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Original scientific paper

Corrosion inhibition performance of copper using N-benzylhydrazinecarbothioamide in a 3.5 % NaCl solution

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Abstract

In this report, N-benzylhydrazinecarbothioamide (BHCTA) was investigated as an organic inhibitor for the corrosion of copper substrate in 3.5 wt.% sodium chloride electrolyte at 298 K. The inhibition efficiency of BHCTA was examined using electrochemical, chemical and theoretical tools. The gained outcomes indicated a supreme inhibition efficiency of BHCTA which exceeded 95 % upon addition of 1.00 mM of BHCTA. Such supreme efficiency was discussed on the basis of decisive adsorption of BHCTA molecules on the copper substrate that hinders concurrently the anodic oxidation and cathodic reduction reactions progressions. The adsorption of BHCTA on the copper surface was discovered to obey Langmuir isotherm. The resulting value of $\Delta G_{ads}^0 = -35.7$ *kJ mol*$^{-1}$ *indicates that BHCTA molecules adsorb on the copper surface through a spontaneous mix of physisorption and chemisorption processes. A scanning electron microscope was used to examine the effect of BHCTA adsorption on the morphology of the copper surface. Theoretical calculations showed that BHCTA has good adsorption properties on Cu substrate. There is a good consistency between the applied experimental and theoretical tools, confirming the validity of the gained outcomes.*

Keywords
Copper corrosion; aqueous NaCl; organic inhibitor; adsorption

Introduction

Corrosion of metals is undoubtedly the most significant problem with significant financial consequences associated with utilizing metals in the workplaces. Similar to numerous metals, copper and its alloys are widely utilized in the chemical and electronic sectors because of their exceptional electrical conductivity, ductility, and corrosion resistance [1]. Copper-surface can readily develop an oxide layer in mild environmental conditions which has a slight protective effect, but copper can still sustain significant damage in environments where chloride ions are present. The rate of corrosion is usually reduced when a protective oxide layer forms on the metal surface. Unfortunately, some dissolved chemicals, especially nitrates, sulfates, and chlorides, weaken this barrier by producing soluble products. In water or other humid environments, copper will eventually undergo chemical degradation. As a result of these chemical attacks, the metal dissolves due to oxidation brought by dissolved oxygen. Localized and perhaps more dangerous pitting corrosion resulted from this. Applying corrosion inhibitors, or substances that can stop the corrosion process, strengthens metal resistance to corrosive chemicals. It is worth noting that one of the most important things that distinguishes heterocyclic organic inhibitors from others is that they contain some electron-donating atoms such as nitrogen, sulfur, and oxygen, which help them to adsorb spontaneously onto the surface of the metal and form a protective layer against corrosion.

Finding a potent copper inhibitor in a chloride solution has enormous practical significance. It is commonly agreed that the anodic dissolving of Cu in chloride surroundings is affected by the chloride content. At chloride content lesser than 1 M, the Cu dissolving happens *via* creation of CuCl, that is not sufficiently protecting and is changed to solvable CuCl_2^- *via* reaction with extra chloride [2,3]. The dissolving mechanism of Cu in chloride solutions can be described by equations (1) and (2):

$$Cu + Cl^- \leftrightarrow CuCl + e^- \tag{1}$$

$$CuCl + Cl^- \leftrightarrow CuCl_2^- + e^- \tag{2}$$

Higher complexes of copper, like $CuCl_3^{2-}$ and, $CuCl_4^{3-}$, as well as those with less chlorides, like CuCl and $CuCl_2^-$, are produced at concentrations greater than 1 M [3]. Using organic inhibitors is one of the most crucial strategies for shielding copper from corrosion [4]. Chen *et al.* investigated the organic inhibitor 2,4,6-trimercapto-1,3,5-triazine for copper corrosion in 0.5 M NaCl solution. It was demonstrated that the examined compound is a mixed corrosion inhibitor, with its highest corrosion inhibition efficacy reaching 95.6 % [5]. Liao *et al.* [6] investigated the combined effects of sodium diethyldithiocarbamate as a corrosion inhibitor for copper corrosion in 3 % NaCl solution that achieved 99 % protective efficacy. It is also important to remember that the main characteristic that sets benzyl hydrazine carbothioamide compounds apart from other materials, is their environmental safety. This allows for a variety of uses, particularly in the pharmaceutical and medical industries, where they can be used as effective corrosion inhibitors as well as for anti-inflammatory, analgesic, anti-bacterial, and anti-cancer purposes. In particular, benzyl hydrazine carbothioamide and related compounds are efficient inhibitors of corrosion. The polar groups of these compounds and their capacity to form combinations with the metal surface-an additional benefit-likely contribute to their improved adsorption on metallic surfaces under abrasive conditions. Furthermore, the abundance of π-electrons and pairs of unshared electrons in the nitrogen and sulfur atoms interact with the d-orbitals of any metal to create a shielding coating.

In view of all said above, the present work aims to explore the corrosion inhibition performance of copper by N-benzylhydrazinecarbothioamide (BHCTA) in a 3.5 wt.% NaCl solution at 298 K, using a number of chemical and electrochemical methods. Figure 1 displays the chemical structure of N-benzylhydrazinecarbothioamide (BHCTA). By joining various experimental outcomes and quantum chemical calculations, possible adsorption and inhibition mechanisms of BHCTA on the copper substrate can be revealed. To date, scientists remain interested in enhancing the heterocycles capacity to further inhibit metallic corrosion. Adding additional components or functions to their structure is one of the motivations of this work.

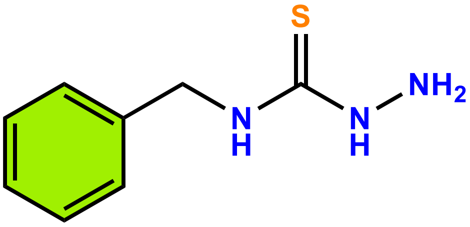

Figure 1. *Chemical structure of BHCTA inhibitor*

Experimental

Chemicals and reagents

All the chemical reagents employed in the experimentation were of analytical quality and not purified additionally. N-benzylhydrazinecarbothioamide with purity 97 % was obtained from Sigma Aldrich Co. USA., and sodium chloride extra pure AR, 99.9 %, ethanol from resident trader El-Nasr Co.

Working electrode (WE) and solution preparation

The working electrode (WE) was built of copper bar with 0.5 cm^2 exposed superficial area. The WE substrate was polished regularly with diverse grades of emery papers to a smooth substrate, and then decreased using ethanol/acetone mixture and blushed with water. For the preparation of the corrosive medium, 35.20 g of NaCl was dissolved in distilled water to obtain a concentration of 3.5 wt.%. Different concentrations (0.05 to 1.00 mM) of the inhibitor molecule (BHCTA) were prepared by dissolving the appropriate amounts of powder in distilled water. 1.00 mM of BHCTA

Weight-loss measurements

Using varying grades of emery papers, rectangular copper coupons of 5.0×3.0×0.3 cm were gradually polished, then degreased with ethanol/acetone mixture, blushing with water, and dried to be ready for tested. The coupons were weighed accurately and immersed in 3.5 wt.% NaCl electrolyte for 12 h, in the absence and presence of different dosages of BHCTA inhibitor at 298 K. The coupons were then removed, meticulously cleaned, rinsed with water, dried, and precisely weighed once again. In this test, three analogous coupons were performed, and the average corrosion rate was calculated. Equations (3)-(5) illustrate how corrosion rate (CR), surface coverage (θ), and corrosion inhibition efficiency (η_{WL} / %) were calculated:

$$CR = \frac{\Delta W}{St} \tag{3}$$

$$\theta = \frac{CR - CR_{\mathrm{Inh}}}{CR} \tag{4}$$

$$\eta_{\mathrm{WL}} = \left(\frac{CR - CR_{\mathrm{Inh}}}{CR} \right) 100 \tag{5}$$

where S is copper substrate area, cm^2; t is exposure time, h; CR and CR_{Inh} are corrosion rates, mg cm^{-2} h^{-1} in the absence and presence of BHCTA inhibitor, respectively.

Electrochemical measurements

Three-electrode setup was used in this study, where the Pt-electrode served as auxiliary electrode, Cu-electrode as WE, and the saturated calomel electrode (SCE) served as reference electrode. Using the Potentiostat/galvanostat Voltalab 80 and Voltamaster 4 software, the open circuit potential (OCP), electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PDP) curves were measured at 298 K. The study examined the corrosion behavior of WE in testing solutions without and with BHCTA inhibitor. EIS measurements were performed at OCP over the frequency range of 100 kHz-30 mHz, with a single amplitude perturbation of 10 mV. The impedance data was examined using ZsimpWIN software in accordance with the relevant equivalent circuit. At a sweep rate of 0.2 mV s^{-1}, the polarization curve was scanned within ±250 mV with respect to E_{corr}. Every electrochemical test was performed at 298 K. Each test included three parallel trials to guarantee the repeatability of data.

Quantum chemical calculations

Using Gaussian 09 software [7], the reaction between the BHCTA molecule and the Cu substrate was theoretically calculated. A 6-311G (d, p) basis set was used in DFT-B3LYP methods for the geometric optimization of the BHCTA molecule. Using Monte Carlo simulation, the strength of the interactions between the investigated chemical and the copper surface was ascertained. The Materials Studio program was used to run these simulations. The Cu (111) surface was used in these simulations, and the details that were used were the crystallographic force area, 303 K temperature, NVT group, and a time step of 1 fs.

Surface morphology examination

In order to evaluate the substrate morphology, copper was submerged in a 3.5 wt.% NaCl solution for a full day, both with and without a 1 mM BHCTA inhibitor. After rinsing the copper substrate with bi-distilled water, it was dehydrated at ambient temperature. The Cu substrate morphological investigations were assessed by JOEL MODEL 6390.

Results and discussion

Open circuit potential (OCP) assessment

Figure 2 shows the OCP fluctuation of Cu electrode in 3.5 wt.% of NaCl electrolyte as a function of time, in the absence and presence of different dosages of BHCTA inhibitor at 298 K.

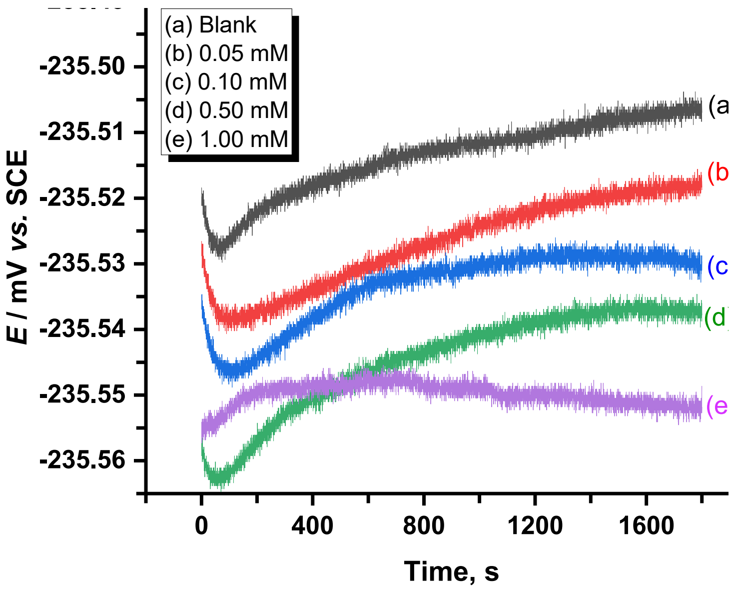

Figure 2. *OCP curves for corrosion of Cu in 3.5 wt.% NaCl solution in the absence and presence of different concentrations of BHCTA inhibitor at 298 K*

The constant potential, which corresponds to E_{corr} of Cu electrode, was easily reached in NaCl solution [8]. Physical electrostatic attraction takes place between the positive charge of the protonated BHCTA molecules and the negative charge of the Cu electrode in inhibited NaCl electrolyte. It was reported [9] that an organic inhibitor can be classified as either anodic or cathodic type inhibitor if its OCP movement differs by at least 85 mV from the measurement made for the blank uninhibited electrolyte. Figure 2 shows that in the presence of the examined inhibitor, the shift in E_{corr} is rather small and so, the BHCTA may be considered as inhibitor of a mixed-type.

Potentiodynamic polarization (PDP) assessment

For assessment of the appropriateness of the BHCTA inhibitor for Cu electrode in 3.5 wt.% NaCl electrolyte, the potentiodynamic polarization (PDP) measurements at 298 K were investigated. Figure 3 displays the PDP for corrosion of Cu tested in 3.5 wt.% NaCl electrolyte in the absence and presence of four different dosages of BHCTA inhibitor. The parameters from the PDP tests such as anodic Tafel slope (β_a), cathodic Tafel slope (β_c), corrosion current density (i_{corr}), and corrosion potential (E_{corr}) were obtained using Voltmaster software attached to Potentiostat/Galvanostat Voltalab 80. It is obvious that by addition of BHCTA inhibitor to the blank electrolyte (3.5 wt.% NaCl), the anodic dissolving of Cu electrode and the cathodic progression decreased. The values of i_{corr} were decreased from 5.1717 µA cm^{-2} for the blank electrolyte to 0.2896 µA cm^{-2} for the inhibited electrolyte with 1 mM of BHCTA. Because it reduces both anodic and cathodic processes, the BHCTA inhibitor can be regarded as a mixed-type inhibitor [10]. The anode dissolution speed slows down as a result of BHCTA molecules being adsorbed on the Cu substrate, limiting the anode reaction active sites. This is owing to the adsorption of BHCTA inhibitor molecules on the active positions of Cu substrate by growing surface handling, and creating a barrier film that delays dissolving of Cu electrode. To assess the efficacy of BHCTA inhibitor to overturn dissolving of the Cu electrode in 3.5 wt.% NaCl electrolyte, the inhibition effectiveness (η_{PDP}, %) was considered using equation (6) [11]:

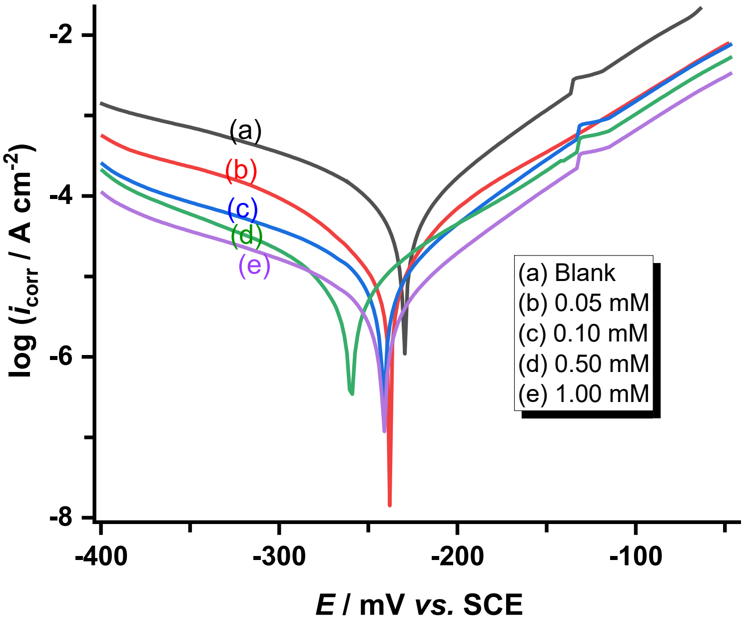

Figure 3. *PDP curves for the corrosion of Cu in 3.5 wt.% NaCl solution in the absence and presence of different concentrations of BHCTA inhibitor at 298 K*

$$\eta_{\text{PDP}} = \left(\frac{i_{\text{corr}}{}^0 - i_{\text{corr}}}{i_{\text{corr}}{}^0} \right) 100 \tag{6}$$

where $i_{corr}{}^0$ and i_{corr} denote the values of corrosion current density (μA cm^{-2}) of the Cu electrode in 3.5 wt.% NaCl electrolyte without and with of BHCTA inhibitor, respectively.

The assessed values of PDP parameters are summarized in Table 1. With varying BHCTA inhibitor doses, the Tafel slopes display key features [12]. The η_{PDP} increases dramatically and the i_{corr} reduces rapidly when the concentration of BHCTA corrosion inhibitors rises. It discloses that the i_{corr} decreased by addition of BHCTA inhibitor, and E_{corr} moves slightly to more negative values. Clearly, the η_{PDP} is improved by using BHCTA as organic inhibitor. The maximum inhibition efficiency (94.4 %) was reached at 1.00 mM of BHCTA inhibitor.

Table 1. *PDP parameters for Cu corrosion in 3.5 wt.% NaCl solution in the absence and presence of different concentrations of BHCTA inhibitor at 298 K*

C_{BHCTA} / mM	$-E_{corr}$ / mV	i_{corr} / μA cm^{-2}	β_a / mV dec^{-1}	$-\beta_c$ / mV dec^{-1}	η_{PDP} / %
0.00 (blank)	229.5	5.17	84	171	-
0.05	237.8	1.61	78	165	68.9
0.10	240.7	0.95	73	153	81.7
0.50	240.9	0.48	76	139	90.8
1.00	258.8	0.29	77	127	94.4

Electrochemical impedance spectroscopy assessment

The behavior of organic inhibitors in inhibiting corrosion process and protective mechanism of inhibitors on metals are usually studied using Electrochemical impedance spectroscopy (EIS) . Figure 4 shows the Nyquist and Bode plots of Cu electrode in 3.5 wt.% NaCl electrolyte without and with various dosages of BHCTA inhibitor at 298 K. Figure 4(a) displays the Nyquist plots of copper in 3.5 % NaCl solutions with and without BHCTA molecules. Depressed semicircular forms are evidently produced. Nyquist curves show that diameter of the semicircle rises when the BHCTA inhibitor is present. This indicates that the inclusion of BHCTA enhances the inhibition process without altering other components of the corrosion mechanism.

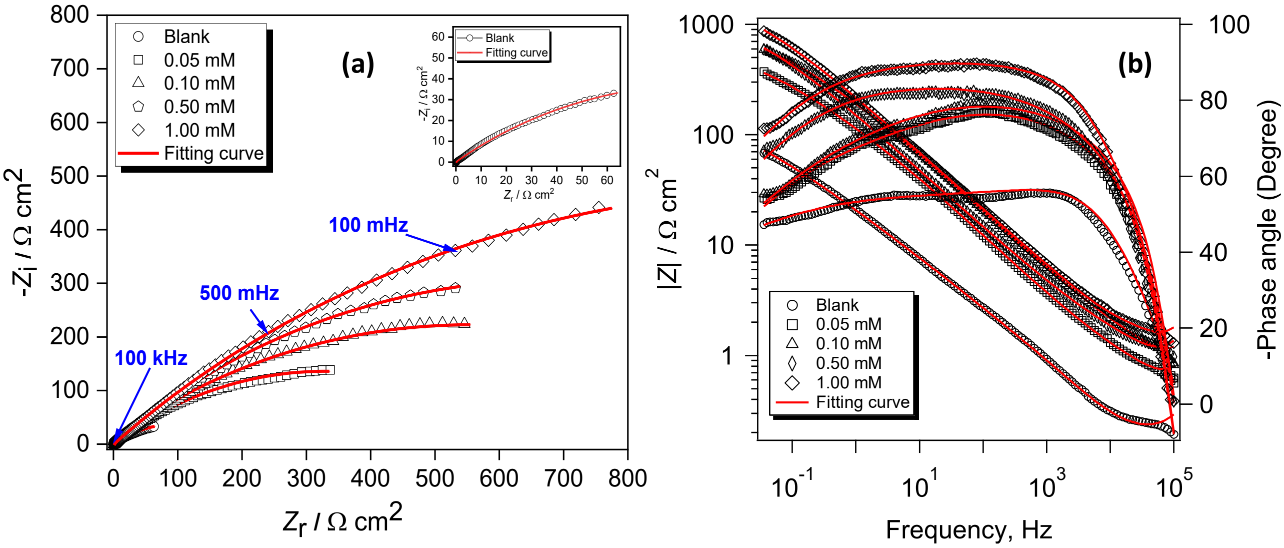

Figure 4. *EIS spectra represented as (a) Nyquist plots and (b) Bode plots for Cu corrosion in 3.5 wt.% NaCl solution in the absence and presence of different concentrations of BHCTA inhibitor at 298 K*

The produced Nyquist plots of copper corrosion in 3.5 % NaCl solutions did not provide ideal semicircles, what is typical behavior of solid electrodes and is frequently ascribed to the roughness caused by the heterogeneity of the electrode surface, and inhibitor adsorption. High-frequency semicircles are frequently thought of as being produced by the charge transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}). As the concentration of BHCTA rises, more molecules of the compound are adsorbed on the Cu surface, forming a more compact protective coating, which causes the diameter of the capacitance arc to be increased [13]. It can be seen in Figure 4(a), that the maximum diameter of capacitance arc is reached when the BHCTA concentration becomes 1.00 mM. At large concentrations, the sulfur, amino groups, and benzene rings present in BHCTA molecules can form molecular collections in the form of hydrogen bonds. This could be the cause of extremely high corrosion inhibition value of BHCTA molecules.

Bode modulus plots for Cu electrode in 3.5 wt.% NaCl solution in the absence and presence of BHCTA inhibitor are presented in Figure 4(b). Bode plots show that the impedance moduli increase markedly with BHCTA concentrations compared with that of the blank electrode. Since BHCTA effectively blocked the copper surface from corroding, the rise in impedance modulus and phase angle can be explained. The impedance data was fitted and analyzed using the equivalent circuits $R_s(Q)R_{ct}$. In this case, R_{ct} is the charge transfer resistance and R_s is the solution resistance. The double-layer capacitor with some pores is represented by the CPE (Q, n), which n values are close to unity. The double-layer capacitors within certain pores are usually represented by CPEs within n values $1 > n > 0$ [14]. Examining the data shown in Figure 4b, increasing measured impedance moduli with increasing inhibitor concentrations may lead to increased CPE impedance and decreased Q values. The R_{ct} can be used to compute the inhibition efficiency (η_{EIS} / %) of BHCTA for the Cu electrode in the manner shown by equation (7) [15]:

$$\eta_{EIS} = \left(\frac{R_{ct} - R_{ct}^{0}}{R_{ct}} \right) 100 \tag{7}$$

where R_{ct}^0 and R_{ct} denote the charge transfer resistances of the Cu electrode in 3.5 wt.% NaCl electrolyte without and with BHCTA inhibitor, respectively. For the copper electrode in the corrosive solution without inhibitor, the R_{ct}^0 value was determined to be 203 Ω cm^2. It was discovered that the R_{ct} values climbed to 652, 1066, 2503 and 3126 Ω cm^2 at concentrations of 0.05, 0.10, 0,50 and 1.00 mM. As a result, the inhibition efficiency increased by 69, 81.1, 91.9 and 93.6 %, respectively. The R_{ct} values rises as the concentration of BHCTA rises because more BHCTA molecules are adsorbed on the Cu electrodes. The findings show that BHCTA molecules have an easy time adhering to the copper surface and achieving an equilibrium of adsorption that prevents copper corrosion.

Weight loss assessment

The corrosion rates and anti-corrosion efficiencies for copper samples inhibited with various concentrations of BHCTA after immersion in 3.5 wt.% NaCl solution for 12 h at 298 K using weight loss test are listed in Table 2 and plotted in Figure 5. As can be seen from Figure 5, the addition of BHCTA inhibits the corrosion of copper at various concentrations. Data in Table 2 show that the corrosion rate decreases with the increase of BHCTA concentration up to 1.00 mM.

Table 2. *WL parameters calculated for corrosion of Cu in 3.5 wt.% NaCl solution in the absence and presence of different concentrations of BHCTA inhibitor at 298 K*

C_{BHCTA} / mM	CR / mg cm^{-2} h^{-1}	θ	η_{WL} / %
0.00 (blank)	0.0131	–	–
0.05	0.00435	0.668	66.8
0.10	0.00257	0.804	80.4
0.50	0.00117	0.911	91.1
1.00	0.00062	0.953	95.3

The weight loss data show that BHCTA has the best inhibiting effect at 1.00 mM at which the maximum inhibition efficiency reached 95.3 %. This demonstrates how the BHCTA molecules prevent copper corrosion. As recorded in Table 2, higher inhibition of BHCTA molecules is related to the active centers of lone pairs of heteroatoms as well as π-electrons of benzene ring that increase the adsorption progression at the Cu substrate [16].

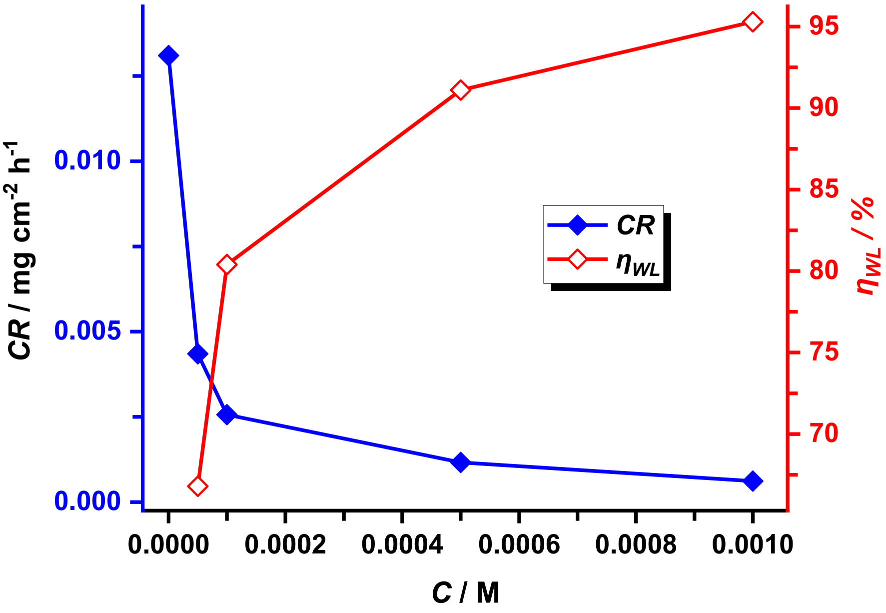

Figure 5. *Variation of CR and η_{WL} of Cu in 3.5 wt.% NaCl solution in the absence and presence of different concentrations of BHCTA inhibitor at 298 K*

Adsorption isotherms

The interaction of organic particles on a metal substrate is a regular dislocation interaction, in which H_2O particles adsorbed at the metal substrate are exchanged by inhibitor molecules. The isotherm parameters of adsorption process make a significant base for elucidation the interaction between the organic particles and the metal substrate. The inhibitor dosage is correlated to the expanse of inhibitor molecules adsorbed on the metal substrate, and displacement adsorption progression is stated by equation (8):

$$\text{Inhibitor}_{(\text{sol})} + x\text{H}_2\text{O}_{(\text{ads})} \leftrightarrow \text{Inhibitor}_{(\text{ads})} + x\text{H}_2\text{O}_{(\text{sol})} \tag{8}$$

where *x* denotes the quantity of H_2O molecules that is replaced by an organic molecule during a displacement process. On the basis of weight loss data, the adsorption behavior of BHCTA molecules on the Cu substrate in 3.5 wt.% NaCl solution in the presence of different concentrations of BHCTA at 298 K was modeled with various isotherms, *i.e.* Langmuir, Temkin, Freundlich and Frumkin isotherms as illustrated in Figure 6(a-d). Among these four types of isotherms, the Langmuir isotherm was found as the best fitting model (R^2 = 0.9998). The Langmuir isotherm design can be represented by equation (9) [17]:

$$\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}} \tag{9}$$

where θ and K_{ads} denote the surface coverage calculated from the weight loss results, and the equilibrium constant of adsorption, respectively.

Figure 6 (a) of Langmuir isotherm which signifies a linear relation between C_{inh}/θ and C_{inh} suggests that BHCTA molecules adsorbed on Cu substrate adapt to Langmuir model. The calculated value of $K_{\text{ads}} = 33.33\times10^3$ L mol^{-1}, demonstrates high adsorption capacity of BHCTA molecules on the Cu substrate. The slope of Langmuir plot was found to be 1.0286, which implies that only one BHCTA molecule may roughly replace one water molecule.

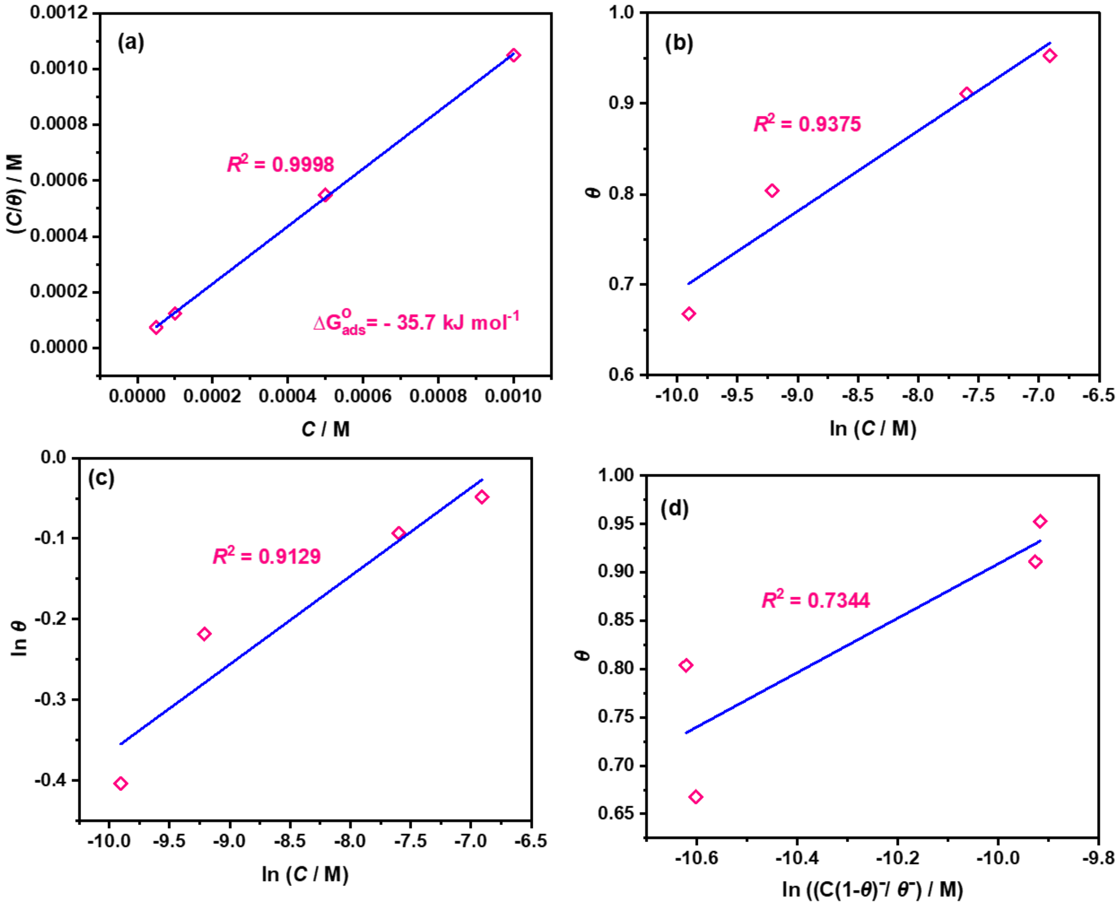

Figure 6. *Adsorption isotherm models of (a) Langmuir, (b) Temkin, (c) Freundlich, and (d) Frumkin, for the corrosion of Cu in 3.5 wt.% NaCl solution in the presence of different concentrations of BHCTA inhibitor at 298 K*

The Gibbs-free energy ($\Delta G_{\text{ads}}{}^0$) can be calculated using the value of K_{ads} *via* equation (10) [18]:

$$K_{\text{ads}} = \frac{1}{55.5}\exp\left(\frac{-\Delta G_{\text{ads}}{}^0}{RT}\right) \tag{10}$$

where R and T display the universal gas constant (8.314 J mol^{-1} K^{-1}) and thermodynamic temperature, K, respectively. The number 55.5 is related to the quantity of H_2O in the electrolyte, mol L^{-1}. An increased spontaneous adsorption reaction is generally indicated by larger K_{ads} and higher negative $\Delta G_{\text{ads}}{}^0$ values. Physisorption is supported by values of $\Delta G_{\text{ads}}{}^0$ about −20 kJ mol^{-1}, whereas chemisorption is implied by values around −40 kJ mol^{-1} or higher. The result of $\Delta G_{\text{ads}}{}^0$, which is −35.7 kJ mol^{-1}, suggests that a combination of physisorption and chemisorption processes is involved in the adsorption of BHCTA molecules on the copper surface.

Quantum chemistry assessment

Quantum chemical calculations are the most efficient way of investigating the connection between corrosion inhibition efficiency and molecular structure of inhibitor molecules [19]. In this investigation, the inhibition effect of BHCTA molecules on the copper substrate was investigated through density functional theory (DFT) calculations. The optimized geometric construction of the BHCTA molecule, as well as the electron densities of the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are displayed in Figure 7.

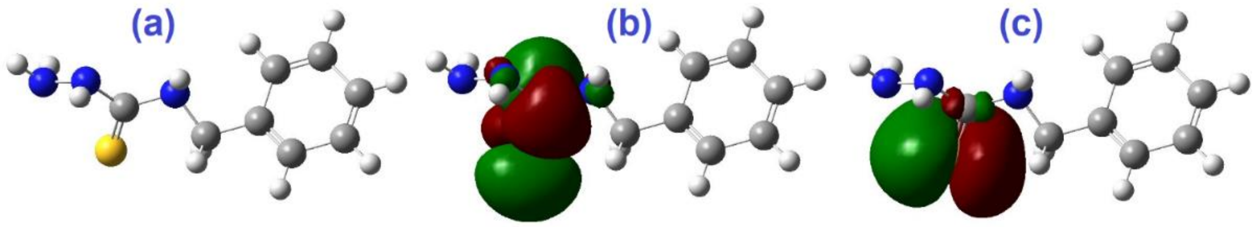

Figure 7. *Optimized structure (a) and frontier orbital distribution of BHCTA molecule (b) LUMO and (c) HOMO*

Generally, higher value of E_{HOMO} of inhibitor molecule denotes a stronger ability to supply metals with electrons [20]. In contrast, higher electron acceptability of inhibitor is indicated by a lower E_{LUMO} value. As a result, BHCTA corrosion inhibitor molecules have good adsorption on the copper surface through electron transfer from the unshared pair of electrons of S and N atoms to the vacant d-orbitals of copper, as well as π-electrons of the benzene ring. They perform well against corrosion in addition to the reverse retransfer of Cu atom valence electrons to BHCTA molecules. As per the Koopman formula, the ionization potential, $I = -E_{\mathrm{HOMO}}$ and electron affinity, $A = -E_{\mathrm{LUMO}}$, were considered as I = 8.261 eV and A = −4.536 eV. The electronegativity (χ), hardness (η) and fraction of electrons transferred (ΔN) can be considered based on equations (11) - (13) [21]:

$$\chi = \frac{I+A}{2} \tag{11}$$

$$\eta = \frac{I-A}{2} \tag{12}$$

$$\Delta N = \frac{\chi_{\mathrm{Cu}} - \chi_{\mathrm{inh}}}{2(\eta_{\mathrm{Cu}} + \eta_{\mathrm{inh}})} \tag{13}$$

The χ_{inh} and η_{inh} values were calculated to be 1.863 and 6.399 eV mol^{-1}, respectively while the values of χ_{inh} and η_{inh} for copper are 4.48 and 0 eV mol^{-1}, respectively. Furthermore, the dipole moment is considered as a crucial indicator for the reactivity of organic molecules as corrosion inhibitor. The higher dipole moment values in conjunction with lower energy gap ($\Delta E = E_{\mathrm{LUMO}} - E_{\mathrm{HOMO}}$) values will encourage the accumulation of the inhibitor on the metal surface, thereby enhancing the inhibition efficiency [22]. The calculated dipole moment for BHCTA molecules was found, μ = 3.131 D, indicating higher inhibition efficiency. According to Lukovits *et al*. [23], the inhibitor efficiency rose as its ability to supply electrons improved if the fraction of electrons transferred (ΔN) was less than 3.6. The computed ΔN of BHCTA inhibitor of 0.205 eV indicates that the BHCTA forms anti-corrosion adsorption layers on the copper surface through electron donor bonding.

Monte Carlo simulation assessment

Monte Carlo simulation was used to understand the inhibitory process and locate low adsorption energy (E_{ads}) sites on the metal surface [24]. This made it possible for researchers to determine the inhibitor preferential adsorption [25]. Preferred adsorption sites on metal surfaces are often described using these techniques. The simulation results and the configurations of the BHCTA molecule adsorption equilibrium on the Cu substrate are shown in Figure 8, where adsorption orientation of inhibitor on the Cu surface is almost flat. Based on Monte Carlo simulation, the adsorption energy (E_{ads}) of the BHCTA molecules was found to be -2025 kJ mol^{-1}. The strong chemical bond that BHCTA molecules create with Cu(111) surface demonstrates the high effectiveness of these molecules in preventing Cu corrosion. Additionally, they highlighted the effects of dipole interactions and electronic transmission from the adsorbate to the substrate. Consequently, it is supposed that the adsorption of BHCTA on the Cu substrate insulates the invasion of Cl^- ions.

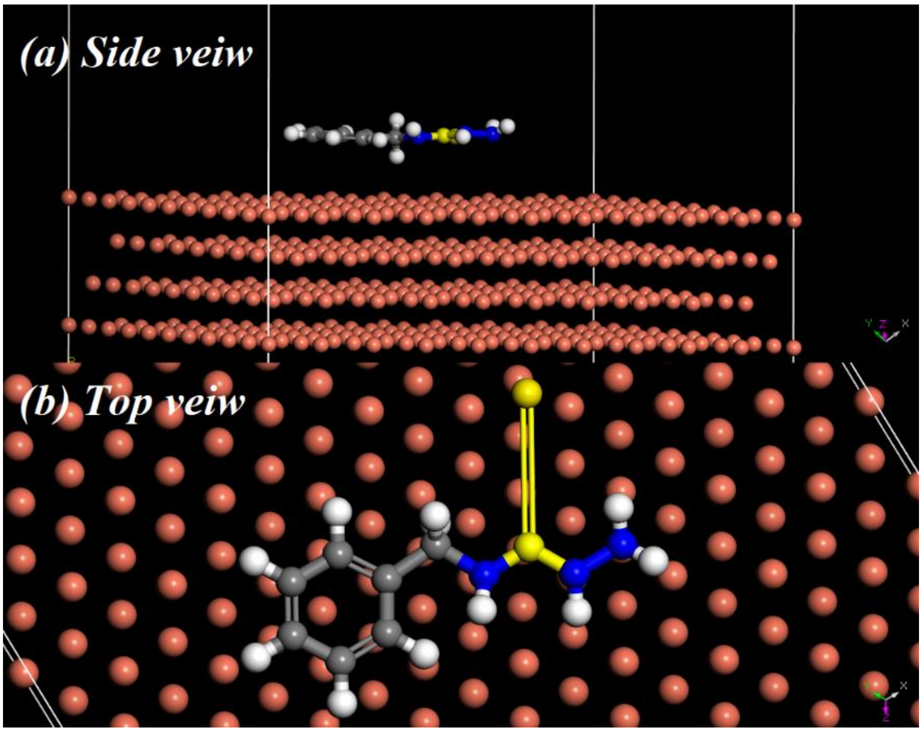

Figure 8. *Side (a) and top (b) views of adsorption position of BHCTA molecule on Cu surface*

Surface inspection

SEM images of the copper substrate after 12 h immersion in 3.5 wt.% NaCl solution without and with 1.00 mM of BHCTA inhibitor, are shown in Figure 9(a) and 9(b), respectively. Figure 9(a) depicts severe damage to the copper substrate as a result of the aggressiveness of corrosive 3.5 % NaCl electrolyte in the absence of an inhibitor. Figure 9(b), on the other hand, shows uniform and protected copper substrate after the addition of BHCTA inhibitor molecules to the corrosive electrolyte. This is due to the significant adsorption of BHCTA inhibitor molecules on the copper substrate, which protects its surface [26].

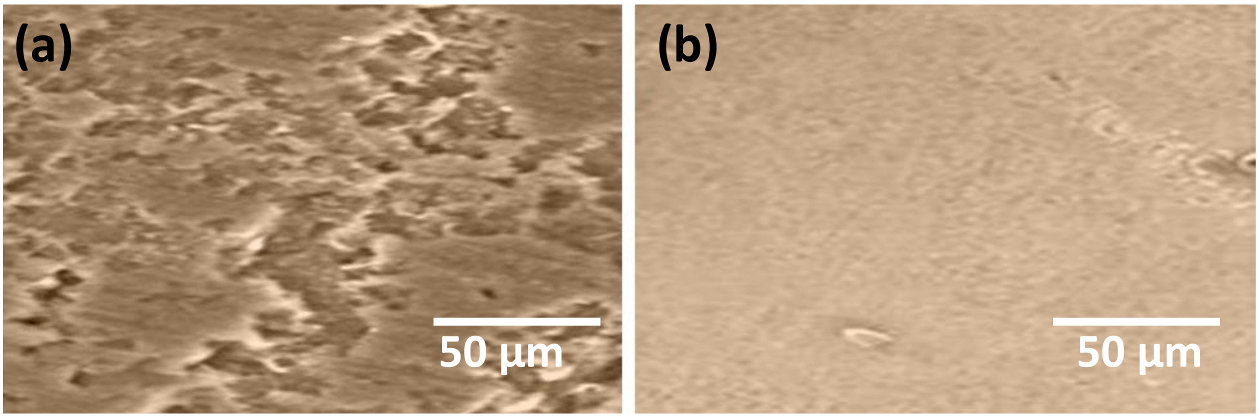

Figure 9. *SEM images of copper substrate after immersion in 3.5% NaCl solution for 12 h (a) without, and (b) with 1.00 mM of BHCTA inhibitor*

Corrosion inhibition mechanism

As illustrated in Figure 10, the postulated inhibition mechanism is based on the measured test and quantum chemistry study. The adsorption of Cl^- ion was substituted by the adsorption of BHCTA molecules on Cu surface [27]. The physical adsorption (electrostatic) and the chemical adsorption created by chemical bonds combine, according to the adsorption results for the BHCTA on the Cu substrate. The presence of charged inhibitor molecules in the solution and the charged metal surface are necessary for physical adsorption. In order to create coordination-type bonds, the inhibitor molecule and the metal surface must share or transfer charges during the chemisorption process. Transition metals with unoccupied low-energy electron orbitals and inhibitor molecules with loosely bonded electrons or heteroatoms with lone pair electrons are necessary for this interaction. By substituting adsorbed Cl^- on the copper substrate with BHCTA molecules, covalent bonds can be formed between the metal surface and π-electrons of the benzene ring and the lone pair of heteroatoms. The Cu is shielded from corrosion by being isolated from the corrosive ions.

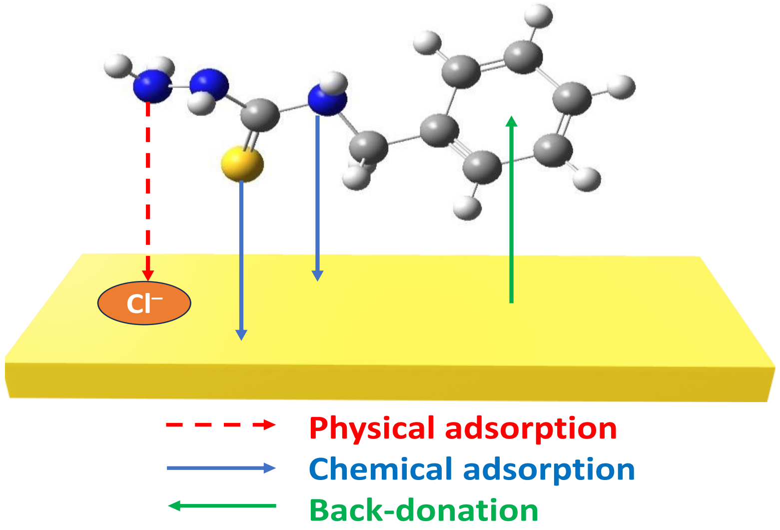

Figure 10. *Schematic diagram of the corrosion inhibition mechanism of BHCTA on copper surface*

Comparison of inhibition efficacy of different heterocyclic derivatives

It is still of interest to compare copper corrosion inhibition in the same media and conditions using BHCTA with the performance of other heterocyclic compounds and the results are summarized in Table 3. It is clear that BHCTA inhibitor has promising efficiency compared to a number of other heterocyclic derivative inhibitors [28-30].

Table 3. *Comparison of the inhibitory efficacy of different heterocyclic derivatives*

Inhibitor	C_{inh} / mM	$C_{\text{NaCl electrolyte}}$ / %	Metal	*IE* / %	Ref.
2-Mercapto-4-amino-5-nitroso- 6-hydroxy pyrimidine (MAP)	1	3.5	Cu	90.7	[28]
1-[(2-Chloro-5-thiazolyl)-methyl]–4,5-dihydro-N-nitro-1H-imidazol-2-amine (IMT)	2	3.5	Cu	97.2	[29]
(2E)–1-[(6-Chloro-pyridin-3-yl)-methyl]-N-nitro-imidazolidin-2-imine (IMP)				98.9	
4-amino-3-methyl-1,2,4-triazole-5-thione (MTSNH)	1	3.0	Copper-nickel (Cu-30Ni)	96.6	[30]
3-methyl-1,2,4-triazole-5-thione (MTS)				65.2	
N-benzylhydrazinecarbothioamide (BHCTA)	1	3.5	Cu	95.3	This work

Conclusions

1) The inhibitory performance of organic molecules BHCTA for copper corrosion was successfully explored in 3.5 wt.% NaCl solution at 298 K.

2) BHCTA molecules are effectively adsorbed on the Cu substrate and hinder concurrently the anodic oxidation and cathodic reduction progressions.
3) Corrosion inhibition efficacy reached more than 95 % upon addition of 1.00 mM of BHCTA.
4) Adsorption of BHCTA on the copper surface agrees with Langmuir isotherm and presents blend of chemisorption and physisorption characteristics.
5) Theoretical calculations show that BHCTA has good adsorption properties on the copper substrate.
6) SEM outcomes provide the foundation of defending layer of BHCTA over the copper substrate.
7) There is good consistency between experimental (PDP, WL, and EIS) and theoretical (DFT calculations and Monte Carlo simulation) tools, which strengthens the results obtained.

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