



Article Corrosion Inhibition Properties of Thiazolidinedione Derivatives for Copper in 3.5 wt.% NaCl Medium

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Abstract: Copper is the third-most-produced metal globally due to its exceptional mechanical and thermal properties, among others. However, it suffers serious dissolution issues when exposed to corrosive mediums. Herein, two thiazolidinedione derivatives, namely, (*Z*)-5-(4-methylbenzylidene) thiazolidine-2,4-dione (MTZD) and (*Z*)-3-allyl-5-(4-methylbenzylidene)thiazolidine-2,4-dione (ATZD), were synthesized and applied for corrosion protection of copper in 3.5 wt.% NaCl medium. The corrosion inhibition performance of tested compounds was evaluated at different experimental conditions using electrochemical impedance spectroscopy (EIS), potentiodynamic polarization curves (PPC) and atomic force microscopy (AFM). EIS results revealed that the addition of studied inhibitors limited the dissolution of copper in NaCl solution, leading to a high polarization resistance compared with the blank solution. In addition, PPC suggested that tested compounds had a mixed-type effect, decreasing anodic and cathodic corrosion reactions. Moreover, surface characterization by AFM indicated a significant decrease in surface roughness of copper after the addition of inhibitors. Outcomes from the present study suggest that ATZD (IE% = 96%) outperforms MTZD (IE% = 90%) slightly, due to the presence of additional $-C_3H_5$ unit ($-CH_2-CH = CH_2$) in the molecular scaffold of MTZD.

Keywords: corrosion inhibitor; copper; thiazolidinedione; EIS; Potentiodyamic polarization; AFM

1. Introduction

In the modern era, copper and its alloys are the most important materials for industrial applications on account of their excellent thermal and electrical conductivity, high tensile strength and thermal expansion capacity [1,2]. Copper and its alloys have wide range of applications in oil and petroleum industries, sheets and pipelines in electronic industries, wire production industry, power stations, desalination plants, heat exchangers, cooling towers and marine industries [3–7]. Additionally, copper has good atmospheric corrosion resistance capability. However, copper and its alloys are prone to corrosion in aggressive environments such as hydrochloric acid and in saline conditions [8–11]. When exposed to



Citation: Lgaz, H.; Saha, S.K.; Lee, H.-s.; Kang, N.; Thari, F.Z.; Karrouchi, K.; Salghi, R.; Bougrin, K.; Ali, I.H. Corrosion Inhibition Properties of Thiazolidinedione Derivatives for Copper in 3.5 wt.% NaCl Medium. *Metals* 2021, *11*, 1861. https:// doi.org/10.3390/met11111861

Academic Editor: Alexandre Emelyanenko

Received: 25 October 2021 Accepted: 15 November 2021 Published: 19 November 2021

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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). such aggressive environments, copper has tendency to undergo severe corrosion damage, leading to a deterioration of appearance and performance. In order to inhibit metallic corrosion, the use of corrosion inhibitors is one of the most effective, inexpensive and practical strategies. A number of organic inhibitors such as triazoles, Schiff bases, imidazoles, natural extract products and amino acids has been reported for the corrosion inhibition of copper and its alloys [2,12–15].

It has been established now, among the several organic inhibitors, that molecules which have heteroatoms (such as N, O, S, P), hetero atomic (>C=O, >C = S, -C = N-, etc.) π -electrons, unsaturated π -bonds and aromatic rings have high adsorption ability on metallic surfaces [16,17]. In these circumstances, thiazolidinedione derivatives are very important heterocyclic organic compounds which have almost all of the above sites in their molecular scaffolds. Their applications comprise diversified fields, from medicinal chemistry to material science [18–21]. However, corrosion mitigation of copper using thiazolidinediones derivatives are still rare in the literature.

In this perspective, the present work reports the synthesis of two thiazolidinediones derivatives namely, (*Z*)-5-(4-methylbenzylidene)thiazolidine-2,4-dione (MTZD) and (*Z*)-3-allyl-5-(4-methylbenzylidene)thiazolidine-2,4-dione (ATZD) and their application in corrosion inhibition performance of copper in 3.5 wt.% NaCl medium. Herein, we have intensely replaced hydrogen atom from the thiazolidinediones unit by $-C_3H_5$ unit ($-CH_2-CH = CH_2$) in the molecular scaffold of MTZD, and thereby producing ATZD. Our intention is to see how this $-C_3H_5$ unit ($-CH_2-CH = CH_2$) affects the corrosion inhibition efficiency of copper in 3.5 wt.% NaCl medium. Electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements were performed to evaluate the corrosion inhibition performance of the synthesized MTZD and ATZD inhibitors. Atomic Force Microscopy (AFM) was used to investigate the surface morphology of copper at the absence and presence of inhibitors.

2. Materials and Methods

2.1. Material and Solutions

The samples used in all measurements were made from industrial copper (99.9% Cu), with 1 cm², and $2.5 \times 2 \times 0.3$ cm³ for electrochemical tests and surface characterization, respectively. Copper samples were polished with abrasive papers (400–2200) to a mirror-like finish, cleaned with deionized water and ethanol, dried in the air then stored in a vacuum desiccator for further use. All chemicals used in the present work were purchased from Sigma-Aldrich (St. Louis, MO, USA) without any further purification.

Analytical-grade sodium chloride (NaCl) in ultrapure water was used to produce 3.5 wt.% NaCl solution, which is considered as a blank. Pre-trial tests were carried out to select the appropriate concentration range, which is fixed between 50 and 300 ppm of inhibitors. No significant increase in inhibition performance was obtained above 300 ppm, therefore, a low concentration was preferred for practical purposes. Unstirred aerated conditions were maintained for all experiments.

2.2. Synthesis of Inhibitors

The title compounds described here were synthesized according to the literature procedures [22].

Synthesis of (Z)-5-(4-methylbenzylidene) thiazolidine-2,4-dione (3): An equimolar mixture of thiazolidine-2,4-dione (1) (0.12 g, 1 mmol), 4-methylbenzaldehyde (2) (1 mmol) in water/ethanol (v/v, 2:1) (10 mL) was treated with sodium hydroxide (1.1 mmol) at 5 °C, then stirred for 5–6 h at room temperature. The completion of the reaction was monitored by TLC. The reaction mixture was acidified with diluted HCl. The solid was filtered and recrystallized from ethanol to give pure product 3.

White solid, yield 110 mg (50%); m.p. 229–231 °C; TLC (cyclohexane–AcOEt: 70–30), $R_f = 0.46$; ¹H NMR (200 MHz, DMSO- d_6) δ , ppm (*J*, Hz): 12.56 (1H, s, NH); 7.73 (1H, s, ArCH = C); 7.46 (2H, d, *J* = 4.4 Hz, H Ar); 7.32 (2H, d, *J* = 4.4 Hz, H Ar); 2.33 (3H, s, CH₃).

¹³C NMR (50 MHz, DMSO) δ , ppm: 167.8 (C = O); 167.3 (C = O); 140.6 (CH = C); 131.8 (C-4 Ar); 130.2 (C-1 Ar); 130.0 (C-2 Ar); 129.8 (C-3 Ar); 122.2 (C-5 TZD); 21.0 (CH₃). MS (ESI⁺): m/z = 220.2 [M + H]⁺.

Synthesis of 3-allyl-5-(4-methylbenzylidene) thiazolidine-2,4-dione (4): A mixture of (*Z*)-5-(4-methylbenzylidene) thiazolidine-2,4-dione 3 (1 mmol), allyl bromide (1.2 mmol) in EtOH/H₂O (v/v; 2:1) (10 mL) was treated with sodium hydroxide (1 mmol), were added. The resulting mixture was stirred and heated at 75 °C for 5–6 h. The completion of the reaction was monitored by TLC. The reaction mixture was cooled and acidified with diluted HCl (4N). The precipitated solid was filtered and purified by recrystallization from ethanol to give pure compound 4.

White solid, m.p. = 116–117 °C (EtOH); TLC (cyclohexane–AcOEt: 70–30), $R_f = 0.77$; ¹H NMR (200 MHz, DMSO-*d*₆) δ , ppm (*J*, Hz): 7.81 (1H, s, ArC<u>H</u> = C); 7.34 (2H, d, , H Ar); 7.21 (2H, d, *J* = 7.2 Hz, H Ar); 5.88–5.69 (1H, m, C<u>H</u> = CH₂); 5.23 (1H, dd, *J* = 12 Hz, 1.4 Hz, CH = C<u>H₂</u>); 5.16 (1H, dd, *J* = 5.7 Hz, 1.4 Hz, CH = C<u>H₂</u>); 4.27 (2H, d, *J* = 6.0 Hz, NCH₂); 2.33 (3H, s, CH₃). ¹³C NMR (50 MHz, DMSO-*d*6) δ , ppm: 167.6 (C = O); 166.0 (C = O); 141.3 (ArCH = C); 134.0 (C-4 Ar); 130.4 (CH = CH₂); 130.3 (C-3 Ar); 130.2 (C-1 Ar); 129.9 (C-2 Ar); 120.1 (CH = CH₂); 118.8 (C-5 TZD); 43.7 (NCH₂); 21.5 (CH₃). MS (ESI⁺): *m*/*z* = 260.0 [M + H]⁺, 282.0 [M + Na]⁺.

2.3. Electrochemical Measurements

Electrochemical studies, including electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization curves (PPC) were carried out using a computer-controlled system Voltalab potentiostat/galvanostat (Corrtest Instruments Corp, Ltd. Wuhan, China) with a three-electrode electrochemical cell and the corresponding CS Studio5 control software. The copper with an exposed area of 1 cm² was used as a working electrode, whereas a mesh of platinum and one of saturated calomel electrode (SCE) were used as counter electrode and reference electrode, respectively. EIS measurements were performed at 298 ± 2 K using various concentrations of inhibitors, then the concentration with higher performance was chosen for immersion time tests. EIS tests versus immersion time were carried out from 1 h to 48 h. Before each EIS measurement, the working electrode was dipped in the test solution for 6 h to ensure a steady-state open circuit potential (E_{OCP}). Thereafter, EIS experiments were recorded using AC signals of amplitude 5 mV peak-topeak, at OCP, on 10⁵ to 10⁻² Hz frequency range. Potentiodynamic polarization curves were recorded at a rate of 0.1 mV/s versus E_{OCP} in the potential range of -500 to 100 mV at temperature 298 ± 2. Electrochemical data were fitted using EC-lab and CS Studio5.

2.4. Surface Characterization

Surface roughness and morphology of uninhibited and inhibited copper were characterized by atomic force microscopy. Copper samples were immersed in 3.5 wt.% NaCl without and with 300 ppm of ATZD for 24 h at 298 K, then cleaned with distilled water and dried before analyses. An AFM (Park XE-100: Atomic Force Microscopy, Suwon, South Korea) was used for surface topography at 10 μ m \times 10 μ m scan range in a contact mode. Gwyddion modular software was used for AFM image visualization and analysis.

3. Results and Discussion

3.1. Electrochemical Impedance Spectroscopy (EIS)

Electrochemical impedance spectroscopy (EIS) has been performed to investigate the inhibition effects of MTZD and ATZD inhibitors on copper in 3.5 wt.% NaCl medium. Nyquist and Bode diagrams for copper electrodes in 3.5 wt.% NaCl medium without and with various concentrations of the investigated inhibitors were shown in Figure 1. It can be seen from the Nyquist as well as Bode plots presented in Figure 1 that there is a presence of two time constants and Warburg impedance.





Figure 1. EIS data for copper in 3.5 wt.% NaCl without and with various concentrations of thiazolidinedione derivatives at 298 K; (**a**,**b**) Nyquist plots, (**c**,**d**) Bode modulus/Phase angle plots.

The obtained impedance spectra in absence and presence of inhibitors were analyzed by fitting of the equivalent circuit model, as shown in Figure 2. Herein, R_s represents the solution resistance, R_f is the film resistance, R_{ct} is the charge transfer resistance, CPE_f and CPE_{dl} are the constant phase elements (CPEs) and W is the Warburg impedance. In the absence of inhibitors, two time constants in Bode plots and a definite diagonal straight line at lower frequencies region of Nyquist plot can be observed. The diagonal straight line corresponds to Warburg impedance and exemplifies the presence of the diffusion layer at the passivated metal-electrolyte interface. In this perspective, the obtained Nyquist plot in absence of inhibitors are applied in the corrosive medium, the whole phenomena become complicated due to existence of multiple number of interfacial regions, i.e., passivated metal-inhibitor layer interface, inhibitor layer-electrolytic solution interface in addition to passivated metal-electrolytic solution interface [1].



Figure 2. Electrical equivalent circuits used to fit the EIS data; (a) blank medium, (b) with inhibitors.

For inhibited NaCl solutions, a significant change in Nyquist plots is observed. Results from these plots as well as from Table 1 show that, for both MTZD and ATZD inhibitors, at 50 ppm concentration, R_f and R_{ct} values increase, whereas the Warburg impedance value decreases. It suggests that the diffusion of the electroactive species, i.e., Cu^+ or Cu^{2+} ions, into the solution decreases. Alternatively, it also suggests that the corrosion of copper in the aggressive NaCl medium decreases. That may be the reason for a lesser diffusion of Cu^+ or Cu^{2+} ions in the solution. On the other hand, at a higher concentration of inhibitors (150 ppm and 300 ppm), the obtained Nyquist plots in the higher frequency region reflects the fact that Warburg impedance is not so much pronounced, rather than charge transfer resistance, which is more prominent. This behavior is well-described by the equivalent circuit model presented in Figure 2b. The observed finding also reflects that the presence of inhibitors limits the process of diffusion, and thereby corrosion phenomenon.

Table 1. EIS parameters for copper in 3.5 wt.% NaCl solution and in presence of thiazolidinedione derivatives at 298 K.

C (ppm)	R_s ($\Omega \ \mathrm{cm}^2$)	R_f (k Ω cm ²)	n_1	$C_{eff, f}$ (µF cm ⁻²)	$\frac{R_{ct}}{(\mathrm{k}\Omega~\mathrm{cm}^2)}$	<i>n</i> ₂	C _{eff, dl} (µF cm ^{−2})	R_p (k Ω cm ²)	W (Ω cm ²)	η (%)
Blank	4.7	0.16	0.86	19.9	1.44	0.75	33.8	1.6	50.35	-
MTZD										
50	4.6	1.12	0.85	8.1	4.12	0.69	11.5	5.24	5.63	70
150	5.8	2.36	0.87	7.3	7.42	0.71	10.4	9.78	-	83
300	6.1	3.64	0.88	5.7	11.85	0.75	6.7	15.49	-	90
ATZD										
50	4.9	2.27	0.84	6.9	5.63	0.67	8.2	7.9	3.77	79
150	5.6	3.31	0.86	5.5	11.84	0.69	6.6	15.15	-	89
300	5.1	5.98	0.86	1.7	32.11	0.68	1.9	38.09	-	96

All the capacitive loops presented in Figure 1 are not perfectly semicircle, whereas they are depressed under the real axis. This is due to frequency dispersion and microscopic roughness of the electrode surface. To overcome this situation, a constant phase element (CPE) is introduced in the equivalent circuit model. There is a relation which correlates CPE with impedance by the following equation [23]:

$$Z_{CPE} = Q^{-1} (i\omega)^{-n} \tag{1}$$

where *Q* is a proportionality coefficient, ω represents angular frequency and *n* refers to surface heterogeneity measure. CPE can be simplified to represent capacitance (*C*), resistance (*R*) and inductance (*L*) based on the *n* values equals to 1, 0, and -1, respectively. The $C_{eff' dl}$, and $C_{eff' f}$ effective capacities can be calculated using the following equations [24,25]:

$$C_{eff'dl} = Q_{dl}^{1/n} \times \left(\frac{1}{R_s} + \frac{1}{R_{ct}}\right)^{\frac{n-1}{n}}$$
 (2)

$$C_{eff'f} = Q_f^{1/n} \times \left(R_f\right)^{\frac{1-n}{n}}$$
(3)

The results obtained from the fitting of electrochemical impedance data are depicted in Table 1.

The R_p represented in Table 1 is the polarization resistance, which consists of two different resistances across the boundaries, such as charge transfer resistance and resistance due to passivation as well as inhibitor layer. It can be seen from Table 1 that with the increase in inhibitor concentration, the $R_p = (R_f + R_{ct})$ value increases concomitantly, indicating that the corrosion resistance ability of copper by MTZD and ATZD inhibitor increases in

3.5 wt.% NaCl medium. To obtain the corrosion inhibition efficiency ($\eta_{\%z}$) of the applied inhibitor molecules, the following equation is used:

$$\eta_{\%z} = \frac{R_p - R_p^0}{R_p} \times 100$$
 (4)

where R_p and R_p^0 signifies polarization resistance with and without the inhibitor molecule, respectively.

At maximum inhibitor concentration, i.e., 300 ppm, the corrosion inhibition efficiency reaches the maximum up to 90% and 96% for MTZD and ATZD, respectively, and thereby follows the order of ATZD > MTZD. The obtained results suggest that the synthesized inhibitor molecules are able to perform at low inhibitor concentration and possess a high degree of corrosion inhibition ability. The reason behind the high corrosion inhibition ability and its order can possibly be explained from the molecular structure of inhibitors. It can be seen from Scheme 1 that inhibitor molecules comprise a thiazolidinedione ring, unsaturated bonds and aromatic rings. The presence of aforesaid units in the molecular skeleton of inhibitors plays a leading role in adsorption onto the copper surfaces; thereby, it shows higher corrosion inhibition behavior. Now, if we consider higher corrosion inhibition behavior of ATZD in comparison with MTZD, it could be seen that one additional $-C_3H_5$ group ($-CH_2-CH = CH_2$) has been incorporated in the molecular scaffold of ATZD, which may provide an additional binding site for the adsorption from its π -electron clouds.



Scheme 1. General procedure for the synthesis of compounds 3 (MTZD) and 4 (ATZD).

In the present investigation, the effect of immersion time on the corrosion inhibition efficiency of the inhibitors has also been performed. The obtained Nyquist and Bode plots with different immersion times (1 h to 48 h) for the ATZD inhibitor at 300 ppm concentration were plotted in Figure 3.



Figure 3. EIS data for copper in 3.5 wt.% NaCl with 150 ppm of ATZD at 298 K and different immersion times; (**a**) Nyquist and (**b**) Bode plots.

The obtained fitted results are tabulated in Table 2. It can be seen from Table 2 that R_p value and corresponding inhibition efficiency increase up to 24 h of immersion and thereby decrease to some extent within 48 h of immersion. With increasing immersion time, increasing corrosion inhibition efficiency suggests that the extent of surface coverage

increases by the applied inhibitor molecules, and thereby two-dimensional layers have been formed on the whole surface of the copper surfaces. The obtained outcome also suggests that the ATZD inhibitor molecule is robust in nature and able to sustain corrosion inhibition efficiency, even after 48 h of immersion time.

Time (h)	R_s ($\Omega \ { m cm}^2$)	R_f (k Ω cm ²)	<i>n</i> ₁	$C_{eff, f}$ (µF cm ⁻²)	R_{ct} (k Ω cm ²)	<i>n</i> ₂	C _{eff, dl} (µF cm ^{−2})	R_p (k Ω cm ²)	W (Ω cm ²)	η (%)
Blank	4.7	0.16	0.86	19.9	1.44	0.75	33.8	1.6	50.35	-
1	5.1	5.98	0.86	1.7	32.11	0.68	1.9	38.09	-	96
12	5.3	7.15	0.87	1.2	38.30	0.66	1.3	45.45	-	96
24	4.7	11.14	0.87	1.0	45.08	0.66	1.1	56.22	-	97
36	5.1	9.83	0.85	1.3	32.02	0.68	1.7	41.85	-	96
48	5.3	5.39	0.87	1.4	26.83	0.69	2.1	32.22	-	95

Table 2. EIS parameters for copper in 3.5 wt.% NaCl solution and in the presence of ATZD at 298 K and different immersion times.

3.2. Potentiodynamic Polarization

Potentiodynamic polarization curves for copper electrode in absence and presence of MTZD and ATZD inhibitors are presented in Figure 4. The curves in this figure represent both anodic and cathodic half reactions in 3.5 wt.% NaCl medium.



Figure 4. PPC of copper in 3.5 wt.% NaCl without and with various concentrations of thiazolidinedione derivatives at 298 K; (a): ATZD, (b): MTZD.

The mechanism of electrochemical dissolution of copper in 3.5 wt.% NaCl medium proceeds as follows [2,26]: (a) it can be seen from Figure 4 that current density first increases till the peak value (i_{peak}) is achieved, which corresponds to the oxidation of Cu to Cu⁺ (Equation (5)); (b) in the solution, Cl⁻ ion is present, which produces an insoluble film of CuCl and thereby the current density decreases from i_{peak} to i_{min} (Equation (6)); (c) the unstable CuCl further reacts with the Cl⁻ ion and produces soluble compound of CuCl₂⁻ and current density shows further increasing trends (Equation (7)) [27].

$$Cu \rightarrow Cu^+ + e^-$$
 (5)

$$Cu^+ + Cl^- \rightarrow CuCl$$
 (6)

$$CuCl + Cl^{-} \rightarrow CuCl_{2}^{-} \tag{7}$$

The reaction between the Cu⁺ and Cl⁻ is faster than that of the reaction between Cu²⁺ and Cl⁻ [28]. Hence, CuCl is the predominately obtained compound in the chloride medium. Therefore, in the chloride medium, anodic dissolution of Cu happens and produces a soluble $CuCl_2^-$ compound, which diffuses to the bulk solution. In the cathodic process, in the absence of inhibitors, oxygen reduction reaction is dominant in the aerated solution as follows [29]:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \tag{8}$$

Additionally, it is also possible for one reaction to happen on the Cu surfaces, as follows [2,30]:

$$CuCl_2^- + 2OH^- \rightarrow Cu_2O + H_2O + 4Cl^-$$
(9)

The oxygen reduction in the cathodic reaction is mainly controlled by mass transport; it is the diffusion of $CuCl_2^-$, which limits the mass transfer process for the oxidative Cu dissolution at the open circuit potential [10,30]. The literature reveals that corrosion of copper in the chloride medium take place by the decomposition of the corrosion product and the formation of chloride compounds. At chloride ion concentrations greater than 1 Molar, the higher chloride complexes $CuCl_3^{2-}$ and $CuCl_4^{3-}$ are formed in addition to the CuCl and $CuCl_2^-$, whereas when the chloride ion concentration is less than 1 Molar, dissolution of Cu mainly formed CuCl, which is unstable in nature and converts to the soluble compound of $CuCl_2^-$ [2,11].

The electrochemical parameters obtained from the extrapolation of Tafel curves such as corrosion potential (E_{corr}), corrosion current density (i_{corr}) and cathodic (β_c) Tafel slope are tabulated in Table 3. The obtained i_{corr} values are used to obtain the inhibition efficiency ($\eta_{\%p}$) for these inhibitor molecules:

$$\eta_{\text{\%P}} = \frac{i_{\text{corr}} - i_{\text{corr}(\text{inh})}}{i_{\text{corr}}} \times 100$$
(10)

where i_{corr} and $i_{\text{corr(inh)}}$ are designated as corrosion current densities for copper immersed in corrosive solutions, without and with added inhibitors, respectively.

C (ppm)	- <i>E</i> _{corr} (mV/SCE)	i _{corr} (μA/cm²)	$egin{array}{c} eta_{ m c} \ ({ m mV}~{ m dec}^{-1}) \end{array}$	η (%)
Blank	206	26	61	-
MTZD				
50	170	6.14	63	76
150	178	2.96	79	88
300	188	1.54	85	94
ATZD				
50	174	4.91	69	81
150	175	2.76	74	89
300	178	0.47	71	98

Table 3. PDP parameters for copper in 3.5 wt.% NaCl solution and in presence of inhibitors at 298 K.

It is seen from the Tafel curves that with the increasing inhibitor concentration of MTZD and ATZD, there is a shifting of anodic as well as cathodic curves towards the lower current densities. It suggests that the inhibitor molecule influences the anodic as well as cathodic reactions. Decreasing current density in the presence of inhibitors suggests the adsorption of inhibitor molecules on the active sites present on the copper surfaces, resulting in a minimizing corrosion attack by the chloride ions [27]. It is also seen from the obtained Tafel curves (*vide* Figure 4) that in presence of inhibitors, cathodic and anodic curves show parallel lines with respect to the uninhibitor molecule categorization such as anodic, cathodic or mixed types is possible from obtained E_{corr} values. Generally, inhibitor molecule categorized to anodic or cathodic nature when the difference between

 $E_{\rm corr}$ value in the absence and presence of inhibitors is >85 mV [31,32]. The obtained results tabulated in Table 3 suggest that $E_{\rm corr}$ values vary \pm 36 mV with respect to the uninhibited ones. It suggests that the synthesized inhibitor molecules perform as mixed type inhibitor behavior. The MTZD and ATZD shows 94% and 98% corrosion inhibition ability at 300 ppm concentration. The obtained results reflect that synthesized inhibitor molecules worked at extremely low concentration and possess high degree of corrosion inhibition.

3.3. Adsorption Isotherm

The adsorption ability of an inhibitor molecule on a metal surface strongly influences its corrosion inhibition efficiency effect. Therefore, finding a relationship between the corrosion inhibition behavior and the adsorption process is significant [33,34]. Herein, the results obtained from EIS measurements can be fitted using adsorption isotherm models to explain the interaction between investigated inhibitors and copper surface in 3.5 wt.% NaCl. Experimental results were fitted to different isotherm models, where the Langmuir adsorption isotherm provided the best fitting (Figure 5). Its mathematical expression is given below [35,36]:

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{11}$$

where C_{inh} and K_{ads} correspond to inhibitor concentration (in mol/L) and adsorption equilibrium constant, respectively.



Figure 5. Langmuir's isotherm plots for adsorption of inhibitors on copper surface in 3.5 wt.% NaCl at 298 K temperature.

The K_{ads} and ΔG_{ads} are related mathematically as per the below equation [35,36]:

$$\Delta G_{ads}^{"} = -RTln(55.5K_{ads}) \tag{12}$$

where *R*, *T* and 55.5 are the gas constant, the temperature of the system and water molecule concentration in the molar.

The calculated values of K_{ads} are 16,253 and 10,449 L/mol for ATZD and MTZD, respectively. These higher K_{ads} values reflect the strong adsorption of these compounds on the copper surface [35]. Generally, values of ΔG_{ads} up to -20 kJ mol/L indicate physical adsorption, whereas those less than -40 kJ mol/L indicate chemical adsorption [37]. In the present study, the ΔG_{ads} values are -37.06 and -38.15 kJ mol/L for MTZD and

ATZD, respectively, which come in between -20 and -40 kJ mol/L. This suggests that the adsorption of both inhibitors on the copper surface involves both physical and chemical interactions [36,38]. These results strengthen those from EIS experiments, confirming that tested inhibitors inhibit the copper corrosion primarily by adsorption onto its surface.

3.4. Atomic Force Microscopy

The AFM is extensively used for the characterization and imaging of surfaces at microto nanometer scales. In corrosion inhibition studies, AFM has been successfully used to visualize the texture of metals and alloys under different experimental conditions. AFM can obtain high-resolution images of the sample surface and its roughness. A lower roughness of a metal surface indicates lower corrosion products and higher protection [39,40]. The 3D and 2D topography maps of copper in blank and inhibited (ATZD) solutions are represented in Figure 6. The roughness of selected area (2D) is represented in Figure 6e,f. The analysis of AFM data shows that the average roughness value of the blank sample is 808 nm, and that of the selected area is 59.1 nm. After the addition of 300 ppm of ATZD to the blank solution, the roughness of the copper surface is decreased to 201.8 nm for the whole scan area, and an average of 5.59 nm for the selected area. It indicates that the copper surface becomes smoother and more compact compared with an uninhibited sample. The addition of the corrosion inhibitor to the NaCl solution decreases its aggressivity, and therefore limiting the dissolution and deterioration of copper. This is mainly achieved by inhibitors' adsorption on the copper surface, creating a protective barrier against corrosion species.



Figure 6. AFM results of copper in 3.5 wt.% NaCl without and with 150 ppm of ATZD at 298 K; (**a**,**b**): 3D, (**c**,**d**): 2D, and (**e**,**f**): Roughness of selected area.

4. Conclusions

In the present work, the corrosion inhibition performance of two thiazolidinedione derivatives was evaluated using electrochemical impedance spectroscopy, potentiodynamic polarization curves and atomic force microscopy for protection of copper in 3.5 wt.% NaCl solution. EIS results indicated that the addition of increasing concentration of inhibitors significantly increased the polarization resistance and decreased the double layer capacitance. In addition, results showed the formation of an inhibitor film that limited the aggressivity of NaCl solution. PPC results confirmed the mixed nature of tested inhibitors, blocking both anodic and cathodic corrosion reactions, while significantly decreasing the current corrosion density. Both inhibitors had a high inhibition efficiency at low concentration. The MTZD and ATZD showed 94% and 98% corrosion inhibition ability at 300 ppm concentration. The Langmuir adsorption isotherm showed that inhibitors inhibited the corrosion of copper through physical and chemical adsorption mechanism. Surface morphology investigation by AFM showed a decreased roughness after the addition of inhibitors to the corrosive solution. Outcomes from the present work showed the high corrosion inhibition properties of the investigated compounds. Hence, future efforts would be devoted to the theoretical investigation of the interaction between these compounds and copper surfaces.

Author Contributions: Formal analysis, data curation, writing—original draft preparation, H.L. and S.K.S.; Conceptualization, methodology, validation, supervision, software, H.-S.L., N.K., R.S. and K.B.; Investigation, F.Z.T. and K.K.; Resources, project administration, funding acquisition, writing—review and editing, I.H.A. and H.-s.L. All authors have read and agreed to the published version of the manuscript.

Funding: The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant number R.G.P.2/56/42. This research was supported by basic science research program through the National Research Foundation (NRF) of Korea funded by the Ministry of Science, ICT and Future Planning (No. 2015R1A5A1037548).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Raw data used for this work is part of ongoing works and cannot be shared at this time.

Acknowledgments: The authors extend their appreciation to the Deanship of Scientific Research at King Khalid University for funding this work through research groups program under grant number R.G.P.2/56/42. This research was supported by basic science research program through the National Research Foundation (NRF) of Korea funded by the Ministry of Science, ICT and Future Planning (No. 2015R1A5A1037548).

Conflicts of Interest: The authors declare no conflict of interest.

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