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RESEARCH ARTICLE

Corrosion Protection of Copper in Salt Medium by Poly 4-Hyroxyaniline Deposited via Electrodeposition Technique

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ABSTRACT

The polymer was used to inhibit the corrosion of copper metal in salt media in different concentrations at room temperature using potentiometric polarization measurement. The polymer was prepared by mixing (0.1 M) 4-Hydroxy aniline (C_6H_7NO) with (0.25M) of ammonium persulfate as the initiator using the electro-deposition technique. The polymer's results showed that copper in (3.5%) NaCl had good corrosion resistance. The findings demonstrate that the %IE for polymer-induced copper corrosion is 89.32% at 10 ppm concentration as a result of the 4-hydroxy aniline polymer's adsorption from salt solution on the surface of copper metal. The numbers from the polarization method and the acquired standard data agree well. The coated copper by polymer lowered the current density icorr compared to uncoated alloy.

Keywords: Anticorrosion, Copper, Electro deposition, Polymer, Saline water

Introduction

Corrosion is the physicochemical interaction between a metal and its environment, which results in changes in the metal's properties and which may lead to significant functional impairment of the metal, the environment, or the technical system of which they form a part.[1] The corrosive environment is either in the form of liquids or the form of air and gases, so it can be classified into two types, namely, wet corrosion where the corrosive environment is liquid (i.e. the environment is brine, acidic solutions, alkaline solutions or water) and dry corrosion, where the corrosive environment is a dry gas and is usually called chemical corrosion.[2] Many of inhibitors that used in industry are organic heterocyclic compounds. Organic heterocyclic inhibitors usually have hetero atoms. The type of mechanism that inhibitors applied was adsorption mechanism, these inhibitors form a preventative film on the metal surface.[3] The substantial difference of corrosion rate between the cathode and anode increases corrosion because of the oxygen concentration difference for example tanks of steel water were filled with water.[4] Due to its outstanding electrical and thermal conductivity and good mechanical workability, copper is a particularly popular metal in many industrial applications. However, when in contact with abrasive solutions, its corrosion resistance is frequently insufficient. In fact, passive film breakdown may happen in some situations that contain ions like chloride, sulfate, or nitrate copper, which can cause corrosion to spread.[5–7] Corrosion inhibitors are chemicals that successfully lower a metal's rate of corrosion when exposed to hostile fluid conditions. There is a lot of interest in using natural compounds as corrosion inhibitors because of the environmental constraints that are now in place for formulations of corrosion inhibitors.[8] Copper and its alloys are widely used in variety of products that enable and enhance our everyday lives. They have

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excellent electrical and thermal conductivities, exhibit good strength and formability. Copper, along with gold and rare meteoric alloys, is one of the few metals that are found in nature in the metallic state and is the only noble metal used as an engineering material.[9] Copper is also used as a material for piping in household water systems. In general, the corrosion process results in the loss of good material properties and economic losses to.[10] The presence of aggressive ions in different environments causes copper deterioration.[11] Chemicals known as inhibitors are adsorbed on a material's surface and work to slow down corrosion by either interacting with the working environment or the material.[12,13] The main functional groups capable of forming chemisorbed bonds with metal surfaces are amino (-NH_2), carboxyl (COOH), and phosphate (-PO_3H_2) although other functional groups or atoms can form coordinate bonds with metal surfaces.[14] Recently, there has been a lot of interest in the use of polymers as corrosion inhibitors. Because polymers can form complexes with metal ions through their functional groups and because these complexes occupy a vast surface area on the metal surface, they are utilized as corrosion inhibitors because they cover the metal's surface and shield it from corrosive chemicals in the solution. The structural relationship between these polymers' inhibitory ability and the heteroatoms (oxygen and nitrogen), which are the main active centers of adsorption, is cyclic rings.[15] These polymers are generally prepared by adding fillers in a polymeric matrix. One very common way, among the several methods for preparing conducting polymer blends or composites, is by mechanical mixing of the components.[16] Therefore, the aim of this research was to examine the resistance of corrosion for Poly 4-Hyroxyaniline in salt solution. According to the results, the polymer can protect copper from corrosion by adsorbing them on the copper surface while maintaining the electrochemical stability and structural integrity of the metal.

Materials and methods

Metal (copper)[9]

According to Table 1, copper was used as a metallic alloy, the chemical composition device was X-ray fluorescence.

Table 1. Chemical composition of the copper specimen.

Metal	Cu	Zn	Ni	P	Al	Mg	Si	Fe	Cr	Ag
Wt%	98.41	0.0040	0.0987	0.0012	0.0410	0.025	0.0012	0.1336	0.0595	1.226

Tools

1. Corrosion cell components
    A. Digital thermometer
    B. ELD Mod.9710
    C. Auto range: ± 200 + ocp
    D. Corrosion cell
    E. Magnetic stirrer
2. FT-IR Spectrophotometer.

Preparation of electrochemical system

The components of the electrochemical deposition system are:

1. Power source: A manually operated potentiostat measures potential E and current density (i) in steps.
2. Potential is measured by a voltmeter (V).
3. Density is measured by an ammeter (i).
4. Graphite electrode.

Methods

1. The first step was preparing **4-amino phenols.**

1- In a beaker, 0.55 gm of the monomer was mixed with 50ml of distilled water and placed for one hour on a magnetic stirrer.
2- The process was repeated at the same time with the initiator taking 1.4gm with 50ml of distilled water and placed on the magnetic stirrer for an hour.
3- Polymerization was conducted by mixing (0.1 M) 4-Hydroxy aniline (C_6H_7NO) with (0.25 M) of ammonium per sulfate as an initiator at 25°C temperature.
4- Precipitation of the material was made after mixing electrically with a voltage of 9.6 V as shown in Fig. 1.
5- Preparing different concentrations of polymer (10–40)[13] ppm.

The second step was using polymer to inhibit the corrosion of copper and before that most sample preparation included:

1. The investigated material was copper. The material was fabricated in circular with dimensions of 0.10 mm.

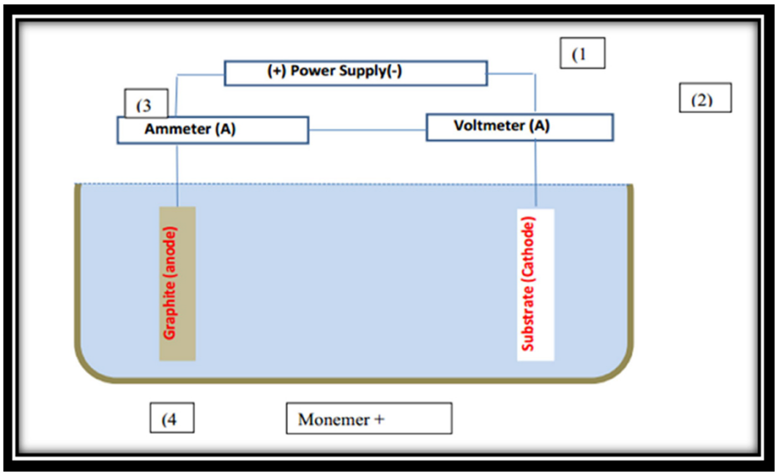

Fig. 1. The electrochemical deposition system.

2. The specimen copper was degreased with acetone and washed with distilled water and finally with ethanol.
3. The specimen was put inside desiccators for protecting and preventing them from oxidation.

Testing techniques

Preparation of corrosion cell

A corrosion cell, an electrode, and a potentiostat make up the electrochemical system.

a. A (1L) pyrex corrosion cell has two vessels: an inside vessel and an external vessel. A chiller was utilized to maintain the water's temperature at 25 °C as it travels through the exterior vessel.
b. Salt solution
   b. The NaCl solution concentration (3.5) %.
   c. In the internal vessel, three electrodes and the thermostat were replaced.

The three electrodes are explained as follows:

4. Reference electrodes are used to determine the working electrode potential according to the potential of the reference electrode. The reference electrode has a well-known and precise potential. It consists of two tubes, with AgCl, Ag, and KCL in the inner tube. The salt solution (3.5% NaCl) was poured into the outer tube. The working electrode was moved 2 mm away from the reference electrode.
5. Platinum metal of the highest purity makes up the (10 cm) long auxiliary electrode.
6. The study and test subject, whose potential will be evaluated, is the working electrode; it is made of a 20 cm metallic wire and attached to the mounted specimen. The corrosion cell[4] and the three electrodes are depicted in Fig. 2.

Fig. 2. The corrosion cell.

Results and discussion

Corrosion measurements evaluation

The polarization curves for copper were conducted by using tafel plots produced from potentiostatic scan ± 200 mv around the open circuit potential of the absence and presence of polymer in the different concentration specimens in 3.5% NaCl solution as shown in Fig. 3.

Tafel plots

Tafel plots provide data for corrosion current densities (icorr) and corrosion potentials (Ecorr), corrosion rates (CR), Tafel slopes, anodic region (βa), and cathodic region (βc), by a polarization curve (Ecorr vs. icorr), are given in Table 2.

The anodic and cathodic curves are moving towards reduced current density when inhibitors are present. Additionally, as inhibitors are added, icorr levels will

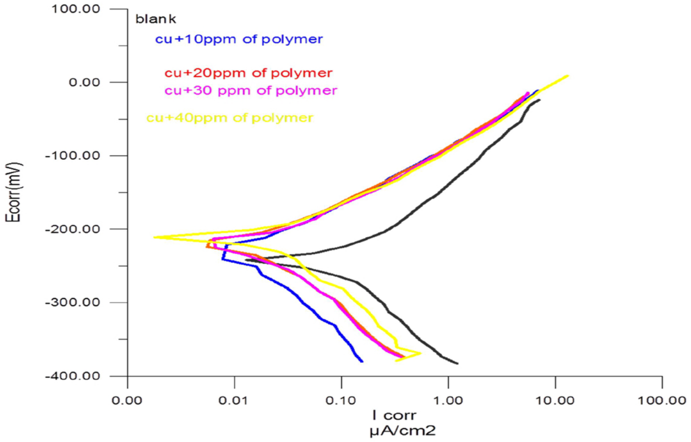

Fig. 3. Polarization plots for the corrosion of copper in 3.5% NaCl in the presence and at various polymer concentrations.

Table 2. Corrosion parameters result from the potentiodynamic polarization of copper in 3.5% NaCl with and without varying polymer concentrations.

Concentration of polymer	I corr μA/cm^2	-E corr (mv)	bc mv/dec	-ba mv/Dec	W.L g/md^2	P.L mm/a
Blank	89.49	241.7	138.9	89.4	1.43E+001	5.87E–001
10 ppm	9.55	230.9	99.8	61.3	3.12E+000	1.28E–001
20 ppm	13.52	221.6	92.8	67.2	3.85E+000	1.57E–001
30 ppm	15.31	223.3	98.2	68.3	4.36E+000	1.78E–001
40 ppm	18.90	210.2	105.2	62.2	5.38E+000	2.20E–001

decline Table 2 and Fig. 3. This demonstrates that inhibitor molecules are adsorbing on the surface of the metal.[17] The table shows that increasing concentration leads to increasing the corrosion current densities icorr. The optimum conditions for polymer in the salty solution are found in 10 ppm inhibition concentration corresponded to the lowest I_{corr} of 9.55 μA.cm^{-2}. The inhibition action is a proportional of the reduction reaction area on copper surface.[18]

Polarization resistances

Evaluating these parameters leads to the determination of the polarization resistance (Rp) as in the following Eq. (1);[19] will decline Table 3.

$$Rp = \frac{bc\ ba}{2.303\left(ba + bc\right) icorr} \qquad (1)$$

The results in the table above indicate that the metal surface is completely covered by the polymer coating at the focus 10 ppm since the polymer is more conductive than bare metals.[20]

Table 3. Values of the polarization resistance (Rp) for copper corrosion in 3.5% NaCl when polymer concentrations were absent and present.

Concentration of polymer	RpΩ/cm^{-2}(copper + polymer)
Blank	0.2639
10 ppm	1.72662
20 ppm	1.25177
30 ppm	1.1424
40 ppm	0.89835

Surface coverage (θ) and Inhibition Efficiency (%IE)

The corrosion protection abilities in saline water (3.5% NaCl), for copper with the presence and absence of polymer specimens were estimated from Tafel extrapolation plots will decline Table 4. The relation determining the inhibition efficiency (PE %) is shown in Eq. (2).[21]

$$\%IE = \frac{icorr* - icorr}{icorr*} \times 100 \qquad (2)$$

The corrosion rates for copper with the presence of polymer specimens decreased and the corrosion protection efficiencies %IE ranged between 89 to 78%.

Table 4. The surface coverage and inhibition efficiency PE% for copper corrosion in 3.5% NaCl in the absence and presence of various polymer concentrations.

Concentration of polymer	T(C°)	θ	%IE
10 ppm	20	0.8932	89.32
20 ppm	30	0.8489	84.89
30 ppm	40	0.8289	8289
40 ppm	50	0.7888	78.88

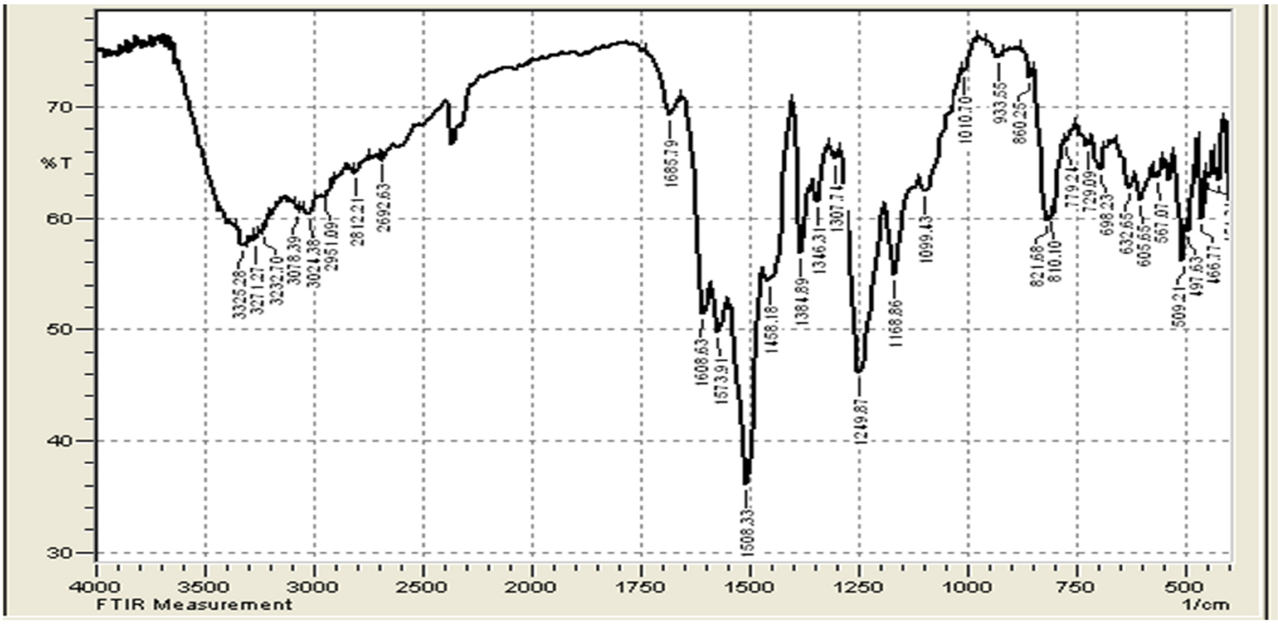

Fig. 4. Absorption of the poly-4-hydroxyaniline FT-IR spectra.

The more confident explanation of this positive enhancement of the %IE may be due to the catalytic action of the conducting polymer on the metal oxide layer which prevents penetration of the aggressive anions (Cl^-) to the substrate, the polymer serves as a mediator between the anodic current passive layer and the reduction of oxygen in the polymer film.[22] The corrosion rates are high in the absence of polymer but the poly4-hydroxy aniline coated ones got less increasing values due to the stability of the polymer layer at this range of concentration of polymer, other reflected facts are the good stabilities of the %IE values in 10ppm of inhibition.[23]

Fourier transform infrared spectrometer of Poly4-hyroxyaniline

Using an iPerkin Elmer FT-IR Spectrophotometer model 1720X, the Prepared Poly4-hyroxyaniline Polymer was identified in Fig. 4 and Table 5., both display the absorption bands.

Table 5. The Poly4-Hyroxyaniline absorption bands.

Vibration groups	Absorption bands (Cm^{-1})
Stretching vibration (O-H)	3323
Stretching vibration band (C-H) aromatic	3078
Stretching vibration (N-H)	2951
Stretching vibration band (C=C) to the benzene ring	1508
bending band (C-H) to the benzene ring	1249
Stretching bend N-ph	1168
Stretching band(C-H)to the benzene ring triplet compensation	810
Stretching vibration C-OH	509

Conclusion

This work describes the corrosion inhibition of copper in salt medium by Poly 4-Hyroxyaniline. Experimental results from potenciodynamic measurements. The results of the inhibition efficiency showed that the use of Poly 4-Hyroxyaniline for corrosion inhibition in salt media, can decrease the corrosion from 89.49 to 9.55 ($\mu A/cm^2$), also the inhibition efficiency reaches 89.32% and its high Rp, as well as its 10 ppm concentration due to, the adsorption of inhibitor from solution attachment to surface of copper in salt Medium copper in malt Medium.

Acknowledgment

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Authors' declaration

- Conflicts of Interest: None.
- We hereby confirm that all the figures and tables in the manuscript are ours. Furthermore, any figures and images, that are not ours, have been included with the necessary permission for re-publication, which is attached to the manuscript.
- No animal studies are presented in manuscript.
- No human studies are presented in manuscript.

- Ethical Clearance: The project was approved by the local ethical committee at University of Baghdad.

Authors' contribution statement

R. A. J.: conducted the preparation, analysis, curation of data, writing –main draft. A. M. F.: was responsible or resources, editing, conceptualization, visualization, analysis. N. J. K.: participated in analysis, writing, studying and organizing data. The final paper has been read and approved by all authors.

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حماية النحاس من التاكل في الوسط الملحي بواسطة ترسيب البولي 4- هيدروكسي انيلين عبر تقنية الترسيب الكهربائي

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المستخلص

استخدمت تراكيز مختلفة من البولمر المحضر لتثبيط تاكل النحاس عند درجة حرارة الغرفة. باستخدام قياس استقطاب الجهد. . تم تحضير البوليمر عن طريق مزج (0.1) مولاري4 -هيدروكسي أنيلين (C6H7NO) مع (0.25) مولاري من بيرسلفات الأمونيوم كبادئ باستخدام تقنيه الترسيب الكهربائي . بينت النتائج بوجود البولمر في 3.5% لكلوريد الصوديوم بانه مقاوم جيد للتاكل . وجد ان كفاءة التثبيط IE%للتاكل النحاس بوجود البوليمر تبلغ 89.32٪ تكون اعلى مايمكن عند تركيز (10ppm) للبولمرنتيجه لامتصاص بوليمر 4- هيدروكسي انلين على سطح معدن النحاس . تتوافق القيم المستحصله من طريقه الاستقطاب والبيانات القياسيه بشكل جيد.والنحاس المغطى بالبوليمر ذو كثافه تيار اوطا مقارنه السبيكه غير المغطى بالبوليمر.

الكلمات المفتاحية: مضادات التاكل، النحاس، طريقة الترسيب الكهربائي، البولمر، محلول ملحي.