This also refers to chemisorption occurring in inhibitor interaction and copper surface where the exchange or move of load from the inhibitor molecules to the copper surface creates a coordinate kind of bond [20].

4. CONCLUSION

Potentiodynamic polarization, open-circuit potential and electrochemical impedance spectroscopy have been approved to use 4-NaTh-thiosemicarbazide as an effective copper corrosion inhibitor in solution comprising 3.5 % NaCl. The mechanism of the corrosion inhibitor is collected by adsorption on the copper surface and followed by the Langmuir adsorption isotherm. The higher efficacy of the corrosion inhibitor is nearly 95 % with a concentration of 10^{-2} of 4-NaTh-3-Thiosemicarbazide.

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